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HANDBOOK OF ADHESIVES AND SURFACE PREPARATION

Technology, Applications and Manufacturing

Edited by

Sina Ebnesajjad

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Sina Ebnesajjad
Chadds Ford, Pennsylvania

Dedicated to the memories of my dear friend
William Andrew Woishnis
Who left the world too early, too young.

Preface

A basic industrial process is the bonding of similar and dissimilar materials to each other. Bonding using an adhesive has proven to be an effective means of attaching materials together.

There are numerous books about adhesives. Several excellent books are available that deal with the subject of adhesives from various viewpoints. Some have looked at adhesives from the perspective of synthesis, chemistry, or bonding techniques. Others have treated the subject from a practical standpoint. Of these, most are attempts to describe adhesion in relation to a variety of materials, including plastics, metals, wood, and so on. A few books regarding applications of adhesives are highly specialized in particular industries, such as metals and construction.

What is different about this book? The present book is focused on practitioners of adhesion technology from an end-user's perspective, thus covering most substrates, such as plastics, metals, elastomers, and ceramics. The information is aimed at allowing readers to select the right adhesive and successfully bond materials together. Other than the choice of the appropriate adhesive, surfaces must be pretreated according to specific methods and prior to the application of adhesives. By including generous selections from the recent back catalog of both Elsevier and William Andrew publishing (now part of Elsevier), I aim to provide to an audience of engineers and other professionals working with adhesives, a wide-ranging and practical handbook.

This book describes treatment methods that must be applied to a material surface before successful adhesive bonding is possible. There are numerous examples, ranging from wallpaper in a house and paint on surfaces to parts used in the construction of aircraft. The aim of the contents is to explain, in an accessible yet complete manner, all that is required to achieve successful adhesion bonding of different materials.

Fundamental material considerations have been given priority to facilitate the use of the contents of this book in different industries. The book is both a reference and a source for learning the basics. Additionally, it is useful for all involved in the product value chains, and it offers information helpful to engineers, chemists, students, and all others involved in material adhesion and processing.

Every attempt has been made to enhance the accessibility of the information to create a reader-friendly text. In the balance of practical and theoretical subjects, practical has been given definite precedence. This is a trade-off that the author readily acknowledges. There are numerous good books and sources for the study of the theory and science of adhesion and adhesives.

The references listed at the end of each chapter serve as both bibliography and additional reading sources. Most of the basic practical technology of adhesives was developed decades ago. Older references have been retained wherever they represent the preferred source of information for a specific topic. Readers can find a wealth of information and reports that have been declassified by the Defense Technical Information Center (www.dtic.mil), most of which date to the 1960s.

The book consists of four parts. Part I contains two introductory chapters that describe the fundamental concepts of surface treatment and adhesion. Part II is comprised of chapters that describe surface tension (energy) concepts, surface characterization techniques, and surface preparation methods for metals and thermoplastics, thermosets, and elastomers.

Part III describes the characteristics of adhesives from the standpoints of chemical structure and application. Heat-resistant and UV-cure adhesives are discussed in separate chapters because of their importance to the adhesive industry.

Part IV of the book describes the applications of adhesives with respect to special adherends. Applications of adhesives in aerospace, electronic, and medical/dental have been described in separate chapters because of the importance and breadth of adhesion use in these industries. There are few, if any, adhesives that are not used by these industries, thus rendering the information in the chapters useful to nearly any other industry. After all, the aerospace industry has been a pioneer in the use of structural adhesive bonding in critical applications.

Appendix A discusses Safety, Environmental, Economic Aspects, and Future Trends. Appendix B provides an exact copy of the FDA Guidance for Tissue Adhesive for the Topical Approximation of Skin issued in May 2008. A glossary section rounds off the book.

I hope this book is useful to those who practice the art of adhesion as a profession. None of the views or information presented in this book reflect the opinions of any of the companies or individuals that have contributed to the book. If there are errors, they are an inadvertent oversight on the part of the author. A note indicating suggestions or specific errors to the publisher, for the purpose of correcting future editions, would be much appreciated.

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1 Introduction and Adhesion Theories

Sina Ebnesajjad

1.1 Definition of Adhesives and Adhesive Bonding

An adhesive is a material that is applied to the surfaces of articles to join them permanently by an adhesive bonding process. An adhesive is a substance capable of forming bonds to each of the two parts when the final object consists of two sections that are bonded together.[1] A feature of adhesives is the relatively small quantities that are required compared to the weight of the final objects.

Adhesion is difficult to define, and an entirely satisfactory definition has not been found. The following definition has been proposed by Wu.[2] "*Adhesion* refers to the state in which two dissimilar bodies are held together by intimate interfacial contact such that mechanical force or work can be transferred across the interface. The interfacial forces holding the two phases together may arise from van der Waals forces, chemical bonding, or electrostatic attraction. Mechanical strength of the system is determined not only by the interfacial forces, but also by the mechanical properties of the interfacial zone and the two bulk phases."

There are two principal types of adhesive bonding: structural and nonstructural. Structural adhesive bonding is bonding for applications in which the adherends (the objects being bonded) may experience large stresses up to their yield point. Structural adhesive bonds must be capable of transmitting stress without losing of integrity within design limits.[3] Bonds must also be durable throughout the useful service life of a part, which may be years. In addition to possessing significant resistance to aging, a structural bond is defined as having a shear strength greater than 7 MPa. Nonstructural adhesives are not required to support substantial loads but merely hold lightweight materials in place. This type of adhesive is sometimes called a "holding adhesive." Pressure-sensitive tapes and packaging adhesives are examples of nonstructural adhesives.

The distinction between structural and nonstructural bonds is not always clear. For example, is a hot melt adhesive used in retaining a fabric's plies structural or nonstructural? One may argue that such an adhesive can be placed in either classification. However, the superglues (cyanoacrylates) are classified as structural adhesives even though they have poor resistance to moisture and heat.

1.2 Functions of Adhesives

The primary function of adhesives is to join parts together. Adhesives accomplish this goal by transmitting stresses from one member to another in a manner that distributes the stresses much more uniformly than can be achieved with mechanical fasteners. Adhesive bonding often provides structures that are mechanically equivalent to or stronger than conventional assemblies at lower cost and weight. In mechanical fastening, the strength of the structure is limited to that of the areas of the members in contact with the fasteners.[4] Obtaining adhesive bonds that are stronger than those of the strength of adherends is not unusual.

Smooth surfaces are an inherent advantage of adhesively joined structures and products. Exposed surfaces are not defaced and contours are not disturbed, as happens with mechanical fastening systems. This feature is important in function and appearance. Aerospace structures, including helicopter rotor blades, require smooth exteriors to minimize drag and to keep temperatures as low as possible. Lighter weight materials than are used with conventional fastening can often be used with adhesive bonding because the uniform stress distribution in the joint permits full utilization of the strength and rigidity of the adherends.[4] Adhesive bonding provides much larger areas for stress transfer throughout the part, thereby decreasing stress concentration in small areas.

Dissimilar materials, including plastics, are readily joined by many adhesives, provided that

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proper surface treatments are used. Adhesives can be used to join metals, plastics, ceramics, cork, rubber, and combinations of materials. Adhesives can also be formulated to be conductive. The focus of this book is on adhesives for bonding plastics, thermosets, elastomers, and metals.

Where temperature variations are encountered in the service of an item containing dissimilar materials, adhesives perform another useful function. Flexible adhesives are able to accommodate differences in the thermal expansion coefficients of the adherends, and therefore prevent damage that might occur if stiff fastening systems were used.

Sealing is another important function of adhesive joining. The continuous bond seals out liquids or gases that do not attack the adhesive (or sealant). Adhesives/sealants are often used in place of solid or cellular gaskets. Mechanical damping can be imparted to a structure through the use of adhesives formulated for that purpose. A related characteristic, fatigue resistance, can be improved by the ability of such adhesives to withstand cyclic strains and shock loads without cracking. In a properly designed joint, the adherends generally fail in fatigue before the adhesive fails. Thin or fragile parts can also be adhesively bonded. Adhesive joints do not usually impose heavy loads on the adherends, as in riveting, or localized heating, as in welding. The adherends are also relatively free from heat-induced distortion.[4]

1.3 Classification of Adhesives

Adhesives as materials can be classified in a number of ways, such as chemical structure or functionality. Adhesives are categorized into two classes: natural and synthetic. The natural group includes animal glue, casein- and protein-based adhesives, and natural rubber adhesives. The synthetic group has been further divided into two subcategories industrial and special compounds. Industrial compounds include acrylics, epoxies, silicones, etc. An example of the specialty group is pressure-sensitive adhesives.

1.4 Advantages and Disadvantages of Joining Using Adhesives

The previous discussion highlighted a number of advantages of adhesive bonding. This section will cover both advantages and disadvantages of adhesive bonding, and some points are reiterated.

1.4.1 Advantages

- Uniform distribution of stress and larger stress-bearing area[5,6]
- Joins thin or thick materials of any shape
- Joins similar or dissimilar materials
- Minimizes or prevent electrochemical (galvanic) corrosion between dissimilar materials
- Resists fatigue and cyclic loads
- Provides joints with smooth contours
- Seals joints against a variety of environments
- Insulates against heat transfer and electrical conductance (in some cases adhesives are designed to provide such conductance)
- The heat required to set the joint is usually too low to reduce the strength of the metal parts
- Dampens vibration and absorb shock
- Provides an attractive strength/weight ratio
- Quicker and/or cheaper to form than mechanical fastening

1.4.2 Disadvantages

- The bond does not permit visual examination of the bond area (unless the adherends are transparent)[5–7]
- Careful surface preparation is required to obtain durable bonds, often with corrosive chemicals
- Long cure times may be needed, particularly where high cure temperatures are not used
- Holding fixtures, presses, ovens, and autoclaves, not usually required for other fastening methods, are necessities for adhesive bonding
- Upper service temperatures are limited to approximately 177 °C in most cases, but special adhesives, usually more expensive, are available for limited use up to 371 °C
- Rigid process control, including emphasis on cleanliness, is required for most adhesives
- The useful life of the adhesive joint depends on the environment to which it is exposed

- Natural or vegetable-origin adhesives are subject to attack by bacteria, mold, rodents, or vermin
- Exposure to solvents used in cleaning or solvent cementing may present health problems

1.5 Requirements of a Good Bond

The basic requirements for a good adhesive bond are:[6]

- Proper choice of adhesive
- Good joint design
- Cleanliness of surfaces
- Wetting of surfaces that are to be bonded together
- Proper adhesive bonding process (solidification and cure)

1.5.1 Proper Choice of Adhesive

There are numerous adhesives available for bonding materials. Selection of the adhesive type and form depends on the nature of adherends, performance requirements of the end use, and the adhesive bonding process.

1.5.2 Good Joint Design

Imparting strength to a joint by design is possible.[8] A carefully designed joint yields a stronger bond than one not carefully designed when advantages of the mechanical design are combined with adhesive bond strength to meet the end use requirements of the bonded part.

1.5.3 Cleanliness

To obtain a good adhesive bond, starting with a clean adherend surface is essential. Foreign materials such as dirt, oil, moisture, and weak oxide layers must be removed, lest the adhesive be bonded to weak boundary layers rather than to the substrate. Various surface treatments exist that remove or strengthen the weak boundary layers. Such treatments typically involve physical or chemical processes, or a combination.[9]

1.5.4 Wetting

Wetting is the displacement of air (or other gases) present on the surface of adherends by a liquid phase. The result of good wetting is greater contact area between the adherends and the adhesive over which the forces of adhesion may act.[10]

1.5.5 Adhesive Bonding Process

Successful bonding of parts requires an appropriate process. The adhesive must not only be applied to the surfaces of the adherends; the bond should also be subjected to the proper temperature, pressure, and hold time. The liquid or film adhesive, once applied, must be capable of being converted into a solid in one of three ways. The method by which solidification occurs depends on the choice of adhesive. The ways in which liquid adhesives are converted to solids are:[6]

- Chemical reaction by any combination of heat, pressure, and curing agents
- Cooling from a molten liquid
- Drying as a result of solvent evaporation

Requirements to form a good adhesive bond, as well as processes for bonding, analytic techniques, and quality control procedures, are discussed in this book.

1.6 Introduction to Theories of Adhesion

Historically, mechanical interlocking, electrostatic, diffusion, and adsorption/surface reaction theories have been postulated to describe mechanisms of adhesion. Theories have recently been postulated for adhesive bonding mechanisms (Table 1.1). It is often difficult to fully ascribe adhesive bonding to an individual mechanism is often difficult. A combination of different mechanisms is most probably responsible for bonding. The extent of the role of each mechanism may vary for different adhesive bonding systems. An understanding of these theories is helpful to those who work with adhesives.

An important facet of adhesion bonds is the locus of the proposed action or the scale to which the adhesive and adherend interact. Table 1.1 shows a scale of action for each mechanism, which is intended to aid in the understanding of these mechanisms. Of course, adhesive—adherend interactions always take place at the molecular level, discussed later in the chapter.

Table 1.1 Theories of Adhesion

Traditional	**Recent**	**Scale of Action**
Mechanical interlocking	Mechanical interlocking	Microscopic
Electrostatic	Electrostatic	Macroscopic
Diffusion	Diffusion	Molecular
Adsorption/surface reaction	Wettability	Molecular
	Chemical bonding	Atomic
	Weak boundary layer	Molecular

The *microscopic* parameter of interest in *mechanical interlocking* is the contact surface of the adhesive and the adherend. The specific surface area (i.e., surface area per unit weight) of the adherend is an example of one such measure. Surface roughness is the means by which interlocking is thought to work. It can be detected by optical or electron microscopy. In the *electrostatic* mechanism, the surface charge is the *macroscopic* factor of interest. The charge in question is similar to that produced in a glass rod after rubbing it with a wool cloth. *Diffusion* and *wettability* involve molecular and atomic scale interactions, respectively.

Readers who wish to gain an in-depth understanding of the interaction forces, adhesion mechanism, and thermodynamics of adhesion are recommended to consult *Fundamentals of Adhesion*, edited by Lieng-Huang Lee.[11] This reference provides a qualitative and quantitative treatment of adhesion, complete with derivation of force interaction equations.

1.6.1 Mechanical Theory

According to this theory, adhesion occurs by the penetration of adhesives into pores, cavities, and other surface irregularities on the surface of the substrate. The adhesive displaces the trapped air at the interface. Thus that an adhesive penetrating into the surface roughness of two adherends can bond them is concluded. A positive contribution to the adhesive bond strength results from the "mechanical interlocking" of the adhesive and the adherends. Adhesives frequently form stronger bonds to porous abraded surfaces than they do to smooth surfaces. However, this theory is not universally applicable, for good adhesion also occurs between smooth surfaces.[12]

Enhanced adhesion after abrading the surface of an adherend may be due to (1) mechanical interlocking, (2) formation of a clean surface, (3) formation of a highly reactive surface, and (4) an increase in contact surface area. It is believed that changes in physical and chemical properties of the adherend surface produce an increase in adhesive strength.[13] It can be debated whether mechanical interlocking is responsible for strong bonds or an increase in the adhesive contact surface enhances other mechanisms. Thorough wetting and extensive chemical bonding are expected consequences of increased contact surface area.

There are supportive data in the literature that relates joint strength and bond durability to increased surface roughness. There are also observations indicating, contrarily, that increased roughness can lower joint strength.[14]

1.6.2 Electrostatic (Electronic) Theory

This theory proposes that adhesion takes place due to electrostatic effects between the adhesive and the adherend.[15–18] An electron transfer is supposed to take place between the adhesive and the adherend as a result of unlike electronic band structures. Electrostatic forces in the form of an electrical double layer are thus formed at the adhesive–adherend interface. These forces account for the resistance to separation. This theory gains support by the fact that electrical discharges have been noticed when an adhesive is peeled from a substrate.[13]

The electrostatic mechanism is a plausible explanation for polymer–metal adhesion bonds. The contribution of the electronic mechanism in nonmetallic systems to adhesion has been calculated and found to be small when compared to that of chemical bonding.[19,20]

1.6.3 Diffusion Theory

This theory suggests that adhesion is developed through the interdiffusion of molecules in between the adhesive and the adherend. The diffusion theory is primarily applicable when both the adhesive and the adherend are polymers with relatively long-chain molecules capable of movement. The nature of materials and bonding conditions will influence whether and to what extent diffusion occurs. The diffuse interfacial (interphase) layer typically has a thickness in the range of 10−1,000 Å (1−100 nm). Solvent cementing or heat welding of thermoplastics occurs due to diffusion of molecules.[13]

No stress concentration is present at the interface because no discontinuity exists in the physical properties. Cohesive energy density (CED, Eqn (1.1)) can be used to interpret diffusion bonding, as defined by Eqn (1.2). Bond strength is maximized when solubility parameters are matched between the adhesive and the adherend.

$$\mathrm{CED} = \frac{E_{\mathrm{coh}}}{V} \tag{1.1}$$

$$\delta = \sqrt{\frac{E_{\mathrm{coh}}}{V}} \tag{1.2}$$

E_{coh} is the amount of energy required to separate the molecules to an infinite distance, V is the molar volume, and δ is the solubility parameter.

A relevant example is the adhesion of polyethylene and polypropylene to a butyl rubber. The adhesive bond is weak when two polymers are bonded at temperatures below the melting point of the polyolefin. Bond strength increases sharply when the adhesion process takes place above the melting temperature of polyethylene (135 °C) and polypropylene (175 °C). Figure 1.1 illustrates the bond strength (peel strength) as a function of bonding temperature. Inferentially, interdiffusion of polyolefins and butyl rubber increases at elevated temperatures, generating higher bond strength.

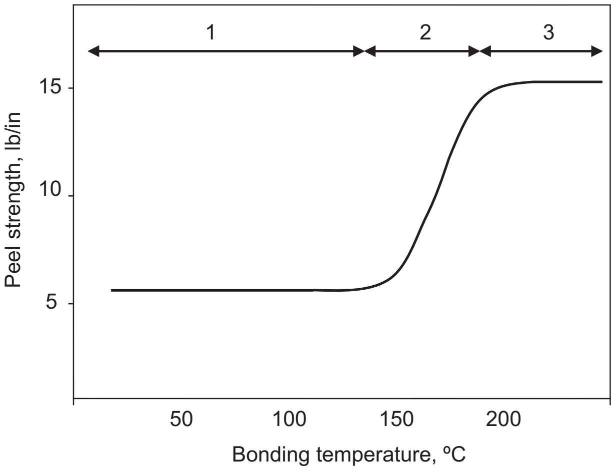

Figure 1.1 Peel strength of polypropylene and butyl rubber vs. bonding temperature: (1) adhesive failure; (2) adhesive/cohesive failure; (3) cohesive failure.[2]

1.6.4 Wetting Theory

This theory proposes that adhesion results from molecular contact between two materials and the surface forces that develop. The first step in bond formation is to develop interfacial forces between the adhesive and the substrates. The process of establishing continuous contact between the adhesive and the adherend is called *wetting*. For an adhesive to wet a solid surface, the adhesive requires a lower surface tension than the critical surface tension of the solid. This is precisely the reason for surface treatment of plastics, increasing their surface energy and polarity.

Van der Waals forces are extremely sensitive to the distance (r) between molecules, decreasing by the inverse of the seventh power ($1/r^7$) of the distance between two molecules and the cubic power of the distance between two adherends. These forces are normally too small to account for the adhesive bond strength in most cases.

Figure 1.2 illustrates complete and incomplete wetting of an adhesive spreading over a surface. Good wetting results when the adhesive flows into the valleys and crevices on the substrate surface. Poor wetting results when the adhesive bridges over the valley and results in a reduction of the actual contact area between the adhesive and the adherend, resulting in a lower overall joint strength.[13] Incomplete wetting generates interfacial defects, thereby reducing the adhesive bond strength. Complete wetting achieves the highest bond strength.

Most organic adhesives readily wet metal adherends. On the other hand, many solid organic substrates have surface tensions lower than those of common adhesives. Criteria for good wetting require adhesives to have a lower surface tension than that of the substrate, which explains, in part, why organic adhesives such as epoxies have excellent adhesion to metals but offer weak adhesion on untreated

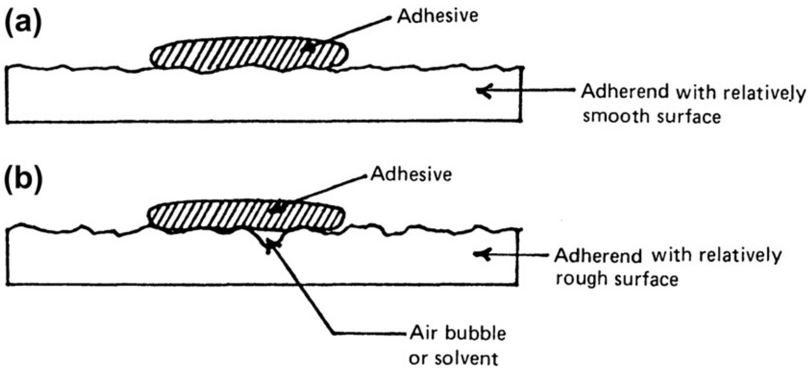

Figure 1.2 Examples of (a) good and (b) poor wetting by an adhesive spreading across a surface.[13]

polymeric substrates such as polyethylene, polypropylene, and fluoroplastics.[13] The surface energy of plastic substrates can be increased by various treatment techniques to allow wetting.

1.6.5 Chemical Bonding

This mechanism attributes the formation of an adhesion bond to surface chemical forces. Hydrogen, covalent, and ionic bonds formed between the adhesive and the adherends are stronger than the dispersion attractive forces. Table 1.2 lists examples of these forces and their magnitudes. In general, there are four types of interactions that transpire during chemical bonding: *covalent bonds*, *hydrogen bonds*, *Lifshitz–van der Waals forces*, and *acid–base* interactions. The exact nature of the interactions for a given adhesive bond depends on the chemical composition of the interface.

Covalent and ionic bonds (Table 1.2) are examples of *chemical bonding* that provide much higher adhesion values than those provided by secondary forces. Secondary valence bonding is based on the weaker physical forces exemplified by hydrogen bonds. These forces are more prevalent in materials that contain polar groups, such as carboxylic acid groups, than in nonpolar materials, such as polyolefins. The interactions that hold the adhesive and the adherends together may also receive contributions from mechanical interlocking, diffusion, or electrostatic mechanisms.

Table 1.2 Examples of Energies of Lifshitz–van der Waals Interactions and Chemical Bonds

Type	Example	*E* (kJ/mol)
Covalent	C–C	350
Ion–ion	$Na^+ \ldots Cl^-$	450
Ion–dipole	$Na^+ \ldots CF_3H$	33
Dipole–dipole	$CF_3H \ldots CF_3H$	2
London dispersion	$CF_4 \ldots CF_4$	2
Hydrogen bonding	$H_2O \ldots H_2O$	24

The definitions of intermolecular interactions are listed below:

Dipole (polar molecule): A molecule whose charge distribution can be represented by a center of positive charge and a center of negative charge, which do not coincide

Dipole–dipole forces: Intermolecular forces resulting from the tendency of polar molecules to align themselves such that the positive end of one molecule is near the negative end of another

Hydrogen bonding: A special type of dipole–dipole interaction that occurs when a hydrogen atom that is bonded to a small, highly electronegative atom (most commonly F, O, N, or S) is attracted to the lone electron pairs of another molecule

London dispersion forces (dispersion forces): Intermolecular forces resulting from the small, instantaneous dipoles (induced dipoles) that occur because of the varying positions of the electrons during their motion about the nuclei

Polarizability is defined as the ease with which the electron cloud of an atom or molecule is distorted. In general, polarizability increases with the size of an atom and the number of electrons on an atom. The importance of London dispersion forces increases with the atom size and number of electrons

Covalent chemical bonds can form across the interface and are likely to occur in cross-linked adhesives and thermoset coatings. This type of bond is usually the strongest and most durable. However, it requires that mutually reactive chemical groups exist. Some surfaces, such as previously coated surfaces, wood, composites, and some plastics, contain various functional groups that under appropriate conditions can produce chemical bonds with the adhesive material. There are ways to intentionally generate these conditions, such as by surface treatment of plastics with techniques like corona or flame treatment.

Organosilanes are widely used as primers on glass fibers to promote the adhesion between the resin and the glass in fiberglass-reinforced plastics. They are also used as primers or integral blends to promote adhesion of resins to minerals, metals, and plastics. Essentially, during application, silanol groups are produced, which then react with the silanol groups on the glass surface or possibly with other metal oxide groups to form strong ether linkages. Coatings containing reactive functional groups, such as hydroxyl or carboxyl moieties, tend to adhere more tenaciously to substrates containing similar groups. Chemical bonding may also occur when a substrate contains reactive hydroxyl groups, which may react with the isocyanate groups from the incoming coating in thermoset polyurethane coatings.

Most likely, chemical bonding accounts for the strong adhesion between an epoxy coating and a substrate with a cellulose interface. The epoxy groups of an epoxy resin react with the hydroxyl groups of cellulose at the interface.

1.6.5.1 Acid−Base Theory

A special type of interaction, the acid−base interaction is a fairly recent discovery. It is based on the chemical concept of a Lewis acid and base, which is briefly described. The acid/base definition was proposed separately by J. N. Bronsted and G. N. Lewis. Restatement of these definitions by Lewis in 1938 led to their popularity and acceptance. The Lewis definitions are: "an acid is a substance which can accept an electron pair from a base; a base is a substance which can donate an electron pair."[21] By this definition, every cation is an acid in addition to chemical compounds such as BF_3 and SiO_2. Conversely, anions and compounds like NH_3, PH_3, and $C_6H_5CH_2NH_2$ are bases. According to the acid−base theory, adhesion results from the polar attraction of Lewis acids and bases (i.e., electron-poor and electron-rich elements) at the interface. This theory is attributed to the work by Fowkes et al.,[22−25] Gutmann,[26] and Bolger and Michaels.[27]

In BF_3, the higher electronegativity of fluorine atoms preferentially displaces the shared electrons away from the boron atom. Thus, a bipolar molecule is created that has positive charge on the boron side and negative charge on the fluorine side. On the other hand, NH_3, by a similar analogy, has a negative nitrogen end that renders it a Lewis base. Naturally, the positive boron end of BH_3 and negative nitrogen end of NH_3 interact.

A special case of acid−base interaction is hydrogen bonding, such as among water molecules that exhibit both acidic and basic tendencies. Table 1.2 shows that the hydrogen bond strength, while substantially less than ionic and covalent bond energies, is one of the most significant among the secondary interactions. The reader can refer to inorganic chemistry texts[28,29] to learn about Lewis acids and bases and their chemical reactions. In summary, the interactions between compounds capable of electron donation and acceptance form the foundation of the acid−base theory of adhesion.

1.6.6 Weak Boundary Layer Theory

This theory was first described by Bikerman. It states that bond failure at the interface is caused by either a cohesive break or a weak boundary layer.[30] Weak boundary layers can originate from the adhesive, the adherend, the environment, or a combination of any of these factors.

Weak boundary layers can occur in the adhesive or adherend if an impurity concentrates near the bonding surface and forms a weak attachment to the substrate. When failure takes place, it is the weak boundary layer that fails, although failure appears to take place at the adhesive−adherend interface.

Polyethylene and metal oxides are examples of two materials that may inherently contain weak boundary layers. Polyethylene has a weak, low-molecular weight constituent that is evenly distributed throughout the polymer. This weak boundary layer is present at the interface and contributes to low failing stress when polyethylene is used as an adhesive or an adherend. Some metal oxides are weakly attached to their base metals. Failure of adhesive joints made with these materials occurs cohesively within the oxide. Certain oxides, such as aluminum oxide, are very strong and do not significantly impair joint strength. Weak boundary layers, such as those found in polyethylene and metal oxides, can be removed or strengthened by various surface treatments. Weak boundary layers formed from the bonding environment, generally air, are very common. When the adhesive does not wet the substrate, as shown in Figure 1.2, a weak boundary layer (air) is trapped at the interface, causing a reduction in joint strength.[13,31]

1.7 Definition of Failure Modes

A hypothetical adhesion bond is shown in Figure 1.3. Assume the bond is tested in the tensile mode, during which the two adherends are pulled apart in a direction perpendicular to the bond. There are different possibilities for the occurrence of failure. The surfaces involved in bond failure are called the *locus* of failure.

If the bond failure occurs between the adhesive layer and one of the adherends, it is called *adhesive failure* (Figure 1.3a). A failure in which the separation occurs in such a manner that both adherend surfaces remain covered with the adhesive, is called *cohesive failure* in the *adhesive layer* (Figure 1.3b). Sometimes, the adhesive bond is so strong that the failure occurs in one of the adherends away from the bond. This is called a *cohesive failure* in the *adherend* (Figure 1.3c). Bond failures often involve more than one failure mode and are ascribed as a *percentage* to cohesive or adhesive failure. This percentage is calculated based on the fraction of the area of the contact surface that has failed cohesively or adhesively.

It is important to determine the exact mode(s) of bond failure when a problem occurs. Determination of the failure mode allows action to be taken to correct the true cause and to save time and money.

Tables 1.3–1.5 show the result of analyses of several bonds between a substrate and a polyvinyl fluoride film using an acrylic adhesive. All surfaces were analyzed by electron spectroscopy for chemical analysis (ESCA). ESCA yields chemical analysis of organic surfaces in atomic percentage, with the exclusion of hydrogen, which is undetectable by this technique. To determine the type of bond failure, ESCA results for the failed surfaces are compared with those of the adhesive and the polyvinyl fluoride film.

In a pure cohesive failure, the two surfaces involved should have virtually identical chemical compositions, which is nearly the case in Tables 1.3 and 1.4. In a 100% adhesive failure, one of the surfaces should have the same chemical composition as the adherend and the other the same as the adhesive. The examples presented in Tables 1.3 and 1.4 illustrate cohesive failure cases for polyvinyl fluoride (adherend) and the adhesive. Table 1.5 gives an example of an adhesive failure. One can see from the chemical composition that the adhesive and polyvinyl fluoride surfaces have been separated in a "clean" manner.

1.8 Mechanisms of Bond Failure

Adhesive joints may fail adhesively or cohesively. Adhesive failure is an interfacial bond failure between the adhesive and the adherend. Cohesive failure occurs when a fracture allows a layer of adhesive to remain on both surfaces. When the adherend fails before the adhesive, it is known as a cohesive failure of the substrate. Various modes of failure are shown in Figure 1.3. Cohesive failure within the adhesive or one of the adherends is the ideal type of failure because with this type of failure the maximum strength of the materials in the joint has been reached. In analyzing an adhesive joint that

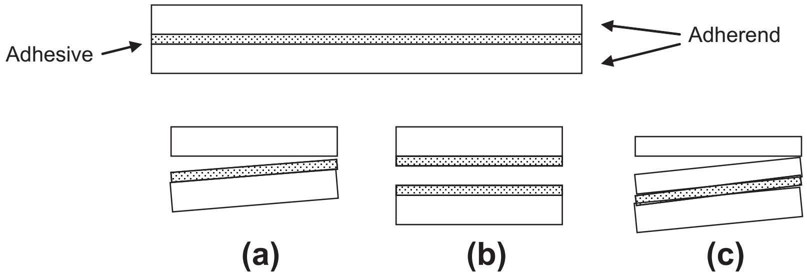

Figure 1.3 Schematics of adhesive bond failure modes: (a) adhesive failure; (b) cohesive failure in the adhesive layer; (c) cohesive failure in the adherend.

Table 1.3 Surface Chemical Analysis (ESCA) in a Cohesive Failure of Adhesive Bond

		Atomic Concentration (%)			
	F	**O**	**N**	**C**	**Si**
As-is adhesive (control)	nd	26.0	2.1	71.6	nd
As-is film (control)	29.3	6.6	nd	64.4	nd
Polyvinyl fluoride film facing the substrate	nd	24.9	2.5	72.6	nd
Substrate facing the polyvinyl fluoride film	nd	25.0	2.1	72.9	nd

nd, not detectable.

Data were provided by Dr. James J. Schmidt at the DuPont Company, 2003.

Table 1.4 Surface Chemical Analysis (ESCA) in a Cohesive Failure of Polyvinyl Fluoride

		Atomic Concentration (%)			
	F	**O**	**N**	**C**	**Si**
As-is adhesive (control)	nd	26.0	2.1	71.6	nd
As-is film (control)	29.3	6.6	nd	64.4	nd
Polyvinyl fluoride film facing the substrate	31.0	4.0	nd	63.2	1.7
Substrate facing the polyvinyl fluoride film	30.0	5.4	nd	62.6	2.0

nd, not detectable.

Data were provided by Dr. James J. Schmidt at the DuPont Company, 2003.

Table 1.5 Surface Chemical Analysis (ESCA) in a Adhesive Failure of Polyvinyl Fluoride

		Atomic Concentration (%)			
	F	**O**	**N**	**C**	**Si**
As-is adhesive (control)	nd	26.0	2.1	71.6	nd
As-is film (control)	29.3	6.6	nd	64.4	nd
Polyvinyl fluoride film facing the substrate	31.6	2.1	nd	66.4	nd
Substrate facing the polyvinyl fluoride film	nd	26.4	3.2	70.5	nd

nd, not detectable.

Data were provided by Dr. James J. Schmidt at the DuPont Company, 2003.

has been tested to destruction, the mode of failure is often expressed as a percentage cohesive or adhesive failure, as shown in Figure 1.3. The ideal failure is a 100% cohesive failure in the adhesion layer.

The failure mode should not be used as the only criterion for a useful joint.[3] Some adhesive–adherend combinations may fail adhesively, but exhibit greater strength than a similar joint bonded with a weaker adhesive that fails cohesively. The ultimate strength of a joint is a more important criterion than the mode of joint failure. An analysis of failure mode, nevertheless, can be an extremely useful tool in determining whether the failure was due to a weak boundary layer or due to improper surface preparation.

The exact cause of premature adhesive failure is very difficult to determine. If the adhesive does not wet the surface of the substrate completely, the bond strength is certain to be less than maximal. Internal stresses occur in adhesive joints because of a natural tendency of the adhesive to shrink during setting, and because of differences in physical properties of adhesive and substrate. The coefficient of thermal expansion of adhesive and adherend should be as close as possible to minimize the stresses that may develop during thermal cycling or after cooling from an elevated temperature cure. Fillers are often used to modify the thermal expansion characteristics of adhesives and limit internal stresses. Another way to accommodate these stresses is to use relatively elastic adhesives.

The types of stress acting on completed bonds, their orientation to the adhesive, and the rates at which they are applied are important factors in determining the durability of the bond. Sustained loads can cause premature failure in service, even though similar unloaded joints may exhibit adequate strength when tested after aging. Some adhesives break down rapidly under dead load, especially after exposure to heat or moisture. Most adhesives have poor resistance to peel or cleavage loads. A number of adhesives are sensitive to the rate at which the joint is stressed. Rigid, brittle adhesives sometimes have excellent tensile or shear strength but have very poor impact strength. Operating environmental factors are capable of degrading an adhesive joint in various ways. If more than one environmental factor (e.g., heat and moisture) is acting on the sample, their combined effect can be expected to produce a synergistic result of reducing adhesive strength. Whenever possible, candidate adhesive joints should be evaluated under simulated operating loads in the actual environment the joint is supposed to encounter.

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2 Introduction to Surface Preparation and Adhesion

Sina Ebnesajjad

2.1 Definition of Surface Preparation, Adhesives, and Adhesive Bonding

Surface preparation or *treatment* is defined as one or a series of operations including cleaning, removal of loose material, and physical and/or chemical modification of a surface to which an adhesive is applied for the purpose of bonding. In plastics bonding, surface preparation is aimed at increasing the surface polarity, improving surface wettability, and creating sites for adhesive bonding. Metal surfaces are typically covered with oxide layers, rendering the surface highly polar and fit for good adhesive bonding. Surface preparation is intended to enhance the bonding strength to metal surfaces. But the main reason for preparing a metal surface is to improve the durability of the bond, especially when exposed to humidity.

An adhesive is a material that is applied to the surfaces of articles to permanently join the articles by a bonding process. An adhesive is a substance capable of forming bonds to each of the two or more parts of which the final object consists.[1] A feature of adhesives is the relatively small quantities (also thickness) that are required relative to the weight of the final objects.

Adhesion is difficult to define and an entirely satisfactory definition has not been found. The following definition has been proposed by Wu:[2]

> Adhesion *refers to the state in which two dissimilar bodies are held together by intimate interfacial contact such that mechanical force or work can be transferred across the interface. There is unifying theory of adhesion that relates the physical-chemical properties of materials to the actual physical strength of an adhesive bond.*[3] *The interfacial forces holding the two phases together may arise from van der Waals forces, chemical bonding, or electrostatic attraction. The mechanical strength of the system is determined not only by the interfacial forces, but also by the mechanical properties of the interfacial zone and the two bulk phases.*

The primary function of adhesives is to join parts together. Adhesives accomplish this goal by transmitting stresses from one member to another in a manner that distributes the stresses much more uniformly than can be achieved with mechanical fasteners. Adhesive bonding often provides structures that are mechanically equivalent to or stronger than conventional assemblies, at lower cost and weight. In mechanical fastening, the strength of the structure is limited to that of the areas in contact with the fasteners.[4] It is not unusual to obtain adhesive bonds that are stronger than the strength of the adherends (surfaces that are to be bonded together).

2.2 Introduction to Surface Treatment

There are a number of reasons for surface treatment of materials. The main reasons for applying surface treatments prior to bonding are as follows:

(1) To remove or prevent the later formation of a weak layer on the surface of the substrate

(2) To maximize the degree of molecular interaction between the adhesive or primer and the substrate surface

(3) To optimize the adhesion forces that develop across the interfaces to ensure sufficient initial joint strength and during the service life of the bond

(4) To create specific surface microstructure on the substrate

Normally, optimum surface energy and structure is achieved by chemical surface treatment. The chemical composition and the morphology of the surface are changed, so that the surface energy of the substrate is maximized for adhesion. Chemical

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treatments also increase the chances that hydrogen, dipole, van der Waals ionic and/or covalent bonding can form at the substrate/adhesive interface. A quick and dirty test for adequate chemical treatment is to place a bead of water on the surface of the part and note if the water spreads. If so, the contact angle it forms with the surface is very small. There are special fluids called *dyne* liquids that bracket the numeric value of the surface energy of a material surface and fairly precisely.

Alternative methods to chemical treatment (with similar surface changes) include plasma, corona, and flame treatment methods. These act in ways similar to chemical treatments, with less hazardous waste generation. Mechanical abrasion is another means of surface preparation. This method of surface preparation is superior to other methods because of the simplicity of the process and significantly less waste generation. Mechanical abrasion works because it provides a clean surface and increases the contact area between the substrate and adhesive. In ordinary gluing of objects together, these methods are not needed because optimal adhesion is not always necessary. When strong adhesion bond is required, the minimum surface preparation required is cleaning and removing of dirt and grease from the contact surfaces.[5]

More recently, novel techniques have been developed to treat the surfaces at the nano scale. For example, the interfacial adhesion energy between the lithography resist and the substrate is very important in nanoimprinting because of problems with the resist sticking or pulling off during separation of the mold from the substrate. Substrate surface treatments with a self-assembled monolayer or oxygen plasma provide good adhesion between a resist coating and a silica substrate.[6]

2.2.1 Degreasing

Removal of all traces of oily contamination and grease from the substrate surfaces to be bonded is vital to the formation of strong adhesive bonds. Different methods, which should be carried out even though the contact surfaces may appear clean, are available for degreasing.

A part may be submerged in trichloroethylene or perchloroethylene vapors even though the vapors are pure uncontaminated solvent. As the vapors condense on the part, contaminants are dissolved and drip off the part with the condensed solvent. When a vapor degreasing unit is not available, the joint surfaces can be wiped with a cloth soaked with trichloroethylene, followed by complete evaporation from the joint surfaces. These solvents are toxic in both liquid and vapor form, requiring the work environment to be well ventilated.

Another technique consists of scrubbing the joint surfaces in a solution of a detergent. Metals can be immersed in or sprayed with an alkaline degreasing agent, followed by rinsing with clean hot water and thoroughly drying by hot air, steam, or ambient air.

Ultrasonic degreasing is known to produce excellent results for small components. Trichloroethylene, acetone, methylene chloride, tetrachloroethylene, and so on are among good solvents for ultrasonic degreasing. Alcohol, gasoline, and paint thinners are not recommended. An effective solvent is 1,1,1-trichloroethane because of its low toxicity and flammability. To verify the cleanliness of a surface that has been degreased, water or dyne liquids are used. If a drop of water forms a film of the surface, then it is free from contamination. If a drop retains its shape, degreasing of the surface must be repeated.

2.2.2 Abrasion

Abraded rough surfaces usually form stronger adhesive joints than do highly polished surfaces, primarily due to larger contact surfaces. A properly abraded surface should not contain any smooth or polished areas. Abrasion treatment should be followed by a second degreasing treatment to ensure the removal of loose particles. Grit-blasting removes surface deposits such as tarnish, rust, or mill scale from metal surfaces. If grit-blasting equipment is not available, or the metal is too thin to withstand blast treatment, clean the joint surfaces with a wire-brush, emery cloth, or sandpaper. Painted surfaces should be stripped down to substrate with a stripper prior to preparation, otherwise the adhesive joint will not be strong.

2.2.3 Chemical Treatment

Degreasing alone, or degreasing followed by abrasion and further degreasing, is sufficient for many adhesive bonds. To obtain maximum strength, reproducibility and resistance to deterioration a chemical or electrolytic pretreatment is required. Careful attention should be paid in the preparation of chemical solutions to assure correct proportioning of components required for formation of adequate bond strengths. Exposure time in the solution application is critical. If the application is too short, it does not sufficiently activate the surfaces. Overexposure to the solution builds up a layer of chemical reaction products that may interfere with the adhesion bond formation.

Some of the surface preparation treatments use chemicals that have serious health effects, unless used with extreme caution. As with all chemicals, consult the Material Safety Data Sheet (MSDS) before using. Organic solvents must be handled with care because their use may raise a fire and/or toxic hazard. Read the material safety data sheet before handling. Acids and sodium hydroxide are aggressive (corrosive) chemicals. Always wear protective clothing and a face shield when using. Read material safety data sheets of all materials before using. Never add water directly to an acid; always add acid to water slowly.

2.3 Requirements of a Good Adhesive Bond

The objective of any surface treatment method is to enhance the adhesive bond strength and durability when it is exposed to environmental factors of service. There are, however, other considerations for the formation of an adequate adhesive bond. The basic requirements for a good adhesive bond are the following[7]:

- Proper choice of adhesive
- Good joint design
- Cleanliness of surfaces
- Wetting of *adherends* (surfaces that are to be bonded together).
- Proper adhesive bonding process (solidification and cure)

2.3.1 Proper Choice of Adhesive

There are numerous choices available for bonding materials. Selection of the adhesive type and form depends on the nature of adherends, performance requirements of the end use, and the adhesive bonding process.

2.3.2 Good Joint Design

Imparting strength to a joint by design is possible.[8] A carefully designed joint can yield a stronger bond than one not designed carefully, by combining the advantages of the mechanical design with adhesive bond strength to meet the end use requirements of the bonded part.

2.3.3 Cleanliness

To obtain a good adhesive bond, starting with a clean adherend surface is essential. Foreign materials such as dirt, oil, moisture, and weak-oxide layers must be removed, or else the adhesive will bond to these weak-boundary layers rather than to the substrate. There are various surface treatments that may remove or strengthen the weak-boundary layers. A number of such treatments will be discussed in Chapters 5−7. These treatments generally involve physical or chemical processes or a combination of both.[7,9]

2.3.4 Wetting

Wetting is the displacement of air (or other gases) on the surface of adherend by a liquid phase. The result of good wetting is greater contact area between the adherends and the adhesive over which the forces of adhesion may act.[7,10] Surface treatment techniques are applied to modify the adherend surface to increase wettability.

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3 Surface Tension and Its Measurement

Sina Ebnesajjad

3.1 Introduction

Surface science is an important branch of physical organic chemistry that studies the behavior and characteristics of molecules at or near a surface or interface. The interface can form between solids, liquids, gases, and combinations of these states. Complex apparatus has been developed to identify and quantify surfaces and interfaces. Polymer surfaces are of special interest in industrial and biological applications; examples of the latter include dental implants and body part prosthetic devices. *Modification* of surfaces of these devices allows formation of controlled interfaces to achieve characteristics such as bondability and compatibility.

Adhesion is an interfacial phenomenon that occurs at the interfaces of adherends and adhesives. This is the fact underlying the macroscopic process of joining parts using adhesives. An understanding of the forces that develop the interfaces is helpful to the selection of the right adhesive, proper surface treatment of adherends, and effective and economical processes to form bonds. This chapter is devoted to the discussion of the thermodynamic principles and work of adhesion that quantitatively characterize surfaces of materials.

3.2 What is an Interface?

Two solid or liquid phases in contact have atoms/molecules on both sides of an imaginary plane called the *interface*. The interfacial particles differ energetically from those in the bulk of each phase due to being on the boundary of the respective phase and interacting with the particles of the other phase. The composition and energy vary continuously from one phase to the other through the interface. This region has a finite thickness, usually less than 0.1 μm.[1,2]

3.3 Surface Tension

The molecules of a liquid are held together by attraction forces. The sum of all attractive forces on any molecule present in the bulk of a liquid averages zero. The net force (also known as *cohesion* force) on a surface molecule is a nonzero quantity in the direction toward the bulk (Fig. 3.1). This is the force that must be counteracted to increase the surface area; the energy consumed by this process is called *surface energy*. The unbalanced forces on the interface cause it to contract to the minimum. Water droplets are spherical because a sphere has minimum surface area for a given volume among all geometric shapes. Although surface tension and surface free energy of a liquid are equal, the same is not true for a solid surface.

Surface tension is defined as the work required to increase the area of a surface isothermally and reversibly by unit amount. Surface tension (γ) is expressed as surface energy per unit area and alternatively as force per unit length. Surface tension of liquids can be measured directly and expressed in the units of work or energy per unit area (erg/cm^2), which is then simplified (erg/cm^2 = dyne.cm/cm^2 =

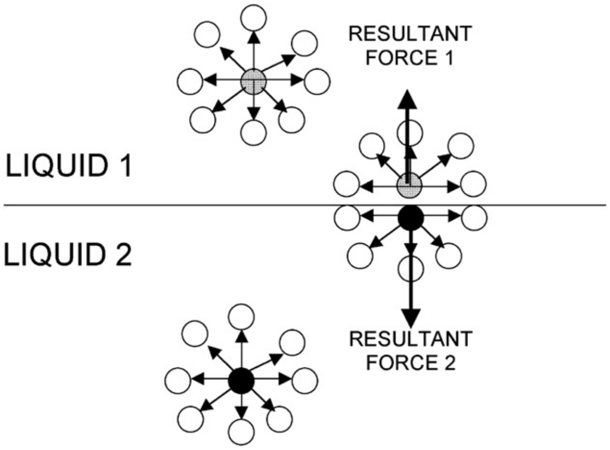

Figure 3.1 Liquid–liquid interface and balance of forces on molecules of liquids.

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dyne/cm) to dyne/cm. There are a number of methods for measuring surface tension of liquids, including ones devised to make measurements for unusual liquids such as molten metal and ionic liquids.[3–5] The challenge has been to find methods to determine the surface tension of solids surfaces.[6]

Surface tension of polymers can be divided into two components: *polar* (γ^p) and *dispersion* (γ^d), to account for the type of attraction forces at the interfaces.[7] Chemical constitution of the surface determines the relative contribution of each component to the surface tension. Polar component is comprised of various polar molecular interactions, including hydrogen bonding, dipole energy, and induction energy, whereas the dispersion component arises from London dispersion attractions. The attractive forces (van der Waals and London dispersion) are additive, which results in the surface tension components being additive: $\gamma = \gamma^p + \gamma^d$.

3.4 Surface Free Energy

A hypothetical example is used to describe the concept of surface free energy. Suppose a box with a sliding cover is filled with a liquid (Fig. 3.2). The sliding cover is assumed to have no interfacial tension with the liquid. If the cover is slid back to uncover a surface area of dA, the necessary reversible work will be (γ dA). For a pure substance, the increase in the free energy of the system at constant temperature and pressure is defined by Eqn (3.1).

$$dG = \gamma \, dA \tag{3.1}$$

The total free energy of the system is comprised of the energy of the bulk liquid and the surface liquid. The latter is equal to the surface free energy per unit area (G_s) multiplied by the surface area as shown in Eqn (3.2). Combining Eqns (3.1) and (3.2) results in Eqn (3.3), which illustrates that free surface energy of a pure substance is equal to its surface tension.

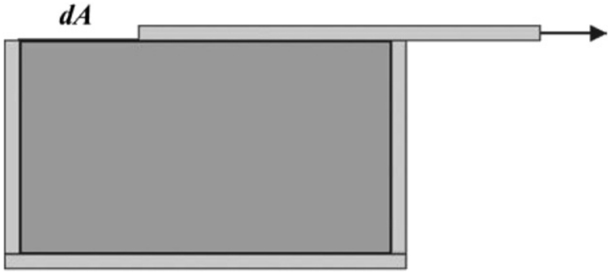

Figure 3.2 An "ideal liquid" box.

$$dG = G_s \, dA \tag{3.2}$$

$$G_s = \left(\frac{dG}{dA}\right)_{T,P} = \gamma \tag{3.3}$$

In a reversible system, the heat (q) associated with it can be related to entropy (S) or *surface entropy* (Eqn (3.4)), where S_s represents surface entropy per unit area. Equation (3.5) is a thermodynamic relationship applied to the liquid surface in which T represents absolute temperature. Equation (3.6) is obtained by substituting for G_s from Eqn (3.3).

$$dq = T \, dS = T \, S_s \, dA \tag{3.4}$$

$$\left(\frac{dG_S}{dT}\right)_P = -S_S \tag{3.5}$$

$$\frac{d\gamma}{dT} = -S_S \tag{3.6}$$

The total surface energy (Eqn (3.7)) can be calculated by applying the enthalpy relationship with Gibbs free energy and entropy to the liquid surface.

$$H_S = E_S = G_S + TS_S \tag{3.7}$$

Equation (3.8) is the result of substitution from Eqn 3.6 into 3.7.

$$E_S = G_S - T\frac{d\gamma}{dT} \tag{3.8}$$

Surface tension of most liquids decreases with increasing temperature in a linear manner. A well-known expression (Eqn (3.9)), defining the relationship between temperature and surface tension, has been attributed to EôTVôS.[8]

$$\gamma V^{2/3} = k(T_c - T) \tag{3.9}$$

V is the molar volume, k has the same value for most liquids (2.1 erg/K), T_c is the critical temperature of the liquid, and T is the liquid temperature. The expectation is that surface tension of a liquid will approach zero at its critical temperature. There are other equations that express the behavior of liquids as a function of temperature.[1,7]

Techniques have also been developed for estimation of the free surface energy of polymers. For example, a method for measuring the surface energy of solids and resolving the surface energy into contributions from dispersion and dipole-hydrogen bonding forces has been developed. It is based on the measurement of contact angles with water and methylene iodide. Good agreement has been obtained with the more laborious γ_c (critical surface tension method). Evidence for a finite value of liquid−solid interfacial tension at zero contact angle is presented. The method is especially applicable for the surface characterization of polymers.[9]

3.4.1 Surface Energy of Solids

A solid is defined as a material that is rigid and resists stress. A solid surface may be characterized by its surface free energy and surface energy. Surface energy (tension) of a solid cannot be measured in a similar manner to that of a liquid due to the difficulty caused by the reversible formation of its surface. The methods for the determination of surface energy of solids are described in this chapter.

Solid material surfaces can be divided into two categories of high and low surface energy.[10] High surface energy materials include metals and inorganic compounds such as oxides, silicates, silica, diamond, and nitrides. Surface tension of high-energy materials is 200−500 dynes/cm. Low-energy materials are mainly comprised of organic compounds including polymers with critical surface tension <100 dynes. Polymer surfaces have themselves been classified[11] as being of low, medium, and high surface energy. Low surface energy solids have critical surface tension in the range of 10−30 dynes/cm, medium energy from 30 to 40 dynes/cm, and high energy >40 dynes/cm.

Low-energy materials, such as oils, are spontaneously absorbed by the high-energy surfaces because of the reduction in the free surface energy of the system. This means that a clean, high-energy surface exposed to the normal ambient environment will not remain clean for long because of the absorption from the environment of water and organic contaminants thereon. Accordingly, a surface cleaning operation is included in many processes just before the actual application of the adhesive or coating to prevent prolonged exposure of the cleaned substrate (adherend) to the factory environment. Another approach is to apply a protective film to the clean surface, which is removed immediately prior to the adhesive coating step.

3.4.2 Work of Adhesion

The work of adhesion is defined as the reversible thermodynamic work that is needed to separate the interface from the equilibrium state of two phases to a separation distance of infinity. Equation (3.10) shows the work of adhesion for a liquid−solid combination. This definition is attributed to the French scientist A. Dupre.

$$W_a = \gamma_L + \gamma_S - \gamma_{SL} \tag{3.10}$$

γ_L is the surface energy (tension) of the liquid phase, γ_S is the surface energy of the solid phase, γ_{SL} is the interfacial surface tension, and W_a is the work of adhesion. A rise in the interfacial attraction results in an increase in the work of adhesion. Equation (3.10) can be rewritten to determine the work of cohesion (W_c) when the two phases are identical and no interface is present, as shown in Eqn (3.11) for a solid phase.

$$W_c =^2 \gamma_S \tag{3.11}$$

3.5 Contact Angle (Young's Equation)

Most liquids wet solid surfaces to some extent and exhibit a contact angle. A contact angle in a static system can be measured at equilibrium. Figure 3.3 illustrates the contact angle in an ideal system where the solid surface is homogeneous, smooth, planar, and rigid. The interfacial tensions designated as γ represent equilibrium values at the point where three phases intersect. The subscripts L, S, and V denote liquid, solid, and vapor phases, respectively. γ^o is used to indicate that the solid surface must be in equilibrium with the liquid's saturated vapor; that is, a film of the liquid is absorbed on the solid surface. Young[12] described Eqn (3.12) without presenting a proof. It has since been proven by different researchers.[13−15]

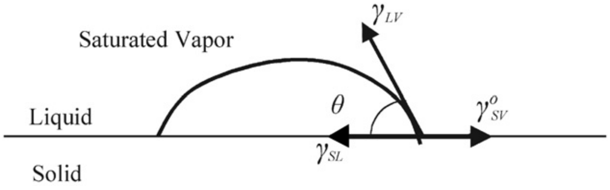

Figure 3.3 Equilibrium contact angle on an ideal surface.

$$\gamma_{LV}\cos\theta = \gamma^{o}_{SV} - \gamma_{SL} \tag{3.12}$$

One route to prove Young's equation is by using the Gibbs free energy of the wetting, proposed by Poynting and Thompson.[16] After the liquid droplet forms the meniscus and reaches equilibrium, the variation in Gibbs free energy is zero. An assumption in Eqn (3.13) is the neglect of the gravitational force.

$$\mathrm{d}G = 0 \tag{3.13}$$

$$\mathrm{d}G = \gamma_{LV}\,\mathrm{d}A_{LV} + \gamma^{o}_{SV}\,\mathrm{d}A_{SV} + \gamma_{SL}\,\mathrm{d}A_{SL} = 0 \tag{3.14}$$

In Eqn (3.14), dA represents small incremental increases/decreases in the surface or interface area. Changes in the interfacial areas are given by Eqns (3.15) and (3.16), because any increase in the solid–liquid interface is countered by a decrease in the solid–vapor interface. Substitution from these two equations in Eqn (3.14) will yield Young's equation (Eqn (3.12)).

$$\mathrm{d}A_{SL} = -\mathrm{d}A_{SV} \tag{3.15}$$

$$\begin{aligned}&\mathrm{d}A_{LV} = \cos\theta\,\mathrm{d}A_{SL}\\&\gamma_{LV}(\cos\theta\,\mathrm{d}A_{SL}) + \gamma^{o}_{SV}(-\mathrm{d}A_{SL}) + \gamma_{SL}\,\mathrm{d}A_{SL} = 0\end{aligned} \tag{3.16}$$

$$\gamma_{LV}\cos\theta = \gamma^{o}_{SV} - \gamma_{SL} \tag{3.12}$$

The difference between the equilibrium surface energy of solid–vapor and solid–liquid is sometimes called adhesion.[17] It must be noted that the work of adhesion and adhesion tension involves the solid–vapor equilibrium instead of the solid–liquid equilibrium.

$$A_{SLV} = \gamma^{o}_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta$$

Most surfaces have heterogeneous composition and are not perfectly smooth. Wetting of such a surface may reach equilibrium or remain in a metastable state. In the case of an ideal surface, the addition or removal of a small volume of liquid from the drop will result in the advancement or recession of the drop. The contact angle will return to its equilibrium value. In the case of a real surface, which may contain roughness and heterogeneity, there is a delay in the movement of the liquid drop in response to the addition or removal of liquid. This phenomenon is called *hysteresis*, which requires a revision of the definition of contact angle.

The contact angle formed as a result of the addition of liquid to the drop is dubbed the *advancing angle*. The angle formed because of the removal of liquid is called the *receding angle*. The contact angle of a liquid on a real surface is measured in both contacting and advancing modes. Typically, after the addition or removal of the liquid there is a delay followed by a sudden motion in the drop of the liquid. The maximum angle for the advancing mode and the minimum angle for the receding mode are defined, respectively, as *advancing* and *receding contact angles*.

Harkins and Livingston[18] proposed a correction to Young's equation, concerning the surface of the solid carrying a film of the liquid's vapor. The surface energy of a solid surface that contains an adsorbed vapor layer (γ_{SA}) is less than that of a "clean" solid surface. This concept has practical significance because clean surfaces tend to adsorb the ambient vapors and oils and must therefore be protected prior to the application of adhesive. Hankins' and Livingston's correction, known as *spreading coefficient* (π_E), is shown in Eqn (3.17); thus, resulting in Eqn (3.18) after substitution in Eqn (3.12).

$$\begin{aligned}&\gamma^{o}_{SV} = \gamma_{SA} - \pi_E\\&\gamma_{LV}\cos\theta = \gamma_{SA} - \pi_E - \gamma_{SL}\end{aligned} \tag{3.17}$$

$$\gamma_{SA} = \gamma_{LV}\cos\theta + \gamma_{SL} + \pi_E \tag{3.18}$$

The spreading coefficient can be measured by a technique developed by Padday. In this method, it has been shown[19] that such a sessile drop, when successively increased in volume, reaches some constant maximum height (h) for a given solid–liquid system, provided the system is aged to reach equilibrium. It has also been shown that this maximum height is related to the spreading coefficient by Eqn (3.19). In this equation, ρ is the density of the liquid and g is the gravitational acceleration.

$$\pi_E = -\frac{\rho g h^2}{2} \tag{3.19}$$

Finally, by substituting for the interfacial tension from the modified Young's equation (Eqn (3.12)) into the work of adhesion (Eqn (3.20)) for a solid−liquid system, the equation for the work of adhesion can be simplified to Eqn (3.21), also known as Young−Dupre's equation.

$$W_a = \gamma_{LV} + \gamma^o_{SV} - \gamma_{SL} \tag{3.20}$$

$$W_a = \gamma_{LV}(1 + \cos\theta) \tag{3.21}$$

This means that the work of adhesion can be calculated by measuring the contact angle and the surface tension of the liquid.

3.6 Laplace's Equation

This equation is the governing relationship for the shapes of all bubbles and drops of liquids. It is also the basis for measuring the static surface/interface tensions of fluids. Laplace's equation states that the pressure drop across a curved surface is proportional to the capillary forces as shown in Eqn (3.22).[12]

$$\begin{aligned} \Delta P &= P_a - P_b \\ P_a - P_b &= \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \end{aligned} \tag{3.22}$$

P_a and P_b are pressures in the two phases and R_1 and R_2 are the main radii of curvature. Dimensionless forms of Laplace equation that are more convenient to apply have been derived.[20] For a spherical surface $R_1 = R_2$; simplify Eqn (3.22) to the following form:

$$\Delta P = P_a - P_b = \frac{2\gamma}{R} \tag{3.23}$$

3.7 Effect of Temperature on Surface Tension

An important variable of surface tension is temperature, which has practical value during the adhesion bonding of plastics. Surface tension of both adhesive and polymer is affected by temperature. Guggenheim's equation (Eqn (3.24)) is applicable to liquids that have small molecules.[21] It has also been found to be applicable to polymers. In this equation, γ_0 is surface tension at $T = 0$ K and T_c is the critical temperature (K) of the liquid. The values of γ_0 and T_c can be determined by fitting a line to the surface tension data as a function of temperature. According to the Guggenheim equation, surface tension decreases with an increase in temperature.[22] The rate of surface tension decrease as a function of temperature is 0.1 dynes/°C cm for liquids with small molecules.[21,23]

$$\gamma = \gamma_0\left(1 - \frac{T}{T_c}\right)^{11/9} \tag{3.24}$$

3.8 Surface Tension Measurement

Surface tension measurement techniques are classified into methods for solids and liquids. There are two modes for measuring surface tension of liquids: static and dynamic. Values reported in the literature are often for static surface tensions of liquids. Tables 3.1 through 3.3 present a brief description of the common techniques for surface tension measurement of liquid and solid materials. Some of these methods have been described in further detail.

Several standards have been written to define methods for measuring contact angle for different applications (Table 3.4). The objective of these methods is to provide procedures for the comparison of surface energy of industrial materials.

3.8.1 Measurement for Liquids: Du Nouy Ring and Wilhelmy Plate Methods

The du Nouy ring and Wilhelmy plate methods (Fig. 3.4) are two most frequently used techniques of measuring surface tension at the liquid−air interface or interfacial tension at a liquid−liquid interface. Only the du Nouy method can be applied to measure interfacial tension. Both of these techniques are based on pulling an object with a well-defined geometry off the surface of liquids and measuring the pull force. These techniques are also known as *pull-force* methods. In the Wilhelmy method, a plate is the pull object, whereas in the du Nouy technique a ring is used. These techniques are ascribed to two scientists who conducted some of the earliest research in the area of surface tension measurement. In 1863, Wilhelmy[24] described measurement of capillary constants in a paper, without a detailed calculation of surface tension. Lecomte du Nouy illustrated the

Table 3.1 Static Surface Tension Measurement Methods for Liquids

Technique	Brief Description
du Nouy Ring	Traditional method for the measurement of surface and interfacial tension. Maximum pulling force on a ring by the surface is measured. Wetting properties of liquids have no influence on this technique.
Wilhelmy Plate	This technique is broadly applicable to liquids, especially when surface tension must be measured over a long time period. A vertical plate with known perimeter is attached to a balance and submerged in the liquid. The force due to wetting is measured by the balance.
Spinning Drop	Suitable for low interfacial tensions. The diameter of a drop within a heavy phase is measured when both are being rotated.
Pendent Drop	Surface and interfacial tensions are measured by this method.

Table 3.2 Dynamic Surface Tension Measurement Methods for Liquids

Technique	Brief Description
Bubble Pressure	This method is used for determining surface tension at short surface ages. The actual measured variable is the maximum pressure of each bubble.
Drop Volume	A method employed for determining interfacial tension as a function of time (interface age). The time between two consecutive drops is measured when liquid of one density is pumped into a second liquid of a different density.

Table 3.3 Surface Tension Measurement Methods for Solids

Technique	Brief Description
Sessile Drop	This method involves measurement of the contact angle optically and is used to estimate wetting properties of a localized region on a solid surface. The angle between the baseline of the drop and the tangent at the drop boundary are determined. This technique is ideal for curved samples or when one side of the sample surface has different properties than the other side.
Dynamic Wilhelmy	This method requires uniform geometry for calculating average advancing and receding contact angles on solids. Both sides of the solid must have the same properties. Wetting force on the solid material is measured as the solid is submerged in, or withdrawn from, a liquid of given surface tension.
Single Fiber Wilhelmy	This is a dynamic Wilhelmy method, applied to single fibers to measure advancing and receding contact angles.
Powder Contact Angle	This procedure allows the measurement of average contact angle and adsorption speeds of powders and other porous species. The change in the weight as a function of time is measured.
Liquid Homolog Method (Zissman)	Called *critical surface tension*, it is based on measuring the contact angle of several liquids and plotting the cosine of the angle versus surface tension of the liquids. The surface tension at which cosine of the contact angle is equal to one, obtained by extrapolation, is the critical surface tension of the solid.

Table 3.4 Standard Contact Angle Measurement Methods for Various Materials

Technique	*Title*—Scope
ASTM D724-99	*Standard Test Method for Surface Wettability of Paper*. Method covers the quantitative determination of the resistance of paper surfaces to wetting by measuring the behavior of a drop of liquid applied directly to the paper surface.
ASTM D5725-99	*Standard Test Method for Surface Wettability and Absorbency of Sheeted Materials using an Automated Contact Angle Tester*. Method measures the contact angle of a test liquid on a flat sample of a film or a paper substrate under specified conditions.
ASTM C813-90 (1994)e1	*Standard Test Method for Hydrophobic Contamination on Glass by Contact Angle Measurement*. Method covers the detection of hydrophobic contamination on glass surfaces by means of contact angle measurement.
ASTM D5946-96	*Standard Test Method for Corona-treated Polymer Films using Water Contact Angle Measurement*. Method covers the measurement of contact angle of water droplets on corona-treated polymer film surfaces; the results are used to estimate the film's wetting tension.
TAPPI T458*	*Surface Wettability of Paper*. In this method, the contact angle between air and liquid on a paper surface is taken as a measure of the resistance of the paper surface to wetting by the liquid. The initial angle of contact or initial wettability is considered to be a measure of the ruling quality of the paper. The rate of change in the wettability is considered to be a measure of the writing quality.

**See TAPPI (Technical Association of the Pulp and Paper Industry) Web site: www.tappi.org.*

shortcomings of the past surface tension determination methods in a paper published in 1919.[25]

Equation (3.25) shows the relationship for the calculation of surface tension by the du Nouy ring method. In this equation, P_T is the total force on the ring which is measured, P_R is the weight of the ring, R is the radius of the ring, and γ_{ideal} is the ideal surface tension. In practice, a meniscus correction factor is required because the size and shape of the surface inside and outside the ring are not the same. Surface tension must, therefore, be corrected for the shape of the ring by a factor (f), as shown in Eqn (3.26). The correction factors have been determined and tabulated.[23,26,27]

$$P_T = P_R + 4\pi R\gamma_{ideal} \tag{3.25}$$

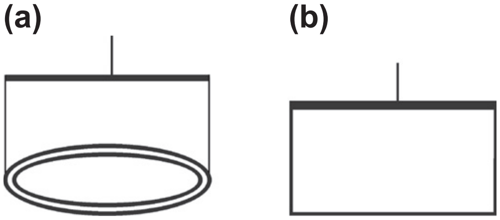

Figure 3.4 Schematic of (*a*) du Nouy Ring and (*b*) Wilhelmy Plate.

$$\gamma = f\gamma_{ideal} \tag{3.26}$$

The Wilhelmy method does not require a correction factor for meniscus shape. Though it does require correction if the plate is partially or completely submerged in the liquid. In Equation (3.27), P_T is the total force on the plate that is measured, P_P is the weight of the plate, p is the perimeter of the plate, and γ_{ideal} is the ideal surface tension. A buoyant force term must be added or subtracted to/from the second part of the equation, depending on whether the plate is above or below the level of the free liquid. In Eqn (3.28), h is the height above or below the free liquid level, A is the cross-sectional area of the plate, and γ is the surface tension.

$$P_T = P_P + p\gamma_{ideal} \tag{3.27}$$

$$P_T = P_P + p\gamma + \rho ghA \tag{3.28}$$

The total force (P_T), acting on the ring (du Noy) or the plate (Wilhelmy), can be measured by a balance connected to either device. Substituting for the total force and other parameters in Eqn (3.28) allows the value of surface tension (γ) to be calculated.

3.8.2 Measurement for Solids: Liquid Homolog Series

Surface tension of solid plastics cannot be measured directly and is thus determined indirectly, usually by contact angle methods. The problem with the direct measurement of surface tension arises from the difficulty in the reversible formation of a solid surface. Table 3.3 shows a list of methods that can be applied to measure the surface energy of solids.

An alternative method uses a concept called *critical surface tension*, proposed by Fox and Zissman[10,28,29] to characterize the surface energy of solids. A plot cosine of the contact angle (cos θ), and liquid−vapor surface tension (γ_{lv}), yields a straight line for a homologous series of liquids (Fig. 3.5). Nonhomologous liquids yield a curved line that may not be easily extrapolated. The intercept of the line at cos (θ) equal to one is defined as the *critical surface tension* of the polymer (γ_c). Values of 18 dynes/cm for polytetrafluoroethylene and 30 dynes/cm for polyethylene are obtained according to this procedure (Figs 3.5 and 3.6). Tables 3.5 and 3.6 present surface free energies of solids and surface tension of liquids.

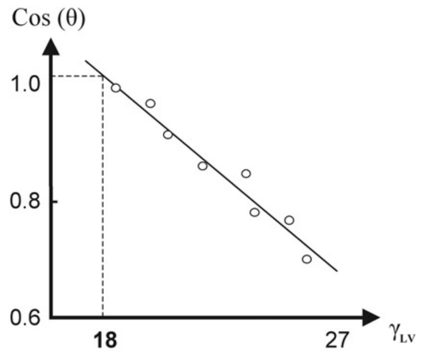

Figure 3.5 Zissman plot for polytetrafluoroethylene using *n*-alkanes as the testing liquids.[4,23]

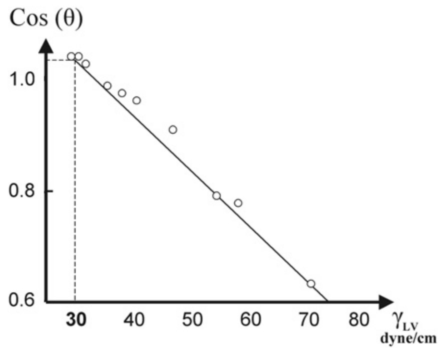

Figure 3.6 Zissman plot for polytethylene using *n*-alkanes as the testing liquids.[4,23]

Table 3.5 Surface Free Energy of Select Plastics

Plastic Material	Surface Free Energy, dynes/cm
Polytetrafluoroethylene	18−19
Polytrifluoroethylene	22
Polyvinylidene Fluoride	25
Polyvinyl Fluoride	28
Polypropylene	29
Polyethylene	30−31
Ionomer (low) Polystyrene	33
Ionomer (high) Polystyrene	37
Polymethylmethacrylate	38
Polyvinyl Chloride	39
Cellulosics	42
Polyester	43
Nylon	46

One can obtain a relationship (Eqn (3.29)) between the critical surface tension and the solid−vapor surface tension by setting the contact angle to zero in Young's equation (Eqn (3.12)). Critical surface tension is therefore smaller than solid−vapor surface

Table 3.6 Surface Tension of Select Liquids

Liquid	Surface Free Energy, dynes/cm
n-Hexane	18
Alcohols	22
Cyclohexane	25
Toluene, Xylene	29
Phenol	41
Aniline	43
Glycol	47
Formamide	58
Glycerol	63
Water	72

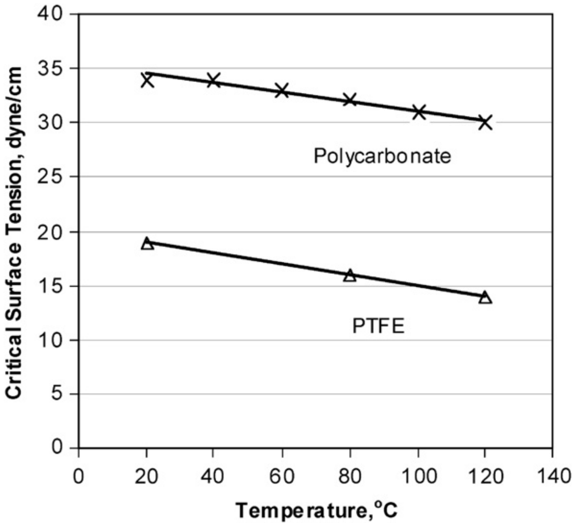

Figure 3.7 Effect of temperature on critical surface tension of two plastics.[24]

tension. Figure 3.7 shows the effect of temperature on critical surface tensions of two plastics.[30] Surface energy of plastics decreases with temperature.

$$\gamma_c = \lim_{\theta \to 0}(\gamma_{LV} \cos\theta) = \gamma_{SV} - \gamma_{SL} \tag{3.29}$$

In summary, the experimental and analytical methods described in this chapter enable the reader to both measure and calculate surface energy of liquids and solids. Surface preparation techniques are partly aimed at changing surface energy of materials, which can be determined using the methods provided in this chapter.

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4 Surface and Material Characterization Techniques

Sina Ebnesajjad

4.1 Introduction

In the analysis of adhesion bonding, possessing knowledge of the composition and structure of the adherend surface is important. Characterization of bonding surfaces aids both in design and failure analysis of a bond, should the adhesion bond fail.

Surface analysis is the use of microscopic chemical and physical probes that give information about the surface region of a sample. (The term "sample" refers to any piece of material, structure, device, or substance that is under study). The probed region may be the extreme top layer of atoms (the only true surface, for purists), or it may extend up to several microns (millionths of a meter) beneath the sample surface, depending on the technique used. Analysis provides information pertaining to chemical composition, level of trace impurities, and physical structure or appearance of the sampled region. Such information is important to researchers and manufacturers who must understand the materials in order to verify a theory or to create a better product.[1]

Many of the techniques used to probe surfaces utilize a beam of ions (e.g., secondary ion mass spectroscopy, SIMS) to strike the surface and knock atoms off the sample material. These atoms are ionized and identified and measured using a technique known as mass spectrometry. Another technique is ion scattering spectroscopy (ISS), which probes the outermost layer of the surface. If a beam of ions is directed at a sample surface, then a certain number will be elastically reflected. Measurement of the energy of the backscattered particles can be used to identify the mass of these atoms. The intensity of the scattered ions, as a function of angle of emission, provides information regarding the surface crystallographic structure. The variation in the intensity of the scattered beam is partly due to the shadowing of substrate atoms by adsorbed atoms. Using scattering theory, knowledge of the sites that the surface atoms occupy can be derived.[2,3]

Other probes strike the surface with electrons (Auger spectrometry; energy dispersive X-ray spectroscopy, EDS or EDAX) or X-rays (electron spectroscopy for chemical analysis, ESCA or total reflection X-ray fluorescence, TXRF) and measure the resulting electron or photon emissions to probe the sample. Measurements of the way high-energy helium nuclei bounce off a sample can be used as a sensitive measure of surface layer composition and thickness (Rutherford backscattering spectrometry, RBS).

Surface structure on a microscopic scale is observed by using scanning electron microscopy (SEM), optical microscopy, and atomic force or scanning probe microscopy (AFM/SPM).

NOTE: All of these techniques must be performed in a high-vacuum environment—characterized is the substrate under those conditions, not atmospheric conditions under which most bonding processes are done.

Table 4.1 and Fig. 4.1 show a comparison of the sampling depth of traditional methods with those of new techniques. These analyses can focus on a much shallower thickness of the surface, and virtually yield analyses of the outermost layers of a polymer article.

In addition to surface specific methods, a number of other analytic techniques that can be applied to characterize the bulk properties of materials are discussed in this chapter.

4.2 Infrared Spectroscopy

During analysis by infrared spectroscopy (IR), a sample is subjected to electromagnetic radiation in the infrared region of the spectrum. The wavelengths that are absorbed by the sample depend on the nature of the chemical groups present. These wavelengths are defined by a wave number (cm^{-1}) that is obtained by dividing the number 10,000 by the wavelength in microns. The ranges of various wave numbers are given in Table 4.2. Absorbance is defined per Eqn (4.1) and varies from 0 (100% transmission) to infinity (0% transmission). Absorbance is related to concentration of the absorbing species by Beer's law (Eqn (4.1)).

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Table 4.1 Comparison of Average Sample Depth for Various Surface Analysis Techniques[4]

Analysis Method	**Sampling Depth**
Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, conventional secondary ion mass spectroscopy (conventional SIMS)	<2 μm
Energy dispersive X-ray (EDS or EDAX)	$<5{,}000$ Å
Rutherford back scattering (RBS)	<400 Å
Surface secondary ion mass spectroscopy (surface SIMS)	<300 Å
Electron spectroscopy for chemical analysis (ESCA) also called X-ray photoelectron microscopy (XPS)	<100 Å
Auger electron spectroscopy (AES)	<100 Å
Ion scattering spectroscopy (ISS), also called low-energy ion scattering (LEIS)	<2 Å
Time-of-flight secondary ion mass spectroscopy (TOF-SIMS)	1.3 Monolayers
Atomic force microscopy (AFM) or scanning probe microscopy (SPM)	0.1 Å

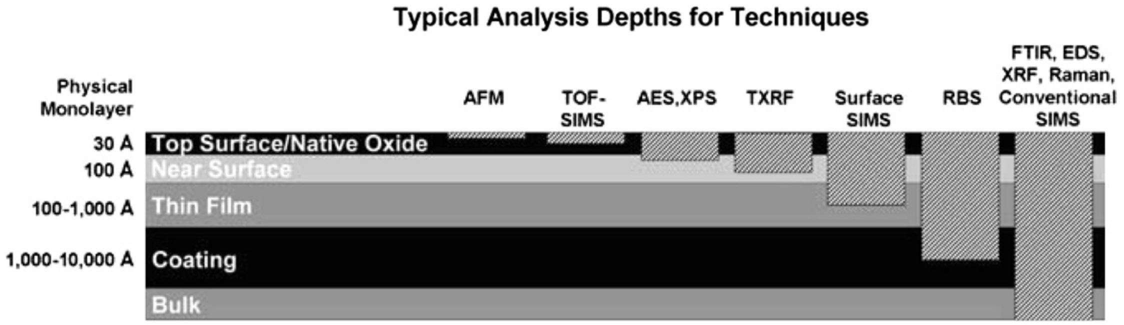


Figure 4.1 Sampling depth for surface analysis techniques.[1]

Table 4.2 Definition of Electromagnetic Wave Ranges

Definition of Range	**Wave Number (10^4 cm^{-1})**	**Wave Length (μm)**
Ultraviolet	5–2.5	0.2–0.4
Visible	2.5–1.42	0.4–0.7
Near IR	1.42–0.4	0.7–2.5
IR	0.4–0.02	2.5–50
Far IR	0.02–0.0012	50–830

$$\text{Absorbance} = \text{Log}\frac{100}{\%\ \text{Transmission}} \tag{4.1}$$

$$\text{Absorbance} = Kcl \tag{4.2}$$

K = a constant that is occasionally called the *extinction coefficient,*

c = concentration of the absorbing species, and

l = sample thickness

Equation (4.2) can be used to determine the concentration of a compound in a solution, if the value of K is known for that compound. Chemical bonds such as C−O, O−H, and so on, absorb different amounts of infrared energy over various wavelengths. Absorption patterns vary from sharp to broad for different bonds. Peak IR absorption wavelength (wave number) is characteristic of a chemical bond. Absorption over the infrared *spectrum* is a fingerprint characteristic of an organic material. Qualitative identification can be achieved by obtaining and analyzing the IR spectrum of a material.

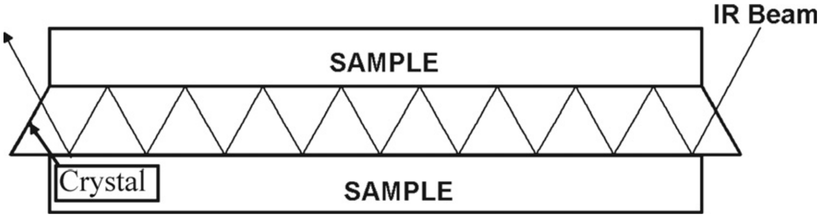


Figure 4.2 Schematic of the sample configuration relative to the reflective crystal in attenuated total reflectance IR.

Infrared spectra can also be obtained by reflecting the IR beam on the surface of a sample. This technique is applied when obtaining an IR spectrum by a transmission technique is not possible. Attenuated total reflectance (ATR), also known as ATIR (attenuated total internal reflectance), is based on multiple internal reflectances of the IR beam on the sample surface using a high refractive index crystal (e.g., thallium bromo-iodide). The IR beam is entered into the crystal at an angle, and after about 25 internal reflections (5 cm), a spectrum similar to that of the transmission is obtained. The sample is in tight contact with both surfaces on the crystal, as seen in Fig. 4.2.

Modern infrared spectrometers use Fourier transform for the calculation of results. The method is called Fourier transform infrared spectroscopy, abbreviated as *FTIR*.

4.3 Raman Spectroscopy

When incident light strikes a sample, part of the light is scattered. Most of the scattered light has the same wavelength as the incident light; this is called Rayleigh scattering. Some of the light is scattered at a different wavelength; this is called Raman scattering. The energy difference between the incident light and the Raman scattered light is called the Raman shift. It is equal to the energy required to vibrate or rotate the molecule. Several different Raman shifted signals will often be observed in a single sample; each is associated with different vibrational or rotational motions of molecules in the sample. The particular molecule and its environment will determine what Raman signals are observed. In practice, because the Raman effect is so slight, a laser is used as the source of the incident light. A plot of Raman intensity versus the frequency of the Raman shift is a Raman spectrum. It usually contains sharp bands that are characteristic of the functional groups of the compounds or materials. This information can be interpreted to determine chemical structure and to identify the compounds present. It is complementary to FTIR in that it uses a different method to measure molecular vibrations.

Raman spectroscopy is a good technique for qualitative analysis and discrimination of organic and/or inorganic compounds in mixed materials. A Raman spectrum can be obtained from samples that are as small as 1 μm.[1] The intensities of bands in a Raman spectrum depend on the sensitivity of the specific vibrations to the Raman effect and are proportional to concentration. Thus, Raman spectra can be used for semiquantitative and quantitative analyses. The technique is used for identification of organic molecules, polymers, biomolecules, and inorganic compounds both in bulk and as individual particles. Raman spectroscopy is particularly useful in determining the structure of different types of carbon (diamond, graphitic, diamond-like-carbon, etc.) and their relative concentrations.

4.4 Scanning Electron Microscopy (SEM)

SEM is a useful technique for the analysis of plastics surfaces. Actually, it is useful for any surface that survives in a vacuum. Almost all SEMs start by sputtering the surface with a thin layer of gold metal. If it is not already conductive, this makes the surface conductive, which is a requirement; so, you are often not looking directly at the surface. It involves a finely collimated beam of electrons that sweeps across the surface of the analysis specimen. The beam is focused into a small probe that scans across the surface of a specimen. The beam interactions with the material result in the emission of electrons and photons as the electrons penetrate the surface. The emitted particles are collected with the appropriate detector to yield information about the surface. The final product of the electron beam collision with the surface topology of the sample is an image (Fig. 4.4).

For example, Fig. 4.4 shows the result of topical SEM analysis of a drug-infused polymer coating on

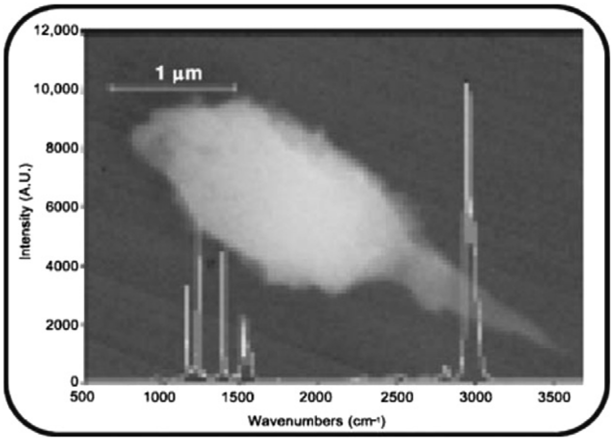


Figure 4.3 Raman spectroscopy identified this micron-sized particle as polyethylene.

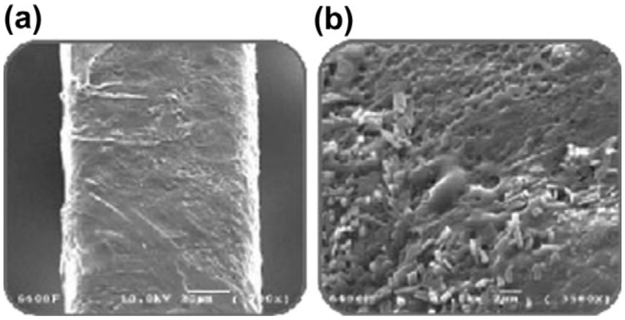


Figure 4.4 SEM images of a polymer-coated device: (*a*) 750 times magnification and (*b*) 35,000 times magnification.[1]

a stainless steel device. SEM of the surface at 750 times magnification is shown in Fig. 4.4(a) and at 35,000 times magnification in Fig. 4.4(b). The higher magnification revealed the presence of crystals on the surface of the coating.

A helpful attachment to the SEM is the *electron microprobe*. An electron beam is focused on a sample surface, causing ionization to a depth of a few micrometers. Energies and wavelength of the emitted X-ray during the de-excitation cycle are characteristic of the elements present in the top layers of the sample. The result is not a true surface analysis, but the electron microprobe allows analysis of various spots of the sample surface.[5]

4.4.1 Environmental Scanning Electron Microscopy (ESEM)

The first commercial environmental scanning electron microscopy (ESEM) was introduced in 1988. Although it is extremely expensive to modify a standard scanning electron microscope (SEM) to perform as an ESEM, a microscope designed for dual function (ESEM/SEM) can operate well in both modes.[6]

One advantage of using the environmental scanning electron microscope (ESEM) is that by operating it in "wet mode" the need to make nonconductive material conductive is eliminated. Material samples do not need to be desiccated and coated with carbon or gold–palladium and thus their original characteristics can be preserved for further testing or manipulation. One may image the sample, modify the sample, and image the sample again, ad infinitum, without destroying its usefulness by having coated it to make it conductive.

Dynamic experiments can also be performed with the ESEM in the wet mode; one of the hot stages may be used to heat a small sample to as high as 1500 °C and image it during every step of the heating/cooling process. After a certain temperature is passed, above 1100 °C, bias actually needs to be adjusted to reject thermal electrons, but this can be done easily.

The Peltier heating/cooling stage[7] allows working within 20 °C above or below ambient temperature, and the combination of low temperature (e.g., 4 °C) and high water vapor pressure (e.g., 6.1 Torr) permits achievement of 100% relative humidity (RH) at the sample surface. At 100% RH, samples are not dehydrated during the imaging process. At less than 100% RH, a moist sample constantly loses water as the vacuum in the chamber pumps on it; in the "scope," it appears as constant movement of the sample.

4.5 Rutherford Backscattering Theory

RBS is based on collisions between atomic nuclei and derives its name from *Lord Ernest Rutherford*, who in 1911 was the first to present the concept of nuclei in atoms. It involves measuring the number and energy of ions in a beam, which backscatter after colliding with atoms in the near-surface region of a sample where the beam has been targeted. With this information, determining atomic mass and elemental concentrations versus depth below the surface is possible. RBS is ideally suited for determining the concentration of trace elements heavier than major constituents of the substrate. Its sensitivity for light masses, and for the makeup of samples well below the surface, is poor.

When a sample is bombarded with a beam of high-energy particles, the vast majority of particles are implanted into the material and do not escape. This is because the diameter of an atomic nucleus is on the order of 1e-15 m, whereas the spacing between nuclei is on the order of 2e-10 m. A small fraction of the incident particles undergo a direct collision with a nucleus of one of the atoms in the upper few micrometers of the sample. This "collision" does not actually involve direct contact between the projectile ion and target atom. Energy exchange occurs because of Coulombic forces between nuclei in close proximity to each other. However, using classical physics, the interaction can be modeled accurately as an elastic collision.

The energy measured for a particle backscattering at a given angle depends upon two processes. Particles lose energy while they pass through the sample, both before and after a collision. The amount of energy lost is dependent on that material's stopping power. A particle also loses energy as the result of the collision. The ratio of the energy of the projectile before and after collision is called the kinematic factor.

The numbers of backscattering events that occur from a given element in a sample depend upon two factors: the concentration of the element and the effective size of its nucleus. The probability that a material will cause a collision is called its scattering cross section.

4.6 Energy Dispersive X-Ray Spectroscopy (EDS)

EDS is a standard method for identifying and quantifying elemental compositions in a very small sample of even a few cubic micrometers. In a properly equipped SEM, the atoms on the surface are excited by the electron beam, thus emitting specific wavelengths of X-rays that are characteristic of the atomic structure of the elements. An energy dispersive detector, a solid-state device that discriminates among X-ray energies analyzes the X-ray emissions. Appropriate elements are assigned, thus yielding the composition of the atoms on the specimen surface. This procedure is called energy dispersive X-ray spectroscopy, or EDS, and is useful for analyzing the composition of the surface of a specimen (Figs 4.5 and 4.6).

4.7 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is similar to SEM, except for the fact that the beam passes

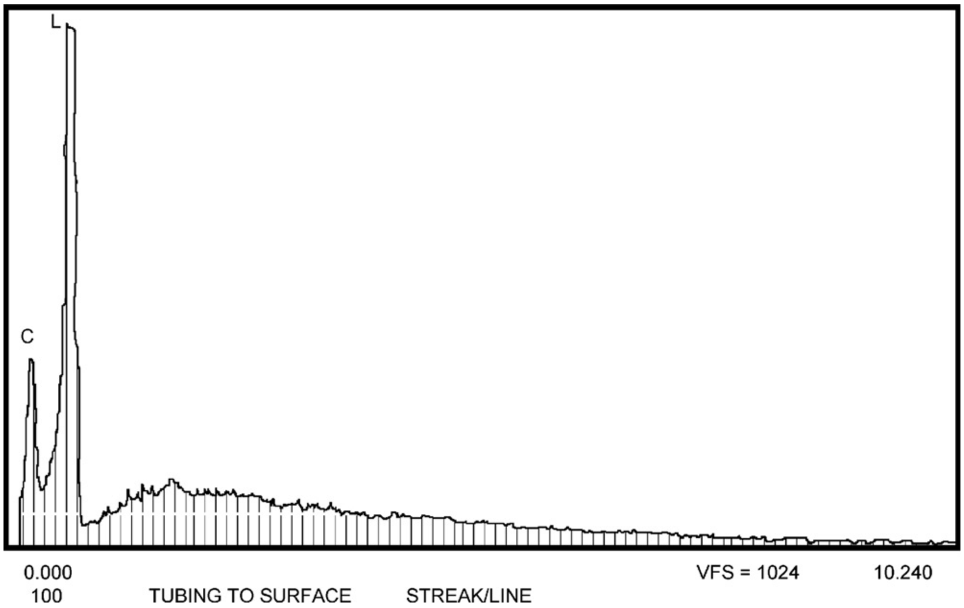


Figure 4.5 EDS elemental analysis of a clean PTFE surface. *(Courtesy of DuPont Fluoroproducts.)*

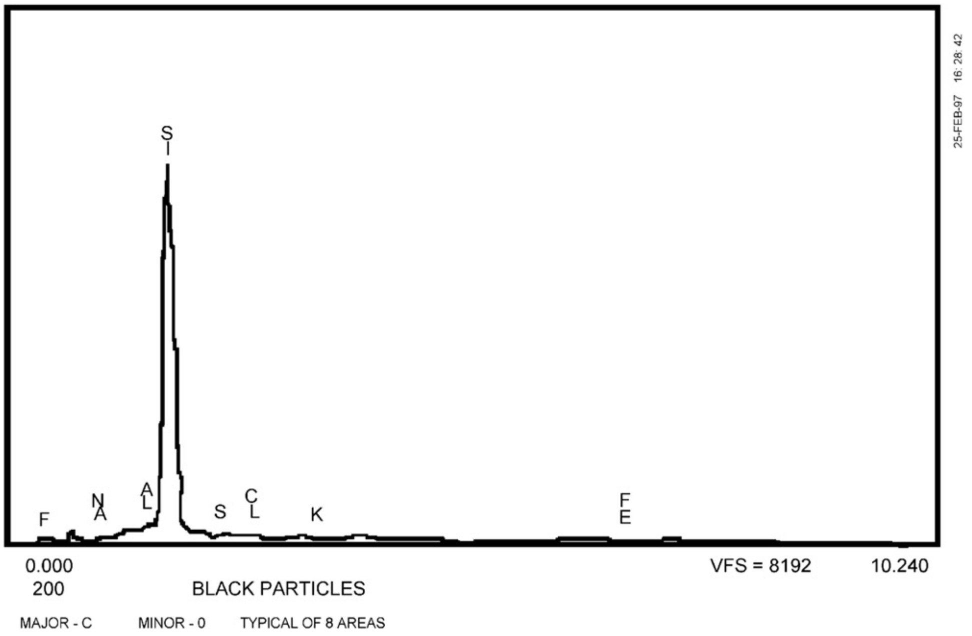


Figure 4.6 EDS elemental analysis of a contamination spot on the PTFE surface. *(Courtesy of DuPont Fluoroproducts.)*

through the sample. A high voltage (80–200 keV), highly focused electron beam is passed through a thin solid sample, typically 100–200 nm in thickness. Electrons undergo coherent scattering or diffraction from lattice planes in the crystalline phase of materials, thus yielding phase identification. Characteristic X-rays that are generated can be detected in a separate detector, permitting qualitative elemental analysis.

Figure 4.7 shows a TEM micrograph of particles of polyvinylidene fluoride that have been produced by emulsion-polymerization in an aqueous phase. Figure 4.8 shows the capability of TEM in revealing the structure of a material. The authors have used nonaqueous miniemulsions to perform polymerizations. Polyvinylpyrrolidone nanoparticles (Fig. 4.8) can be synthesized at temperatures higher than 150 °C in nonaqueous inverse miniemulsions and in the presence of an additional stabilizer. Particle size

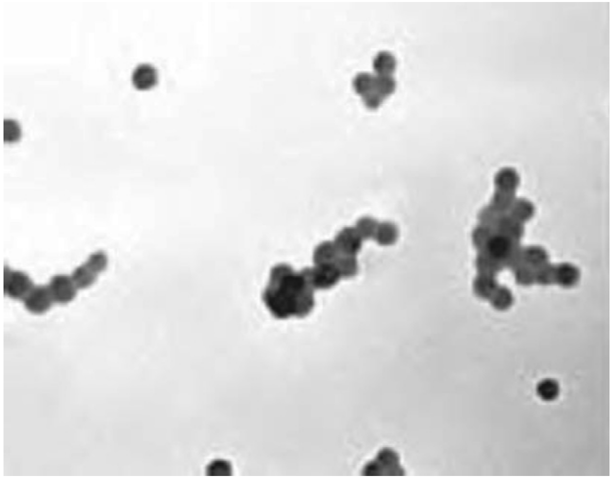


Figure 4.7 Transmission electron micrograph of particles of emulsion-polymerized PVDF particles ($D_p = 128$ nm).[6]

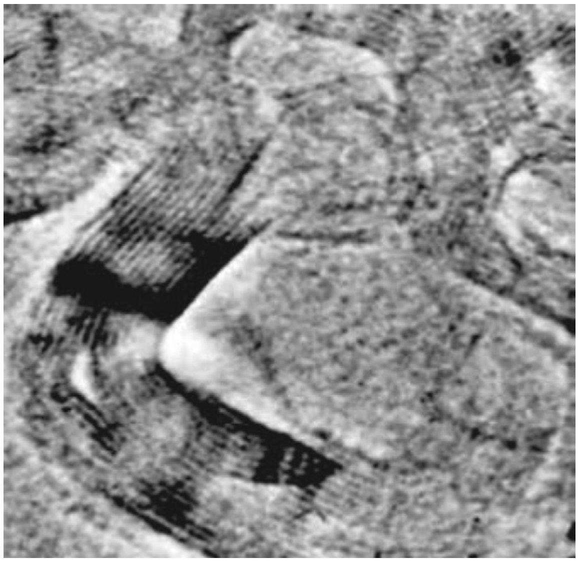


Figure 4.8 TEM micrograph of polyvinylpyrrolidone particles.

and size distribution can be measured from the micrograph because of its excellent resolution.[8]

4.8 Electron Spectroscopy for Chemical Analysis (ESCA)

This is a widely used analytic technique for characterizing polymer surfaces. ESCA is also called X-ray photoelectron spectroscopy (XPS) and is able to detect all elements except hydrogen. A sample is irradiated by X-ray beams, which interact with the inner electron shell of atoms. Photon energy of the X-ray is transferred to an electron in the inner shell, enabling it (*photoelectron*) to escape from the sample surface. An analyzer measures the kinetic energy of the photoelectron, which is equal to the binding energy of this electron. Knowledge of the binding energy allows identification of the element. The chemical bond of an atom to other elements shifts the bonding energy of the photoelectron to higher or lower values. This shift in binding energy provides structural information for a molecule.

Operation and maintenance of ESCA equipment and interpretation of its data are quite complex. Samples intended for ESCA and other surface analysis must be handled carefully because minute contamination can mask the surface structure of the samples. To alleviate this type of complication, the sample surface can be washed with volatile solvents such as methanol, acetone, hydrocarbons, and fluorocarbons using an ultrasound bath. Typically, analysis is conducted before and after the surface wash while studying a sample that has been handled and/or contaminated. Another application of surface wash is removal of loose material that may be weakly bound to the surface. The working details and data interpretation for ESCA are outside the scope of the present book. The interested reader is encouraged to refer to other sources to gain an in-depth understanding of ESCA.[4,9–13]

A typical spectrum of ESCA shows peaks as a function of binding energy, as shown in Fig. 4.9 for polytetrafluoroethylene. C1s and F1s peaks on a "clean" surface indicate that the PTFE surface is comprised of only carbon and fluorine. The energy shift can be curve-fitted by trial and error to determine the functional groups on the surface. The most simplified report that ESCA generates is a survey of the atomic composition of the surface elements, with the exception of hydrogen. A helpful tool to investigate surface changes of a polymer is the ratio of other elements to carbon, as shown in Table 4.3, for the effect of sodium etching on the surface composition of a few different fluoropolymers.

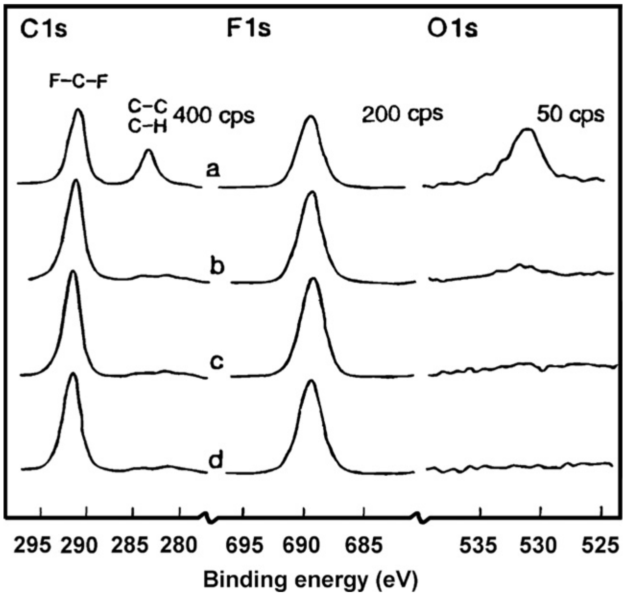


Figure 4.9 XPS spectra of polytetrafluoroethylene (*a*) before cleaning and after cleaning with an ultrasonic cleaner in (*b*) methanol, (*c*) acetone, and (*d*) *n*-heptane.[13]

4.9 Auger Electron Spectroscopy (AES)

Auger refers to the mission of a secondary electron after the surface of a solid has been bombarded with electrons. This is a different phenomenon from photoelectron emission (the basis of ESCA), which occurs after bombardment of a solid surface with low-energy X-rays.[15] The energy of the Auger electron depends on the chemical bonding state of the element from which it has emitted. The depth of the escape of an Auger electron is less than 1 nm, with metals having shortest escape depth and organic material the deepest. Lateral resolution of AES is around 1 μm. Auger spectroscopy, thus, characterizes the surface of materials.

This method uses a low-energy electron gun, with a power less than 5 keV, to lessen the heating and decomposition of the surface. The number of electrons and their energies are detected by a counter and energy analyzer. The energy of the electron identifies the element, whereas the number of emitted electrons indicates the surface concentration of the element.

Table 4.3 Effect of Sodium Etching on the Surface Composition and Adhesion Bond Strength of Fluoropolymers[14]

Polymer	Treatment	Surface Chemical Analysis (%) by ESCA						
		F/C Ratio	Cl/C Ratio	O/C Ratio	Cl	C	F	O
PTFE	–	1.60	–	–	–	38.4	61.6	–
PTFE	Tetra-Etch®[1] (1 min)	0.011	–	0.20	–	82.2	0.9	16.9
PTFE	N/1 min[2]	0.005	–	0.14	–	87.2	0.4	12.4
PVF	–	0.42	–	–	–	70.4	29.6	–
PVF	Tetra-Etch®[1] (30 min)	0.21	–	0.026	–	80.7	17.2	2.1
ECTFE	–	0.64	0.27	–	14.1	52.5	33.4	–
ECTFE	Tetra-Etch®[1] (1 min)	0.16	0.05	0.12	3.8	74.9	12.2	9.1

[1] *Supplied by WL Gore Corporation.*
[2] *Treatment with 1 mole solution naphthalenide in tetrahydrofuran at room temperature.*

4.10 Ion Scattering Spectroscopy (ISS)

When a beam of ions hits a solid surface, part of the projectiles will be scattered back into the vacuum after one or more collisions with target atoms of the top few layers.[16] Measurement of the energy of the backscattered particles can be used to identify the mass of these atoms. The technique is called ion scattering spectroscopy (ISS). The term encompasses several techniques, depending on the energy of the primary ion beam. LEIS (low energy ion scattering) spectroscopy refers to primary energies in the range of 100 eV—10 keV, medium energy ion scattering (MEIS) to a range from 100 to 200 keV, and high energy ion scattering (HEIS) to energies between 1 and several MeV. Often the LEIS technique is called ion scattering spectroscopy (ISS); the term we will use below means LEIS, while HEIS technique is best known as *Rutherford backscattering spectroscopy* (RBS).

LEIS is attractive as a surface-specific technique. Spectra are usually obtained using noble gas ion beams from 0.5 to 3 keV.[17] Due to strong electron affinity of inert-gas ions, the probability of electron transfer is very high, even in the initial collision with a surface atom. After two or more collisions, most ions are neutralized so that a detector set to analyze only ions of the same type as those in the incident beam detects ions that have almost entirely had only one collision with a target atom. Projectiles entering the solid are discarded because they require several scattering events to return to the surface and exit.

The practical use of IIS is determined by its extreme sensitivity to only the top surface layer (for standard experimental arrangements) or two monolayers (for grazing incidence). Typical applications include composition of catalytic surfaces, thin film coatings, and adhesion, as well as arrangement of surface atoms, including the localization of adsorbed atoms. Quantification of surface analysis, using low-energy ions, is hampered by the uncertainty of the inelastic losses and the neutralization rate, depending on ion trajectories. In addition, overlapping peaks and multiple scattering have to be considered, and here computer simulation becomes an indispensable tool.

4.11 Secondary Ion Mass Spectroscopy (SIMS)

This is a valuable technique for identifying the structure and composition of polymer surfaces, and it complements ESCA. ESCA spectra for similar materials are difficult to resolve, whereas SIMS can differentiate among different polymers. This is partly due to the smaller sampling depth required by SIMS. In a typical analysis, the surface of the polymer sample is bombarded by a primary ion at low current density, principally intended to minimize alteration of the sample surface because of irradiation. The polymer surface generates positive and negative ions, which are analyzed using a mass analyzer. The results of detailed analysis provide chemical structure and composition data about the surface. A traditional shortcoming of SIMS, however, is its inability to perform quantitative analysis.

A different type of analyzer called *time of flight* (TOF-SIMS) can be utilized to determine the structure of the sample as a function of sampling depth. TOF-SIMS is used to measure the mass of an ion, so it is a mass analyzer. It can be useful in determining stratification of resins in coatings or diffusion of atoms into an area underneath a surface.[18,19,19A] TOF-SIMS works best for samples that do not degrade by exposure to ion irradiation, such as inorganic material.

Quantitative analysis of organic materials by TOF-SIMS is intrinsically difficult because of their tendency to decompose under ion irradiation. Techniques have, however, been devised to circumvent radiation-induced degradation. In a study, principal component analysis (PCA) was applied as a means of compensation for the spectral degradation caused by this decomposition and this improved the accuracy of the quantitative analysis.[20]

Two organic additives were used that had quite different composition and vulnerability to decomposition under ion irradiation in polystyrene. This enabled the extraction of a principal component related to their content that is independent of the decomposition. It proved the effectiveness of the approach in quantitative analysis of organic additives content in polymers without loss in accuracy due to spectral degradation.

4.12 Mass Spectroscopy (MS) or spectrometry

MS is applicable to both organic and inorganic substances. It is a quantitative technique that allows the study of the structure of organic matter. A sample is degraded, often bombarded with electrons, into fragments that are identified through fractional mass differences in atoms of the same principal mass number.[21] There are two types of mass analyses: one is high resolution that differentiates between fractional mass differences and the second is mass analysis that only differentiates principal mass number. The latter is more common. The method requires extremely low pressure (high vacuum), and the fragments must be volatile. Charged fragments are ejected into vacuum; strictly speaking, this does not mean that they are volatile (implies evaporation). The determination relies on the pattern of fragmentation of a molecule upon ionization. These patterns are distinct, can be reproduced, and are additive for mixtures. A mass spectrum is a graph that shows the measured values of ion intensities per unit charge (*m*/*e*, mass divided by charge). Mass spectrum is unique for each compound (Fig. 4.10). In a high-resolution spectrum, the deviation of the molecular weight of each fragment from an integral value is used to determine the elemental composition.

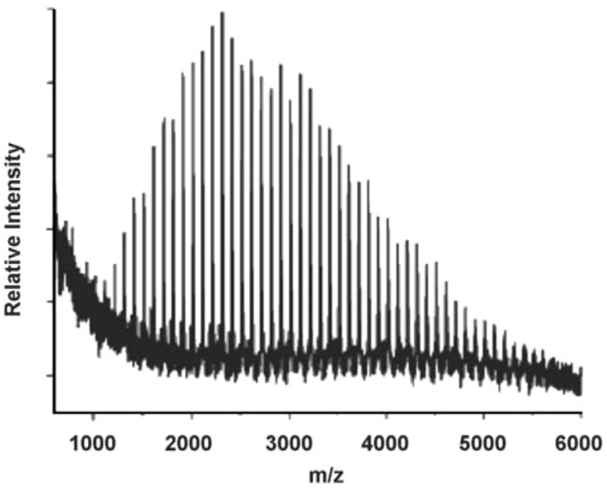


Figure 4.10 Matrix-assisted laser description ionized time-of-flight (MALDITOF) mass spectrum of poly (methylmethacrylate) (PMMA).[22,24]

There are several methods for ionization of organic compounds including particle bombardment, chemical and field ionization, electron impact, field desorption, and laser pulse. For example, in laser micromass analysis methods, a laser pulse is used to supply the necessary energy to volatilize a sample from the surface for mass spectroscopy.[22] Mass spectrometry is often used in conjunction with gas chromatography to identify the separated components. The working technology of mass spectrometry is quite complex.[23]

4.13 Gas Chromatography (GC)

Chromatography separates a mixture into its components, which are then analyzed by one of many detectors. In GC, the sample is passed during the vapor phase through an appropriated solid bed placed in a column. An oven supplies heat to the column, through which the vapor is carried using a constant stream of a gas such as nitrogen or helium. The time required to elute each component (*retention* time) is monitored. (Analysis times can run for more than an hour.) GC refers to the use of solid absorbent or molecular sieve columns. In the majority of GC columns, the packing is coated with a stationary liquid phase. Separation takes place by partitioning between the liquid coating and the carrier gas.

There are a variety of column packing material and liquid phases. Sometimes a very long capillary column is used without a solid packing and is only coated with a liquid on the wall. The oven can be operated isothermally at a given temperature or according to a program where temperature varies as a function of time.

There are different types of detectors, including thermal conductivity and electron capture types. The most common detector is the *flame ionization* variety (FID). A hydrogen flame is utilized to combust the column effluents. Thermal conductivity detectors do not degrade the effluents and are not as sensitive as flame ionization detectors. Electron capture detection is especially sensitive to halogenated compounds.

Retention time of a compound is a characteristic of that compound under a set of conditions. To resolve an overlap of retention time, a combination of GC with MS or IR is employed. Figures 4.11 and 4.12 show examples of GC/MS spectra for two isomers. Note the similarity that is typical of the GC/MS spectra of various isomers.

4.14 Nuclear Magnetic Resonance (NMR)

NMR is a unique technique that depends on the magnetic nature of a few isotopic nuclei, primarily ^{1}H, ^{13}C, ^{19}F and ^{31}P. In a strong magnetic field, a nucleus processes about the direction of the magnetic field with a frequency proportional to the field strength. A nucleus is bombarded with radio frequency electromagnetic waves at right angles to the magnetic field. When the spinning nucleus and the radio frequency become equal, resonance happens. The energy transfer is the basis of the NMR spectrum of the nucleus and is measured and depicted as a band. The resonance frequency at which the energy absorption occurs depends on the chemical nature of the sample and the environment (e.g., solvent). The nature of the bonds in a molecule can be identified by NMR (Fig. 4.13), by the use of reference spectra and characteristic frequencies for different types of chemical bonds.

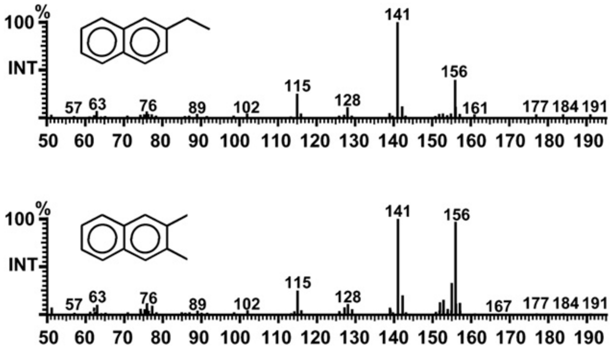


Figure 4.11 GC/MS spectra of alkylated polycyclic aromatic hydrocarbon (PAH) isomers.[23]

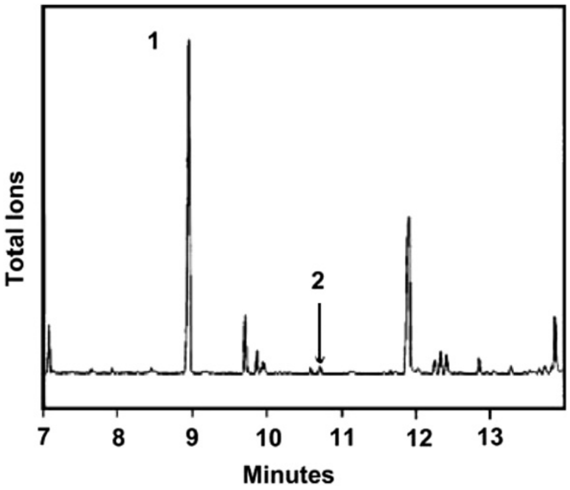


Figure 4.12 GC/MS thermal desorption chromatogram of silicon oil causing poor adhesion of thermally bonded package; peak 1: octamethylcyclotetrasiloxane, peak 2: decamethylcyclopentasiloxane.

If a strong magnetic field is applied to the nuclei, a difference can be found between alignment in the direction of the applied magnetic field and alignment in the opposite direction of the applied magnetic field. In NMR, the constraint that leads to quantized transitions is applied by the spectrometer. Due to this, the frequency of absorption varies with the applied magnetic field and thus there is no absolute frequency or wavelength for a given absorption. NMR spectra are not plotted as absorption versus wave number, as IR spectra are, but are plotted as absorption versus *chemical shift*, d. The chemical shift for proton NMR is the difference between the frequency of absorption of the sample and a standard, tetramethylsilane (TMS), normalized by the frequency of absorption of TMS, which is expressed in parts per million (ppm). Therefore, the above equation is multiplied by 10^{6}.[25]

In IR we consider two states for a bond: vibrating and nonvibrating. The transition associated with the

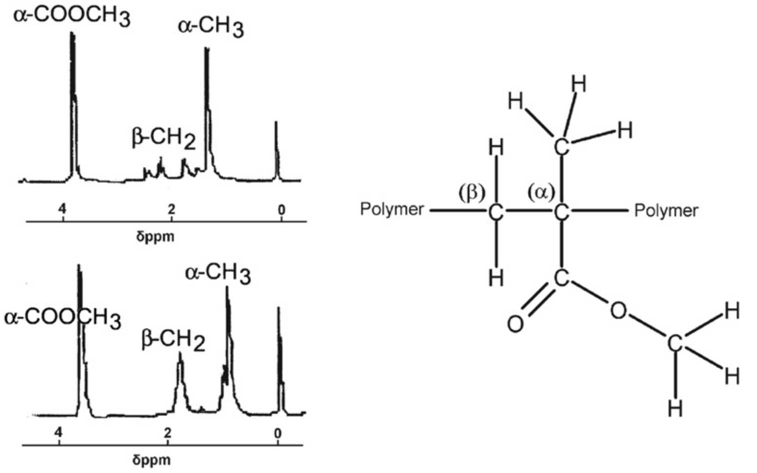


Figure 4.13 Example of NMR frequency shift in elucidating chemical structure of a polymethyl methacrylate.

change from nonvibrating to vibrating leads to the absorption at fixed wave numbers. In NMR several states are possible depending on the spin quantum number. The permitted states are given by the allowable values for the magnetic quantum number, $mI = I, I - 1, \ldots -I$. For $I = 1/2$ there are two states possible, $mI = 1/2$ and $mI = -1/2$. For $I = 1$ three states are possible, $mI = 1, 0, -1$. For protons the two allowable states are generally spoken of as parallel and antiparallel to the applied field.

PMMA was one of the first polymers studied in depth for tacticity, using proton NMR. For syndiotactic PMMA (bottom), three main absorptions are observed, α-CH_3 at 0.91, β-CH_2 at 1.9, and α-$COOCH_3$ at 3.6. For the isotactic polymer (top curve), the α-CH_3 is more deshielded at 1.20, the β-CH_2 becomes a quartet centered at 1.9 and the α-$COOCH_3$ remains a singlet at 3.6. The splittings of the β-CH_2 in what should be a sequence of 1:1:1:1 is due to two types of methylene groups, termed erythro, e (more deshielded), and threo, t (less deshielded), corresponding to the bottom and top protons in the molecular sketch above. Each of these peaks are split into two peaks by the other, leading to an expected splitting of four equal peaks, with a reported J coupling constant of about 0.2 ppm. The e and t protons are separated by 0.7 ppm, which can be verified by molecular modeling. A higher resolution NMR can resolve higher order stereosequences, as shown below for isotactic and atactic PMMA. You should compare the information content of the 60 MHz spectrum above to the 500 MHz spectra below. (Again, 60 MHz refers to the natural resonance frequency of a proton for a given magnetic field of the instrument, ν a B_0.)[26]

4.15 Differential Scanning Calorimetry (DSC)

DSC is one of the best known techniques among a group called *thermal analysis* methods. Others include *differential thermal analysis*, *dynamic mechanical analysis*, and *thermogravimetric analysis* methods; all will be covered in the following sections.

DSC is a thermal analysis technique that is used to measure the heat flows related to transitions in materials, as a function of time and temperature.[28] These measurements provide qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. Any event, such as loss of solvent, phase transitions, crystallization temperature, melting point, and degradation temperature of the plastic sample, results in a change in the temperature of the sample. The available DSC systems have a wide range of temperature capability, from −60 °C to >1500 °C.

Two types of systems are commonly used: *power compensation* and *heat flux* DSCs. In the former apparatus, temperatures of the sample and the reference are controlled independently by using separate but identical furnaces. The power input to the two furnaces is adjusted to equalize the temperatures. The energy required for the temperature equalization is a measure of the enthalpy or heat capacity of the sample relative to the reference. In *heat flux* DSC, the sample and the reference are interconnected by a metal disk that acts as a low-resistance heat-flow path. The entire assembly is placed inside a furnace. Changes in the enthalpy or heat capacity of the sample cause a difference in its temperature in relation to the reference. The resulting heat flow is small due to the thermal contact between the sample and the reference. Calibration experiments are conducted to correlate enthalpy changes with temperature differences. In both cases, enthalpy changes are expressed in units of energy per unit mass.

A typical DSC is run isothermally, or with the temperature change at a constant rate under an atmosphere of air, or another gas. In the isothermal case, the heat flow or enthalpy change is plotted against time. In the latter case, heat flow or enthalpy is plotted against temperature or time. Figure 4.14 shows an example of an enthalpy peak generated by an exothermic event or an endothermic event such as melting of the crystalline phase of a semicrystalline or crystalline polymer. Heat of fusion (H_{f0}) represents the enthalpy change at the crystal melting point of T_0. The weight fraction of the crystalline phase (W) can be determined by comparing the measured heat with H_{f0}. A sample of the polymer is heated in a DSC from a temperature of T_1 to T_2, where the polymer becomes amorphous at a temperature of T_0 prior to reaching T_2, as shown by the baseline shift in Fig. 4.14. The enthalpy changes are determined according to the following procedure.

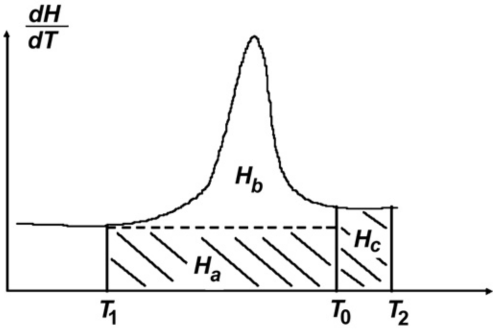


Figure 4.14 Example of a DSC peak.

H_a represents the simple enthalpy change during the heating of the polymer sample from T_1 to T_0. At T_0, the crystalline phase melts and becomes amorphous. The enthalpy of fusion is expressed in Eqn (4.3). The increase in the enthalpy of the amorphous phase as a result of heating from T_0 to T_2 is designated as H_c. If the enthalpy change, calculated from the separation of the DSC curve from the baseline (i.e., area under the curve), is designated as H_T, then Eqn (4.4) can be derived to calculate the weight fraction of the crystalline phase.

$$H_b = WH_{f0} \tag{4.3}$$

$$\begin{aligned} H_T &= H_a + H_b + H_c \\ H_T &= H_a + WH_{f0} + H_c \\ W &= \frac{(H_T - H_a - H_c)}{H_{f0}} \end{aligned} \tag{4.4}$$

An example of a DSC thermogram for two types of polyether ether ketone is given in Fig. 4.15.

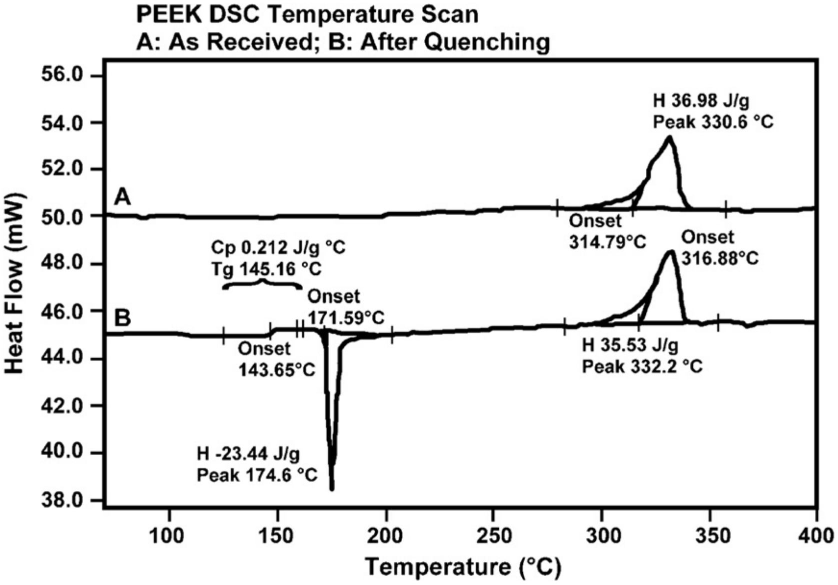


Figure 4.15 DSC thermogram for two types of polyetheretherketone.[27]

4.16 Differential Thermal Analysis (DTA)

This technique measures the temperature difference between a sample and a reference, as temperature is increased. A plot of the temperature difference (thermogram) reveals exothermic and endothermic reactions that may occur in the sample. Temperature for thermal events, such as phase transitions, melting points, crystallization temperatures, and others, can be determined by this method. Maximum temperature capability of DTA is in excess of 1000 °C under air or other gas atmospheres. A typical heat-up rate for DTA is in the range of 10−20 °C/min, although slower rates are possible by using a typical optimum sample weight of 50−100 mg. The sample should be ground to particles finer than 100 mesh.

Melting of a semicrystalline or crystalline polymer manifests itself as an endothermic peak. The peak temperature is correspondent to the actual melting point of the polymer. As in DSC, the area under the peak is proportional to the crystalline fraction of the sample. Mixtures of polymers can be characterized by DTA because the melting points of individual polymers are for the most part unaffected by the mixture. Similar polymers, such as high and low density, are distinguishable by DTA, whereas IR would not be able to easily resolve such subtle differences. Figure 4.16 shows the thermogram of a mixture of polytetrafluoroethylene (PTFE) and perfluoroalkoxy polymer (PFA). Three peaks are noticed: one at about room temperature (19 °C), which is a transition point for PTFE, and two melting points. PTFE and PFA are distinguished by the difference in their melting points.

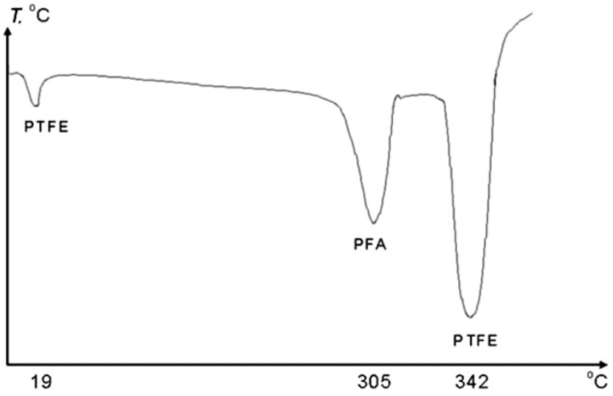


Figure 4.16 Examples of DTA thermogram for PFA and PTFE.

4.17 Dynamic Mechanical Analysis (DMA)

DMA method is generally a more sensitive technique for detecting transitions than are the DSC and DTA methods. This is because the properties measured are the dynamic modulus and damping coefficient, both of which change significantly when crystalline structure transitions to the amorphous phase. The operating principle is that in these transitions, a proportionally larger change occurs in the mechanical properties of a polymer than the change which occurs in its specific heat. DMA is, thus, the preferred method of measurement for glass transition temperature and other minor phase/structure changes of polymers.

The DMA method determines[29] elastic modulus (or storage modulus, G'), viscous modulus (or loss modulus, G''), and damping coefficient (Tan Δ) as a function of temperature, frequency, or time. Results are usually in the form of a graphical plot of G', G'', and Tan Δ as a function of temperature or strain. DMA may also be used for quality control and product development purposes.

The forced nonresonance technique is one of the simpler DMA methods.[30] In the majority of commercially available DMAs, a force is applied to a sample and the amplitude and phase of the resultant displacement are measured. These instruments utilize a linear actuator where the applied force is calculated from knowledge of the input signal to the electromagnetic coils in the driver. An alternative to the above is the use of a force transducer to measure the applied load, with the sample held between this transducer and the magnetic driver. These are the two types of arrangements that are found with the forced nonresonance technique. In each case, the sample is driven at a frequency below that of the test arrangement. Typically, the frequency range of instruments is from 0.001 to 1000 Hz. Any measurements below 0.01 Hz take too long for most analytical experiments, especially if the data are required as a function of temperature. Resonance often occurs at frequencies greater than 100 Hz, depending upon sample stiffness.

Figure 4.17 shows an example of a DMA output for polytetrafluoroethylene. Samples of PTFE were analyzed by DMA in shear mode at a length to thickness ratio of 4:1. Figure 4.17(a) shows the DMA output of stress versus time versus temperature, the results of which have been converted to Fig. 4.17(b) by the *time−temperature superimposition* technique.

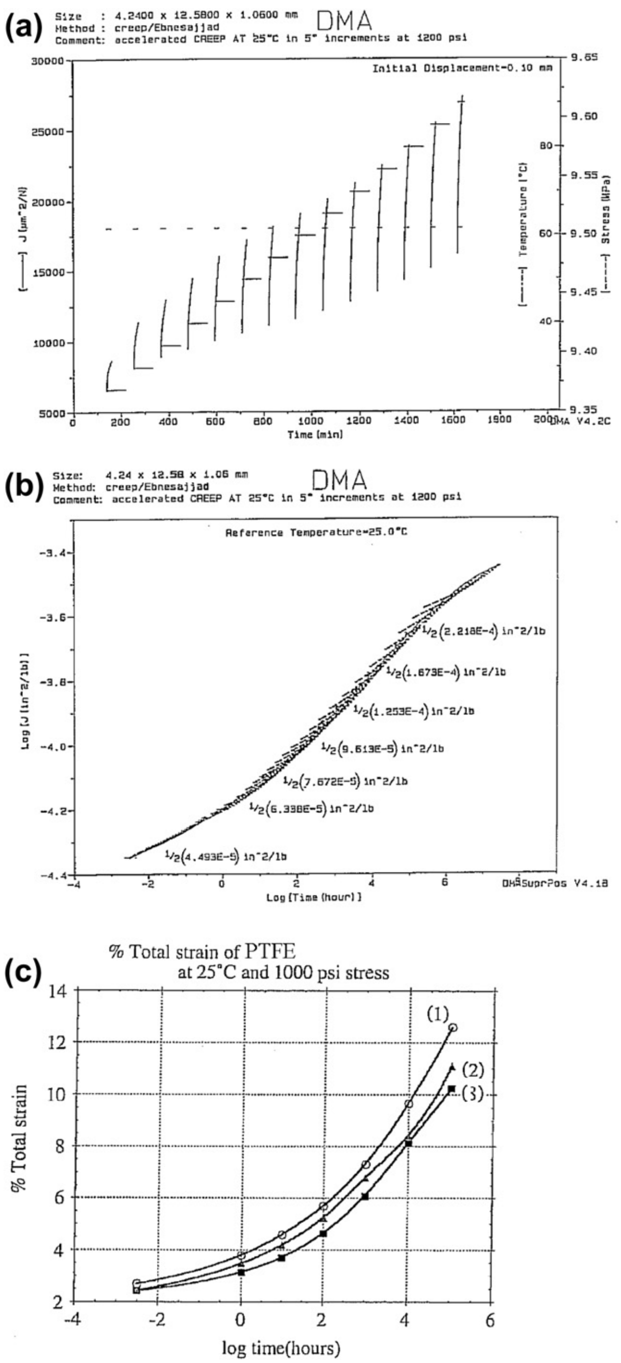


Figure 4.17 Examples of DMA graphs for three grades of PTFE.
(Courtesy DuPont Fluoroproducts.)

Time—temperature superimposition technique allows the prediction of material properties that normally would require measurements over many months or years. To collect the necessary data, measurement of a time-dependent variable is made at a number of temperatures. The curves are shifted mathematically along the time axis until some overlap occurs and a continuous curve is formed covering several decades of time; this curve is called the *master curve*. The master curve can be used to determine the time-dependent property as a function of time. Figure 4.17(c) shows total strain as a function of time and temperature for PTFE.

The choice of geometry will be dependent on the sample under investigation. For example, thin films can only be measured accurately in tension. High-quality dynamic mechanical testers perform well in tension and should apply the required pre-tension forces automatically, including those associated with large modulus changes that may occur at the glass transition. *Pre-tension* is necessary in order to maintain the sample under a net tension in order to prevent buckling that would otherwise occur. Tension should be the first choice for any sample less than 1 mm thick. Samples thicker than 1 mm will be likely too stiff for the instrument in tension; bending mode would be preferable in this case. Materials that creep excessively, such as polyethylene, may be difficult to test in tension, due to creep under the pre-tension force.

Readers interested in a more in-depth understanding of data obtained from DMA measurements can refer to polymer rheology textbooks. Helpful books on this topic include *Transport Phenomena* by Bird, Stewart, and Lightfoot, *Melt Rheology and its Role in Plastics Processing*—Theory and Applications, by J. M. Dealy and K. F. Wissbrun and *Polymer Melt Rheology*—A Guide for Industrial Practice, by F. N. Cogswell.[31,32]

4.18 Thermogravimetric Analysis (TGA)

TGA is a powerful technique for the measurement of thermal stability of materials including polymers. In this method, changes in the weight of a specimen are measured while its temperature is being increased. Moisture and volatile contents of a sample can be measured by TGA. The apparatus basically consists of a highly sensitive scale to measure weight changes and a programmable furnace to control the heat up rate of the sample. The balance is located above the furnace and is thermally isolated from the heat. A high precision hang-down wire is suspended from the balance down into the furnace. At the end of the hang-down wire is the sample pan, the position of which must be reproducible. The balance must be isolated from the thermal effects (e.g., by use of

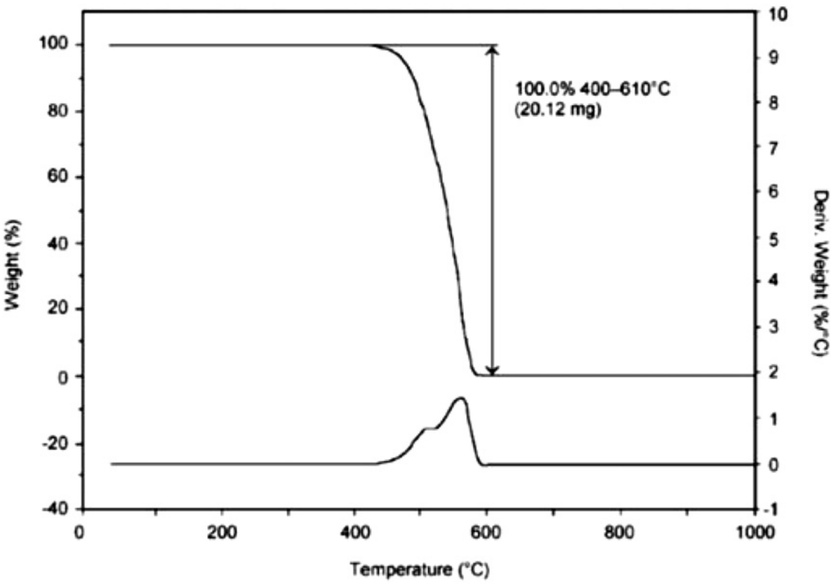


Figure 4.18 TGA thermogram of a neat FEP resin.
(Courtesy DuPont Fluoroproducts.)

a thermostatted chamber) to maximize the sensitivity, accuracy, and precision of weighing. Addition of an infrared spectrometer to TGA allows analysis and identification of gases generated by the degradation of the sample.

TGA apparatus is equipped with a microfurnace, which can be rapidly cooled. The heating element is made of platinum (reliable up to 1000 °C). An external furnace with a heating element made of an alloy of platinum and 30% rhodium can extend the temperature range to 1500 °C.

A modern apparatus is usually equipped with a computer that can calculate the weight-loss fraction or percentage. A commercial TGA is capable of >1000 °C, 0.1 μg balance sensitivity and a variable controlled heat-up rate under an atmosphere of air or another gas. Heat up rate capability of TGA may vary from 0.1 to 200 °C/min.

Figures 4.18 and 4.19 show the TGA spectra for the FEP resins, DSCs of which have been shown in the Figs 4.20 and 4.21. A comparison of these figures indicates deterioration in the thermal stability of FEP after incorporation of pigment. Figure 4.22 represents the TGA thermogram for a PTFE (31% wt.) compounded with carbon black (18% wt.) and silica (50.5% wt.). The 0.5% difference is due to the evolved volatile gases, which have not been shown in Fig. 4.22.

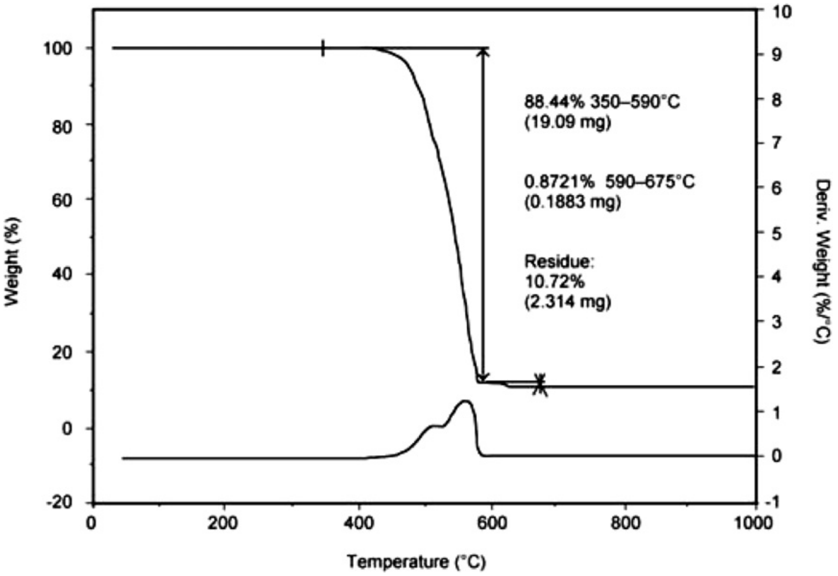
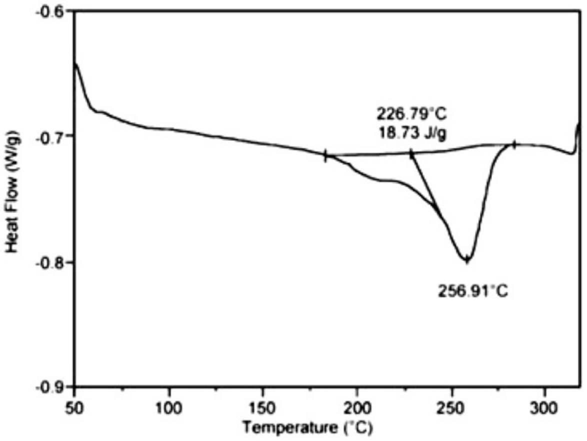
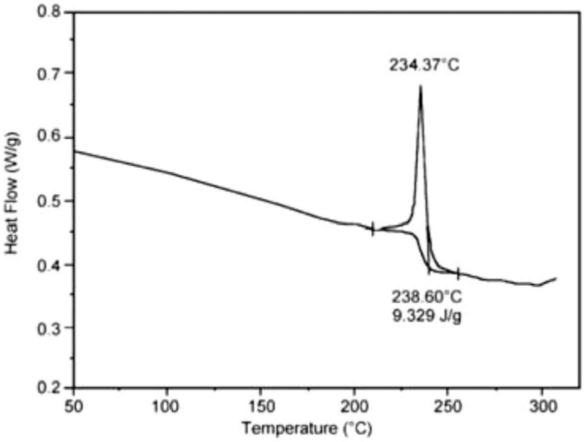


Figure 4.19 TGA thermogram of a pigmented FEP resin.
(Courtesy DuPont Fluoroproducts.)

(a) First heat cycle



(b) Cooling cycle



(c) Second heat cycle

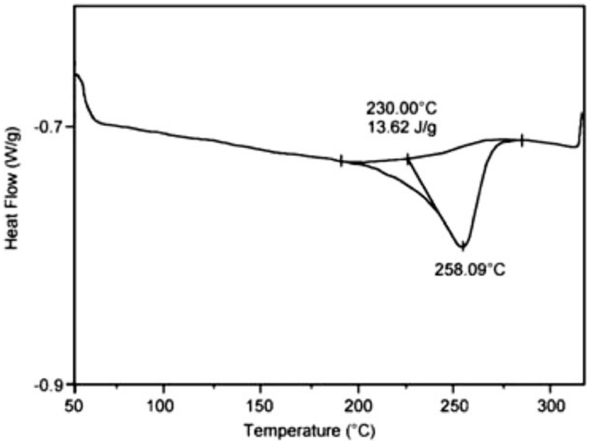
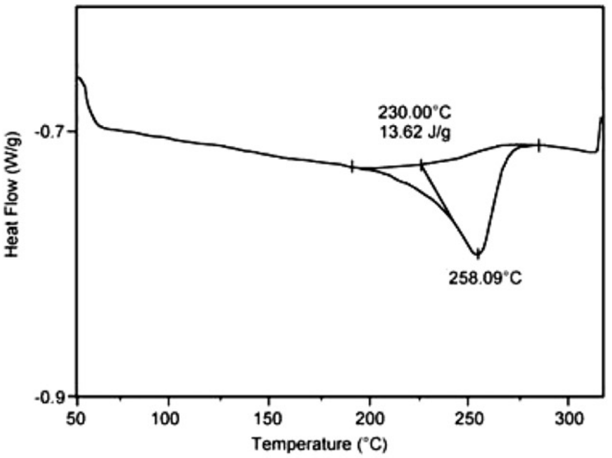


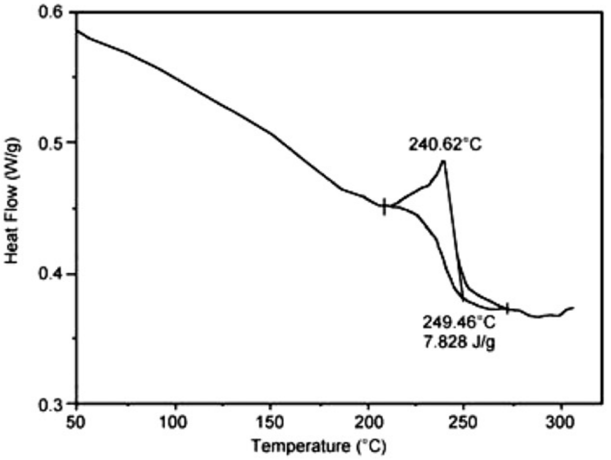
Figure 4.20 DSC thermograms of a neat FEP resin (melt flow rate = 30 g/10 min).

(Courtesy DuPont Fluoroproducts.)

(a) First heat cycle



(b) Cooling cycle



(c) Second heat cycle

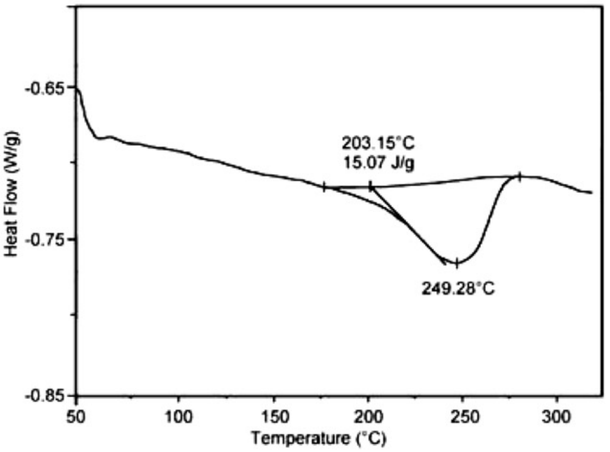


Figure 4.21 DSC thermograms of a pigmented FEP resin (melt flow rate = 30 g/10 min).

(Courtesy DuPont Fluoroproducts.)

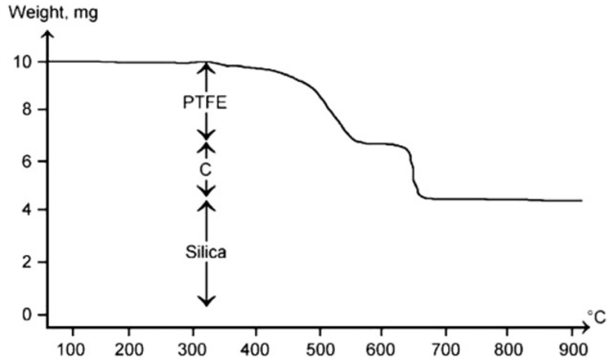


Figure 4.22 TGA thermograms of a pigmented PTFE resin.[35]
(Courtesy DuPont Fluoroproducts.)

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5 Material Surface Preparation Techniques

Sina Ebnesajjad

5.1 Introduction

Surface treatment and preparation for adhesive bonding is complex because of the material-specific nature of the required methods. This chapter and the next two are arranged in a comprehensive fashion to facilitate learning and referral. This chapter is devoted to delineating in a general manner the surface preparation and treatment techniques. Emphasized is the method instead of the specific material (adherend). Proceeding chapters focus on material-specific surface treatment processes and conditions for metallic and plastic/elastomer substrates, respectively.

Chapter 5 is organized to separate the sections for metallic and nonmetallic (plastics and elastomers) materials. Sections 5.3, 5.4, and 5.5 describe the surface treatment techniques of metals and Section 5.6 describes those of plastics and elastomers. Fluoroplastics are extremely difficult to treat and to adhere. They have been treated as a special case and are covered in Section 5.7. In Section 5.7, methods to assess the effectiveness of surface treatment are covered. Finally, Section 5.8 looks at the important topic of treatment age, which may affect bond strength and durability.

5.2 General Considerations

Adhesive bonding is a surface phenomenon; thus, preparation prior to adhesive bonding is the keystone of successful bonding. Surface preparation, or *surface pretreatment* as it is interchangeably known, is carried out to render adherend surfaces receptive to the development of strong, durable adhesive joints. It is desirable, although not always practical, to expose the basic adherend material directly to the adhesive, with no intervening layer of oxide film, paint, chromate coating, chromate-free coating, phosphate coating, or silicone release agent. Such layers are called "weak boundary layers," and in their presence the adhesive never directly contacts the adherend surface.[1]

Selection of the exact surface preparation method to use for a particular adherend requires careful evaluation. A number of factors, some obvious and others not, influence the choice. The size of component parts and the availability of equipment and facilities are obvious considerations. Less obvious factors include the rapid depletion of active chemicals in an immersion bath or the accumulation of foreign materials in the bath that gives rise to weak boundary layers.[1]

In order to place surface preparation in proper perspective, the adherend-to-organic material (i.e., adhesive) interface must be considered from design through fabrication. Joint design, adhesive selection, and processing must be considered. These factors are interdependent. The use of an optimum surface preparation is of little value when an unsuitable adhesive is used, the bond is not properly processed, or the joint design involves peel or cleavage stress.[2]

Proper surface preparation ensures that the weakest link in an adhesive joint exists within the adhesive or organic material layer and not at its *interface* within the adherend. In adhesive bonds, this type of fracture is known as *cohesive* failure: when a layer of adhesive remains on both adherends. *Adhesive* failure is when fracture of failure occurs at the adhesive-to-adherend interface. Many American Society for Testing Material (ASTM) prescribe reporting the mode of failure of fracture as a certain percentage cohesive and a certain percentage adhesive. From a surface preparation viewpoint, the ideal type of failure of a bonded joint or test specimen is one with 100% cohesive failure.[2]

Table 5.1 shows the different surface treatment processes for metallic and nonmetallic substrates and includes a short description of the effect of the treatment on the material surface.

5.3 Surface Treatment of Metals

Preparing the surface of a metallic sample involves multiple steps, and the sum of these steps are not always applied. Obtaining a quality adhesive bond without cleaning (and abrading) the metal

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Table 5.1 Surface Treatment of Materials to Enhance Adhesion

Substrate	Treatment method	Effect of treatment
Metals	Degreasing	Cleaning of the surface
Metals	Grit blast	Loose material (weak boundary) removal from the surface and increase in contact surface area
Metals	Acid etch/liquid pickling	Surface oxidation
Plastics	Corona treatment	Weak boundary layer removal and surface oxidation
Plastics	Flame treatment	Weak boundary layer removal and surface oxidation
Plastics	Chemical etching	Weak boundary layer removal and surface oxidation
Fluoroplastics	Chemical etching	Surface defluorination and oxidation

surface is not possible. Metals have high-energy surfaces and absorb oils and other contamination from the atmosphere. These steps are as follows:

1. Cleaning (using a solvent or other chemical) (Always)
2. Removal of loose materials (mechanical, e.g., grit blasting) also increases contact surface (Often)
3. Improvement of corrosion resistance (Almost always)
4. Priming (applying a material to the surface) (Sometimes)
5. Surface hardening (mechanical or chemical to strengthen the surface) (Occasional)

Metal surfaces are best cleaned by vapor degreasing with an organic solvent such as trichloroethane, although effective aqueous systems have been developed. This treatment is followed by grit blasting to increase the adhesive contact surface area by roughening the metal surface. Chemical etching removes weakly bonded oxides from the metal surface and forms an oxide that is strongly bonded to the bulk of the part. Another useful step is the *priming* of the part surface, which can improve the wettability of the surface and protect it from oxidation.

The optimum surface preparation to provide durability and uniform quality is ordinarily a chemical immersion or spray process. In the case of very large parts, the application is often carried out by the use of reagents in paste form. Low-energy surfaces, mainly plastics, require entirely different types of surface treatment that often alter the chemical nature of the surfaces.

The choice of the process used is desirable only if the production process of the entire system will accommodate it. Cost must also be considered and balanced against the requirement for reliability, maintainability, and critical roles of the joint.

Table 5.2 illustrates the importance of proper surface preparation for five different metal adherends, using two different adhesives and a variety of surface treatment techniques.[3] Figure 5.1 shows how various surface treatments impact the durability of the aluminum bond under adverse conditions. Surface treatment is particularly important for the durability of aluminum. The exact ranking order of results may change in studies of this type, depending on the adhesive primer and type of alloy being used.[4]

More recently, new surface treatments using non-isothermal, low-temperature plasma have drawn a great deal of interest. Plasma-chemical methods suitable for coating and surface treatment replace conventional galvanic methods, because they are not as harmful to the environment as the classical ones[5] (see Section 5.4.2).

5.4 Cleaning (Degreasing) Metals

Before adhesive bonding, thoroughly cleaning the adherends is essential. Unclean adherends will not be receptive to optimal adhesion, regardless of the quality of materials used, or the stringent control of the application process. Proper surface preparation is extremely important in assuring strong and lasting bonds. For many adherends, surface preparation requirements go far beyond simple cleanliness.

After cleaning is done to remove obvious surface contamination, such as soil, grease, oil, finger marks,

Table 5.2 Effect of Metal Substrate Surface Preparation in Adhesive Bonded Joints[3]

Adherend	Treatment	Adhesive	Shear strength, MPa
Aluminum	As received	Epoxy	3.06
Aluminum	Vapor degreased	Epoxy	5.77
Aluminum	Grit blast	Epoxy	12.1
Aluminum	Acid etch	Epoxy	19.0
Aluminum	As received	Vinyl-phenolic	16.8
Aluminum	Degreased	Vinyl-phenolic	19.9
Aluminum	Acid etch	Vinyl-phenolic	35.7
Stainless steel	As received	Vinyl-phenolic	36.0
Stainless steel	Degreased	Vinyl-phenolic	43.5
Stainless steel	Acid etch	Vinyl-phenolic	49.7
Cold-rolled steel	As received	Epoxy	20.0
Cold-rolled steel	Vapor degreased	Epoxy	19.9
Cold-rolled steel	Grit blast	Epoxy	29.6
Cold-rolled steel	Acid etch	Epoxy	30.8
Copper	Vapor degreased	Epoxy	12.3
Copper	Acid etch	Epoxy	16.1
Titanium	As received	Vinyl-phenolic	9.35
Titanium	Degreased	Vinyl-phenolic	21.4
Titanium	Acid etch	Vinyl-phenolic	46.5
Titanium	Acid etch	Epoxy	21.8
Titanium	Liquid pickle	Epoxy	22.9
Titanium	Liquid hone	Epoxy	26.9
Titanium	Hydrofluorosilicic acid etch	Epoxy	27.6

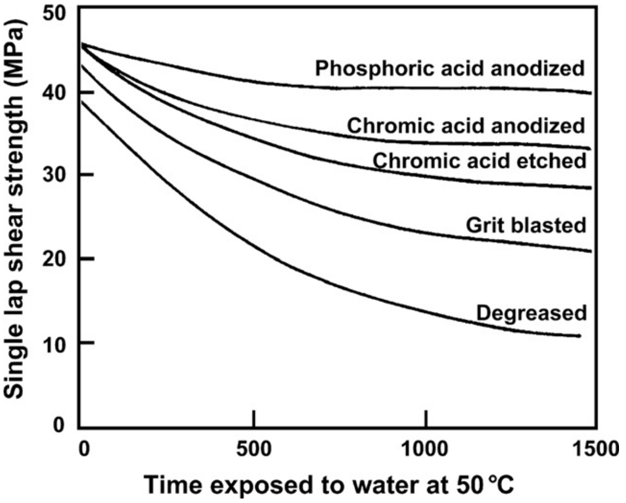

Figure 5.1 Effect of surface pretreatment on the performance of aluminum-alloy epoxy joints subjected to accelerated aging in water at 50 °C.[4]

and so on, specific chemical or physical treatments are usually required to produce a surface receptive to adhesion. Polytetrafluoroethylene (PTFE) and other fluorinated polymers are good examples of surfaces having this requirement. Adhesion bond strength to clean, pure PTFE is close to zero and it is only after severe chemical treatment, which alters the surface chemically and physically, that the surface is receptive to adhesion.

Magnesium is somewhat similar, requiring considerable treatment beyond simple cleaning. In the case of magnesium, however, strong initial adhesion is possible with clean magnesium. Even so, the chemically active nature of the metal means the permanency of this adhesion is poor. With many organic materials, such as adhesives, reactions occur at the metal-to-organic material interface, producing by-products having low cohesive properties. These by-products subsequently degrade the initially good adhesion to an unacceptable level. For this reason, using chemical or anodic treatments after cleaning magnesium is necessary. Such treatments result in the formation of thin inorganic chemical films, which adhere tenaciously to the magnesium and at the same time are receptive to adhesion to organic materials, such as adhesives. The treatment film laid down in this manner also functions as a barrier between the metal and organic material, preventing any chemical reaction between them. The term "cleaning" has come to mean removal of dirt, contaminants, and oils, and also specific chemical surface treatments for adhesive bonding.[2]

5.4.1 General Sequence of Cleaning

Any surface preparation requires completion of one, two, or three of the following operations:[2]

- Solvent cleaning
- Intermediate cleaning
- Chemical treatment

Priming, discussed later, may also be carried out in some cases in order to ensure superior durable bonds under particularly adverse environments.

5.4.1.1 Solvent Cleaning

Solvent cleaning is the process of removing soil from a surface with an organic solvent, without physically or chemically altering the material being cleaned. This includes various methods such as vapor degreasing, spraying, immersion, and mechanical or ultrasonic scrubbing. Solvent cleaning can be an end in itself, as in the case of vapor degreasing of an aluminum honeycomb core before bonding. It may also be a preliminary step in a series of cleaning and chemical treatment operations.[2]

The four basic solvent cleaning procedures are as follows[2]:

1. Vapor degreasing
2. Ultrasonic vapor degreasing
3. Ultrasonic cleaning with liquid rinse
4. Solvent wipe, immersion, or spray

5.4.1.1.1 Vapor Degreasing

Vapor degreasing is a solvent cleaning procedure for the removal of soluble soils, particularly oils, greases, and waxes, as well as chips and particulate matter adhering to the soils from a variety of metallic and nonmetallic parts. The principle step of vapor degreasing is scrubbing the part with hot solvent vapors. These vapors condense on the part at a sufficient rate to form liquid flow, which dissolves and washes the soil from the part as the condensed solvent drains by gravity. Vapor degreasing requires both the proper type of solvent and degreasing equipment. The solvents used must have certain properties, including the following:[2]

1. High solvency of oils, greases, and other soils
2. Nonflammable, nonexplosive, and nonreactive under conditions of use
3. High vapor density, compared with air, and low rate of diffusion into air to reduce loss
4. Low heat of vaporization and specific heat to maximize condensation and minimize heat consumption
5. Chemical stability and noncorrosiveness
6. Safety in operation
7. Boiling point low enough for easy distillation and high enough for easy condensation (for recycling and reuse of dirty solvent or regeneration of clean solvent from used)
8. Conformance to air pollution control legislation

The eight common vapor degreasing solvents are as follows:

1. Methyl chloroform (1,1,1-trichloroethane)
2. Methylene chloride (dichloromethane)
3. Perchloroethylene (tetrachloroethylene)
4. Trichloroethylene
5. Trichlorotrifluoroethane
6. Trichlorotrifluoroethane-acetone azeotrope
7. Trichlorotrifluoroethane-ethyl alcohol azeotrope
8. Trichlorotrifluoroethane-methylene chloride azeotrope

These materials have a wide range of boiling points, from a low of 39 °C for methylene chloride to a high of

121 °C for perchloroethylene. Trichloroethylene and perchloroethylene are the solvents most commonly used for vapor degreasing, particularly the former. Considerable attention to detail regarding equipment is required, and the vapor degreasing process is given in Ref. 2.

5.4.1.1.2 Ultrasonic Vapor Degreasing

Vapor degreasers are available with ultrasonic transducers built into the clean solvent rinse tank. The parts are initially cleaned either by the vapor rinse or by immersion in a boiling solvent. They are then immersed for ultrasonic scrubbing, followed by rinsing with vapor or spray plus vapor. During ultrasonic scrubbing, high-frequency inaudible sound waves (more than 18,000 cycles per second) are transmitted through the solvent to the part, producing rapid agitation and cavitation. The cavitation (repeated formation and implosion or collapsing of the bubbles in the solvent) transmits considerable energy to the parts and to the soil on them. Particulate materials, insolubles, and strongly adherend soils are quickly removed from a part, even on remote surfaces and blind holes. The ultrasonic frequency and intensity for optimum cleaning must be selected by test. It depends on the type of part being cleaned, soil removed, and particular solvent in the system. Some ultrasonic degreasers have variable frequency and power controls. The most common frequency range for ultrasonic cleaning is from 20,000 to 50,000 cycles per second. Power density may vary widely, but 2, 5, and 10 W/in^2 are common.[2]

5.4.1.1.3 Ultrasonic Cleaning With Liquid Rinse

Ultrasonic cleaning is a common procedure for high-quality cleaning, utilizing ultrasonic energy to scrub the parts and a liquid solvent to rinse away the residue and loosened particulate matter. This procedure, rather than using the vapor degreasing technique for precleaning and final rinsing, utilizes manual application of liquid solvents. The process is not limited to any particular solvents and, indeed, organic solvents need not be used. It is widely used with aqueous solutions: surfactants, detergents, and alkaline and acid cleaners. The only real limitations are that the cleaning fluid must not attack the cleaning equipment, fluids must not foam excessively, and the fluids must cavitate adequately for efficient cleaning.[2]

The process is not as efficient as vapor rinse, solvent wipe, immersion, or spray, but it is suitable for many surface preparation applications and pretreatments. One or a combination of these techniques may be used. A large number of solvents are recommended. Solvent wiping is the most portable and versatile of these methods, but is also the least controllable. There is always a danger of incomplete removal of soil, and spreading of soil in a uniform manner, causing its presence not to be readily visible, and contamination of a surface with unclean wiping materials.

For general cleaning, wiping materials should be clean, freshly laundered cotton rags, new cheese cloth, or cellulose tissues. For special super-clean applications whereby cleaning must occur in a controlled "clean" room, specially processed lint-free polyurethane foam wiping materials are available (from Sills and Associates, Glendale, CA). The solvent should be used only once, and it should be poured onto the wiping material. The wiping material should never be immersed in the solvent. Solvent containers with small openings should be wiped systematically with the solvent-soaked cloth or tissue. The wiping material should be discarded, and the surface should be cleaned again with new solvent and cloth or tissue. This cycle should be repeated until there is no evidence of soil on either the cloth or the cleaned surface.

Although immersion and soaking in a solvent is often sufficient to remove light soil, scrubbing may be required for heavier soils. The most efficient scrubbing method is ultrasonic, as discussed earlier. Other scrubbing techniques include tumbling, solvent agitation, brushing, and wiping. After the parts are soaked and scrubbed they must be rinsed. The quality of cleaning produced by the immersion process depends primarily on the final rinse. The solvent spray cleaning method is efficient because of the scrubbing effect produced by the impingement of high-speed solvent particles on the surface. The solvent impinges on the surface in sufficient quantity to cause flow and drainage, which washes away the loosened soil. Also, because only clean solvent is added to the surface, and scrubbing and rinsing occur, there is no danger of contamination, as there is with the immersion process.

5.4.1.1.4 Safety

Four safety factors must be considered in all solvent cleaning operations: toxicity, flammability, hazardous incompatibility, and equipment. The solvents must be handled in a manner that prevents toxic exposure of the operator. Where flammable solvents are used, they must be stored, handled, and used in a manner preventing any possibility of ignition. In a few cases, knowledge of the hazardous incompatibility of the solvents, cleaning equipment, and materials to be cleaned is essential. Safe equipment and proper operation are also critical. Snogren lists maximum acceptable concentrations (MACs), the term being synonymous with threshold limit values (TLVs), for a number of solvents used in cleaning. These values are given in parts per million (ppm) (e.g., acetone, 1000 ppm; methyl alcohol, 200 ppm; and methyl chloroform, 500 ppm). Obviously methyl alcohol, which requires less concentration to incapacitate than do methyl chloroform and acetone, is the solvent with the greatest exposure to danger. It should be pointed out that TLVs are merely guides in the control of health hazards, and represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect.[2]

All flammable solvents should be stored in metal containers, such as safety cans, and must be applied using metal containers. The container should be grounded during pouring or dispensing. Snogren gives flammability limits in terms of percentage by volume in air (lower and upper) for the solvents commonly used. Some of the solvents he lists are nonflammable. The flammable solvents must be used only in areas ventilated to prevent accumulation of vapors and fumes. Other obvious precautions must also be taken. Unstabilized methyl chloroform, trichloroethylene, and perchloroethylene are subjected to chemical reaction on contact with oxygen or moisture, forming acid by-products. These acids are highly corrosive to metals. Only stabilized grades of these solvents should be used. Strong alkalies, such as caustic soda, may react with trichloroethylene to form explosive mixtures (dichloroacetylene). Fluorocarbon solvents may react violently with highly reactive alkaline earth metals.[2]

5.4.1.2 Intermediate Cleaning

Intermediate cleaning is the process of removing soil from a surface by physical, mechanical, or chemical means without altering the material chemically. Small amounts of parent material may be removed in this process. Examples include grit blasting (most common technique), wire brushing, sanding, abrasive scrubbing, and alkaline or detergent cleaning. Solvent cleaning should always be carried out before this step. Intermediate cleaning operations may be an end in themselves. Examples of such a situation include cleaning stainless steel with uninhibited alkaline cleaner or detergent scrubbing epoxy laminates.[2]

5.4.1.2.1 Grit Blasting (contributed by Dr Laurence W. McKeen)

Grit blasting is the method most commonly used to obtain good adhesion of fluoropolymer coatings. Grit blasting should precede preheating of ferrous metals to retain the protective oxide formed. With other clean substrates, the order of these two operations is not important.

Grit blasting is a relatively simple process. Hard grit is propelled by compressed air, or occasionally by high-pressure water, directed at the substrate that needs cleaning or roughening.

Grit blast profiles are commonly measured in microinches or root mean square by means of a profilometer (see Section 5.3). A profilometer drags a diamond stylus across the substrate and measures the depth of the peaks and valleys (Table 5.3).

Surface profiles in excess of 100 microinches (2.5 μm) are recommended and 200−250 microinches (5.1−6.5 μm) are frequently employed. On hard substrates, aluminum oxide grit from #40 to #80 is commonly used at air pressures ranging from 80 to 100 psi (5.8−7.3 kg/cm^2) at the gun. Aluminum and brass are commonly used at air pressures ranging from 80 to 100 psi (5.8−7.3 kg/cm^2) or below. Maximum air pressures on stainless steel may exceed 100 psi (7.3 kg/cm^2).

It should be noted that profiles measured by common profilometers indicate only the depth of profile. They measure neither uniformity or coverage of the grit nor the sharpness of the peaks. Full coverage of the grit blast is indicated by lack of gloss on the metal surface when viewed at a flat grazing angle.

There are numerous types of grit. The choice of which grit to use depends on its intended purpose, the substrate, and the expense. Important properties of the grit include hardness (grit needs to be harder than the substrate to roughen it). Denser materials have more momentum and impart more energy to the substrate.

Sometimes minimal damage to the substrate is required. This could be due to the relative softness

Table 5.3 Grit Blast Media Properties

Media	Hardness, Moh	Density, g/cm^3	Bulk density, lb/ft^2 (g/cm^3)	Relative cost volume basis
Walnut shells	1–4		40–80 (0.64–1.28)	19
Silicon carbide	9	3.2	95 (1.52)	50
Aluminum oxide	9	3.8	125 (2.00)	25
Glass bead	6	2.2	100 (1.60)	18
Plastic grit	3–4	1.45–1.52	45–50 (0.72–0.80)	30
Steel shot	6	7.87	280 (4.49)	27
Steel grit	6	7.87	230 (3.68)	
Sand, silica, (silicon dioxide)	7	2.6		11
Sodium bicarbonate	2.5	2.16		

of the substrate or because the texture of or pattern machined in the substrate needs to be maintained. Plastic grit, walnut shells, or sodium bicarbonate can clean the substrate or remove the previous coating.

Occasionally, the abrasive is propelled by pressurized water. Sodium bicarbonate slurries have been used to remove fluorocarbon coatings in this fashion.

Aluminum oxide is usually offered in a size range of 16–240 grit. It is angular in shape. It is the most popular cleaning blast media. Aluminum oxide conforms to major industrial and government standards including MIL A21380B and ANSI B74.12-1982.

Silicon carbide is usually offered in a size range of 16–240 grit. It is angular in shape. Silicon carbide is an extremely hard sharp grain that is more friable than aluminum oxide. It is used in blasting of extremely hard materials, and it is expensive.

Sand, silicon dioxide, or silica, is considered too smooth and uniform. It breaks down too rapidly to be useful in preparing metal substrates and, though it is cheap and naturally occurring, it is not recommended.

Glass beads are made from chemically inert soda-lime glass. Blasting with glass bead will produce a metallurgically clean surface for parts and equipment. The beads are spheres of uniform size and hardness. Glass beads can meet OSHA standards for cleaning operations. Another advantage of using glass beads is the disposability; spent glass is environmentally friendly. This can simplify the disposal and reduce cost. Glass beads are often used for stress relief. Mil-spec (MIL-G-9954A) glass beads are available.

Crushed glass is available in a range of sizes from coarse to very fine. Crushed glass is an excellent low-cost alternative to various reclaimed blast abrasives. Although it breaks down relatively easily, it is silica free with minimal iron content (2%) and produces a luster-white metal finish.

Steel grit and shot are generally available with diameters of 0.007–0.078 in. Steel grit is angular in shape, whereas shot is round. Steel grit and shot have one of the lowest breakdown rates of all blast media and can, therefore, be recycled and reused. The density is also high, which helps impart more energy to the substrate being cleaned. Steel grit is excellent for use in large blast room applications. It should not be used on stainless steel where iron impregnation is a concern. Cast stainless steel shot is available for nonferrous castings or for other items where ferrous contamination is a problem.

Walnut shells are not very hard. This media is offered in sizes 10/14, 14/20, 20/40. The abrasive is soft, friable dried shells or nuts. It is sometimes called "organic," or agrishell abrasive and is often used for removing contaminants, such as carbon deposits or old paint from delicate parts, or for removing soft materials, such as aluminum. It is also good for blast cleaning with portable equipment.

Plastic grit is another soft medium, typically in a size range of 12–60 mesh. It is often made from recycled or waste plastic. Like walnut shells, plastic grit is typically used to clean surfaces and remove old paint without harming the substrate.

Blasting of baking soda is unique because of its biodegradable characteristics. Cleanup after use is easy, because it is water soluble and can be literally "washed" away. Baking soda is commonly used where one-pass coverage with no recovery is acceptable or desirable, and the substrate is delicate or sensitive. Typical applications for baking soda include graffiti removal, boat hulls, and large printing press rolls. It is often made into waterborne slurry and propelled by high-pressure water.

5.4.1.3 Chemical Treatment

Chemical treatment is the process of treating a clean surface by chemical means. The chemical nature of the surface is changed to improve its adhesion qualities. Solvent cleaning should always precede chemical treatment and, frequently, intermediate cleaning should be used in between.[2]

5.4.2 Surface Treatment of Metals—Atmospheric Plasma Jet

In addition to using plastics, glass, or polymers, plasma treatment for cleaning of the contaminants and surface modifications are used in various applications. This produces the new functional surfaces, for thermally sensitive substrates can be used for treatment. Plasma pretreated metal products have new applications in the field of automobile, printed circuit board manufacturing, and electromagnetic interference shielding materials, and so on, which affects environmental nonpollution. This indicates that for these applications, the surfaces must be cleaned and activated, resulting in enhancing the adhesion properties between metal−metal and metal−polymer interfaces.[6,7]

Kim et al.[5] have reported the investigations of surface modification phenomena of different metal surfaces by atmospheric plasma jet treated under the condition of nearly atmospheric pressure. The aims of our study are to obtain the optimum conditions with high surface energy and to understand the surface phenomena for increasing the adhesion property.

5.5 Priming

An adhesive primer is usually a dilute solution of an adhesive in an organic solvent applied to the adherend producing a dried film with a thickness of 0.0015−0.05 mm. Some of its functions are as follows:

- Improves wetting[8]
- Protects the adherend surface from oxidation after surface cleaning, extending the time that may elapse between surface preparation and adhesive application. (Such an extension may increase the usable time for aluminum adherends from 12 h to up to 6 months)[2]
- Helps inhibit corrosion (corrosion inhibiting primes)[8]
- Modifies the properties of the adhesive to improve certain characteristics, such as peel[9]
- Serves as a barrier coat to prevent unfavorable reactions between adhesive and adherend[8]
- Holds adhesive films or adherend in place during assembly. This type of primer retains tack or develops tack at room or elevated temperatures[9]

The use of primers provides (1) more flexible manufacturing scheduling, (2) high reliability of joints, (3) less rigorous cure conditions, (4) wider latitude in choice of adhesive system, and (5) more durable joints.[8] Primers are usually not fully cured during their initial application. They are dried at room temperature and some are force-dried for 30−60 min at 65.5 °C. These steps, frequently called "flashing," provide a dry nontacky surface that can be protected from contamination and physical damage by wrapping with clean paper, sealing in polyethylene bags, or covering with a nontransferring adhesive-backed paper.[2]

When primers are desirable, the manufacturer's literature will ordinarily specify the best primer to use. The primers, such as the adhesives, are usually proprietary in nature and are made to match the adhesives.[9]

5.6 Surface Treatment of Plastics

An important and relevant difference between metals and plastics is their surface energy. Polymers have inherently lower surface energy than metals (assuming they are contamination-free), and tend to form intrinsically poor adhesion bonds without some type of treatment. Adhesion is the mechanical resistance to separation of a bonded system and involves the outer surface of a material. Treatment only

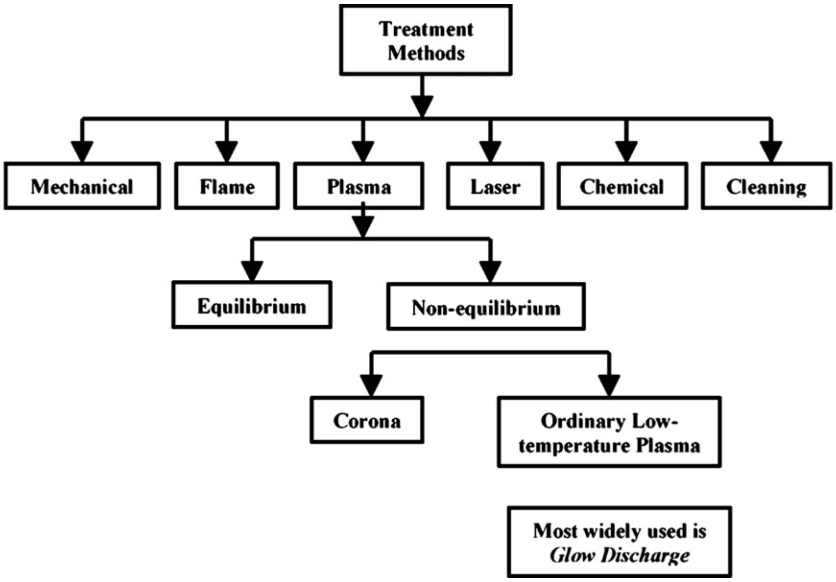

Figure 5.2 Classifications of plastic treatment techniques.

impacts the region near the surface and does not alter the bulk properties of the plastic parts.

During the dawn of plastic technology, chemical priming was the only method of surface preparation. Soon after, the first rudimentary machines were developed to treat polymer surfaces, increasing their polarity and surface energy and making them acceptable for the various laminating, coating, and decorating processes. The flame and corona treatment methods gradually evolved through the 1960s and 1970s. With solvent-based systems predominant, major breakthroughs came slowly. The advent of waterborne—and then energy-cured—systems changed the pace of development. Suddenly, marginal treatment levels (34—38 dynes/cm) caused serious adhesion bond quality problems. Films that had been readily printable exhibited pinholes, fisheyes, ink liftoff, and other defect types. The remedy was to increase the treatment level to a part surface energy of 40 dynes/cm or higher.

There are now chemical, physical, and bulk treatment methods available for adhesion enhancement. Chemical modification techniques include those usually requiring wet or chemical reactions as the primary means of altering the surface; such as wet etching, grafting, acid-induced oxidation, and plasma polymerization. Physical surface treatment methods include corona discharge, ion or electron beam, photon beams (laser, ultraviolet light, and X-ray), plasma discharge, and flame oxidation. Bulk methods involve additives, blending, or recrystallization, all of which affect the bulk properties of plastics.

This section describes the significant techniques available for the treatment of plastic surfaces to enhance adhesion (Fig. 5.2). Not all methods have wide commercial application. Some of the techniques are limited in the scope of their use. For example, chemical treatment (acid-induced oxidation) is the most frequently used method to impart adherability to plastic surfaces. Plasma treatment is limited to smaller components and parts. Flame and corona treatments are effective for continuous films (often called webs) and thin sheets of plastic, usually operated at high speed.

5.6.1 Effect of Treatment on Plastic Surfaces

The changes that occur in the surface of plastics by applying the treatment methods are the result of the four processes of *cleaning*, *ablation*, *cross-linking*, and *surface chemical modification* (mostly oxidation). Common treatment methods include corona, flame and plasma treatment, and chemical etching, all of which serve to increase the surface energy of plastics. The polar component of surface energy should be increased by 15—20 dynes/cm to achieve proper adhesive bonding in polymers such as polyolefin, polyphenylene sulfide, polyaramide, and others.[10] The other changes in the plastic surfaces include removal of weak materials, strengthening of the surface (by cross-linking), and increased surface roughness.

The increase in surface energy of plastic occurs through the surface oxidation of the polymer chains of the plastic part. For halogenated polymers, such as chlorinated and fluorinated polymers, surface modification involves significant dehalogenation, which is the removal of chlorine and fluorine atoms from the surface molecules. In general, each surface treatment can be viewed as a transfer of energy to the surface of plastics. In almost every case, the dissipation of treatment energy on the plastic surface results in more than one change to the surface; these changes are described later.

Cleaning, or removal of contamination, including process oils, dirt, waxes, mold release agent, and exuded plasticizer, is an important change that occurs as a result of surface treatment. Methods involving chemicals such as solvent cleaning and etching, if not properly used, can leave behind a residue that may interfere with adhesive bond formation. Clean surfaces must be protected because of rapid reacquisition of contamination from the ambient atmosphere.

Plastic surfaces often contain a low-molecular-weight polymer such as an oligomer or loosely bonded matter, also called a *weak boundary layer*. There is some debate about production of low-molecular-weight polymers as a result of surface treatment.[11] The low-molecular-weight polymer is also the normal product of most polymerization reactions. Loosely bonded material may originate from the plastic part itself and additives incorporated such as pigments, processing aids, and mold release agent. They may also have been acquired externally as a result of contact with contaminated surfaces or exposure to a contaminated environment. The treatment methods remove loose material from the part surface. One mechanism for removal of material from the part surface material is *ablation,* which is the degradation and conversion of organic matter into volatile species.

The electrical discharge at the plastic surface during *corona-treatment* reacts with the polymer molecules generating free radicals. The presence of free radicals allows cross-linking and funtionalization of the plastic surface with and without chain scission. The radicals rapidly react with ambient oxygen and produce peroxide groups that can decompose and give rise to a variety of polar groups. These groups include hydroxyl (OH), carbonyl (C=O), and carboxylic acid (O=C−OH), the presence of which has been confirmed by electron spectroscopy for chemical analysis (ESCA or XPS).

Corona treatment is believed to roughen the plastics by the degradation of amorphous regions of the polymer surface.[12] The belief is that corona treatment does not impact the crystalline region of the surface, preferentially attacking the relatively weak amorphous regions. Degradation and subsequent removal of the amorphous material leads to the increased roughening of the surface of plastics such as polyethylene.[13–15] A rough surface provides a much larger adhesive contact area than a smooth surface.

Plasma treatment oxidizes the surface of the polymer in the presence of oxygen. It can, thus, remove organic contaminants from its surface. Early studies have concluded cross-linking of low-molecular-weight surface species as the mechanism for elimination of a weak boundary layer.[16] More recent research has attributed the effectiveness of plasma treatment to surface cleaning, ablation of surface polymer chains, surface cross-linking of polymer chains, and introduction of polar functional group that result in increased surface energy.[17]

The mechanism of *flame treatment* is thermal oxidation of the polymer surface. Flame temperature may exceed 2000 °C. It can clean the surface and remove the weak boundary layer by vaporizing surface contamination and low-molecular-weight polymers.

Chemical treatment, or etching, oxidizes the plastic surface similarly to corona treatment. For instance, chromic acid is used to etch the surface of polyethylene and polypropylene (PP). An increase in etching time and temperature intensifies the surface treatment by increasing the degree and depth of oxidation.

5.6.2 Surface Cleaning

Nonmetallic material, namely plastics, should be degreased, if necessary, with an aqueous detergent solution followed by a thorough rinse with clean water and dried. The detergent can be substituted by a solvent. Either solvent or detergent solutions can remove mold-release agents or waxes from the plastic part surface. Effective solvents include methyl ethyl ketone, acetone, and methanol, depending on the plastic type. Resistance of the plastic to the solvent should be considered in their selection to prevent dissolving or degrading the plastic during cleaning. The chemical surface cleaning step is skipped if the treatment technique can accomplish adequate cleaning; in addition to surface modification, such as plasma treatment.

5.6.3 Mechanical Treatment (Surface Roughening)

Surface roughening and sanding of plastics accomplishes the same purposes as those of metals. Essentially, loose and unstable polymers are removed from the surface, thus increasing contact surface area. This step is not pertinent, if there are decorative and aesthetic considerations that require an even, smooth surface. For instance, if a plastic part is painted or laminated to a thin film, the application of surface roughening and sanding may not be possible or limited. When applicable, plastic surfaces are usually hand-sanded or sand-blasted to impart roughness (increased contact surface area) to the part surface.

5.6.4 Corona Treatment

Corona discharge takes place at atmospheric pressure in contrast to low-temperature (or cold) plasma that requires vacuum. Corona is a stream of charged particles, such as electrons and ions, that is accelerated by an electric field. It is generated when a space gap filled with air or other gases is subjected to a sufficiently high voltage in order to set up a chain reaction of high-velocity particle collisions with neutral molecules, resulting in the generation of more ions. Corona discharge has been applied to treat the surface of plastics to render them adherable (Fig. 5.3). In this method, the plastic article is exposed to a corona discharge produced by high-frequency, high-voltage alternating current.

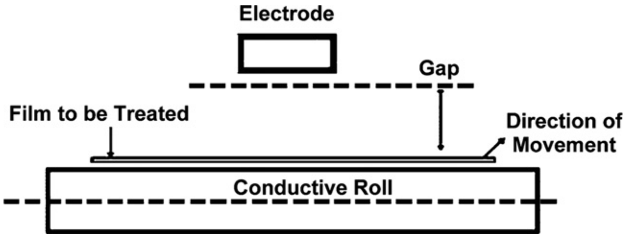

Figure 5.3 Conceptual schematic diagram of a film corona treatment system.

There are three types of treating configurations (two of which are shown in Fig. 5.4), and all consist of the same parts, including an electrode, an electrical insulator or dielectric, and a return path or ground. The differences among the three configurations are in the location of the electrode. In a conventional system (Fig. 5.4a), the web passes over a roll, which is covered with insulating material such as a silicone rubber. A metal electrode is suspended above the roll so that an air gap of 1.5−2.5 mm exists between the electrode and the insulated roll. High voltage operates across the air gap, ionizing it and forming a corona discharge curtain between the electrode and the material (e.g., film) that is being treated. The conventional configuration can be used only with nonconductive material. The second configuration is called *bare roll* (Fig. 5.4b), in which the electrode is covered with a dielectric (usually ceramic), and the roll is made of anodized aluminum. In the third configuration, called *double dielectric*, the roll and the electrodes are covered with dielectric material.

The main parameters for the control of the treatment process include voltage, width of the air gap between electrodes, film/web speed, and width of the electrodes. Most machines allow treatment of one

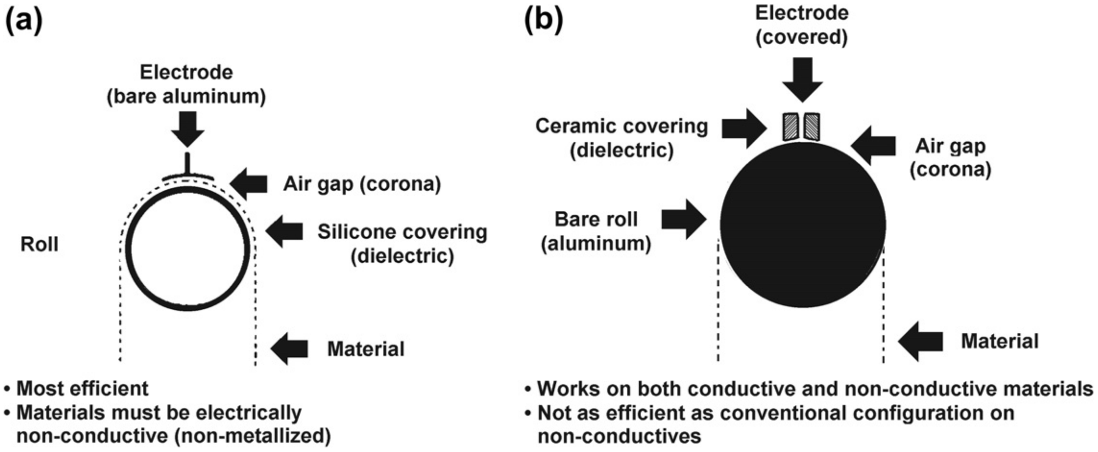

Figure 5.4 Configurations of corona treatment equipment. (*a*) Conventional configuration. (*b*) Bare-roll configuration.[15]

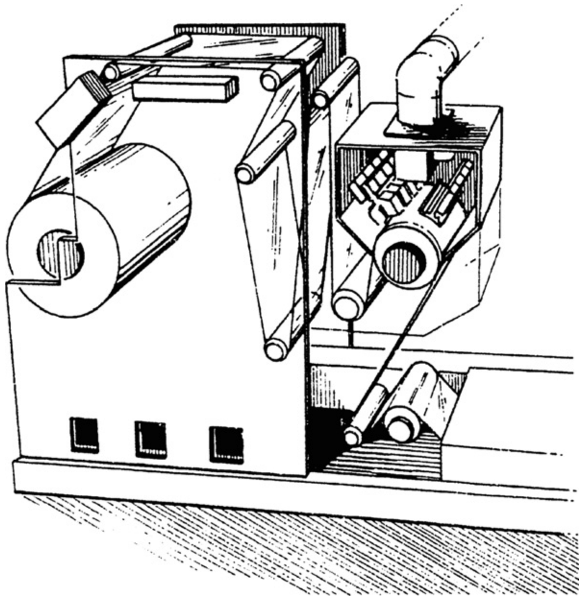

Figure 5.5 A typical single side corona treatment machine.

side of the web (Fig. 5.5), and require two passes for two-sided treatment. There are machines that are equipped with two sets of electrodes for one-pass two-sided treatment.

The appropriate treatment voltage to turn the air in the electrode gap into a conductor depends mainly on the size of the gap. It is possible to reduce the voltage to about 300 V independent of the gap size (within the operating range) by increasing the current. The color of a stable corona discharge is purple, resembling a natural gas flame across the gap.

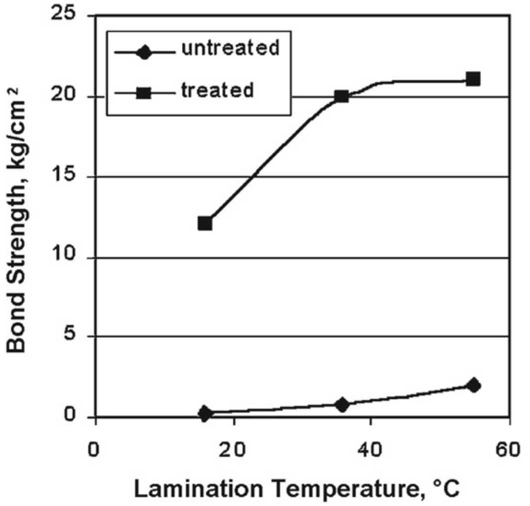

Figure 5.6 Adhesion bond strength of polyethylene (PE) to itself as a function of lamination temperature for untreated and corona-treated PE.

Effect of corona treatment on adhesion of polyethylene to itself (autohesion) has been studied as a function of lamination temperature and density, as shown in Figs 5.6 and 5.7.[18,19] Corona treatment has a dramatic effect on the increase of adhesion bond strength over that achieved with untreated polyethylene. Increase in lamination temperature enhances the bond strength of treated film.

Effectiveness of corona treatment depends on the type of polymer. Examples of bond strengths of corona-treated PP and a polyetherimide can be found in Fig. 5.8. PP is affected by the treatment, as seen by the increase in adhesive bond strength in contrast to the bond for the polyetherimide, which is unchanged.

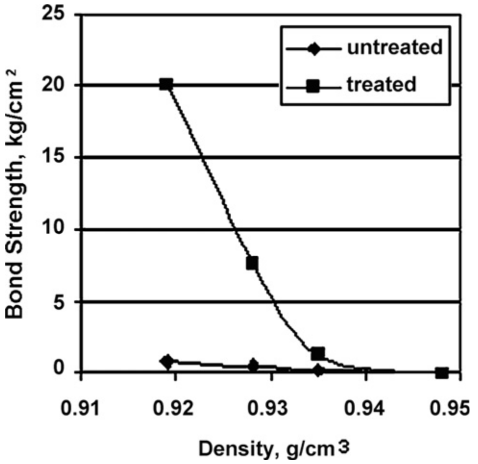

Figure 5.7 Adhesive bond strength of polyethylene (PE) to itself versus density at lamination temperature of 36 °C for untreated and corona-treated PE.

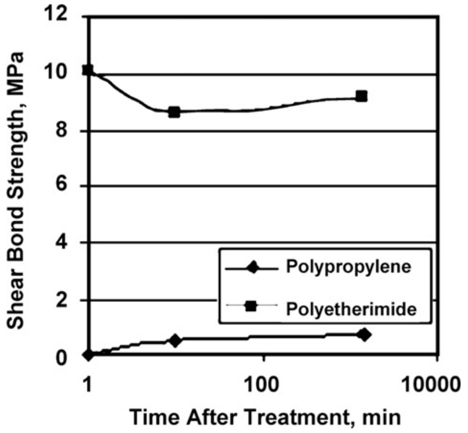

Figure 5.8 Bond strength (shear) of corona-treated polypropylene, bonded to aluminum using an epoxy adhesive (Araldite AW 136 H/hardner HY994).

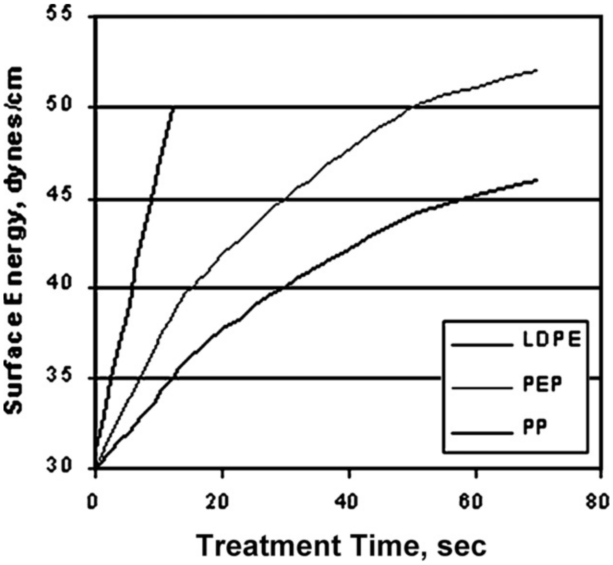

Figure 5.9 Surface energy of plastics versus duration of corona discharge treatment.

The duration of corona discharge treatment in air has a strong influence on the surface energy of the plastic. Figure 5.9 illustrates this relationship for low-density polyethylene, polyethylene–propylene copolymer (PEP), and PP. Surface energy increases more slowly as the crystallinity of the polymer being treated increases (from lower to higher, PE → PEP → PP); thus, a longer exposure time is required to achieve the same level of surface energy.

5.6.4.1 Three-Dimensional Corona Treatment

Problems with flame treating are manifold. Heat easily distorts the surface it is meant to treat if it is not calibrated and recalibrated frequently and exactly. Complex three-dimensional (3D) objects may need to be manipulated several times to get the treatment into every corner or into closed areas, which can be a very tedious and time-consuming process. The gas/air mixture has to be closely monitored and frequently recalibrated to ensure any measure of consistency.[20]

3D corona treatment, as the name indicates, is aimed at surface modification of objects with a third dimension, compared with a web (two dimensional). Plastic objects are treated by 3D corona discharge to promote adhesion for printing, painting, coating, bonding, and labeling.[21–24]

A 3D corona discharge head has a dielectric enclosure with two small electrodes made of medium thickness, bare aluminum, or stainless steel wire and is connected to a high-voltage power supply and a fan (Fig. 5.10).[25] When a high voltage exceeds the air breakdown value (30 kV/cm), an electrical arc occurs. This high current arc is blown out from the enclosure by the air stream and is usually several centimeters long and 1 mm in diameter.

When the arc strikes a solid object, it goes across the surface and returns into the enclosure.[26] The treatment is achieved by moving the object under the discharge head or by moving the head over the object. The arc is essentially a one-dimensional object (such as a wire), and a treatment of 3D surfaces requires at least two heads. It is difficult to treat objects with complicated geometry, especially with internal cavities or channel structure, including tubing. The average power required for one head operation is about 500 W. The effective power dissipated in the arc could be as low as 50 W. Most of the ions and electrons travel between the two electrodes along the arc trajectory, where the main transfer of energy occurs.

Although the fan cools the arc continuously, it still has a fairly high core temperature. The air stream created by the fan is usually unstable. The arc constantly changes, following the random pulsation of the air, leading to a nonuniform surface treatment. To increase uniformity, the exposure time should be significantly increased, cutting down the production

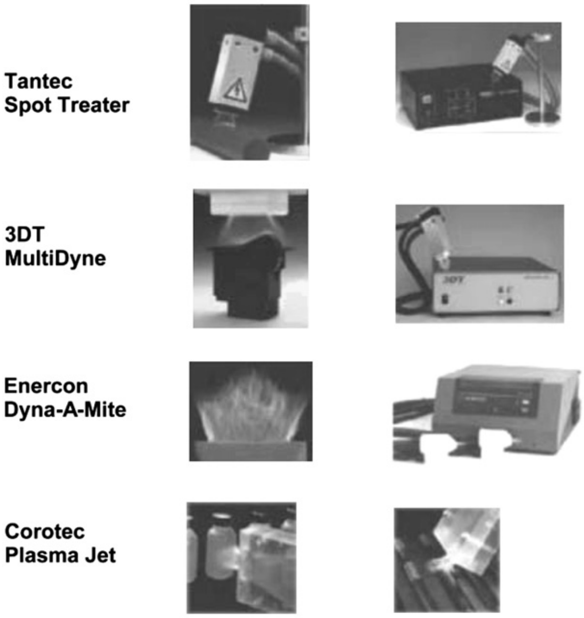

Figure 5.10 Examples of 3D Corona Treater offered by four equipment manufacturers.[25]

rate. On the other hand, high current density within the arc makes the arc plasma very hot and limits exposure time by the thermal damage threshold of the surface.

The plasma effect on the material strongly depends on the exposure time because each material requires a minimum exposure time to activate its surface. The required level of surface modification depends on the application (e.g., printing, bonding, and coating), as well as on the applied ink, adhesives, coatings, and curing process. Occasionally, there is not a sufficient window for the necessary exposure time and thermally safe material handling for the 3D corona treaters. It especially relates to tough treating materials ("plasmaphobic") when the surface gets burned rather than modified. This is also the case for heat-sensitive materials, thin wall plastic objects, wires with thin insulation, fiber optics, thin coating layers, and so on. The problem is partly solved by installation of several discharge heads along the process line. If the problem is not solved, other techniques are used.

"3D" corona treaters also generate ozone. To reduce high ozone concentration, special filters are required to comply with clean room environment regulations for the medical and semiconductor industries. High voltage signal, when applied to the electrodes, usually has an audible frequency (60 Hz and up). Electrical breakdown takes place each half period of the cycle and produces a small shock wave with distinctive sound. This could generate significant amounts of noise in multiple head discharge systems, requiring noise abatement and hearing protection.

5.6.4.2 Corona Treatment of Fluoroplastics

Corona discharge treatment of FEP and PTFE films in air has been reported[27] to improve adherability of these films, as indicated by higher values of peel strength. The bond was inconsistent and fairly weak. Later, corona treatment of FEP was reported[28] under an atmosphere of gases other than air (Fig. 5.11). Typically, process conditions included a voltage in the range of 10,000−30,000 V, pulsing peak voltage of 100,000−500,000 cycles per second, and less than 5% by volume of a suitable gas in nitrogen. A suitable gas had to have a vapor pressure of 0.25 mm of mercury at 60 °C. Examples included glycidyl methacrylate, tetrahydrofuran, carbon tetrachloride, vinyl butyl ether, and methyl vinyl ketone.

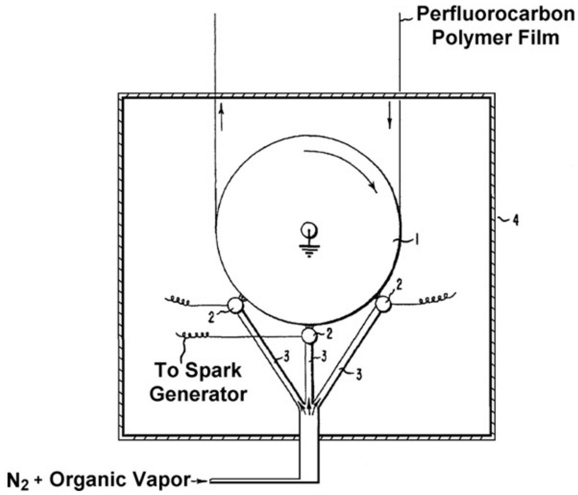

Figure 5.11 Schematic diagram of a corona treater under an organic vapor.[22] (1) Metal roll, (2) stationary hollow tube, (3) distributor duct, and (4) enclosed chamber.

For example, consider McBride and Wolinski[28] corona-treated FEP film (0.25-mm thick) under the atmosphere (0.5% by volume) of various chemicals. A voltage was applied in the range of 10,000−30,000 V, with pulsating peak voltages of up to 100,000 V, whereas the film moved at a speed of 1.5 m/min. The treated film was stuck to a strip of cold-rolled steel using an epoxy containing 1% amine hardener. Bond strength was then measured at a peel angle of 90° in a Suter tester, which is essentially an extensiometer equipped with jaws that can be separated at a controlled speed. Table 5.4 shows the bond strength for various atmospheric chemicals; film treated without a vapor phase chemical developed a weak bond.

Kreuz and Zytkus[29] reported corona treatment of FEP under an atmosphere of acetone (<5%−40% by volume in nitrogen), which had the advantage over the previous atmospheric compounds of producing a film that did not block in roll form. Treated FEP could be printed and marked with inks, was heat sealable, and adhered well to metals. Adhesion of FEP film (25 μm thick) to metal was accomplished by first laminating it to a thin polyimide (PI) film (13 μm thick) using a nip roll at 250−270 °C and at a pressure of 270 kPa. The treated FEP surface was then laminated to a 13-μm-thick (Fig. 5.12) aluminum foil in a nip roll at a speed of 6−9 m/min. In some cases, the laminate was postheated to test the effect of heat on the bond strength and the locus of bond failure (Table 5.5).

Table 5.4 Bond Strength of Corona-Treated FEP under an Atmosphere of Different Chemicals[22]

Atmosphere Chemical	Bond Strength, g/cm
None	39.7−119
N-vinyl-3-pyrrolidone	3571
Acrylonitrile	2500
p-Chlorostyrene	1190
Toluene-2,4-diisocyanate	1952
Vinyl acetate	1913
Xylene	1389
Hexane	1349
Carbon tetrachloride	1587
Tetraisopropyl titanate	1428

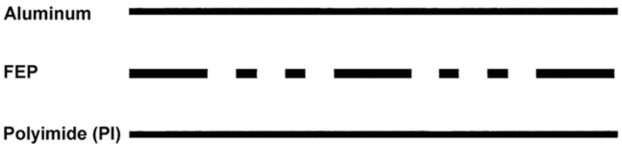

Figure 5.12 FEP laminate to aluminum foil and polyimide.

The importance of the role of acetone in the corona treatment atmosphere is shown by the data in Table 5.6. In this case, a FEP film at a thickness of 13 μm was treated in an atmosphere of acetone (3.1% by volume) and nitrogen. The treated film was heat sealed to a 25-μm-thick PI film, both corona treated and untreated, at different temperatures. Untreated PI produced a weaker bond, whereas FEP treated in air (vs. acetone/N_2) yielded almost no bond strength.

5.6.5 Flame Treatment

Flame treatment is a commercial process to render polyolefins and polyethylene terephthalate adherable. The polymer article (e.g., film) is passed over an oxidizing flame formed by an oxygen-rich (relative to stoichiometry) mixture of hydrocarbon gas. Variables affecting the extent of oxidation include the flame characteristics (e.g., excess oxygen) and the speed of the article movement. Gas flame contains excited fragments and species such as atomic oxygen (O), NO, OH, and others that can abstract hydrogen from the surface of the polymer that is replaced by oxygenated functional groups (mostly $-C{=}O$ and $-OH$).

Polyethylene and PP have a surface tension of 30 dynes/cm, which has to be raised to a minimum of 38 dynes/cm, but preferably raised to 42 dynes/cm, in order to render their surfaces adherable. Flame treatment is the most widely used method of pretreatment. It is flexible and reliable if carefully controlled. It enables uneven and curved surfaces to be treated. It uses a mixture of air at 138−345 kPa and a fuel gas at a (low) pressure of 1.7 kPa. The gas can be butane, propane, natural gas (methane), and coal gas.

For the flame to be effective, it must be oxidizing; that is, blue. Correct flame control is very important. A basic flamer will do simple work, but for routine operations and long production runs, it is recommended to use specially designed flame control systems. These are fitted with gas and air control valves to compensate for pressure fluctuations, ensuring that the mixture is always at its optimum. Safety devices, such as flame failure shutdown, are fitted as standard. Automatic ignition is also normal. Flame nozzle design is important for these normally single- or double-row ribbon burners. This will give

Table 5.5 Bond Strength of Corona-Treated FEP Under the Atmosphere of Acetone[23]

Lamination Temperature, °C	Postheat treatment	Bond strength, g/cm	Failure interface
230	Yes	137	FEP-Al
230	No	161	FEP-Al
235	No	167	FEP-Al
241	No	127	FEP-Al
240	Yes	182	FEP-Al and PI-FEP
272	Yes	244	PI-FEP
272	No	226	PI-FEP

Table 5.6 Effect of Corona Treatment and Heat Sealing Variables on Bond Strength of FEP[24]

FEP corona treatment atmosphere	FEP film speed, m/min	Bond strength, g/cm at heat seal temperature of 315 °C		Bond strength, g/cm at heat seal temperature of 350 °C	
		Treated PI	Untreated PI	Treated PI	Untreated PI
Air	15.1	13.5	–	15.5	–
Air	24.2	16.3	–	13.9	–
Acetone	15.1	208	110	416	253
Acetone	24.2	196	50	287	138

a more stable flame shape and characteristic. “Flame throwers” are inefficient and unreliable. Flame control and position of the item in the flame are critical. Setting up the flamer is also very important (see Fig. 5.13). Overflaming will damage the surface of the product, whereas underflaming can cause the ink not to stick/adhere.

It is imperative to find the correct flame treatment suitable to the component in question. Key factors include the gas type, gas-to-air ratio, burner type, gas flow rate, flame distance, and flame passage speed (treatment time). Excessive treatment of the surface results in degradation of the PP, and therefore poor adhesion. Insufficient treatment, however, does not modify the surface adequately, thus leading to poor adhesion. It is often a rather delicate procedure to find the proper conditions, and great care has to be taken in the experimentation.

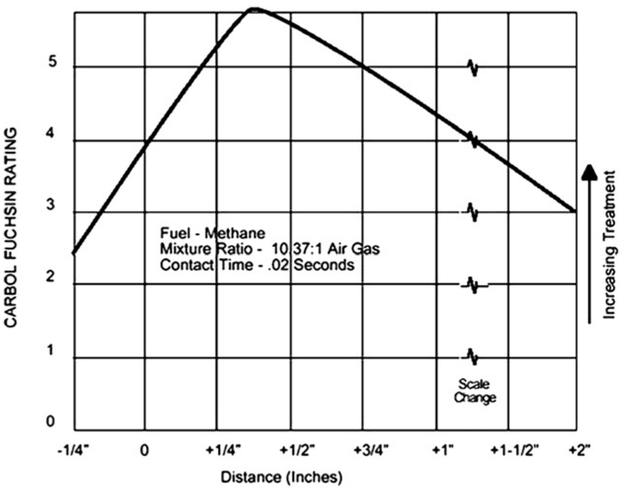

Figure 5.13 Effect of distance between part and inner cones of flame.[26]

During flame treatment, all hydrocarbon gases combine with oxygen to produce heat, as shown here for methane:

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$$

The above equation indicates complete combustion of the fuel gas methane. The volume of air required for complete theoretical combustion of gas (such as methane) is called the *stoichiometric* volume (100%). A flame containing an excess (>100% stoichiometry) of air is referred to as an *oxidizing* flame; a flame that does not have sufficient air (<100% stoichiometry) to complete combustion is a *reducing* flame. Figure 5.14[30] shows the effect of using more or less air than the stoichiometric volume on tape peel strength of polyethylene or PP. A maximum value develops at about 115% stoichiometry or 15% excess air.

In Fig. 5.15,[31] the influence of the flame passage speed over the plastic on the adhesion (shown as percentage of maximum adhesive bond strength)

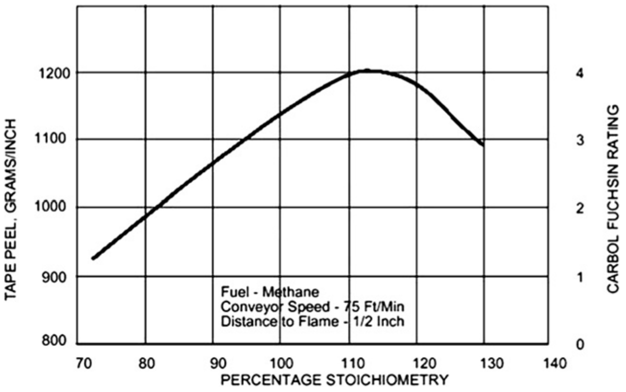

Figure 5.14 Effect of air/gas ratio on treatment level.[26]

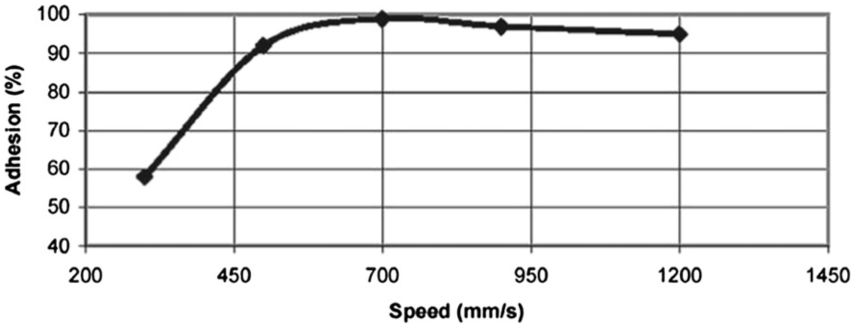

Figure 5.15 An example of measured influence on burner speed on the adhesion of molded GMT. Where the optimum is situated depends on the whole system.[27]

between the adhesive and glass matte-reinforced thermoplastic is presented. The machine supplier often provides assistance with the optimization of the system.

Speed of the conveyer greatly affects the flaming. As a rule, the higher the speed of passage of the item through the flame, the less likelihood there is to damage the surface. High gloss surfaces are susceptible to blooming, reducing the gloss. Higher speeds help to reduce blooming. Conveyers are constructed from metal mesh, which must be of sufficient length to allow the mesh to cool. Hot meshes will mark plastic components.

Flame treatment is not effective in the adhesion treatment of perfluoroplastics. The data in Table 5.7 reveal a large increase in the bond strength of polyvinyl fluoride (PVF) and ethylene chlorotrifluoroethylene (ECTFE) after flame treatment. Fluorine-to-carbon ratio (F/C) of PVF remained unchanged but O/C ratio increased significantly. In the case of PTFE, F/C ratio actually increased, which could explain the drop in the bond strength as a result of flame treatment. Flame probably removed contamination that had previously masked (covered) some of the F-atoms on the surface.

5.6.6 Plasma Treatment

Plasma (glow discharge) sometimes refers to the fourth state of the matter. It is produced by exciting a gas with electrical energy (Fig. 5.16). It is a collection of charged particles containing positive and negative ions. Other types of fragments, such as free radicals, atoms, and molecules, may also be present. Plasma is electrically conductive and is influenced by a magnetic field. Plasma is intensely reactive, which is precisely the reason that it can modify surfaces of plastics.[32] It can be used to treat parts to make their surfaces harder, rougher, more or less wettable, and more conducive to adhesion.

Table 5.7 Effect of Flame Treatment on the Surface Composition and Adhesion Bond Strength of Fluoropolymers

Polymer/ treatment	Surface chemical analysis (%) by ESCA*							Bond strength, N**
	F/C ratio	Cl/C ratio	O/C ratio	Cl	C	F	O	
PVF								
No	0.41	–	0.011	–	70.4	28.8	0.8	360
Yes	0.41	–	0.065	–	67.6	28.0	4.4	3240
ECTFE								
No	0.61	0.27	–	14.3	53.2	32.5	–	240
Yes	0.25	0.12	0.087	8.0	68.8	17.2	6.0	2980
PTFE								
No	1.60	–	–	–	38.4	61.6	–	420
Yes	1.94	–	–	–	34.0	66.0	–	80

*Electron spectroscopy for chemical analysis.

**Bond strength in Newton (N) using lap-shear test and an epoxide adhesive.

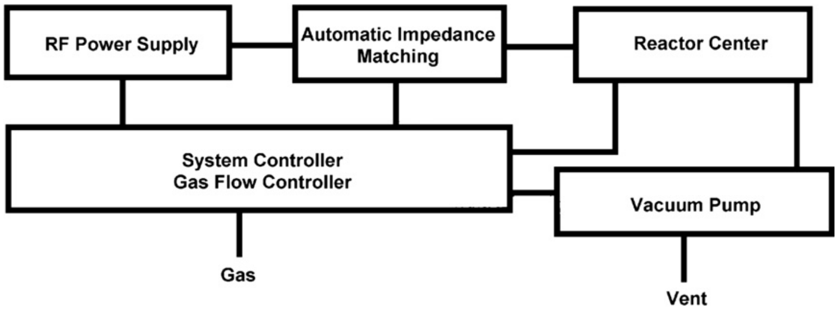

Figure 5.16 Schematic diagram of a plasma system.[31]

In 1966, Schonhorn and Hansen[33] reported on a highly effective treatment for the surface preparation of low-surface-energy polymers for adhesive bonding. The techniques consisted largely of exposing the polymer surface to an inert gas-plasma at reduced pressure generated by electrodeless glow discharge (i.e., radio-frequency field). For polyethylene, only very short treatment times were necessary (ca. 9 s), whereas larger contact times were required for other polymers, such as PTFE.[34] Plasma gases used (O_2, He, and N_2) can be selected to include a wide assortment of chemical reactions. In the process, atoms are expelled from the surface of the polymer to produce a strong, wettable, and cross-linked skin.[3]

Plasma treatment can be carried out on a variety of plastic parts, and even on powder additives such as pigments and fillers. In practice, plasma treatment is used sparingly in the industry because it is conducted under vacuum process, and so it is both expensive and inconvenient. Nevertheless, plasma treatment is a well-researched topic that is replete in academic literature.

The plasma used for treating material surfaces is called *cold plasma*, meaning its temperature is about room temperature. Cold plasma is created by introducing the desired gas into a vacuum chamber (Fig. 5.17), followed by radio frequency (13.56 MHz), or microwave (2450 MHz) excitation of the gas. The energy dissociates the gas into electrons, ions, free radicals, and metastable products. Practically any gas may be used for plasma treatment, but oxygen is the most common. The electrons and free radicals created in the plasma collide with the

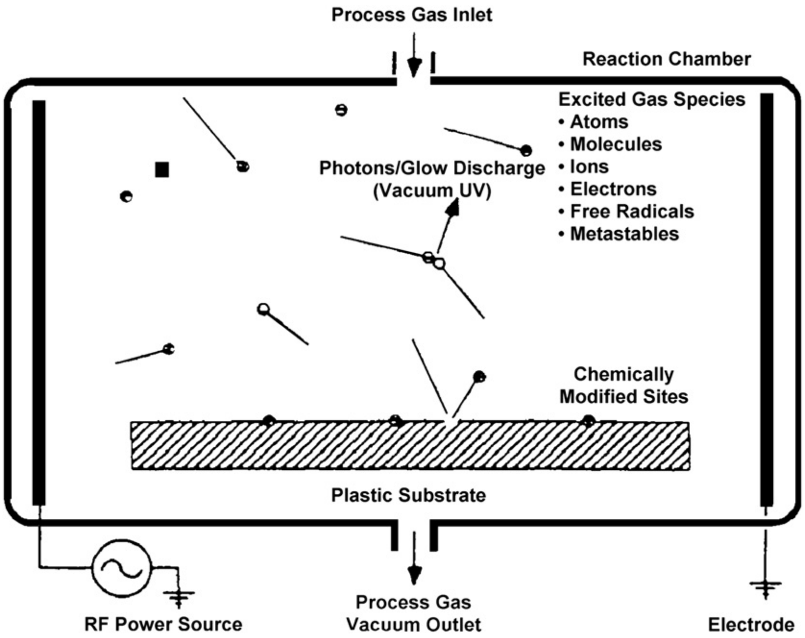

Figure 5.17 Schematic of the surface modification of plastic in a gas-plasma reactor.

Table 5.8 Effect of Plasma Treatment on Lap-Shear Joint Strength (kg/cm) of High-Density Polyethylene Sheet (1.6 mm thick)[32]

Treatment type (duration)	13-mm wide lap shear	6-mm wide lap shear
Oxygen (30 min)	80	245
Oxygen (1 min)	84	248
Helium (1 min)	84	242
None—solvent wiped	9.3	–

Table 5.9 Effect of Plasma Treatment Duration on Lap-Shear Joint Strength and Failure Mode of Polyethylene (3.2 mm thick)[32]

Treatment type	Duration, min	Bond strength, Mpa	
		High density	Low density
None—solvent wiped	–	2.2 (A, PE)	2.6 (A, PE)
Oxygen	0.5	13.7 (A, PE)	–
Oxygen	1	9.2 (A, Al)	10 (C, PE)
Oxygen	30	16.8 (A, Al)	10.1 (C, PE)
Helium	0.5	6.4 (A, PE)	9.6 (C, PE)
Helium	1	9.4 (A, PE)	9.5 (C, PE)
Helium	39	21.6 (C, PE)	9.1 (C, PE)

Table 5.10 Effect of Plasma Treatment Duration on Lap-Shear Joint* Strength of Polycarbonate and Polypropylene Sheet[32]

Treatment type	Duration, min	Bond strength, MPa	
		Polycarbonate (1.6-mm-thick sheet)	Polypropylene (0.12-mm film)
None—solvent wiped	–	2.8 (A, PC)	2.6 (A, PP)
Oxygen	0.5	5.5 (A, PC)	12.9 (A, PP)
Oxygen	30	6.4 (A, PC)	21.2 (A, PP)
Helium	0.5	4.6 (A, PC)	3.1 (A, PP)
Helium	30	5.8 (A, PC)	1.4 (A, PP)

A = adhesive failure, C = cohesive failure (see Section 5.2 for definitions of bond failure), PE = polyethylene, Al = aluminum, PC = polycarbonate, PP = polypropylene.

**Bonded to etched aluminum coupons using a cross-linked epoxy (a blend of Epon® 828 and Versamid® 140, 70/30 parts by weight).*

polymer surface and rupture covalent bonds, thus creating free radicals on the surface of the polymer. The free radicals in the plasma may then recombine to generate a more stable product. After a predetermined time or temperature is reached, the radio frequency is turned off. The gas particles recombine rapidly and the plasma is extinguished.

Plasma-treated polymers usually form adhesive bonds anywhere from two to four times stronger than bonds formed by traditional chemical or mechanical preparation. Researchers at Picatinny Arsenal conducted and reported a study of a number of polymers using activated gas plasma treatment.[35] Another study covered other plastics (Valox® polybutyl terephthalate polyester, polyethersulfone, polyarylsulfone, polyphenylene sulfide, ECTFE fluoropolymer, nylon 11, nylon 6/12, and nylon 12).[36] Tables 5.8–5.11 illustrate the effectiveness of this process for a number of polymers. Clearly, plasma treatment is not equally efficient in rendering different plastics adherable.

5.6.6.1 Atmospheric Plasma[1]

Atmospheric plasma systems have been developed in response to a number of issues with 3D corona treatment systems that were discussed in Section 5.6.4.1. Even though the same physical phenomenon, electrical breakdown of gases at atmospheric pressure (electrical discharge), is used, the methods of creation and application of this discharge are completely different.[37]

The plasma system is designed to create a uniform plasma cloud that completely surrounds small objects or spreads into the boundary layer of the surface. It can also be placed in the internal cavities, channels, and so on. The same plasma system can treat the internal surfaces of a 50-μm capillary and cover a 50-mm diameter (and higher) surface area. For example, one design of a machine[38] is based on the well-known physical phenomenon.[38] The strength of the electrical field considerably increases in the vicinity of small radius objects. Applying a high-voltage signal to the sharp edge body (e.g., a needle) causes electron leakage from the edge to the gaseous environment (e.g., air). These free electrons, accelerated by the strong electrical field, have enough energy to ionize neutral gas molecules and produce other free electrons and ions.

These electron avalanches, however, do not develop into an arc but gradually decay as they move away from the edge, creating a uniform glowing cloud near the electrode. Because there is no well-defined second electrode, the currents in the plasma cloud are extremely low (100 μA), and plasma occupies a finite volume at near to room temperature. The overall power to initiate and maintain this glow discharge usually does not exceed 100 W. The low-temperature plasma cloud may be applied directly onto the surface of the treated material or considerably extended with the use of inert gases such as helium, argon, and so on.

This kind of plasma is very effective because most of the microdischarge trajectories end up on the surface of the treated material. A specially designed high-frequency, low-current power supply significantly increases the efficiency by multiplying the number of microdischarges in the cycle. The system is practically noiseless, produces very little ozone when operating in the open air, and generates no ozone when inert gases are used. A small amount of reactive gases may be added into the flow to obtain plasma with unique properties; this is frequently required for chemical surface modification. Thin film deposition by plasma polymerization may also be accomplished on the treated surface by adding monomers (CH_4, C_2H_2, etc.) into the plasma cloud.

A comparison of an atmospheric plasma and a 3D corona treater is given in Table 5.12.

5.6.6.2 In-line Plasma Treatment of Wire Insulation

Some atmospheric plasma treatments allow in-line surface modification of almost any wire insulation material. Examples include polyamides, polyesters, and the fluoropolymers most difficult to treat. A treated surface can then accept inkjet printing for marking purposes. Table 5.13 shows a comparison of the marking durability on ethylene tetrafluoroethylene copolymer (ETFE) and fluorinated ethylene propylene copolymer (FEP) for untreated (U), flame treated (Fl), and plasma treated (Pl) conditions. Some wires have been cross-linked by irradiation (IR) to enhance cut-through resistance of the insulation. Wire suppliers have been identified in each case and all ink was UV curable.

Table 5.14 shows the results of scrape abrasion testing on a Tefzel® ETFE (www2.dupont.com) insulation with and without plasma treatment. Clearly, plasma has a positive effect on enhancing resistance of the marking to removal by scrape abrasion. Contact angle data and calculated surface energy data can be found in Tables 5.15 and 5.16.

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[1] The authors would like to gratefully acknowledge the use of material developed by Dr Igor Morokh, Tri-Star Technologies, El Segundo, CA, in this section.

Table 5.11 Effect of Plasma Treatment Duration on Lap-Shear Joint* Strength of Various Plastics[32]

Treatment type	Duration, min	Bond strength, MPa				
		Polyethylene (0.25-mm-thick film)	**Polystyrene terephthalate (0.25-μm transparent film)**	**Polyvinyl fluoride (25-mm transparent film)**	**Cellulose acetate (15.2-mm-thick sheet)**	**Nylon 6 (76-μm-thick film)**
None—solvent wiped	–	3.9 (A, PS)	3.6 (A, PET)	1.9 (A, PVF)	7.5, 4.5 (A, CAB)	5.8 (A, N)
Oxygen	0.5	–	–	9.4 (A, Al/PVF)	7.8 (A, CAB)	11.2 (A, AL)
Oxygen	1	–	–	–	3.1 (A, CAB)	10.5 (A, AL)
Oxygen	30	21.5 (C, PS)	9.4 (A, PET)	9.8 (A, Al/PVF)	9.5 (A, CAB)	24.1 (A, AL)
Helium	0.5	–	–	9.9 (A, Al/PVF)	9.6 (A, CAB)	9.4 (A, AL)
Helium	1	–	–	–	4.1 (A, CAB)	9.5 (A, AL)
Helium	30	27.7 (C, PS)	11.4 (A, PET)	9.3 (A, Al/PVF)	–	27.3 (A, AL)

A = adhesive failure, C = cohesive failure, Al = aluminum, PS = polystyrene, PET= polyethylene terephthalate, PVF = polyvinyl fluoride, CAB = cellulose acetate butyrate, N = nylon 6.

**Bonded to etched aluminum coupons using a cross-linked epoxy (a blend of Epon® 828 and Versamid® 140, 70/30.*

Table 5.12 Comparison of an Atmospheric and a 3D Corona-Treater[25]

	Atmospheric plasma	3D Corona
Average power	100 W	1000 W
Plasma carrier	Argon	Air
Plasma currents	Low (mA)	High (10 mA)
Main direction of the energy transfer	From the electrode to the substrate surface	Between the electrodes parallel to the substrate surface
Plasma frequency	High (20,000 Hz)	Low (60 Hz)
Noise level	Low	High
Ozone generation	Low	High
Plasma flow temperature	Low (room)	High (>250 °F)
Substrate exposure	Unlimited	Limited to thermal damage
Coverage from single head on the flat surface	Up to 3-in-diameter circle or up to 5 in × 1 in strip	Up to 2 in × ¼ in strip
Ability to treat patterned surfaces	Unlimited	Limited
Ability to treat inner surfaces	Unlimited	Very limited
Ability to introduce special additives into the plasma for chemical surface modification	Limited	Very limited
Overall flexibility	High	Low
Overall efficiency	High	Low

5.6.3.3 Plasma Treatment of Fluoroplastics

Table 5.17 contains data that compares the results of plasma treatment and sodium etching for four perfluoropolymers. Peel strengths of untreated and treated samples were measured by bonding them into T-peel specimens using the flexibilized epoxy adhesive Scotch-Weld® 3553 (available from 3M Corp.; www.3m.com). The laminates were cured for several hours at 70 °C and peel tested at 12.5-cm/min pull rate. PTFE does not accept plasma treatment as well as PFA and FEP, as indicated by its relatively low peel strength. Sodium etching is the only effective method of modifying the surface of PTFE.

A study of adhesion improvement of ETFE by plasma treatment using oxygen, ammonia, and oxygen + SF_6 gases has been reported.[41] Joints were made using commercial epoxy adhesives by a double lap-shear configuration (Fig. 5.18). Bond strength of the plasma-treated ETFE significantly exceeded bond strength of sodium-etched polymer specimen (Table 5.18). A range of values was obtained for bond strength with different adhesives.

Plasma treatment does not impart sufficiently strong adhesive bonds in PTFE, the most common perfluoropolymer. Bond strength of plasma-treated PTFE is at best 60% of that obtained by sodium etching.[42]

An alternative plasma treatment technique is the glow discharge method that can be done at atmospheric pressure. Fluoroplastic films were treated by glow discharge in helium atmosphere.[43] Strips of the treated and untreated films were bonded to 0.2-mm-thick aluminum foils using a urethane adhesive cured at 100 °C for 15 min. The treatment conditions and bond strengths of the samples are given in Table 5.19.

5.6.7 Chemical Etching

Chemical treatment is the most effective method of rendering the surface of plastics optimum for bonding. This technique can alter the physical and chemical properties of the surface. Chemical treatment is often preceded by a cleaning operation that removes surface contamination. The benefits of cleaning the surface in advance include a reduction of the contamination of

Table 5.13 Marketing Durability of Flame- and Plasma-Treated Fluoropolymer Insulated Wires[59]

Insulation type	**ETFE**			**ETFE**			**IR ETFE**						**IR ETFE**			**FEP**		
Wire spec	**M17 5000-14TE1U00**			**M37 500 10TO2T14**			**M17 500 24102T23**			**M13-101364**			**WS191991-20-1**			**MIL-C 17G**		
Wire vendor				**Thermax CDT, Belden Company**			**Teledyne Thermatics**			**Judd wire**			**Delta wire**			**Thermax CDT, Belden Company**		
Treatment testing	U	Fl	Pl	U	Fl	Pl	U	Fl	Pl	U	Fl	Pl	U	Fl	Pl	U	Fl	Pl
Rub (finger)	F	P	P	F	F	P	F	P	P	F	P	P	F	P	P	F	F	F
Rub(eraser)	F	P	P	F	F	P	F	P	P	F	P	P	F	F	P	F	F	P
Alcohol	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P	F	F	P
1,1,1 Trichlor	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P
Freon® TMC	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P
Water	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P
Acetone	F	F	P	F	P	F	F	P	P	F	F	P	F	F	P	F	F	P
Episolve301	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P	F	F	P
Masking tape	F	P	P	F	F	P	F	P	P	F	P	P	F	P	P	F	F	P
Thermal shock	F	P	P	F	F	P	F	P	P	F	P	P	F	F	P	F	F	P
Iso Oil	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P
Pen (40 dyne/cm)	F	P	P	F	P	P	F	P	P	F	P	P	F	P	P	F	F	F
Cold shock	F	P	P	F	P	P	F	P	P	F	P	P	F	F	P	F	F	P

All wires were marked with UV-curable ink; rub (finger): 20 strokes of moderate pressure; rub (eraser) per MIL-M-91531, 4.62; alcohol, trichlor, Freon® TMC (50% methylene chloride, 50% 1,1,2-trichlorotrifluoroethane), water (plus surfactant to promote wetting), acetone, and episolve per MILSTD 202; masking tape: press onto marking, wait 30 s, peel off and read marking; thermal shock per WS 19185; ISO oil: soak for 48 h and rub once; pen: check the spreading on the surface of the wire; cold shock: 5 min at −40 °F, bend and rub.

U = untreated, Fl = flame-treated, Pl = plasma treated. F = fail, P = pass.

Table 5.14 Results of a Scrape Abrasion Test Performed at Raychem, Menlo Park, CA, on Tefzel® Spec 55 Insulated Wire for the Marking Identification Made by M-100J Ink-Jet Wire Marker

Line speed	30 ft/min	60 ft/min	120 ft/min
UV exposure, s	1	0.5	0.25
Average number of cycles plasma off	7	11	12
Average number of cycles plasma on	58	>125	48

Testing method: motor driven, reciprocating cam mechanism, equipped with a reset counter and capable of a 3/8-in stroke at 60 cycles per minute with a clamp for holding specimens. The contact surface is a smooth cylindrical steel mandrel, 0.025 in in diameter. Applied weight is 500 g. One cycle corresponds to two strokes. Note: The tests were stopped after 125 cycles.

Table 5.15 Contact Angles (Degrees) Measurement for the Plasma-Treated FEP Insulated Wire (22759/11-20)

Plasma treatment conditions	Water surface tension 72 dyne/cm	Methylene iodide surface tension 50 dyne/cm	Xylene surface tension 30 dyne/cm
No treatment	101 ± 5	75 ± 4	46 ± 4
Air plasma	94 ± 8	70 ± 3	32 ± 3
Argon plasma	90 ± 4	66 ± 5	23 ± 5
Argon and ammonia	82 ± 4	6 ± 6	20 ± 7

Table 5.16 Surface Energy Calculation Based on Contact Angle Measurement for Plasma-Treated FEP Insulated Wire (22759/11-20)

	Harmonic-mean approximation			Geometric-mean approximation		
Plasma treatment conditions	Dispersive component, dyne/cm	Polar component, dyne/cm	Total, dyne/cm	Dispersive component, dyne/cm	Polar component, dyne/cm	Total, dyne/cm
No treatment	17.3	5.4	22.7	14.3	2.6	16.9
Air plasma	20.5	7.2	27.9	17.7	3.9	21.6
Argon plasma	19.9	9.1	29.0	16.4	6.0	22.4
Argon and ammonia	23.0	11.5	34.5	19.3	8.4	27.7

Table 5.17 Peel Strength of Adhesive-Bonded Fluoropolymers[39,40]

Treatment	Material			
	PTFE	FEP	ETFE	PFA
Untreated	Negligible	0.1	Negligible	0.04
Sodium etched	5	8.2	–	6.4
Plasma treated	2.2	10.4	15.8	8.3

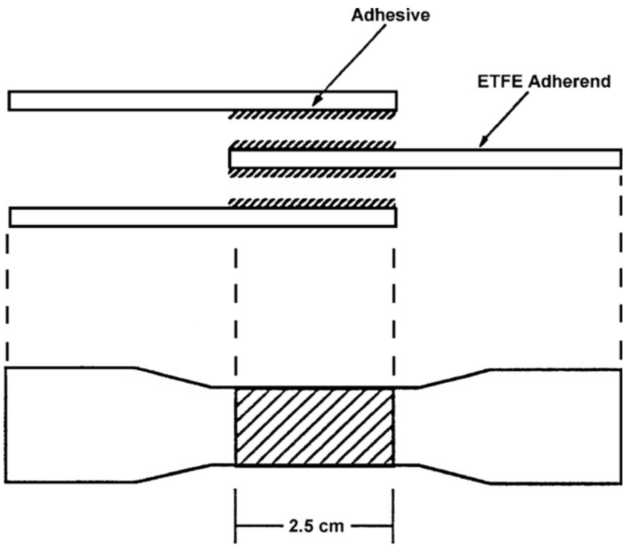

Figure 5.18 Schematic of the double lap-shear test specimen.

Table 5.18 Bond Strength of Plasma-Treated ETFE Using a Double Lap-Shear Test and Epoxy Adhesives[37]

Treatment type	Bond strength, MPa
None	0.07
Tetra-Etch®*	0.78
Plasma ($O_2 + SF_6$)	1.49–2.31
Plasma (O_2)	1.47–1.83
Plasma (NH_3)	1.40–1.72

**Tetra-Etch® by W.L. Gore & Associates, Inc.*

Table 5.19 Effect of Atmospheric Glow Discharge Treatment in He on Bond Strength[38]

Fluoroplastic	Untreated, g/cm	Treated, g/cm
PFA	0	600
FEP	0	640
ETFE	0	430
PVDF	100	830

Treatment conditions: gas flow rate = 5 L/min, discharge frequency = 5 kHz. Treatment time = 60 s.

the chemical solution and improved interaction between the surface and the solution.

Typically, the surface of a plastic part is washed with soap and detergent solution or an organic solvent, followed by immersion in the chemical treatment bath. The solutions include an acid, base, oxidizing agent, chlorinating agent, or other active chemicals.[44] Afterward, the part is rinsed in water, followed by drying at elevated temperature. Concentration of active ingredients must be monitored and maintained at an adequate level to allow effective treatment of successive plastic parts in the same solution. Table 5.20 shows examples of most common chemical etching treatment systems.

Sulfuric acid-dichromate is the most commonly applied chemical etching treatment for many plastics; a list can be seen in Table 5.21. There are few hard rules to determine the composition of these treatment media, although ranges can be found in Table 5.21. The exact formulation should be determined by testing the adhesive bond strength for any given plastic. Combinations of chromic acid, sulfuric acid, and phosphoric acid have been tried successfully.[2,45]

Chromic acid removes amorphous regions of the polymer morphology, leading to the formation of complex (labyrinthine) cavities on the plastic surface. Some surface oxidation takes place. Improved wettability and bond strength has been ascribed to topography of etched plastic surfaces rather than polarity of the surface.[46]

Sodium etching is an extreme treatment technique that is suitable for surfaces that are very difficult to treat. Examples include fluoropolymers and thermoplastic polyesters. A description of sodium etching and its application to fluoroplastics is provided in the next section.

5.6.7.1 Sodium Etching of Fluoroplastics

Perfluorinated fluoroplastics are chemically unaffected by nearly all commercial chemicals. An exception is highly oxidizing substances such as element forms of sodium, potassium, and other alkaline metals. This is the basis for sodium etching of fluoroplastic parts, which is described in this section.

The original method for surface treatment of PTFE for adhesive bonding is etching in a sodium solution in anhydrous liquid ammonia.[47,48] The reagent is prepared by simply dissolving metallic sodium in liquid ammonia to obtain a 0.5–1% by weight concentration. The solution has a dark blue color and should be stirred thoroughly before use. The surface of the fluoropolymer should be cleaned carefully with an organic solvent such as acetone in order to remove oils or grease and other contaminants

Table 5.20 Common Chemical Treatment Solutions[61]

Chemical solution	Polymers	Comments
Sulfuric acid-dichromate etch	Acrylonitrile-butadiene-styrene (ABS), polyacetal, melamine or urea polymer, polyolefin, polyethylene oxide, polystyrene, polysulfone and styrene-acrylonitrile (SAN)	Most common method
Sodium etch	Fluoroplastics and some polyesters	
Sodium hydroxide	Polystyrene, polyesters, polyamide and polysulfone	
Sanitizing	Homopolymer polyacetal	Developed by DuPont, US patent 3,235,426
Phenol	Nylon	
Sodium hypochlorite	Thermoplastics and thermoplastic rubbers	

Table 5.21 Composition and Process Variables for Sulfuric Acid-Dichromate Etching[61]

Ingredient/variable	Typical value, part by weight	Range, part by weight
Potassium or sodium dichromate	5	0.5–10
Sulfuric acid (concentrated)	85	65–96.5
Water	10	0–27.5
Time	–	10 s to 90 min
Temperature	–	Room temperature—71 °C

that can cause poor treatment and weak bonding. Moisture must be kept from the solution by storing it under positive pressure in protective packaging.

The fluoropolymer needs to be in the solution for a brief duration ranging from 2 to 10 s.[49] Ammonia rapidly volatilizes after the article is removed from the bath. Sodium can be removed by dipping the treated article into ethyl alcohol. A lengthy immersion time actually weakens the adhesive bond. The optimum time depends on the freshness of the etching solution. The treated fluoropolymer has a shiny dark brown color, which grows into a dull brown after exposure to air. Analysis of the baths shows the presence of fluoride and/or chloride ions, suggesting defluorination and/or dechlorination of the surface during treatment (Table 5.22).

Table 5.23 gives the bond values of fluoroplastics before and after etching, obtained by the lap-shear test method. Bond strengths of the treated surfaces of PTFE, PVF, and ECTFE are larger than that of the untreated surfaces by an order of magnitude or more.

Etching has a profound effect on the surface chemistry of fluoroplastics. Results of surface chemical composition of fluoroplastics, using ESCA, are summarized in Table 5.23. The consistent changes in surface composition of fluoroplastics due to the treatment are a reduction in fluorine and/or chlorine content, and an increase in carbon content and oxygen content. Treated PTFE surface is composed virtually entirely of carbon and oxygen and a small amount of fluorine.

The change in the surface of the treated fluoroplastics is also reflected in the contact angle. For example, the water contact angle of FEP and PTFE decreases from 109° to 52° (advancing) on sodium/ammonia treatment.[46,50,51] Heating the treated fluoropolymer for a lengthy period can reverse the change in the surface. Water contact angle of treated PTFE increases back to 101° after 96 h exposure to a temperature of 200 °C.

Table 5.23 shows the effect of sodium etching for several fluoroplastics by Tetra-Etch® (www.gore.com), on the surface composition and lap-shear

Table 5.22 Effect of Sodium Etching on the Surface Composition and Adhesion Bond Strength of Fluoropolymers[43]

		Surface Chemical Analysis (%) by ESCA[*]							
Polymer	**Treatment**	**F/C ratio**	**Cl/C ratio**	**O/C ratio**	**Cl**	**C**	**F**	**O**	**Bond strength, MPa[**]**
PTFE	None	1.60	–	–	–	38.4	61.6	–	2.1
PTFE	Tetra-Etch®[†] (1 min)	0.011	–	0.20	–	82.2	0.9	16.9	21.3
PTFE	N/1 min[‡]	0.005	–	0.14	–	87.2	0.4	12.4	21.4
PVF	None	0.42	–	–	–	70.4	29.6	–	1.8
PVF	Tetra-Etch®[†] (30 min)	0.21	–	0.026	–	80.7	17.2	2.1	20.8
ECTFE	None	0.64	0.27	–	14.1	52.5	33.4	–	1.2
ECTFE	Tetra-Etch®[†] (1 min)	0.16	0.05	0.12	3.8	74.9	12.2	9.1	10.0

[*] Electron spectroscopy for chemical analysis.
[**] Lap-shear test.
[†] Supplied by W.L. Gore Corporation.
[‡] Treatment with a 1 mole solution of sodium naphthalenide in tetrahydrofuran at room temperature.

Table 5.23 Effect of Sodium Etching (Tetra-Etch® by W. L. Cole) on the Surface Composition and Adhesion Bond Strength of Fluoropolymers[28]

	Surface Chemical Analysis (%) by ESCA[*]							
Polymer/ treatment	**F/C ratio**	**Cl/C ratio**	**O/C ratio**	**Cl**	**C**	**F**	**O**	**Bond strength, N2**
PVF								
None	0.41	–	0.011	–	70.4	28.8	0.8	360
10 s	0.37	–	0.012	–	72.4	26.7	0.9	800
1 min	0.37	–	0.021	–	75.4	23.0	1.6	2080
60 min	0.13	–	0.015	–	87.3	11.4	1.3	3020
PVDF								
None	0.93	–	0.014	–	51.4	47.9	0.7	1580
1 min	0.17	–	0.12	–	77.4	12.9	9.7	2450
60 min	0.11	–	0.14	–	79.5	9.2	11.3	2940
ECTFE								
None	0.61	0.27	–	14.3	53.2	32.5	–	240
1 min	0.24	0.05	0.095	3.7	72.5	17.7	6.9	3300
PTFE								
None	1.6	–	–	–	38.4	61.6	–	420
10 s	0.01	–	0.13	–	87.6	0.8	11.6	4280
1 min	0.01	–	0.20	–	82.2	0.9	16.9	4260

Bond strength in Newton (N) using lap-shear test. An epoxide adhesive was used for PVF, PTFE, and ECTFE and a cyanoacrylate adhesive for PVDF.
[*] Electron spectroscopy for chemical analysis.

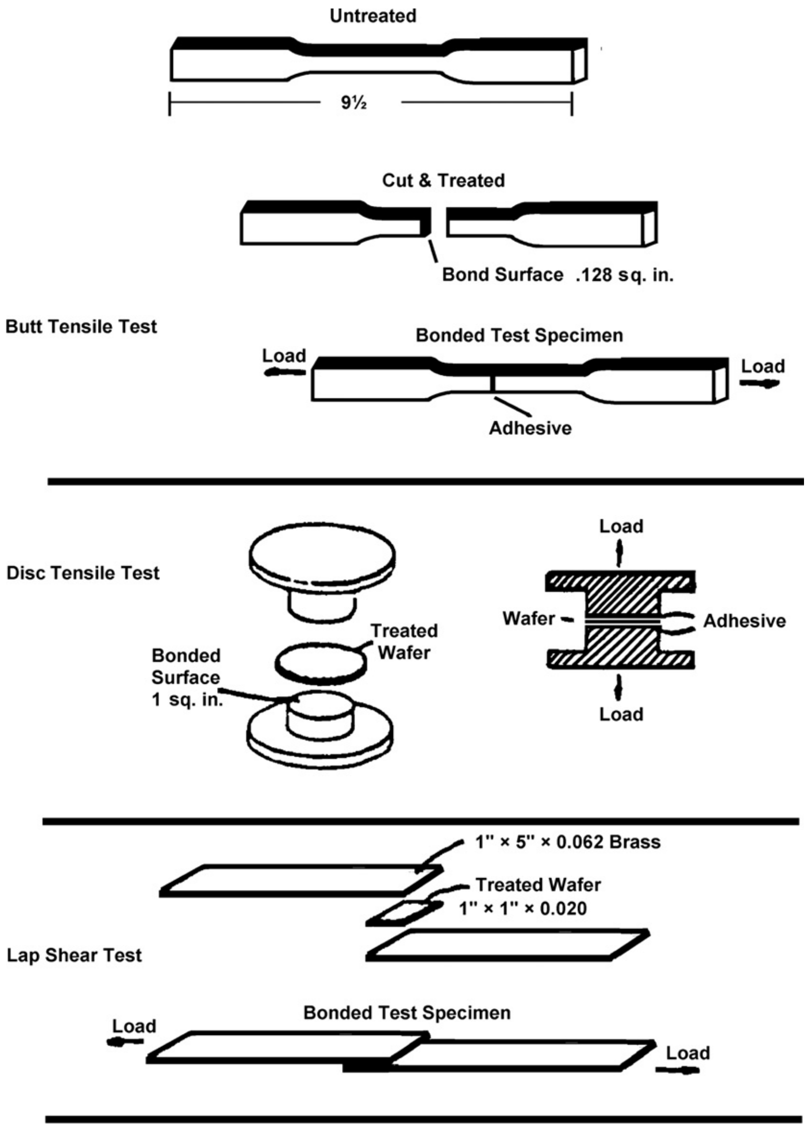

Figure 5.19 Test specimens for determination of bond ability of treated PTFE.[45]

bond strength. In general, the data for various fluoroplastics indicate an increase in the adhesive bond strength with increasing fluorine and chlorine content.

The use of a commercial dispersion of sodium in naphthalene can reduce the preparation time. The shelf life of the bath is 60 days, provided that it is stored in a closed container and isolated from air. The polymer is immersed in the solution for 1−5 min followed by rinsing in alcohol or acetone. Bond strength using epoxy adhesives ranges from 7 to 14 MPa in tensile mode. This broad range of adhesive bond strength is obtained in butt tensile, disk tensile, and lap-shear test configurations, displayed in Fig. 5.19.

Research has shown that defluorination depth of the polymer surface extends about 300 nm (Fig. 5.20) as a result of sodium naphthalenide treatment.[52,53] The researchers reported that exposure to X-rays decreased the defluorination depth to 30−150 Å. The structure of the defluorinated layer is highly porous. The suggested adhesion mechanism is mechanical interlocking of adhesive with this porous structure. Bond failure nearly always occurs by stripping the etched layer, as opposed to cohesive failure of the adhesive.

Etching solutions for in-house treatment can be purchased from a number of sources. They include Fluoro Etch® by Acton Corp. (www.actontech.com) and Tetra-Etch® by W.L. Gore & Associates. Some companies, such as Acton and Goodrich Corporation (Porter Process; www.goodrich.com), provide surface treatment service. Operational safety and waste disposal are two issues concerning parties who deal with etching solutions.

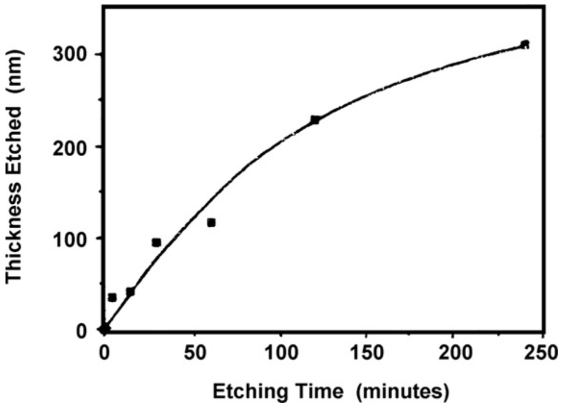

Figure 5.20 Apparent defluorination depth as a function of Na/naphthalene treatment time.[45]

5.7 Methods for Evaluating Effectiveness of Surface Preparation

Before actual bonding, the subjective "water-break" test, or the quantitative and objective contact-angle test, may be carried out. After bonding, the effectiveness of surface preparation may be determined by measuring the bond strength and determining the mode of the failure of the adhesive joint.

5.7.1 Dyne Liquids

This method is common for estimating the treatment level of plastic surfaces in manufacturing/production environments. It involves using solutions made from a mixture of two chemicals that produce liquids (dyne) with surface tension in the range of 30–70 dynes/cm. The test consists of placing droplets of the various dyne liquids on the treated surface and observing the spreading of the drops in 2 s. Successive liquids with different surface tensions allow for narrowing of the surface tension range of the plastic surface. This method is subjective, but it provides a rapid means of assessment of the treatment level, which especially useful in a production environment. There are also pens that operate similarly to dyne liquids. A more quantitative approach is the measurement of contact angle, which decreases with an increase in treatment level. A perfect wetting liquid forms a contact angle of zero on the solid surface.

5.7.2 Water-Break Test

This test depends on the observation that a clean surface (one that is chemically active or polar) will hold a continuous film of water rather than a series of isolated droplets. This is known as a water-break-free condition. A break in the water film indicates a soiled or contaminated area. Distilled water should be used in the test, and a drainage time of about 30 s should be allowed. Any trace of residual cleaning solution should be removed or a false conclusion may be made. If a water-break-free condition is not observed on the treated surface, it should not be used for bonding. The surface should be re-cleaned until the test is passed. If failures continue to occur, the treating process itself should be analyzed to determine the cause of the problem.[2]

5.7.3 Contact-Angle Test

Wettability may also be determined by measuring the contact angle between the polymer surface and the drop of a reference liquid, such as distilled water. A small contact angle indicates that the liquid is wetting the polymer effectively, whereas large contact angles show that the wetting is poor. Every surface has a critical surface tension, γ_c, of wetting. Liquids with surface-free energies below γ_c will have zero contact angles and will wet the surface completely, whereas liquids with surface-free energies above γ_c will have finite contact angles. The critical surface tension is in units of dynes per centimeter at 20 °C. Contact angles for untreated materials vary from 37° to 48° for relatively polar materials, such as nylon, to highs of 100° and 97° for the nonpolar, unbondable silicone, and polyethylene resins. After exposure to activated argon plasma, contact angles are reduced to 40° for polymethyl methacrylate (PMMA) and to 19° or less for nylon, polystyrene, polyethylene, and room-temperature-vulcanizing (RTV) silicone.[6] Zissman and others have written comprehensively on surface-tension phenomena relating to adhesion.[54–56]

Table 5.24 gives the treatment values required for a number of plastics as a function of the adhesive coating system and the manufacturing processes. Notice that, as discussed earlier in this section, in all cases waterborn adhesives require higher surface energy levels than solvent-based systems.

5.8 Surface Exposure Time (SET)

SET is the time elapsed between the surface preparation and actual bonding. After parts have been subjected to surface preparation, they must be protected from contamination during transportation and

Table 5.24 Suggested Surface Energy (Treatment Level) for Various Plastics Adhesion Substrates[50]

		Printing Processes												Other Processes					
	Process	Flexo and Gravure			Litho			Offset, Letterpress			Screen and Pad			Laminating(6)			Coating		
	Coating Type	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV
Substrate	PE(2)	38 44	36 40	38 50	40 46	37 42	40 50	40 46	37 42	42 54	42 48	38 44	44 60	42 50	38 44	42 54	42 48	38 45	44 54
	PP(3)	38 44	36 40	40 50	40 46	38 42	40 50	40 46	37 42	40 54	42 48	38 44	44 60	42 50	38 44	42 54	42 48	38 45	44 54
	PVC(4)	38 44	36 40	36 50	40 45	37 42	36 52	40 45	38 42	40 52	42 48	38 44	42 60	42 50	38 44	42 54	40 48	38 45	42 54
	PET(5)	44 52	40 46	42 54	46 56	42 46	44 56	46 56	42 46	46 60	48 60	42 48	44 62	46 60	42 48	44 62	42 52	42 48	46 60
	PS	38 44	35 40	42 48	40 45	37 42	42 50	40 46	38 44	42 58	42 48	38 44	42 56	42 52	37 44	42 54	42 50	38 46	44 54
	PVDC	40 46	38 42	42 52	42 46	40 42	42 52	42 48	38 44	42 54	42 50	40 45	42 58	42 50	38 44	44 52	42 48	40 46	44 54
	PU	40 46	38 42	38 50	40 46	38 42	38 52	40 45	38 44	42 56	42 50	38 44	42 58	42 50	38 44	42 56	42 48	38 46	44 54
	ABS	42 46	40 44	40 52	42 46	40 45	42 52	42 48	38 46	45 52	42 48	40 45	46 56	42 52	40 45	42 56	42 48	38 46	44 54
	PTFE	40 44	34 39	36 52	40 45	35 40	38 52	40 48	38 44	42 60	42 52	38 46	42 60	42 56	38 46	42 56	42 50	40 48	42 54
	Silicone	40 44	35 40	40 50	40 45	38 42	38 52	40 48	38 44	40 56	42 50	38 46	42 60	42 56	38 46	42 56	42 50	40 48	42 54

Polymer name abbreviations: PE = polyethylene, PP = polypropylene, PVC = polyvinyl chloride, PET = polyethylene terephthalate, PS = polystyrene, PVDC = polyvinylidene chloride, PU = polyurethane, ABS = acrylo butyl styrene, and PTFE = polytetrafluoroethylene.

In most cases, if the substrate is somewhere between the low and high dyne levels cited, a satisfactory bond can be obtained. For demanding production conditions (e.g., high web speeds and/or critical quality process work), it is safest to aim for the top of the range. Use Table 5.24 as a general guideline only; each operation has slightly different requirements. These data are for flame or corona treatment in an oxygen-containing atmosphere. (1) Some values theoretical. (2) Any density, any type, including films, coated board, and molded products. (3) All types; cast or molded. (4) More plasticizer generally requires levels at the high end of these ranges. (5) Unquoted. (6) For heat sealing, the surface energies of the mating PE surfaces should match closely; if both faces are treated, heat sealing can usually be accomplished over a broader and lower temperature range.

storage. The clean surface should never be touched with bare hands or soiled gloves. If more than a few hours are required between cleaning and priming, the parts should be covered, or, for still longer periods, wrapped in clean craft paper until the priming can be carried out. After priming, the dried primer surfaces, if not being bonded immediately, should again be protected by wrapping in craft paper. These steps should be carried out whether or not a primer is used. The period of time for which the parts can be safely stored in this way varies, depending on the nature of the adherends, the adhesive, the surface-preparation method, and the ultimate bond strength required.[34,57,58]

Picatinny Arsenal (now the US Army Armament Research and Development Center) has published a number of reports and papers on SET, using both shear tests and peel tests. Peel tests, in particular the roller peel test, are more sensitive to variation in surface preparation than are shear tests. Peel tests show that, in general, increasing SET tends to reduce the critical joint strength. Up to 30 days may elapse between surface preparation and actual bonding if the frying surfaces are protected and the relative humidity is kept at about 50%, without serious loss in joining strength. Temperatures and relative humidity above normal will cause deterioration in shorter periods of time.[34,57]

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6 Surface Preparation of Metals

Sina Ebnesajjad

6.1 Introduction

The specific preparation and treatment techniques described in this chapter are intended to provide for the production of strong reproducible bonds that fit easily into the bonding operation. It must be noted that the methods for preparing metal surfaces are generally much older than those of plastics because metals have been used for a longer period. Improvements have been made in recent decades, but the pace of upgrades has been slow in recent years. Improvements have often been determined by governments that promulgate environmental interests to reduce emissions and toxic waste generated by the surface preparation methods of metals: an important example is chromate-free etching of aluminum.

6.2 Aluminum

Chemical treatments are usually most effective with aluminum alloys, especially when long-term environmental exposure is required. The sulfuric acid−dichromate etch (*FPL* etch, named after *Forest Products Laboratory*, US Department of Agriculture; www.fpl.fs.fed.us) has been used successfully for many decades. Techniques more recently developed are often modifications of the FPL procedure. Other important methods include chromate conversion coating and anodizing. Corrosion-resistant adhesive primer, as well as anodic and chromate conversion coatings, helps to prevent corrosive failure of adhesion.[1]

Specifics of the procedures are outlined in the following sections.

6.2.1 Immersion Etch (Optimized FPL Process)

This method is specified in ASTM D2651-01 (2008).[2]

1. Remove ink markings and stamped identification by wiping with commercial solvents, such as acetone, methyl ethyl ketone (MEK), lacquer thinner, and naphtha
2. Degrease by vapor degreasing with 1,1,1-trichloroethane or immersion in a nonetching alkaline solution for 10 min at 70−82 °C. A typical solution is made by mixing 3.0 parts by weight sodium metasilicate, 1.5 parts sodium hydroxide, and 0.5 parts sodium dodecylbenzene sulfonate, such as Nacconol® 90G8 (Nacconol® 90G is available from the Stepan Co., www.stepan.com), to 133.0 parts water[3]
3. Immerse for 12−15 min at 66−71 °C in the etching solution (Table 6.1)
4. Rinse with water at 60−65 °C for 30 min
5. Air-dry in an oven or use infrared lamps not above 65.5 °C

Caution should be taken in making the solution. Add the acid to 60% of the water, stir in the dichromate, and then add the rest of the water. Never add the water to concentrated acid![4]

6.2.2 FPL Paste Etch

FPL paste etch is used for secondary bonding of parts that contain previously bonded areas, for repair of assemblies or when the size of parts makes immersion impractical. The parts should be bonded in the temperature range of 21−32 °C. A paste is

Table 6.1 Composition of FPL Etching Solution

Solution Component	Parts by Weight
Sulfuric acid (specific gravity 1.84)	10
Sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$)	1
Distilled water	30

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Table 6.2 A Comparison of Corrosion Protection Performance of Chromate Free Iridite NCP with Chromate[6]

Corrosion Performance							
Aluminum alloy	5052	6022	3003	1100	6111	6061	A356
Salt spray hours							
Iridite NCP	1000+	1000+	1000+	1000+	1000+	1000+	576
Chromate	1000+	1000+	168	432	432	648	1000+

prepared by mixing the sulfuric acid—sodium dichromate solution described above with finely divided silica (available from Stepan Chemical Co[5]) or Fuller's earth (composed mainly of alumina, silica, iron oxides, lime, magnesia, and water) and this is then applied to the surface. The paste is applied by brushing and should not be allowed to dry after application. Polypropylene (or similar) brushes should be used because of their chemical resistance. The paste should be allowed to remain in place for 20—25 min. Extra coats may be applied to prevent the paste from drying out or turning green. Clean dry cheesecloth moistened with water should be used to remove all traces of the paste at the end of the exposure period. Water may be sprayed if desired. Drying should be carried out at a maximum of 66 °C. As might be expected, bond strengths obtained by this technique are somewhat lower than those obtained by immersion.[2]

6.2.3 Chromate-Free Etch Process

Acid chromate etching solution is not only toxic and hazardous during use but also highly harmful if released into water supplies. Equally effective chromate-free etching solutions have been developed (Table 6.2). Iridite® 14-2 by MacDermid is a chemical process that produces a protective chromate conversion film on aluminum and aluminum alloys. Application is by dip, brush, swab, or spray, producing coatings ranging from clear to dark yellow. The darker coatings provide the greatest corrosion protection. The coating can be used as a final finish or can be dyed various colors. It can also serve as a base for paints and high performance top coats or lacquers, or as a base for rubber bonding. The operating range of Iridite® 14-2 is extremely flexible. Suitable adjustments of the Iridite® 14-2 concentration can accommodate wide variations in immersion time, achieve the corrosion protection (film thickness) desired, and the alloy to be treated.

Russell and Garnis[7] found that an etching solution recommended for the precleaning of aluminum prior to resistance welding gave excellent results. This solution consisted of nitric acid and sodium sulfate (N—S). In later modifications, a "P" etch was developed containing sulfuric acid, sodium sulfate, nitric acid, and ferric sulfate.

When aluminum was treated, the presence of nitric acid resulted in the production of oxides of nitrogen. These oxides are toxic and must be vented. In an effort to eliminate the necessity for venting the toxic etching fumes, a new etchant composition called "P2" was developed, which does not give off any appreciable fumes and produces good bond strength and improved durability.[7—9]

Degreasing or solvent cleaning may be carried out prior to using the P2 etch, by using the procedure described in Section 6.2.1. The composition of P2 etching solution is given in Table 6.3.

To prepare a 1-L solution, the acid is added to approximately a half liter of water, with constant stirring. Ferric sulfate is then added and mixing is continued. Water is added next to bring the volume to 1 L. The solution is heated to 60—65 °C, and the parts are immersed in this solution for 12—15 min. Rinsing follows in agitated tap water for 2 min. A second rinse, also at room temperature, using deionized water is sprayed on the part to remove the tap water.[7,10] This sulfuric acid-ferric sulfate etch yields bonds at least equal to those made using the FPL etch. When used as a deoxidizer prior to phosphoric acid anodizing (PAA) (see below), the results are essentially equal to those using the FPL etch. In a variation of this process, the

Table 6.3 Composition of P2 Etching Solution

Solution Component	Concentration
Sulfuric acid (6.5—9.5N)	27—36%
Ferric sulfate	135—165 g/L
Water	30

final rinse lasts 1−3 min in demineralized water at ambient air temperature of up to 71 °C, followed by drying in ambient air of up to 71 °C.[10]

6.2.3.1 Recent Etching Research Results

In 1996, Critchlow and Brewis[11] conducted an extensive review of 41 mechanical, chemical, electrochemical, or other identified treatments specifically designed to modify the surface of aluminum to enhance bond durability. They listed a number of useful conclusions that indicate the direction for future research into these aluminum pretreatment techniques.

These surface modifications methods may be combined with a range of chemical "add-ons," such as primers, coupling agents, or hydration inhibitors, to stabilize the surface during storage or to further enhance bond durability. A number of useful analytical techniques were identified, ranging from wettability, optical inspection methods, to more complex techniques such as Auger electron spectroscopy and electron spectroscopy for chemical analysis.

Although satisfactory *initial* bond strengths can be achieved when bonding to aluminum surfaces that have been degreased, surface modification is generally regarded as being required to optimize durability of the bond strength. A diverse range of mechanical, chemical, and electrochemical treatments have been developed to achieve this objective.

In comparative trials, PAA usually produces the best durability. It is clear that the modified aluminum surface should not be considered in isolation. For optimum durability, any treatment should be matched, when appropriate, to a suitable primer and adhesive. It is not possible to fully explain the relative durabilities provided by the various pretreatments because of the large number of combinations of alloys, pretreatments, and adhesives.

A number of factors have, however, been shown to be important, including: (1) a stable oxide is important as this can prevent or minimize the formation of a relatively weakly bound inorganic layer; (2) a topography that favors mechanical keying and provides an increased area over which interfacial interactions can occur is clearly beneficial. In the case of phosphoric acid anodized aluminum, the adhesive is thought to form a "composite" with the oxide structure. Strong interaction between the adhesive and the substrate is necessary to prevent the displacement of the adhesive by water.

The use of adhesive-bonded aluminum joints for automotive applications has several advantages in comparison with other joining techniques.[12] Dissimilar materials can be bonded with a reduced risk of galvanic corrosion, and thereby better control of tolerances is obtained. Other benefits include improved stiffness, rigidity, impact behavior and energy absorption, less vibration, and sound deadening. However, a major concern is deterioration of the mechanical performance of the joints as a result of exposure to a wet and corrosive environment. In this regard, the pretreatment of the aluminum substrate is essential. To obtain a strong and stable bond between the metal and the adhesive, the naturally formed surface oxide on aluminum has to be removed and replaced with a new, continuous, solid, and corrosion-resistant oxide layer. The most widely used treatments in the aerospace industry all utilize hexavalent chromium in their processing, and PAA or chromic acid anodizing is an essential step in their pretreatments. For automotive applications, simpler, cheaper, and environmentally friendly processes are required.

In a study published in 2002,[12] AA6060-T6 grade aluminum extrusions were subjected to various chrome-free pretreatments, including thin film AC anodizing in hot sulfuric acid, alkaline etching and a phosphate-permanganate conversion coating. A chromic-sulfuric acid pretreatment (FPL etch), commonly used for bonding of aluminum, was included as a reference. Hot AC anodizing is a process developed to prepare aluminum strip or sheet for painting on a continuous basis. The method should also be of interest as a batch pretreatment process. In addition to being chrome-free, no degreasing or etching stage is necessary because of the cleaning action of hydrogen evolved from the surface during the cathodic cycle of the AC current. Consequently, processing time is very short.

Degradation of adhesive joints is associated with diffusion of water to the adhesive/substrate interface, causing hydration of the oxide conversion coating and loss of adhesive strength.[12] A moderate temperature increase, which in the absence of water does not have an adverse effect on a structural joint, leading to a much more pronounced loss in strength. Presence of chloride ions is further expected to accelerate the loss of adhesion, for example, by propagation of localized corrosion of the metal beneath the adhesive.

Surface characteristics and durability of adhesive bonded AA6060 aluminum alloy joints with different pretreatments have been studied.[12] The results

Table 6.4 Elemental Composition of Test Samples Including Two Batches of AA6060[13]

	Cu	Mg	Mn	Fe	Si	Ti	Zn	Cr	Zr
AA6060 (1)	0.006	0.46	0.022	0.21	0.42	0.0013	0.0069	0.0003	0.0020
AA6060 (2)	0.002	0.46	0.021	0.18	0.40	0.01	0.015	–	0.01
$AlMg_{0.5}Si_{0.4}$	0.001	0.47	0.001	<0.001	0.38	0.0015	0.0015	0.0009	0.0002

indicate that thin film AC anodizing in hot sulfuric acid is promising as a simple, very rapid, and environmentally friendly pretreatment for adhesive bonding. Hot AC anodized single lap joints subjected to standard filiform corrosion (FFC) test conditions exhibited no significant loss in strength after 50 days of exposure at 82% RH and 40 °C. Reference FPL etched joints also showed no significant strength loss after similar exposure but had a slightly lower tensile strength than AC anodized joints.

Pretreatment of the AA6060 material by alkaline etching in hot NaOH solution resulted in the formation of a scalloped surface with a Mg-enriched hydroxide film.[12] A significant reduction in joint strength of about 7% was observed for these specimens, as a result of corrosion testing. Desmutting in nitric or sulfuric acid to remove the Mg-enriched hydroxide film resulted in still higher losses in strength. Application of a phosphate-permanganate conversion coating to the alkaline-etched substrate also had no beneficial effect. However, all pretreatments employed are superior to acetone degreasing alone.

Examination of fractured surfaces after tensile testing revealed evidence of FFC on the alkaline-etched, phosphate-permanganate coated, and FPL-etched specimens.[12] Corrosion filaments provide paths for ingress of moisture to the substrate/adhesive interface and corrosion products may also have contributed to a loss of adhesion by creating transverse stresses. To what extent the rate of degradation of adhesive bonded joints is affected by FFC requires further investigation.

In another study, Lunder et al.[13] subjected extruded AA6060 aluminum (Table 6.4) to various surface pretreatments before application of a one-component structural epoxy adhesive, XD4600. The durability of joints was assessed by wedge adhesion and FFC testing of panels coated with adhesive.

The following surface pretreatments were employed prior to adhesive bonding of the wedge and lap-shear test samples:

1. NaOH etched and deoxidized: Degreased in a commercial degreasing agent (AD Chemicals Z19, 50 g/L, pH 1.6, 50 °C, 20 s), rinsed in tap water, etched in 100 g/L NaOH solution (60 °C, 50 s), rinsed in tap water, deoxidized in fluoride/sulfuric/phosphoric acid-based solution (4% Alfideox 73, 25 °C, 1 min), rinsed in tap and then distilled water, and dried in hot air stream
2. Ti—Zr-based treatment, pH 2.9: Pretreated as in pretreatment 1 followed by immersion in hexafluorotitanate/zirconate-based solution (4% Gardobond X4707, 90 s, 20 °C, adjusted to pH 2.9 by Gardolene 6800), rinsed in tap and then distilled water, and dried in hot air stream
3. Ti—Zr-based treatment, pH 4.0: As pretreatment 2, except that conversion coating was performed in a solution of pH 4.0
4. Chromated: Pretreated as in pretreatment 1 followed by immersion in chromate solution (15 g/L Alodine C6100, 3 min, pH 2, 20 °C), rinsed in tap and then distilled water, and dried in hot air stream. Ti—Zr-based pretreatments 2 and 3, differing from each other only by the pH of the conversion bath, were employed to produce specimens with "low" and "high" coating weights in a controlled manner. Care was taken to maintain similar convection conditions in the baths during coating formation. Two additional pretreatments were included in the FFC test:
5. NaOH etched: As pretreatment 1 but without the deoxidation step
6. Degreased: Degreased in acetone

A chromate-free Ti—Zr-based pretreatment provided improved durability relative to an alkaline etch and deoxidation pretreatment but was clearly inferior to chromating in terms of adhesion and FFC resistance. Excessive Ti—Zr oxide deposition occurred in the vicinity of intermetallic α-Al(Fe,Mn)Si particles during pretreatment, which significantly reduced the performance of bonded joints during wedge test. The intermetallics, furthermore, played a crucial role in promoting FFC, as demonstrated by complete FFC immunity of an AA6060 model analog alloy ($AlMg_{0.5}Si_{0.4}$) free from α-Al (Fe,Mn)Si particles. The Ti−Zr-based pretreatments provided limited protection against FFC on AA6060 apparently because of a limited effect of the Ti−Zr oxide conversion coating in reducing the cathodic activity of the intermetallic particles. In the search for chromate-free pretreatments for painted or adhesive-bonded aluminum, inhibition of the cathodic activity on Fe containing particles is suggested as an important factor to prevent FFC.

Ti−Zr-based pretreatment provided[13] improved durability of epoxy-bonded AA6060 aluminum joints relative to an alkaline etch and deoxidation pretreatment but was inferior to a chromate treatment in terms of adhesion and resistance against FFC. The presence of cathodic intermetallic α-Al(Fe,Mn)Si particles in AA6060 is detrimental:

- The particles cause excessive Ti−Zr oxide deposition in their vicinity during pretreatment, resulting in poor durability of epoxy-bonded joints in humid environments
- The particles promote FFC in the presence of chlorides. A particle-free $AlMg_{0.5}Si_{0.4}$ model alloy similar to AA6060 was virtually immune against FFC, independent of pretreatment
- As the amount of Ti−Zr oxide deposited during Ti−Zr-based pretreatment is affected by the type, fractional area and distribution of cathodic particles present on the aluminum surface, the pretreatment conditions should be adapted to the specific alloy to achieve optimum performance
- Although the Ti−Zr-based pretreatment promoted adhesion, such treatment did not provide significant protection against FFC because the Ti−Zr oxide deposit did not inhibit the cathodic activity on the particles as effectively as a chromate pretreatment. Effective passivation of the cathodic particles, which are always present in commercial aluminum alloys, should be an important issue in the search for chromate-free pretreatments exhibiting high FFC resistance

Prolongo and Urena[14] conducted a detailed study of the effect of pretreatment applied, on the surface characteristics of aluminum substrates and on the adhesive strength of epoxy−aluminum joints (Fig. 6.1). They analyzed the variation of the density, composition, and aspect of the adherends as a function of the applied pretreatment. To determine the influence of alloying elements, they used two different aluminum alloys, A1050 and A2024 (Table 6.5). The adhesive strength was measured by the lap shear test, using several epoxy resins to analyze the influence of the adhesive nature.

The following surface pretreatments were employed prior to adhesive bonding of the lap-shear test samples:

1. Mechanical abrasion and degreasing: Abraded with Scotchbrite and wiped with MEK
2. Alkaline cleaning: Pretreated as in pretreatment 1 followed by immersion in 100 g/L NaOH solution, at 60 °C for 1 min, and rinsed in tap water

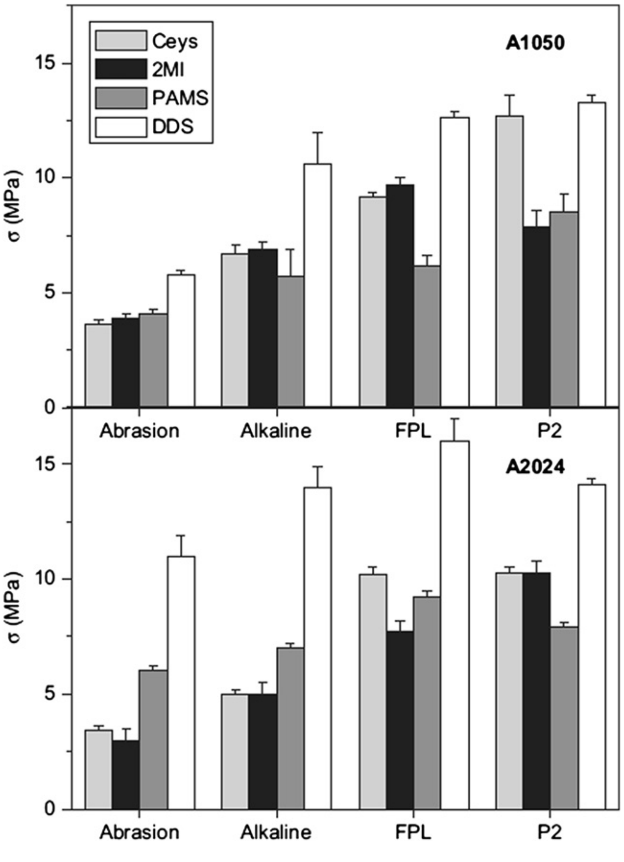

Figure 6.1 Adhesive strength of epoxy-aluminum joints as a function of the applied etching pretreatments: (a) abrasion, (b) alkaline, (c) optimized FPL, and (d) P2 (adhesives Ceys, 2MI, PAMS, and DDS are based on diglycidyl ether of bisphenol A, Diglycidyl ether of bisphenol-A(DGEBA), and differ in composition and/or cure conditions).[14]

Table 6.5 Elemental Composition of A1050 and A2024 Alloys[14]

	Cu	Mg	Mn	Fe	Si	Ti	Zn	Cr
A1050	–	–	0.01	0.29	0.09	0.01	0.01	–
A2024	4.67	1.34	0.63	0.25	0.15	0.06	0.02	0.01

3. Optimized FPL treatment: Pretreated as in pretreatment 2 followed by immersion in a water solution with 330 mL/L sulfuric acid (97% v/v) and 50 g/L potassium dichromate, at 60 °C for 15 min, and rinsed in tap water
4. P2 treatment: Pretreated as in pretreatment 2 followed by immersion in a water solution with 185 mL/L sulfuric acid (97%) and 127 g/L ferric sulfate, at 65 °C for 8 min, and rinsed in tap water (percentages by weight: 48% H_2O, 37% H_2SO_4, and 15% $FeSO_4$)

The chromate-free treatment based on the sulfuric acid-ferric sulfate etch provided an improved joint strength compared with dichromate-sulfuric acid etching, alkaline etching, or mechanical abrasion. This increase is associated with the porous oxide layer formed, but it depends on the adhesive nature used. The joints with Al–Cu–Mg alloy substrates generally presented higher adhesive strength values than those with pure aluminum adherends because of the selective etching of other elements and intermetallic compounds, which have different electrochemical potential.

6.2.4 Anodization

The anodization process is sometimes used for bare (nonclad) aluminum machined or chem-milled parts that must be protected against corrosion. Anodic coatings include chromic, sulfuric, and phosphoric acid types. Anodizing process involves electrolytic treatment of metals, during which stable films or coatings are formed on the surface of the metals. Anodic coatings can be formed on aluminum alloys in a wide variety of electrolytes, using either alternating or direct current (DC). PAA is a widely used method, as described in ASTM D3923-98 (2004).[15] In short, the process involves immersing the part in a 9–12% solution of phosphoric acid at 19–25 °C at anywhere from 9 to 16 V under DC for 20–25 min. Rinsing, drying, inspecting, and priming (Table 6.6) follow this step. Durability data obtained by this method are slightly better than those obtained by using an etch.[15]

PAA was studied by Boeing Aircraft in the early 1960s and commercially introduced in 1974. This process is less critically dependent than etching on processing variables such as the time between treatment and rinsing. It is also possible to use polarized light as a quality control test for the anodizing pretreatment. The oxide layer formed by this process is much thicker and the "whiskers" are longer than with chromic acid etching, although the thickness of the anodic oxide is dependent on the nature of the aluminum alloy being treated. PAA produces surfaces that are more resistant to hydration than those produced with other anodizing methods, including chromic acid.[16] PAA is also known to give more consistent results in durability studies than is chromic acid etching.

6.2.5 Brush Plate Bond Etch (Stylus Method)

This method of electrochemical surface preparation is not broadly known but has been effectively applied for small batch runs where tanks and other capital-intensive methods might have been used. Almost all of the solutions, "brushes" (or styli), and electrical power supplies, are proprietary. When this method is used, the entire "family" of proprietary items should be used; mixed usage of items between

Table 6.6 Phosphoric Acid Anodization (PAA) Conditions

Solution Component	Value
Phosphoric acid, 85%	9–12 weight%
Temperature, °C	19–25
Voltage, DC volts	9–11 (single rack) 14–16 (multirack)
Anodizing time, min	20–25

vendors should not occur. Additional details can be found in ASTM D2651-01.

6.3 Beryllium

Beryllium and its alloys must be heated with care. Handling or processing produces dust, chips, scale, slivers, mists, or fumes. Air-borne particles of beryllium and beryllium oxide are extremely toxic and have serious latent effects. Abrasives and chemicals used with beryllium must be property disposed.[1] One procedure is to degrease with trichloroethylene (TCE), followed by immersion in the etching solution (Table 6.7) for 5–10 min at 20 °C:[17]

Rinse in distilled water after washing in tap water and oven-dry for 10 min at 121–177 °C. Caution should be exercised because beryllium reacts quickly with methyl alcohol, fluorocarbons, perchloroethylene, and MEK/Freon® and can be pitted by long-term exposure to tap water containing chlorides or sulfates.[17]

A proprietary coating used to provide a corrosion-resistant barrier is Berylcoat "D," currently available from Brush Wellman, Inc., 17876 St. Clair Avenue, Cleveland, OH 44110.

6.4 Brass

Brass is an alloy of copper and zinc. Sandblasting or other mechanical means of surface preparation may be used. The following procedure combines mechanical and chemical treatment:[18]

1. Abrasive blast, using either dry or wet methods. Particle size is not especially critical
2. Rinse with deionized water
3. Treat with a 5% solution of sodium dichromate in deionized water
4. Rinse in deionized water
5. Dry

Another method is the following:[17,19]

Table 6.7 Composition of Etching Solution for Beryllium

Solution Component	Parts by Weight
Sodium hydroxide	20–30
Distilled water	170–180

Table 6.8 Composition of Brass Etching Solution

Solution Component	Parts by Weight
Zinc oxide	20
Sulfuric acid, concentrated	460
Nitric acid, 67% (specific gravity 1.41)	360

1. Degrease in TCE
2. Immerse for 5 min at 20 °C in the etching solution (Table 6.8).
3. Rinse in water below 65 °C
4. Re-etch in the acid solution for 5 min at 49 °C
5. Rinse in distilled water after washing
6. Dry in air (temperatures of washing and drying must not exceed 65 °C)

6.5 Bronze

Bronze is an alloy of copper and tin. The surface treatment involving zinc oxide, sulfuric acid, and nitric acid given above for brass is satisfactory for bronze.

6.6 Cadmium

Cadmium is ordinarily used as a coating on steel. It can best be made bondable by electroplating with silver or nickel. Another procedure is the following:[20]

1. Degrease or solvent clean with TCE
2. Scour with a commercial, nonchlorinated abrasive cleaner[21] (such as Ajax®, from Colgate Palmolive; www.colgate.com)
3. Rinse with distilled water
4. Dry with clean, filtered air at room temperature

It may be desirable to use a primer or sealant. Adhesive choice is particularly important with cadmium coatings.[20]

6.7 Copper and Copper Alloys

Copper is used in three basic forms: pure, alloyed with zinc (brass), and alloyed with tin (bronze). Copper has a tendency to form brittle amine compounds with curing agents from some adhesive systems. The most successful surface treatments are black oxide given below, as are chromate conversion coatings, which are especially recommended when the adhesive is slightly corrosive to copper. Other treatment methods have also been listed.

6.7.1 Nitric Acid, Sodium Chlorite (Black Oxide)

This method is intended for relatively pure copper alloys containing more than 95% copper.[2] It tends to leave a stable surface. It is not recommended for use with adhesives that contain chlorides or for hot bonding to polyethylene.

Procedure:

1. Degrease
2. Immerse in the etching solution for 30 s at room temperature. The solution is made by mixing 30 parts of nitric acid (70% technical) and 90 parts of water, all by volume
3. Rinse in running water and transfer immediately to the next solution without allowing the parts to dry
   Immerse for 2–3 min at 93–102 °C in the bath shown in Table 6.9. This solution should not be boiled
4. Rinse thoroughly in running water until a neutral test is produced when touched with pH indicator paper
5. Air-dry
6. Bond as soon as possible within 12 h of surface treatment

6.7.2 Nitric Acid/Ferric Chloride

1. Degrease (see Section 6.2.1)
2. Immerse for 1–2 min at room temperature in the following solution by weight:
   197 parts water
   30 parts nitric acid (sp. gr. 1.42)
   15 parts ferric chloride solution (42%)
3. Rinse thoroughly
4. Dry as quickly as possible
5. Apply adhesive immediately

Table 6.9 Composition of Copper Stabilization Bath

Solution Component	Concentration, g/L
Sodium chlorite	31.6
Trisodium phosphate	10.5
Sodium hydroxide	5.3

6.7.3 Nitric Acid

1. Bright dip in concentrated nitric acid at 16–21 °C for 15 s or until all corrosion has disappeared
2. Rinse thoroughly
3. Dry as fast as possible
4. Apply adhesive immediately

6.7.4 Acid Etch (FPL-Ferric Sulfate)

1. Remove surface contamination by sanding, wire brushing, or sand blasting, if necessary
2. Degrease
3. Immerse for 10 min at 66 °C in the solution given in Table 6.10
4. Rinse (water at or below room temperature)
5. Dry
6. Immerse the parts until a bright clean surface has been obtained in the following solution described in Table 6.11
7. Rinse using cold tap water
8. Dip in concentrated ammonium hydroxide
9. Rinse in cold tap water
10. Dry quickly
11. Apply adhesive immediately

6.8 Gold

Use methods given for platinum.

Table 6.10 Composition of Copper Etching Solution

Solution Component	Parts by Weight
Sulfuric acid (specific gravity 1.84)	75
Ferric sulfate (commercial grade)	1
Distilled water	8

Table 6.11 Composition of FPL Etching Solution

Solution Component	Parts by Weight
Sulfuric acid (specific gravity 1.84)	2
Sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$)	1
Distilled water	17

6.9 Magnesium and Magnesium Alloys

The surface preparation methods for magnesium alloys are closely associated with corrosion prevention. Because magnesium is highly reactive, corrosion-preventive coatings must be applied for most service applications. The major problem is to apply a sufficient thickness of coating to prevent corrosion, but not so thick that the bond fails cohesively in the coating.[2]

6.9.1 Alkaline-Detergent Solution

1. Degrease using the procedure described in Section 6.2.1 (use caution, because contaminants, such as metal particles, oils, etc., may result in a fire or explosion hazard)
2. Immerse for 10 min at 60−71 °C in an alkaline-detergent solution, described in Table 6.12
3. Rinse thoroughly
4. Dry at a temperature below 60 °C

6.9.2 Hot Chromic Acid

1. Degrease (see cautions in Section 6.9.1)
2. Immerse for 10 min at 71−88 °C in the solution comprised 1 part chromic oxide (CrO_3) and 4 parts distilled water
3. Rinse thoroughly
4. Dry at a temperature below 60 °C

The methods in Sections 6.9.1 and 6.9.2 can be run consecutively with an aqueous wash in between to give improved bond strengths.

6.9.3 Sodium Hydroxide-Chromic Acid

1. Degrease (see cautions in Section 6.9.1)

Table 6.12 Composition of Magnesium Etching Solution

Solution Component	Parts by Weight
Sodium metasilicate	2.5
Trisodium pyrophosphate	1.1
Sodium hydroxide	1.1
Sodium dodecylbenzene sulfonate (Nacconol® 90G)	0.3
Distilled water	95

2. Immerse for 5−10 min at 63−79 °C in a solution of 12 parts by weight water and 1 part sodium hydroxide (commercial grade)
3. Rinse in water at or below room temperature
4. Immerse for 5−15 min at room temperature in the solution described in Table 6.13
5. Rinse thoroughly
6. Dry at a temperature below 60 °C

6.9.4 Anodic Treatments

Light anodic treatment and various corrosion-preventive treatments produce good surfaces for adhesive bonding. These treatments have been developed by magnesium alloy producers, such as Dow Chemical Company (www.dow.com), Midland, MI, and others. Details are available from *ASM Metals Handbook, Vol. V*[22] and MIL-M-45202, Type I, Classes 1, 2, and 3.[23]

6.9.5 Conversion Coatings and Wash Primers

Some dichromate conversion coatings and wash primers designed for corrosion protection can be used for adhesive bonding.[2] Preliminary tests should be carried out to determine the suitability of the process before acceptance. Details are found in *ASM Metals Handbook, Vol. V*[22] and MIL-M-3171.[24]

Table 6.13 Composition of Magnesium Etching Solution

Solution Component	Parts by Weight
Chromic oxide (CrO_3)	24
Chromic nitrate	1.1
Distilled water	123

6.10 Nickel and Nickel Alloys

Steps for surface treatment of nickel and its alloys are described below.

6.10.1 Abrasive Cleaning

1. Solvent clean, preferably using vapor degreasing
2. Abrade with 180–240-grit paper, or grit blast with aluminum oxide 40-mesh abrasive
3. Solvent clean again according to step 1[1]

6.10.2 Nitric Acid Etch

1. Vapor degrease in TCE
2. Etch for 4–6 s at room temperature (~20 °C) in concentrated nitric acid (sp. gr. 1.41)
3. Wash in cold and hot water, followed by a distilled water rinse
4. Air-dry at 40 °C[18]

6.10.3 Sulfuric-Nitric Acid Pickle

1. Immerse parts for 5–20 s in the solution shown in (Table 6.14) at room temperature
2. Rinse in cold water
3. Immerse in a 1–2% ammonia solution for a few seconds
4. Rinse thoroughly in distilled water
5. Dry at temperatures up to 65.5 °C[1,25]

6.10.4 Cleaning and Treatment of Plated Parts

Thinly nickel-plated parts should not be etched or sanded.[26] Two unique problems are often encountered when preparing and bonding plated metals:[18]

- Vigorous mechanical treatment may penetrate and destroy the plating
- Plating-to-base adhesion may be inadequate

Table 6.14 Composition of Nickel Etching Solution

Solution Component	Amount
Sodium chloride	30 g
Sulfuric acid (60 °Be’)	1.5 L
Nitric acid (40 °Be’)	2.25 L
Distilled water	1.0 L

Because the plating process produces a clean, bondable surface, freshly plated surfaces often do not require additional preparation. Keep in mind, however, that plating changes surface properties such as adhesion, porosity, and surface stress of the metal deposit. Current density, composition of the plating bath (including brightener content), and bath temperature affect the bondability of the plated surface.

When mechanical pretreatment is used, abrade the surface lightly. Fine grades of sand or abrasive paper will minimize penetration. The correct chemical treatment depends on the type of metal, which is deposited during the plating process.

If the plating does not adhere tightly to the base metal, the plating process itself should be investigated. Application of Chemlok® 205 or 207 primer (0.1–0.2 mil, 2.5–5 μm) (www.lord.com) often improves adhesion to plated metals.

A recommended practice is light scouring with a nonchlorinated commercial cleaner, rinsing with distilled water, drying at below 49 °C, and then priming as soon as possible.

6.10.5 Nickel-Base Alloy Treatments

Monel® (nickel-copper), Inconel® (nickel-iron-chromium), and Duranickel® (primarily nickel) (www.specialmetals.com) are the major types of nickel-base alloys. According to Keith et al.,[27] procedures recommended for stainless steel will give at least satisfactory results with these alloys.

6.11 Platinum

6.11.1 Abrasive Cleaning

1. Solvent clean, preferably by vapor degreasing (avoid immersion and wiping, unless these steps can be followed by vapor rinsing or spraying)
2. Abrade lightly with 180–240-grit paper
3. Solvent clean again as in step 1[1]

6.11.2 Abrasive Scouring

1. Scrub surfaces with distilled water and nonchlorinated scouring powder
2. Rinse thoroughly with distilled water (surfaces should be water-break-free)[1]

6.12 Silver

Use the methods given above for platinum or use the following methods.

6.12.1 Chromate Conversion Coating

1. Solvent clean
2. Immerse for 5−10 s in the solution shown below (Table 6.15) at room temperature
3. Rinse in distilled water
4. Dry at temperatures up to 66 °C[1]

6.12.2 Degrease-Abrade-Prime

1. Vapor degrease
2. Abrade lightly with emery cloth
3. Prime coat with an adhesive such as Lord Corp's Chemlok (silicone-type polymer) diluted with 5−10 volumes of methanol or ethanol[28]

6.13 Steel

Compared with aluminum, relatively little research has been carried out on optimum surface treatments for steel preparatory to adhesive bonding. Steel alloys are usually used where high temperatures and other rigid requirements are expected. As a result, problem areas such as corrosion, thermal degradation of adhesives and primers, and moisture effects become important. Surface preparation is even more critical in bonding steel than it is with many other metals. Initial adhesion may be good, but bonds degrade rapidly under rigid environmental exposure. For this reason, primers are desirable. Many steel alloys will form surface oxides rapidly; therefore, drying cycles after cleaning are critical. Alcohol rinses after water rinses tend to accelerate drying and reduce undesirable surface layer formation. Mild steel (carbon steel) may require no more extensive treatment than degreasing and abrasion to give excellent adhesive bonds. Tests should be carried out with the actual adhesive to be used to determine whether a chemical etch or other treatment is essential.[20,29,30]

Table 6.15 Composition of Chromate Conversion Solution for Silver[1]

Solution Component	Amount
Kenvert No. 14 powder (supplied by Gallade Chemical, www.galladechem.com), g	10.6
Distilled water, L	3.6

Brockmann[31] suggests that in contrast to aluminum and titanium alloys, where the surfaces are usually treated by chemical methods, etching procedures for different types of steel, except for stainless steel, are not recommended. According to Brockmann, the best results are usually obtained by using mechanical roughening techniques, such as grinding with corundum (Al_2O_3), as the grit material. Brockmann states the only chemical treatment required is etching for stainless steel in an aqueous solution containing oxalic acid and sulfuric acid (see below).

DeLollis[32] suggests that the most common method for preparing steel surfaces for bonding is probably sandblasting, preceded by vapor degreasing to remove any oily film present. Because a clean steel surface is easily oxidized, it is particularly important that the compressed air source used in sandblasting is dry and free of oil. Although some methods call for rinsing in a clean volatile solvent such as MEK or isopropyl alcohol, it should be remembered that these solvents frequently contain small amounts of water that may cause subsequent rusting (xylene or toluene are preferable solvents). Furthermore, when volatile solvents evaporate from a metal surface, the surface is chilled. In a humid environment, such an effect may result in condensation of moisture, which nullifies the cleaning effort. After sandblasting, the best treatment is to blow the particulate matter off the surface with clean, dry air. Solvent wiping should be used only as a last resort.

DeLollis[32] suggests that vapor honing or vapor blast can be used for small steel parts without danger of warping or any significant change in tolerance. A wetting agent and rust inhibitor are usually present in the abrasive-water suspension used in this method. These agents must be rinsed off thoroughly in clean water. After this step, a clean, dry, water-compatible solvent must be used to remove the water. Finally, clean, dry compressed air or nitrogen should be used to blow off the solvent. Abrasive treatments may result in warping of thin sheet-metal stock. In this type of application, any of the acid-etch solutions used with stainless steel can be used with carbon steels. They must be used carefully, however, because they would react more rapidly with carbon steel than with stainless steel. Chemical treatments for carbon steel are to be used only when abrasive equipment is not available, and they are described below.

6.13.1 Acid Treatment

1. Prepare one of the solutions as shown in Table 6.16 or 6.17
2. Degrease in a vapor bath of TCE
3. Immerse for 10 min in the orthophosphoric acid solution (Table 6.16) at 60 °C or for 5–10 min at 20 °C in the hydrochloric acid solution (Table 6.17)
4. Remove the black residue formed on the metal with a clean, stiff brush while holding the metal under cold, running distilled or deionized water
5. Dry the metal by heating at 120 °C for 1 h. If the steel part cannot be stored immediately in an area of low humidity (less than 30% RH) apply the adhesive immediately after cleaning[29]

6.13.2 Potassium Iodide-Phosphoric Acid Method

This is a surface treatment process based on the oxidation of the steel to produce a continuous epsilon oxide (Fe_2O_3). It is reported to give strong durable bonds and to improve the salt-spray and humidity resistance of polymer-coated steel. The steps are

1. Vapor degrease
2. Alkaline clean in a solution containing 3% trisodium phosphate and 3% sodium carbonate for 5 min at 82 °C
3. Rinse in deionized water
4. Immerse in a solution of 50 g potassium iodide (KI) per liter of 1:1 concentration phosphoric acid:water (v/v) at 93 ± 11 °C for 2–10 min
5. Rinse in deionized water
6. Dry at 11–71 °C[33]

Table 6.16 Composition of Etching Solution for Steel

Solution Component	Parts by Weight
Orthophosphoric acid (specific gravity 1.73)	1
Ethyl alcohol, denatured	1–2

Table 6.17 Composition of Etching Solution for Steel

Solution Component	Parts by Weight
Hydrochloric acid, concentrated	1
Distilled water	1

6.13.3 ASTM Suggested Methods

ASTM D2651-01[2] lists the following mechanical and chemical methods for surface preparation of carbon steel.

6.13.3.1 Mechanical Method

Carbon steel may be prepared using the same general methods as stainless steel (Section 6.14). Sand blast, grit blast, or vapor hone may be used. Thin sheet steel may be warped due to peening action of the blasting abrasives.

6.13.3.2 Method for Stainless Steel

Thin parts and sheet materials may be prepared using methods for stainless steel. The major problem is in preventing oxidation of the surfaces. Oxidation can occur in a very short time, even before the parts are dry. Parts must be bonded immediately. The adhesive or adhesive primer must be applied immediately after drying.

6.13.3.3 Nitric-Phosphoric Acid Etchant

The nitric-phosphoric etchant is environmentally acceptable. It produces a smut-free surface that can be treated by other chemical processes, by immersion for 5 min at 23 °C in the solution given in Table 6.18.

6.14 Stainless Steel

Stainless steel, or corrosion-resistant (CRES) steel, has a high chromium content (11% or higher) as the primary alloying element. There have been a large number of surface preparation methods reported in the literature. An excellent report prepared in 1968 by Battelle Memorial Institute workers[34] gives details of 12 surface preparation methods and discusses the relative advantages and disadvantages of each. In addition to mechanical methods, strong acids and strong alkalis are used. A wet-abrasive blast with a 200-grit abrasive, followed by thorough rinsing to remove the residue, is an acceptable procedure for some uses but does not produce high bond strengths. Strong acid treatments are usually used for general bonding to produce strong bonds with most adhesives. Passivation in nitric acid solution and concentrated sulfuric acid-saturated sodium dichromate solution both produce high-strength bonds but with low or marginal peel strengths. Such joints may fail under vibration stress, particularly when a thin stainless steel sheet is bonded with low-peel-strength adhesives.

The acid-etch process outlined below can be used to treat Types 301 and 302 stainless steel. This process results in a heavy black smut formation on the surface. This material must be removed if maximum adhesion is to be obtained. The acid-etch process produces bonds with high peel and shear strength. The 400 series of straight-chromium stainless steels should be handled in the same manner as for the plain carbon steels. The precipitation-hardening stainless steels each present an individual problem. Processes must be adopted or developed for each one.[1,23,34]

6.14.1 Acid Etch (for Types 301 and 302 Stainless Steel)

This method has been used successfully with modified epoxy adhesive (such as 3M's Scotch-Weld®, www.3m.com), achieving excellent stressed durability results at 60 °C and 95% RH. The procedure is as follows:

1. Degrease—Wash with acetone to remove grease, oil, markings, and solvent-removable soils. Follow with vapor degreasing using a suitable safe solvent
2. Sulfuric acid etch—Immerse the parts for 4 min at 60 °C in a solution of 25–35% by volume of sulfuric acid (sp. gr. 1.84) in deionized water. Do not start timing until gassing is evident. A piece of 1020 steel may be rubbed across the parts to start the etching process
3. Rinse in running tap water at service-water temperature for 2 min
4. Smut removal—Immerse parts for 5 min at 66 °C in a solution of 22–28 parts by weight of sulfuric acid (sp. gr. 1.84) and 2–3 parts by weight of sodium dichromate in deionized water
5. Rinse in running tap water at service-water temperature for 2 min
6. Dry the parts at 60 °C for 30 min in a preheated air-circulating oven
7. Packaging–Wrap the parts in clean craft paper until ready to bond[35]

6.14.2 Oxalic-Sulfuric Acid Process for Maximum Heat Resistance

1. Immerse for 10 min at 90 °C in the solution of Table 6.19
2. Remove the solution and brush the black smut deposit with a good stiff brush (nylon is suggested)
3. Rinse with clean running water
4. Dry in a stream of hot air
5. Return to the desiccator[36]

Lord Corp.[37] (www.lord.com) recommends soaking parts in a commercial steel cleaner of high alkalinity before immersing in the oxalic-sulfuric acid solution.

Table 6.18 Composition of Etching Solution for Steel

Solution Component	Volume, %
Nitric acid, 40° Baume	5
Phosphoric acid—85% weight	30
Surfactant (Triton® X200)	0.01
Deionized water	64.99

Table 6.19 Composition of Etching Solution for Stainless Steel

Solution Component	Amount
Sulfuric acid, concentrated	10 mL (18.4 g)
Oxalic acid	18.5 g
Distilled water	150 mL

6.14.3 Bromophosphate Treatment

This treatment is a modification of the iodophosphate treatment described above for carbon steel. No chloride ion is used in the method. KBr is used instead of KI and 1–5% by volume of concentrated H_2SO_4 should be added to the treating solution in the case of difficult-to-etch CRES steels to ensure the removal of the existing surface layers.[33]

1. Vapor degrease
2. Alkaline clean in a solution of 3% trisodium phosphate and 3% sodium carbonate for 5 min at 82 °C
3. Rinse in deionized water
4. Immerse in a solution of 50 g potassium bromide (KBr) per liter of 1:1 concentrated phosphoric acid:water for 2–10 min at 93 ± 11 °C. In the case of difficult-to-etch CRES steels, to ensure removal of the existing surface layer, use 50 g KBr per liter of 1:9:10 concentrated sulfuric acid:concentrated phosphoric acid:water
5. Rinse in deionized water and dry at 15.6–71 °C

This method can be adapted to spraying techniques.

6.14.4 ASTM Suggested Methods

ASTM D2651-01[2] lists the following mechanical and chemical methods for surface preparation of stainless steel.

6.14.4.1 Mechanical Methods

Mechanical methods such as wire brushing, rubbing with metal wool, hand sanding, dry sandblast, grit blast, or vapor honing may be used to prepare stainless steel. Care should be exercised to ensure that abrasive materials such as grit, sand, cloth, sandpaper, or brushes are free from contamination that may be spread or rubbed onto the steel. Dry grit or sand blasting tends to warp thin sheet materials; these methods are suited only for thick-section parts. Vapor blasting by water or steam and an abrasive is the most effective method and does not warp parts, if done carefully. Peening action of any blast process may work harden the surface of some base metals. Hand sanding, rubbing with metal wool, and wire brushing is the least effective method. Exercise care in using any mechanical method to prevent deep gouges or rough surfaces, which are not conducive to good bonding. Wash, vaporize, degrease, and brush or air blast (dry oil-free air) surfaces to remove all traces of the abrasives. Apply the primer or adhesive immediately after the treatment.

6.14.4.2 Acid Etch

1. Etch for 10 min at 65–71 °C in the following solution by weight: 90 parts water, 37 parts sulfuric acid (sp. gr. 1.84), and 0.2 parts sodium dodecylbenzene sulfonate such as Nacconol® 90G[3]
2. Rinse thoroughly and remove smut with a stiff brush if necessary
3. Immerse for 10 min at room temperature in the bright dip solution of Table 6.20

6.14.4.3 Acid Etch

Immerse for 2 min at approximately 93 °C in the solution of Table 6.21 heated by a boiling water bath.

6.14.4.4 Acid Etch

Immerse for 15 min at 63 ± 3 °C in a solution by volume of 100 parts sulfuric acid (sp. gr. 1.84) to 30 parts saturated sodium dichromate solution.

6.14.4.5 Sodium Metasilicate

Immerse for 15 min at 63 ± 3 °C in the solution of Table 6.22.

6.14.4.6 Acid Etch

1. Immerse for 10 min at 60–65 °C in the solution described in Table 6.23
2. Rinse thoroughly

Table 6.20 Composition of Etching Solution for Stainless Steel

Solution Component	Part by Weight
Nitric acid (specific gravity 1.42)	15
Hydrofluoric acid (35.35%, specific gravity 1.15)	2
Deionized water	88

Table 6.21 Composition of Etching Solution for Stainless Steel

Solution Component	Part by Weight
Hydrochloric acid (specific gravity 1.2)	200
Orthophosphoric acid (specific gravity 1.8)	30
Hydrofluoric acid (35.35%, specific gravity 1.15)	10

3. Immerse for 5 min at 50–65 °C in FPL solution used for preparing aluminum (Table 6.1)
4. Rinse thoroughly
5. Dry at a temperature below 93 °C

6.14.4.7 Commercial Household Cleaner

Some batches of stainless steel may be prepared by vigorous scouring with a wet cloth and a commercial household cleaner. This method should be used only in cases where other methods are unavailable. Somewhat lower bond strength results from this method compared with other techniques described.

6.15 Tin

Solvent cleaning with methylene chloride, chloroform, or TCE is recommended prior to abrading. Scraping, fine sanding, or scouring are suitable methods of abrading, which should be followed by solvent cleaning.[1] This is one of the few metals for which abrasion may be used without being followed by an acid etch.[20]

Table 6.22 Composition of Etching Solution for Stainless Steel

Solution Component	Part by Weight
Sodium metasilicate	1
Sodium salt anionic surfactant, polyether sulfonate type (Triton® X200K)	1.8
Water	47.2

Table 6.23 Composition of Etching Solution for Stainless Steel

Solution Component	Parts by Weight
Hydrochloric acid (specific gravity 1.2)	50
Formalin solution (40%)	10
Hydrogen peroxide (concentration, 30–35%)	2
Water	45

6.16 Titanium

Titanium is a very important metal, with uses in many industries. Titanium is a space-age metal used widely in aerospace applications, requiring high strength-to-weight ratios at elevated temperatures above 300 °C.[32] Adhesive-bonded helicopter rotor blades consisting of titanium skins in the form of sandwich panels have been in use since the 1950s. This section provides a somewhat chronological description of the surface treatment methods. The methods published by ASTM method D2651-01 are presented in Section 6.16.7.

The earliest surface treatment methods for these titanium surfaces were based on cleaning and etching in alkaline mixtures. These processes provided good joint strength. However, they were sensitive to the chemical composition of the titanium alloy and, within the same alloy, were sometimes affected by batch-to-batch variations. At a later date, a stainless steel for pickling etchant was used. This etchant was based on mixtures of nitric and hydrofluoric acids. However, when intermediate-curing-temperature adhesives were developed, these adhesives did not give as high strengths with titanium as they did with aluminum alloys. Consequently, the phosphate-fluoride process was developed, described later in this section. This process had been the most widely used surface preparation procedure for titanium for aerospace applications. It has been described in ASTM D2651-01[2] and MIL-A-9067.[38]

In the late 1960s, Army helicopters in Southeast Asia began to develop severe debonding problems in sandwich panels of titanium and glass-reinforced epoxy composite skins bonded to aluminum honeycomb core. These failures were attributed to the ingress of moisture into the interface. The combined effects of moisture and stress would have, thus, accelerated joint failures. As a result of this problem, a number of research programs were undertaken to explain the mechanism of failure in hot/humid environments and to improve the environmental resistance of titanium adhesive-bonded joints. One such program resulted in the development of a modified phosphate-fluoride process by Picatinny Arsenal workers.[39] At a later date, two commercial surface preparations, Pasa-Jell and VAST, became available as alternatives. These procedures are described in Section 6.20. Many surface preparation methods were developed in the 1970s and 1980s because of the need for superior adhesive bonds of titanium joints in aerospace and other applications.[40]

One of the problems that requires close control in titanium processing is hydrogen embrittlement. The formation of hydrogen gas is inherent in the acid etching and anodizing processes, and hydrogen adsorption on titanium surfaces can lead to embrittlement. Extreme caution must be taken when treating titanium with acid etchants that evolve hydrogen. Immersion times must be closely controlled and minimized.[1]

6.16.1 Titanium as Biomaterial

In recent times, titanium has become a biomaterial of choice for musculoskeletal implants, such as artificial hip and knee prostheses; screws, plates, nails, and intramedullar fixation devices; and dental implants.[41,42] Titanium and its alloys are recognized within the biomaterials because of their excellent biocompatibility and high chemical inertness of the oxide that covers their surfaces, as well as their mechanical and their osseointegration properties that promote their regular use in biomedical applications.[43−45]

In the case of titanium implants, surface roughness is one of the most important surface characteristics in reducing the period of osseointegration, stimulating greater bone regeneration and improving mechanical stability by interlocking the surrounding bone tissue with the implant.[46] Indeed, the modifications introduced by surface treatments developed for cementless and endosseous implants are based on the empirical evidence that there is a surface roughness range where the osseointegration is optimized.

Within the great variety of surface treatments used in biomaterials to improve osseointegration and to reduce the healing time, nowadays, blasting, acid etching, and a combination of both (blasting C acid etching) are widely used.[47] Many surface treatments that are used in cementless and endosseous implants modify the topography and the roughness to increase the implantbone contact area and thus favor biomechanical anchorage, shortening the period of osseointegration. Nevertheless, the effects that the surface treatments can have on the fatigue life of the material are not generally considered. In this sense, the superficial condition of the component is one features that affects the fatigue strength, especially the fatigue crack nucleation.

Pazosa et al.[41] have studied the fatigue behavior of annealed commercially pure titanium grade 4 as a function of surface treatment methods. They used acid etching, shot blasting, and a dual treatment of blasting C acid etching. An as-machined surface condition was used as a reference. Topography, roughness, surface defects, microstructural changes, and residual stresses were characterized in each case.

Rotating−bending fatigue tests of each surface condition were conducted at room temperature with a frequency of 33 Hz. S−N curves and Basquin equations were obtained based on the results of these tests. In 1910, Basquin noticed that Stress-Life data could be modeled according to a power equation, yielding a straight line on a log−log scale. This observation corresponds to elastic material behavior in the Strain-Life approach. The Basquin equation can be expressed in terms of true elastic strain amplitude.[48] Tested samples were also characterized to evaluate fatigue damage.

The acid etching decreases the fatigue endurance, whereas the blasting and blasting C acid etching treatments showed a similar behavior with respect to the reference condition. For acid etching, the modifications introduced (stress raisers) contributed to accelerate the nucleation of cracks. On the other hand, the treatments with a blasting stage besides generating stress raisers introduced compressive residual stresses and superficial plastic deformation that tend to improve the fatigue endurance of the material.

6.16.2 Stabilized Phosphate-Fluoride Treatment

This method, developed by Wegman at Picatinny Arsenal, is an improvement over the basic phosphate-fluoride method described in MIL-A-9067.[35] The improvement is achieved by the addition of sodium sulfate in the pickle. The method is reported to give good initial bond strength and excellent durability under adverse conditions, including high temperature/high humidity (60 °C and 95% RH under load). In this method, the proper crystalline structure is established by the phosphate-fluoride process, which is then stabilized by the incorporation of sodium within the crystalline structure.

1. Vapor degrease or clean with acetone
2. Alkaline clean by immersing parts in alkaline cleaner (nonsilicated), 5−10% by volume, for 5 min at 66 °C. For suitable formulations, contact Chemetall Oakite Products (Berkeley Heights, NJ, www.chemetallamericas.com)
3. Rinse in running tap water at 40 °C for 2 min
4. Modified HF Acid-Nitric Acid Pickle: Immerse for 2 min at room temperature in the following solution (Table 6.24)
5. Rinse in running tap water at service temperature
6. Phosphate-fluoride etching is done by soaking parts for 2 min at room temperature in a solution given in Table 6.25
7. Rinse in running tap water at service temperature for 2 min
8. Immerse in deionized water at 66 °C for 15 min.
9. Rinse in water at room temperature to 71 °C for 15 min
10. Dry at 60 °C for 30 min in a preheated air-circulating oven
11. Wrap the parts in clean craft paper until ready to bond

This method yields excellent durability for both 6,4 titanium and chemically pure (CP) titanium. The former, however, exhibits a loss of lap-shear strength after 5 years outdoor weathering. The CP titanium does not show this effect.

6.16.3 Alkaline Cleaning

Use steps 1, 2, 3, 10 and 11 in Section 6.16.4 only, under the procedure for the Stabilized Phosphate-Fluoride Method in Section 6.16.2. The results, however, give poorer durability than with that method.[35]

Table 6.24 Composition of Etching Solution for Titanium

Solution Component	Amount
Hydrofluoric acid, 70% wt. concentration	15.7−23.6 g/L
Sodium sulfate, anhydrous	23.6 g/L
Nitric acid, 70% wt. concentration	315−394 g/L
Deionized water	To make 1 L

Table 6.25 Composition of Phosphate Fluoride Etching Solution for Titanium

Solution Component	Amount
Trisodium phosphate	51.2−55.1 g/L
Potassium fluoride	19.7−23.6 g/L
Hydrofluoric acid, 70% wt. concentration	17.3−19.7 g/L
Deionized water	To make 1 L

6.16.4 Alkaline Etch

1. Vapor degrease or clean with acetone
2. Alkaline clean: Immerse parts in nonsilicated alkaline cleaner for 5 min at 66 °C. Examples of commercial products include Oakite Pyrene 1038 in water (for a reliable recommendation, contact Chemetall Oakite Products, Berkeley Heights, NJ, www.chemetallamericas.com)
3. Rinse in running tap water at 40 °C for 2 min
4. Rinse in running deionized water for 1 min at service temperature
5. Alkaline etch: Immerse for 5−10 min at <100 °C in a cleaner (such as Cleaner AD-25, available from Turco Products Division of Henkel Surface Technologies, Madison Heights, Michigan, www.henkel.com)
6. Rinse under running tap water at service temperature for 2 min
7. Rinse under running deionized water at service temperature for 1 min
8. Dry at 60 °C for 30 min in a preheated air-circulating oven
9. Wrap the parts in clean craft paper until ready for bonding[36]

6.16.5 Pasa-Jell® Treatment

Pasa-Jell® (www.bergdahl.com/PasaJell.htm) is a proprietary chemical marketed by Semco Division, Products Research and Chemical Corp., Glendale, CA. This formulation is available either as a thixotropic paste suitable for brush application or as an immersion solution for tank treatment. Pasa-Jell® 107 is a blend of mineral acids, activators, and inhibitors, thickened using inorganic agents, to permit application in localized areas. The approximate chemical constituents are 40% nitric acid, 10% combined fluorides, 10% chromic acid, and 1% couplers, and the balance is water. The immersion process requires nonmetallic tanks made of polyvinyl chloride (PVC), polyethylene, or polypropylene. A recommended mixture uses 1:1 dilution for 12 min. With the thixotropic Pasa-Jell® paste, a reaction time of 10−15 min assures durable bonds.[35]

6.16.6 VAST Process

VAST is an acronym for Vought Abrasive Surface Treatment and is a development of Vought Systems of LTV Aerospace Corp., Dallas, now Vought Aircraft Industries (http://www.voughtaircraft.com). In the VAST process, titanium is blasted in a specially designed chamber with slurry of fine abrasive containing fluorosilicic acid under high pressure. The particles are made of aluminum oxide at about 280 mesh in size, and the acid concentration is maintained at 2%. The process produces a gray smut on the surface of 6A1-4V-Ti alloy, which must be removed by a rinse in 5% nitric acid. The joint strength that results is superior to that provided by the unmodified phosphate fluoride process. The film produced is crystalline, having an anatase structure containing Ti, O, Si, F, Pb, and C. The oxide is stable up to 175 °C but starts converting to rutile structure at higher temperatures.[40,49]

The VAST process, because of its need for special equipment, has found limited use. The process details are as follows:[29]

1. Wipe surface with MEK
2. Alkaline clean
3. Rinse with deionized water at room temperature
4. Use VAST process for 5−10 min in a suitable chamber. The slurry consists of 2000 mL of 2% hydrofluorosilicic acid (H_2SiF_6) plus 500 mL of 240-grit purified aluminum oxide (Al_2O_3). The white aluminum oxide (available from the St. Gobain Abrasives Carborundum Division, Niagara Falls, NY 14302) is acceptable.
5. Rinse with tap water spray at room temperature
6. Immerse for 1 min in 5% nitric acid solution (optional, depending on titanium alloy)
7. Rinse in deionized water at room temperature
8. Air-dry
9. Bond within 4 days after treatment to be safe, although experiments have shown no changes up to 9 days

6.16.7 Alkaline-Peroxide Etch [Royal Aircraft Establishment (RAE) Etch]

When titanium is immersed in alkaline hydrogen peroxide solutions, depending on the concentration of sodium hydroxide and hydrogen peroxide, the metal is either etched or oxidized. The concentrations that produce gray oxides produce adhesive-wettable surfaces. A recommended mixture is 2% caustic soda and 2.2% hydrogen peroxide. Exposure to the oxidizing solution may be at room temperature, but 10−36 h are required under these conditions to produce high-strength durable joints. Good bonding surfaces are produced within 20 min at 50−70 °C. Oxidized adherends are washed with plain and acidified water before rinsing with acetone and drying at 100 °C.[40]

High bond strengths (50−55 MPa) are produced if the titanium surface is subjected to alumina blasting prior to treatment. Alkaline-peroxide etch has many advantages over the acid-based treatments. The chemical constituents are less toxic; the treatment does not require acid-resistant containers; the process is free from hydrogen pick-up, and the waste material is easily disposed. The process, however, is limited to batch production because of the high instability of hydrogen peroxide at high exposure temperatures. This process was developed jointly by *British Aerospace* (www.baesystems.com) and the RAE. Durability is reported to be excellent, with 91−92% of initial joint strength (control) being retained after 4 years in a warm/wet environment.

6.16.8 ASTM Suggested Methods

ASTM D2651-01[2] lists the following mechanical and chemical methods for surface preparation of stainless steel.

6.16.8.1 Mechanical Abrasion

See Section 6.14.4.1.

6.16.8.2 Chemical Methods

1. Acid etch (hydrochloric, orthophosphoric, hydrofluoric)
2. Immerse for 2 min at room temperature in the following solution: 841 mL orthophosphoric acid (reagent grade, 85–87%) to 63 mL hydrofluoric acid (reagent grade, 60%)
3. Rinse
4. Oven-dry for 15 min at 88–93 °C

6.16.8.3 Acid Etch (Nitric Hydrofluoric)

1. Immerse for 15 min at 76 °C in the following solution: 6–8 fl oz of a caustic cleaner, such as Turco® (www.henkelna.com) Vitro-Klene 10, or equivalent, to 3.6 L (1 gal) water
2. Rinse in cold tap water
3. Immerse for 5 min at room temperature in the following solution by weight: 48% nitric acid (sp. gr. 1.5), 3% ammonium bifluoride (technical), to 49% water
4. Rinse in cold tap water
5. Air-dry at room temperature
6. Immerse for 2 min at room temperature in the following solution: 50.0 g trisodium phosphate (technical), 8.9 g sodium fluoride (technical), 26.0 mL hydrofluoric acid (48%), to water to make 3.6 L (3.6) of solution
7. Air-dry at room temperature

6.16.8.4 Stainless Steel Methods

Processes used to prepare titanium alloys for adhesive bonding can be much the same as for stainless steel. Good bond strengths have resulted by bonding titanium alloys that have been anodized by proprietary processes.

6.16.8.5 Chromic Acid/Fluoride Anodizing

Stainless steel surface processes, as described in Section 6.14.4.4–6.14.4.6, have been found satisfactory.

6.17 Tungsten and Alloys

6.17.1 Hydrofluoric-Nitric-Sulfuric Acid Method

1. Degrease in a vapor bath of TCE
2. Abrade the surface with medium-grit emery paper
3. Degrease again as in step 1
   Using equipment constructed of fluoropolymer resins, polyethylene, or polypropylene, prepare the solution given in Table 6.26.
   Blend the hydrofluoric acid and the nitric acid with water. Then slowly add the sulfuric acid, stirring constantly with a polytetrafluoroethylene or polyethylene rod. Add a few drops of 20% hydrogen peroxide.
4. Immerse for 1–5 min in the above solution at room temperature
5. Rinse under tap water
6. Finish rinsing in distilled water
7. Dry in an oven at 71–82 °C for 10–15 min[19]

6.18 Uranium

For any adhesive to bond well with this metal, the uranium must be freshly pickled and dried. The dark-colored, loosely adherent surface oxide layer must be removed. Cleaning is satisfactory when the metal surface becomes bright and shiny.

6.18.1 Abrasive Method

This method, developed by Picatinny Arsenal workers, involves degreasing the uranium in a vapor bath of TCE and then sanding the bonding surfaces in

Table 6.26 Composition of Etching Solution for Tungsten

Solution Component	Parts by Weight
Nitric acid, specific gravity 1.41	30
Sulfuric acid, specific gravity 1.84	50
Hydrofluoric acid, 60% wt. concentration	5
Deionized water	15

a pool of the adhesive to be used for bonding.[29] This is done to prevent further oxidation of the uranium block by exposure to air after sanding and also to prevent contamination of the surrounding area with radioactive particles. Polyamide-epoxy and polyurethane adhesives are recommended. The problem of oxidation remains, however, when only the two bonding surfaces of the uranium block are cleaned and adhesive coated. Under these conditions, the oxide layer spreads from the uncleaned side of the uranium until the bonding surfaces themselves are completely oxidized. By sanding all six sides of each uranium block and then coating with a protective layer of adhesive, the problem is solved.

6.18.2 Acetic Acid-Hydrochloric Acid Method

This method is used with aluminum-filled adhesives when no primer or surface coating is to be applied.[29]

1. Pickle uranium bars clean in 1:1 nitric acid-water
2. Rinse briefly in distilled water
3. Immerse in 9:1 acetic acid-hydrochloric acid bath for 3 min. Note that 200 mL of this bath can accommodate no more than 4 bars of 11.4 cm × 2.5 cm × 0.3 cm dimensions without a rigorous reaction taking place and a black film forming on the uranium surface
4. Rinse briefly in distilled water
5. Rinse in acetone
6. Air-dry

6.18.3 Nitric Acid Bath

This method is to be used when a primer or surface coating is applied.[30]

1. Pickle clean in 1:1 nitric acid-water
2. Rinse in acetone
3. Immerse for 10 min in coating bath of 1.0 g purified stearic acid dissolved in 95–99 mL of acetone and 1–5 mL of nitric acid
4. Air-dry
5. Rinse with carbon tetrachloride spray
6. Air-dry
7. Store in distilled water in a polyethylene bottle at 60 °C

6.19 Zinc and Alloys

The most common use of zinc is in galvanized metals. Zinc surfaces are usually prepared mechanically. One mechanical and two chemical methods follow.

6.19.1 Abrasion (for General-Purpose Bonding)

1. Grit or vapor blast with 100-grit emery cloth
2. Vapor degrease in TCE
3. Dry at least 2 h at room temperature or 15 min at 93 °C to remove all traces of TCE[17]

6.19.2 Acid Etch

1. Vapor degrease in TCE
2. Abrade with medium-grit emery paper
3. Repeat the degreasing in step 1
4. Etch for 2–4 min at room temperature in the solution specified in Table 6.27[19]

6.19.3 Sulfuric Acid/Dichromate Etch

1. Vapor degrease in TCE
2. Etch for 3–6 min at 38 °C in the solution described in Table 6.27
3. Rinse in running tap water
4. Rinse in distilled water
5. Dry in air at 40 °C[17]

6.19.4 Conversion Coatings

Phosphate and chromate conversion coatings are available for zinc from commercial sources as proprietary materials.

Table 6.27 Composition of Etching Solution for Zinc

Solution Component	Parts by Weight
Sulfuric acid, conc., specific gravity 1.84	2
Sodium dichromate (crystalline)	1
Deionized water	8

6.20 Weldbonding Metals

Chemical etching is essential to assure high-strength weld-bond joints. There are differences in the surface requirements after cleaning for welding and bonding. To achieve Class A resistance welds, it is necessary to have a chemically active surface that may have a high surface resistance. Final selection of the surface preparation method should be based on the end use of the hardware and consideration of the relative importance of weld quality and adhesive joint strength.[50]

Lockheed workers Kizer and Grosko[51] have studied weldbonding using four different surface preparation techniques on aluminum. A technique developed for aluminum by the Northrop Grumman Corporation for the Air Force follows. It was found to be superior to the previously recommended FPL etch plus 60-min dichromate seal.[52,53]

1. Vapor degrease in trichloroethane vapor for 60 s, followed by spray rinse of condensed trichloroethane fluid for an additional 60 s. All parts must be free of water prior to vapor degreasing
2. Alkaline clean in Cleaner® 85 solution. (Cleaner® 85 is available from Turco Products Division of Henkel Surface Technologies, Madison Heights, MI.)
3. Immediately spray-rinse in cold deionized water for at least 5 min and inspect for water-break-free condition. Should water breaks occur, repeat the above steps
4. Immerse the alkaline-cleaned parts in a deoxidizer solution consisting of 8−16% by volume of nitric acid and 20.1−24.6 g/L Amchem® 7 for 7−10 min at room temperature. When chemical addition is required to maintain the strength of the solution, use Amchem® 17 instead of Amchem® 7. (These products are available from Amchem® Products, Inc., Ambler, PA, www.amchemproducts.com)
5. Immediately spray-rinse in cold deionized water for at least 5 min
6. Anodize at 1.5 ± 0.2 V for 20−25 min in a solution of 10.1 ± 1.1 g/L phosphoric acid and 10.1 ± 1.1 g/L sodium dichromate. Anodizing should be conducted in a room-temperature solution using a "Ripple-free" DC power supply
7. Immediately spray-rinse in cold deionized water for at least 5 min
8. Oven-dry 30−60 min at 60−66 °C
9. Cleaned parts must be handled only with clean white cotton gloves and may be stored for periods up to 21 days prior to weld bonding by wrapping in chemically neutral paper

For titanium, Nothrop Grumman Corporation has developed two surface treatments for the US Air Force. They are given below.[54]

6.20.1 Vapor Honing/Pasa-Jell® 107M Procedure

1. Remove organic contaminants by MEK solvent rinse.
2. Remove inorganic contaminants by immersion in nonetch alkali (such as Oakite® 61 B) at 60 °C. (Oakite® 61 is available from Chemetall Oakite Products, Berkeley Heights, NJ, www.aerospace.chemetall.com)
3. Immerse in Pasa-Jell® 107M solution at ambient temperature for 10 min. (This is a proprietary solution containing HNO_3, $Na_2Cr_2O_7$, H_2SiF_6, and proprietary surfactants supplied by Semco® Division, Products Research and Chemical Corp., Glendale, CA.) Semco® Pasa-Jell® 107 is inorganically thickened to permit application in localized areas. Semco® Pasa-Jell® 107-M does not contain the inorganic thickener permitting immersion of large surfaces. Semco® Pasa-Jell® 107 (www.bergdahl.com/pasaJell_107.htm) is designed to provide a balanced ratio of components that will maintain the effectiveness of the etch rate and inhibit embrittlement as long as the total acid content is maintained above 20%[55]
4. Use VAST process[56] of surface impingement in suitable chamber. The slurry consists of 2% hydrofluorosilicic acid (H_2SiF_6) and 500 mL of 240-grit purified aluminum oxide (Al_2O_3), such as white aluminum oxide available from the St. Gobain Abrasives Carborundum Division, Niagara Falls, NY 14302
5. Rinse with tap-water spray at room temperature
6. Immerse 1 min in 5% nitric acid solution (optional, depending on titanium alloy)

7. Rinse in deionized water at room temperature
8. Air-dry
9. Bond within 4 days after treatment. (Experiments have shown, however, that no changes have taken place up to 9 days)

6.21 Conclusions

Metals require surface treatment to remove contamination and prepare their surfaces for adhesion bonding. Both initial bond strength and bond durability are affected by the surface preparation technique. Most metals require unique methods of treatment for formation of optimal bond strength. Most treatment methods for surface preparation use or generate chemicals that may have a variety of adverse health effects and must be used with extreme caution.

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7 Surface Preparation of Thermoplastics, Thermosets, and Elastomers

Sina Ebnesajjad

7.1 Introduction

This chapter describes the methods used for the preparation of specific plastic adherends, emphasizing practical techniques. These procedures provide relatively simple ways to obtain strong reproducible adhesive bonds that readily fit in commercial processes. To add to the usefulness of this chapter, the author has made liberal citation of commercial plastics when describing treatment techniques. It is difficult to describe surface preparation methods of specific plastics without identifying them. After all, plastic manufacturers are the most frequent sources of basic preparation methods.

7.2 Thermoplastics

Plastics have continued to play an important role as material of construction for parts in key industries such as automotive, aerospace, medical devices, consumer, electronic, and others. Fabrication processes, such as injection molding, are capable of producing complex shape parts. In spite of this adhesion of plastic surfaces to other plastics, elastomers, metals, and ceramics are still required to produce parts with intricate design.

Thermoplastic surfaces, unlike thermosetting, ordinarily require physical or chemical modification to achieve acceptable adhesion bonding. This is especially true in the case of crystalline thermoplastics such as the polyolefins (primarily polyethylene [PE] and polypropylene [PP]), linear polyesters, and fluoropolymers.

Surface-preparation methods are usually suggested for conventional bonding, where an adhesive is applied to the bonding surfaces. Solvent cementing and thermal welding do not require chemical treatment of the plastic surface. As with metallic substrates, the effectiveness of treatment imparted to plastic surfaces decreases with time. Therefore, carrying out the priming or bonding steps as soon as possible after surface preparation is important.[1]

7.2.1 Recent Plastics Treatment Research Results

In recent times, new technologies have spurred the development of novel and unusual surface treatment techniques. These methods are often highly specialized and developed, around specific applications.

7.2.1.1 Ultraviolet Light Treatment

In a pilot study,[2] it was discovered that an ultraviolet zone (UVO) based method, which has been developed for surface treating wool fibers, could be used to oxidatively modify polymer surfaces. Electron spectroscopy for chemical analysis (ESCA) and contact angle results indicated that the treatment was effective on PE and a polyetheretherketone (PEEK). It produced changes in surface oxygen chemistry and free energy, which increased polarity and improved wettability of the surface. Composite lap shear tests showed that the treatment gave a marked improvement in adhesion and that an optimum joint strength is achieved at low treatment times (<1 min).

There is an increase in the amounts of initial oxygen functionalities (Table 7.1) and the development of a new oxidized species at a binding energy of 289.0 eV, which is most likely due to the development of COOH/COOR. Significant increases in adhesion are achieved as a result of the treatment after 1 min (Fig. 7.1); however, at longer exposure times, the adhesion level begins to deteriorate. This is most likely due to the production of low molecular weight, weakly bound fragments, by scission of the PEEK structure. These reactions appear to dominate any surface cross-linking reactions caused by the treatments.

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Table 7.1 Relative Amount of Carbon Species in Untreated and UVO Treated PEEK for 10-min Study[2]

Untreated			**UVO Treated**		
C Type	**Binding Energy, eV**	**Atom, %**	**C Type**	**Binding Energy, eV**	**Atom, %**
C–C/C–H	284.8	72.4	C–C/C–H	284.8	54.8
Ring C–O	286.3	15.5	Ring C–O	286.3	24.1
C=O	287.1	3.2	C=O	287.1	9.2
			O–C=O	289.0	11.9

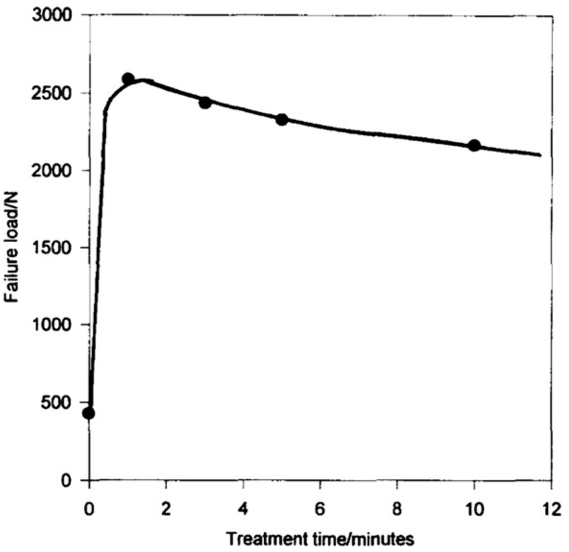

Figure 7.1 Effect of UVO treatment on the adhesion of PEEK to epoxy using a composite lap shear test study.[2]

The data obtained in the study indicated that the overall effects of the treatment are similar to those observed for certain plasma treatment and flame treatment, even though the actual mechanisms of the surface chemical changes may be different. Unlike glow discharge treatments, the process can be applied under ambient conditions as a continuous treatment method. The data presented indicate that the method may be commercially exploitable for film treatment and further, that the method might be particularly useful for the applications where a controlled level of surface oxidation is required, for example, for surface pretreatment or preparation of delicate films.

7.2.1.2 Atmospheric Plasma

Another area of continuing progress has been[3] in corona discharge treatment of plastics. This technique is ineffective for the treatment of plastics in the field of emerging applications such as printing of plain PP films with water-borne inks. Plasma treatment is effective for treating the surface of the majority of plastics. It is operated under highly reduced pressure using expensive gases. Plasma thus has major drawbacks because of relatively high investment and the running costs of the gases.

A process has been developed, which is more efficient than the corona discharge technique and has a much lower running cost than the plasma method. In this process, air is substituted with specific gaseous mixtures into the treatment area; Aldyne® is a major improvement of corona. It provides plastic films with high and stable surface energy, improved wettability, adhesion, and modulation of coefficient of friction (COF), allowing treated substrates to be fully suitable for printing, lacquering, coating, and laminating.

To substitute air into the discharge area with a gaseous mixture, specific components are added: first, injection of the chosen gaseous mixture and, second, to control the flow of gaseous atmosphere into the discharge area (thus the name *atmospheric plasma*). As a matter of fact, since it contains 21% of oxygen, the air boundary layer attached to the moving film surface has to be removed before its entry into the discharge area, in order to control the performances of the process. Specific Aldyne© components are, therefore, placed at the entry of the hood to remove the air boundary layer.[3]

7.2.1.3 Ion-Assisted Reaction Treatment

Antireflection (AR) coatings are widely used in various applications such as display panels, solar cells and, optical lenses.[4–7] AR coatings are usually applied to glass surfaces, but in many applications the glass substrates are being replaced with polymers. Coatings on polymer substrates are made at room temperature because of the low heat resistance of polymers.[8] These films, however, often exhibit low optical transmittance and poor adhesion. Methods such as ion beam mixing, heat treatment, and buffer-layer deposition have been used to improve the adhesion. In ion beam mixing and heat treatment, the excessive energy deformed the plastic substrates, and buffer layers, such as Cr and SiO_X films that reflected and/or absorbed the light, resulting in a loss of optical transmittance. These approaches are, therefore, not suitable for optical devices.

With high optical transmittance (>90% in the visible range) and a high deformation temperature (>140 °C), polycarbonates (PCs) are a promising substrate material for optical lenses and display panels.[9] Despite their excellent physical properties, PC substrates are not widely used because the adhesion is not sufficiently strong between coating and substrate. This poor adhesion is because of the hydrophobic nature of the PC surface and also because of the large difference in thermal expansion coefficients between the coating film and the PC. It has been reported that the wettability of various plastics was improved substantially by irradiating the surface with low-energy argon ions in an oxygen environment.[10,11]

In a more recent study,[4] PC substrates were irradiated with Ar ions in an oxygen environment. The acceleration voltage of the ions was 0.8 kV. A cold cathode hollow ion source was used for generating the ions. Argon ions are the dominant species under these conditions: oxygen ions are seldom seen. The vacuum chamber was evacuated to 2×10^{-5} Torr with rotary and turbo pumps. Working pressure was approximately 1×10^{-4} Torr, with the Ar and O_2 flow rates of 3 and 12 sccm, respectively. The ion-beam current density was measured by a Faraday cup and was fixed at 14.4 $\mu A/cm^2$. The ion doses varied from 1×10^{15} ions/cm^2 to 5×10^{16} ions/cm^2. A detailed description of the setup has been presented in a previous article.

A study[4] showed that adhesion between the AR coating layer and the PC substrate was significantly improved by ion-assisted reaction treatment in which PC substrates were irradiated with low energy Ar ions in an O_2 environment. As Ar ion doses increased, the water contact angles decreased from 76° to 18°, indicating that the nature of the surface had become more hydrophilic. This change was attributed to the increase in the density of functional groups such as C=O and C−O bonds. The ion irradiation had little influence on the optical transmittance and the surface roughness of the substrates. Peel tests showed that the adhesion between the AR coating and the PC substrate improved with an increasing ion dose. At an ion dose of 1×10^{16} ions/cm^2, peeling became negligible.

7.2.2 Acetal Copolymer

The plastic acetal copolymer (Celcon®) is (made by Ticona Corp., www.ticona.com) a highly crystalline copolymer with excellent solvent and chemical resistance. Two suggested surface-preparation methods are as follows:

7.2.2.1 Chromic-Acid Etch

1. Wipe parts with acetone[12]
2. Air-dry
3. Etch the surfaces for 10−15 s in a solution made up as summarized in Table 7.2
4. Flush with tap water
5. Rinse with deionized water
6. Oven-dry at 60 °C

7.2.2.2 Hydrochloric-Acid Etch

1. Immerse parts for 5 min in concentrated hydrochloric acid at the room temperature.[13] Use a glass rod to move fresh acid into contact with the acetal copolymer. About 8−13 μm of acetal copolymer is removed per minute of the etching process.
2. Rinse and then dry at room temperature for 4 h. Heat-formed or machined acetal copolymer should be stress-relieved before etching. A specially developed primer used in very thin coats gives excellent results.

7.2.3 Acetal Homopolymer

Acetal homopolymer (Delrin®) is a highly crystalline polymer (Du Pont Company, www2.dupont.com) that has excellent solvent resistance. The chemical structure and solvent resistance of homopolymer acetal lead to a relatively poor adhesion of solvent-based paints and cements. This is largely

Table 7.2 Composition of Etching Solution for Acetal Copolymer

Solution Component	Parts by Weight
Sulfuric acid	400
Potassium dichromate	11
Distilled water	44

overcome by surface treatment prior to application of the coating. Originally, a chemical etching process, named "satinization", was developed, where by a mildly acidic solution, produced uniformly, distributed anchor points on the surface.[14] This process is no longer used because of the environmental concerns with some of the chemicals in the etching bath. Two methods have been described for surface preparation of homopolymer acetal parts to form relatively strong bonds, as described in Sections 7.2.3.1 and 7.2.3.2.

7.2.3.1 Three-Step Procedure

A more recent three-step etching procedure (Table 7.3), using chemicals that are more compatible

Table 7.3 Three-Step Etching Procedure for Homopolymer Acetal Polymer[5]

	Step 1	**Alternative Step 1 A**	**Step 2**	**Step 3**
Solution	71% o-H_3PO_4 (orthophosphoric acid). Mix 5 vol. parts of commercial concentrated (85%) o-H_3PO_4 with 1 vol. part of DI water (deionized water)	Preparation: Mix 5 vol. parts of (85%) o-H_3PO_4 with 1 vol. part glycerin DAB7[a] and 0.5 −1.0 g/L sodium alkylarylsulfonate[b] (phenysulfonate)	12% NaOH (sodium-hydroxide). Preparation: Dissolve 120 g NaOH in 1 L of DI water	1% acetic acid. Preparation: Add 20 ml glacial acetic acid to 1 L of DI water
Bath temparature	70 °C	85 °C	100 °C	80 °C
Dipping time	5 min	5 min	6 min	10 min
Rinse	Thoroughly 1 min/ 23 °C with water	As for Step 1	As for Step 1	As for Step 1, followed by a supplementary rinse in DI water
Heating elements	Quartz or heating elements coated with TEFLON®	As for Step 1	Stainless steel, titanium, heating elements coated with TEFLON® or quartz	As for Step 2
Material for dipping ranks recommended	PVC, polypropylene (PP), high density polyethylene (HDPE) or glass	PVC, PP, HDPE or glass	Stainless steel, mild steel or glass	PVC, PP, HDPE or glass
Remarks	If the surface of the parts is significantly contaminated (mould release agent, finger prints, traces of oils, etc.,) the parts should be degreased prior to the dipping	The solution of Step 1 A has some degreasing character but may give less good adhesion		

All the above information is subject to disclaimer.
[a] *Heat stabilized type used for explosive manufacture.*
[b] *Common detergent.*

with today's environmental requirements, has also been successfully tested.[15]

7.2.3.2 Chromic-Acid Etch

1. Wipe with acetone or methyl ethyl ketone
2. Immerse in a chromic acid solution (Table 7.4) for 10–20 s at room temperature (20–30 °C): Dissolve the potassium dichromate in clear tap water, and then add sulfuric acid in increments of about 200 g, stirring after each addition
3. Rinse in running tap water for at least 3 min
4. Rinse in distilled or deionized water
5. Dry in an air-circulating oven at 38 °C for about 1 h

Adhesives are strongest in compression and shear modes, but they perform comparatively weakly in tension, cleavage, and peel modes. Adhesion depends on the surface preparation of the parts. Cleaning and degreasing is an absolute minimum requirement. Surface roughening, mechanically with sandpaper or chemically with an etching bath, strongly improves the results. Several types of adhesives are to be considered including two-component epoxy, two-component polyurethane, or cyano-acrylate.[15]

7.2.4 Acrylonitrile-Butadiene-Styrene

This terpolymer may be prepared for bonding by the following techniques.

7.2.4.1 Abrasion With Primer

1. Sand with a medium grit sandpaper[16]
2. Wipe free of dust
3. Dry in an oven at 71 °C for 2 h
4. Prime with a silane primer such as Dow Corning A-4094 or General Electric SS-4101.

Table 7.4 Composition of Etching Solution for Acetal Homopolymer

Solution Component	Parts by Weight
Sulfuric acid, concentrated	300
Potassium dichromate ($K_2Cr_2O_7$)	15
Water	24

7.2.4.2 Warm Chromic-Acid Etch

1. Degrease in acetone[17]
2. Etch in the solution (Table 7.5), for 20 min
3. Rinse in tap water
4. Rinse in distilled water
5. Dry in warm air

7.2.5 Allyl Diglycol Carbonate

The resin allyl diglycol carbonate (CR-39® by PPG Industries, http://corporateportal.ppg.com/NA/chemicals/Optical/CR39/) can be cast in a film form. It was developed in 1940 and is sold in monomer form. It is used to produce highly transparent plastics for optical applications, such as lenses for glasses. The following surface treatment method has been recommended.[18]

1. Degrease in methanol, isopropanol, or detergent
2. Abrade by grit or vapor blast, or use 100-grit emery cloth. Sand or steel shots are suitable abrasives
3. Solvent degrease in methanol or isopropanol

7.2.6 Cellulosics

Cellulosics [cellulose acetate, cellulose acetate butyrate (CAB), cellulose nitrate, cellulose propionate, ethyl cellulose] are ordinarily solvent cemented, unless they are to be bonded to dissimilar adherends, using conventional adhesives. In such cases, the following surface preparation method may be used.

Table 7.5 Composition of Etching Solution for Acrylonitrile–Butadiene–Styrene

Solution Component	Parts by Weight
Sulfuric acid, concentrated	26
Potassium dichromate	3
Distilled water	11

7.2.6.1 Abrasion and Cleaning

1. Solvent-degrease in methyl alcohol or isopropyl alcohol[19,20]
2. Grit or vapor-blast, or use 220-grit emery cloth
3. Repeat step 1
4. Heat for 1 h at 93 °C and apply adhesive while still hot

7.2.7 Ethylene-Chlorotrifluoroethylene Copolymer (ECTFE)

This fluoropolymer has excellent chemical resistance. See Chapter 6 for more information about adhesion treatment of ECTFE.[21]

7.2.8 Ethylene-Tetrafluoroethylene Copolymer (ETFE)

This high-temperature-resistant polymer can be easily processed by conventional methods, including extrusion and injection molding. It can be joined by screw assemblies, snap-fit, press-fit, cold or hot heading, spin-welding, and heat-bonding. See Chapter 6 for more information about the adhesion treatment of ETFE.[21]

7.2.9 Ethylene-Vinyl Acetate (EVA)

This copolymer is really an elastoplast, with properties intermediate between that of a plastic and an elastomer. A suggested surface preparation method is as follows:

SIRA method[18]

1. Degrease in methanol
2. Prime with epoxy adhesive
3. Fuse into the surface by heating for 30 min at 100 °C

EVA material containing 20 wt% vinyl acetate (EVA20) was treated with corona discharge to improve its adhesion to polychloroprene adhesive. Several experimental variables in the corona discharge treatment of EVA20 were considered: corona energy, type of electrode, and number of consecutive treatments. Advancing contact angle measurements (water, 25 °C) showed an increase in the wettability of EVA20 after treatment with corona discharge, which corresponds to an increase in the O/C ratio on the treated surface. The higher the corona energy (i.e., the higher discharge power and longer treatment times), the greater the degree of surface oxidation. Peel strength values of the joints, produced with EVA20 using a polychloroprene adhesive containing 5 wt% isocyanate, increased from 1.5 kN/m (as-received EVA20) to 4.3 kN/m (corona-treated EVA20). A mixed (adhesional + cohesive in EVA20) locus of failure was obtained in all adhesive joints produced with corona discharge-treated EVA20. Finally, the number of consecutive corona discharge treatments and the surface area of the electrode (spherical versus hook-shaped electrode) did not greatly influence the adhesion of EVA20 to polychloroprene adhesive.[22]

7.2.10 Fluorinated Ethylene-Propylene Copolymer (FEP)

This fluoropolymer is a true thermoplastic and is a copolymer of tetrafluoroethylene and hexafluoropropylene. FEP can be heat sealed, heat bonded, laminated, and combined with many materials. It can be used by itself as a hot-melt adhesive.

7.2.11 Ionomer

Ionomers are polymers in which ionized carboxyl groups create ionic cross-links in the intermolecular structure.[19] The properties are similar to those of cross-linked thermosets, even though these resins are processed at conventional temperatures like other thermoplastic resins, for example Surlyn® resins by the Du Pont Company (www2.dupont.com/Surlyn/en_US/). These resins, like PE, do not develop high-strength adhesive bonds. The following surface preparation technique is suggested:

Abrasion[18]

1. Solvent-degrease in acetone or methyl ethyl ketone
2. Grit- or vapor-blast, or use 100-grit emery cloth. ISO-grit alumina is a suitable abrasive
3. Repeat step 1

7.2.12 Nylon (Polyamide)

Both solvent cementing and adhesive bonding are used with nylon (nylon 6,6 is the type most commonly used).[19] The solvents, however, are quite different from those used for cellulosics and PS. Nylon molding resins are not ordinarily cemented by conventional solvent-type cements because of their lack of solubility in ordinary non-toxic solvents. Nylon is frequently bonded to metals, introducing problems not found in nylon-to-nylon bonds. Conventional adhesives must be used in nylon–metal bonds. Nylons are relatively crystalline thermoplastics that are not considered solvent-sensitive, requiring relatively strong solvents for surface preparation. Suitable solvents for cleaning polyamide surfaces include:

Acetone (B.P. 56.5 °C)

Methyl ethyl ketone (B.P. 79.6 °C)

Perchloroethylene (B.P. 121 °C)

1,1,1-Trichloroethylene (TCE) (B.P. 74.1 °C)

Freon® TMC (B.P. 36.2 °C) [a 50/50 mixture of methylene chloride and 1,1,2-trichloro-1,2, 2-triflouoroethane]

Detergents have also been used instead of organic solvents in cleaning nylon. Nylon, like PC, readily absorbs moisture from the air. For this reason, keeping the humidity low before bonding is desirable.

Abrasive method:[12]

1. Wash with acetone
2. Dry
3. Hand-sand with 120-grit abrasive cloth until the gloss is removed
4. Remove sanding dust with a short hair stiff brush

Bonding or priming should be carried out as soon as possible. Parts should be warmed slightly before bonding. Primers recommended include nitrile-phenolic, resorcinol-formaldehyde, vinyl phenolic, silane, and so on. Epoxies have been used on metallic surfaces, with the nylon being bonded to the epoxy.[23]

7.2.13 Perfluoroalkoxy Resins

They combine high-temperature performance with a capability for thermoplastic processing. See Chapter 6 for surface preparation methods.[21]

7.2.14 Phenylene Oxide Based Resins

This family of plastics is composed of PS-modified polyphenylene oxide (Noryl® polyaryl ethers by SABIC, www.sabic-ip.com). These resins have outstanding dimensional stability at high temperatures, broad use-temperature range, and other desirable properties. Solvent cementing is the usual method of joining. Surface preparation bonding consists of sanding or the following acid etch procedure.[24,25]

1. Solvent-clean with isopropanol or aqueous solutions of most commercial detergents
2. Sand or etch with chromic acid. If chromic acid etch is used, etch 1 min at 80 °C in the solution given in Table 7.6
3. Rinse in distilled water
4. Dry

Note that studies made with the original unmodified polyphenylene oxide etched in the above solution for 3 min at 65 °C have revealed that chromic acid solution becomes ineffective after its first use. The evaluation was made with AF-30 nitrile-phenolic adhesive and modified T-peel tests. If it is desired to avoid this possible problem, vacuum blasting, followed by an acetone wipe, can be used.[19]

7.2.15 Polyarylate

The new engineering thermoplastic, Polyarylate (Ardel® by BP plc., http://engpolymer.co.kr/service/site_link/com_maker/pla-maker_1.pdf), announced in 1980, is aromatic polyester based on bisphenol A and phthalic acid. According to the manufacturer, its surface preparation is similar to that of polysulfone (see Polysulfone below).

Table 7.6 Composition of Etching Solution for Polyaryl Ethers

Solution Component	Amount, g
Sulfuric acid, concentrated	375
Potassium dichromate	18.5
Distilled water	30

7.2.16 Polyaryl Sulfone

The engineering thermoplastic, Polyaryl Sulfone (Astrel® 360 plastic),[19] supplied by the 3M Company is structurally useful at temperatures of up to 260 °C. The manufacturer's literature mentions welding by thermal, ultrasonic, or solvent techniques. Air Force studies evaluated sandblasting, acid etch, and solvent-wash methods, with the latter effective for surface preparation for steel–plastic–steel bonds.

Solvent wash is a triple-wash (three successive washes) in a 65/35 mixture by volume of a fluorocarbon and reagent-grade isopropyl alcohol.

7.2.16.1 Sandblast

1. Ultrasonic-clean with an alkaline-etching solution
2. Cold-water rinse
3. Alcohol-wash
4. Sandblast with 150-mesh silica sand
5. Alcohol-wash
6. Dry with dry nitrogen

7.2.16.2 Acid Etch

1. Ultrasonic clean in an alkaline cleaning solution
2. Cold-water wash
3. Bathe 15 min at 66–71 °C in an acid solution (shown in Table 7.7).
4. Cold-water wash
5. Dry at 66 °C in air-circulating oven

Table 7.7 Composition of Etching Solution for Polyaryl Sulfone

Solution Component	Amount, %
Sulfuric acid, concentrated	96.6
Sodium dichromate	3.4

7.2.17 Polycarbonate

Solvent cementing is a common method for bonding the resin PC (supplied as Lexan®—SABIC, Calibre®—Dow Chemical Co., www.dow.com, and Tuffak®—Altumax UK, a division of Atoglas—the Atofina subsidiary, www.atoglas.com/literature/pdf/95.pdf) to itself or to plastics soluble in the same solvents.[19] The latter includes CAB, acrylics, or polyurethane. However, adhesive bonding must be used in bonding to metals, wood, rubber, and most other plastics. Like nylon, PC is hygroscopic. This is the reason that keeping the humidity low before bonding is important.

In surface preparation of PC for adhesive bonding, the customary cleaning solvents include methyl alcohol, isopropyl alcohol, petroleum ether, heptane, VM&P naphtha, and white kerosene. Ketones, toluol, TCE, and benzol should not be used since PC is incompatible with these solvents; they cause crazing or cracking. A number of other cleaning solvents, including paint thinners, are similar to ketones in that they cause grazing or cracking. So, care should be used in the selection of solvents used for cleaning. Light solutions (1%) of detergents, such as alkanox or Joy®, are also suggested.[19,26]

7.2.17.1 Flame Treatment

1. Wipe with ethyl alcohol to remove dirt and grease[27]
2. Pass the part through the oxidizing portions of the flame of a BernzOmatic propane torch (www.bernzomatic.com)
3. Treatment is complete when both sides are polished to a high gloss, free of scratches and visible flaws. The process usually requires 5–6 passes on both sides
4. Allow the part to cool for 5–10 min before bonding

7.2.17.2 Abrasion

1. Wipe with ethyl alcohol, methyl alcohol, or other acceptable solvent or cleaner mentioned above[12]
2. Air-dry
3. Sand with fine-grit (120-grit, 400-grit maximum) abrasive cloth or sandpaper
4. Remove sanding dust with a clean dry cloth or a short hair stiff brush
5. Repeat solvent wipe

7.2.17.3 General Electric Procedure for Use With Room-Temperature-Vulcanized Silicone Adhesives

Room-temperature-vulcanized (RTV) silicone adhesives (www.siliconeforbuilding.com) are effective for applications requiring excellent bond strength, a high service temperature, and good thermal expansion.[28] Silicone adhesives may be used with all standard PC resins, including glass-reinforced grades. For optimum performance, the following procedure should be applied:

1. Lightly abrade mating surfaces with fine emery
2. Clean surface of grease or foreign matter with methyl alcohol or other compatible cleaning solvent
3. Prime abraded surface with GE Silicone Primer SS-4004 and allow a minimum of 1-h drying time. Unprimed surfaces reduce the bond strength significantly
4. Apply silicone adhesive in desired thickness. The final bond thickness may range from 0.127 mm to 0.762 mm.
5. Assemble

7.2.18 Polychlorofluoroethylene (PCTFE)

This resin is a fluoropolymer with excellent chemical resistance.[29] See Chapter 6 for more information about the treatment methods for PCTFE.

7.2.19 Polyester (Saturated)

Thermoplastic polyesters are available as polyethylene terephthalate (PET), used primarily in films (Mylar® and Melinex® by DuPont Co., www2.dupont.com), or in fibers as Dacron® (Koch Industries, www.invista.com) and Hostaphan® (Mitsubishi Polyester Film GmbH, www.m-petfilm.com), and polybutylene terephthalate, and used in molding as Valox® (SABIC), Celanex® (Ticona Corp., Florence, KY, www.ticona.com) and Tenite® (Eastman Chemicals, www.eastman.com/Brands/Tenite/).[19] Glass-filled grades of these resins are also available. Thermoplastic polyesters are generally resistant to solvents and chemicals, including alcohol, ethers, and aliphatic hydrocarbons, most chlorinated hydrocarbons, aqueous salt solutions, and aqueous acid and basic solutions under specified conditions. Specific surface preparations for the above thermoplastic polyesters are described below.

7.2.19.1 Treatments for Valox® Thermoplastic Polyester

1. Abrade-degrease[30,31]
   (a) Sand lightly with 240-grit sandpaper
   (b) Degrease with toluene or TCE. Toluene is a common solvent for the unreinforced Valox®
2. Plasma treatment[32]—Activated gas plasma, using oxygen, argon, or water vapor plasma, has given good bonds 3−4 times stronger than those obtained with the abrasion method.

7.2.19.2 Treatments for Celanex® (www.ticona.co.uk/celanex) Thermoplastic Polyester

1. Abrade-degrease[31]
   (a) Sandpaper
   (b) Degrease by wiping with a solvent such as acetone

7.2.19.3 Treatments for Tenite® Polyterephthalate

Dip parts in methylene chloride for 10−15 s before bonding, preferably with polyurethane adhesives.[33]

7.2.20 Polyetheretherketone

This material is available from Victrex Plc.[34] PEEK is an aromatic polyether, high-performance thermoplastic used in coating, insulation of high-performance wire and cable, and molded parts. Acetone has a slight crazing effect on PEEK, but isopropyl alcohol, toluene and TCE have no effect, and thus may be used in cleaning.

Surfaces to be bonded should be cleaned, dried, and freed of grease. This may be achieved by wiping the joint surfaces with 1,1,1-trichloroethane or a similar degreasing solvent. In addition, roughening of the surfaces with an abrasive will form a more

Table 7.8 Bond Strength[a] of PEEK versus Treatment Method

Surface Treatment	Bond Strength, kg
Abrading + degreasing	40
Abrading + degreasing + flame oxidation	48
Abrading + degreasing + chromic acid etch	37

[a] *Araldite® epoxy adhesive, cured 17 h at 40 °C; lap joint 13 mm wide with 13 mm overlap. Total bond area 170 mm²; substrate aluminum. Testing method: tested shear at 20 mm/min.*

reliable bond. Degreasing should be repeated after abrading. Bond strengths may be further increased by more vigorous surface activation procedures, in particular, flame treatment with a blue (oxidizing) flame, or treatment with a chromic acid etching solution. Table 7.8 shows results obtained with these various treatments when bonding PEEK to aluminum with Araldite® 2010 (HUNTSMAN Corp., www.huntsman.com), a general-purpose epoxy adhesive.

7.2.21 Polyethersulfone (PES) (Victrex Plc)

This is another high-performance engineering thermoplastic.[35] Methyl alcohol, ethyl alcohol, isopropanol and low-boiling petroleum ether are solvents that may be used for cleaning. Acetone, methyl ethyl ketone, perchloroethylene, tetrahydrofuran, toluene, and methylene chloride should not be used, since they have an adverse effect on the plastics. PES can be bonded to itself by solvent cementing adhesives, or ultrasonic welding. Mating surfaces should be degreased with carbon tetrachloride before adhesive bonding.[36]

7.2.22 Polyetherimide

Polyetherimide (Ultem®-SABIC) is an amorphous engineering thermoplastic offered by SABIC.[36] It has a number of desirable properties, including a high heat-distortion temperature. Unlike most amorphous resins, polyetherimide is resistant to a wide range of chemicals, including most hydrocarbons, alcohols, and fully halogenated solvents. Only partially halogenated hydrocarbons, such as methylene chloride and trichloroethane, will dissolve polyetherimide, and these compounds should not be used for cleaning.

7.2.23 Polyethylene

PE has a non-polar, nonporous, and inert surface.[19] For this reason, adhesives cannot link chemically or mechanically to untreated PE surfaces. Although PE is relatively inert to most solvents, solvent cementing cannot be used. For bonding to itself or to other materials, an adhesive with a suitable surface preparation method must be used. There are a number of surface treatment techniques in use, including chemical, electronic, flame, and primer methods. Oxidation treatments are the most successful. These include immersion in a chromic-acid solution, exposure to corona discharge, flame oxidation, immersion in an aqueous solution of chlorine, or exposure to chlorine gas in the presence of ultraviolet light. The chromic acid oxidation method is probably the most convenient for use with molded plastic parts of diverse contour.

7.2.23.1 Chromic-Acid Etch

1. Wipe with acetone, methyl ethyl ketone (MEK) or xylene[19]
2. Immerse in the following chromic-acid solution (Table 7.9) for 60–90 min at room temperature, or 30–60 s at 71 °C
3. Dissolve the potassium dichromate in the clean tap water; then add the sulfuric acid in increments of about 200 g, stirring after each addition
4. Rinse in running tap water for at least 3 min
5. Dry in an air-circulating oven at 38 °C for about 1 h

7.2.23.2 Oxidizing Flame Method

This method utilizes an oxyacetylene burner, which is passed over the faying surface until it

Table 7.9 Composition of Etching Solution for Polyethylene

Solution Component	Parts by Weight
Sulfuric acid, concentrated	300
Potassium dichromate	15
Water	24

appears glossy.[26] To make certain that too much oxide is not formed on the surface, it should be scoured lightly with soap and water. The surface should then be washed with distilled water and dried at room temperature. Flame treatment is fast and provides bond strength greater than with the chromic acid treatment described above. However, it requires very careful control to prevent heat warpage. The procedure is safest with pieces of thick cross section. See Chapter 5 for details about flame treatment.

7.2.23.3 Gas Plasma Treatment

This treatment is very effective and is recommended for use with very complex geometric surfaces, which cannot be sanded or flame-treated adequately where very strong bonds are required.[26]

7.2.24 Polymethylmethacrylate (PMMA)

In bonding PMMA (Plexiglas®—Arkema Corp., www.plexiglas.com) to itself, solvent cementing is ordinarily used. However, when bonding PMMA to a dissimilar substrate, conventional adhesive bonding must be used. Surface treatment is as follows[19]:

1. Wipe with methanol, acetone, MEK, TCE, isopropanol, or detergent
2. Abrade with fine-grit (180−400 grit) sandpaper, or use abrasive scouring with small amounts of water, dry-grit blasting, or wet abrasive blasting
3. Wipe with a clean, dry cloth to remove particles
4. Repeat solvent wipe

7.2.25 Polymethylpentene (TPX®)

This material is now supplied by Mitsui Petrochemical Industries, Ltd.[37] It is a copolymer of 4-methylpentene and is useful up to 204 °C. Chemical behavior is similar to that of other polyolefins. It is attacked by strong oxidizing agents. Some light hydrocarbons and chlorinated solvents can cause swelling and subsequent strength loss. Surface preparation methods include:

7.2.25.1 Degreasing-Abrasion (for General-Purpose Bonding)

1. Solvent-clean in acetone[18]
2. Grit-or vapor-blast, or use 100-grit emery cloth
3. Solvent-clean again in acetone

7.2.25.2 Chromic-Acid Etch

1. Solvent-clean in acetone[18]
2. Immerse for 1 h at 60 °C (Table 7.10)
3. Rinse in tap water
4. Rinse in distilled water
5. Dry in warm air

7.2.25.3 Acid-Permanganate Etch

1. Solvent clean in acetone[18]
2. Immerse for 5−10 min at 90 °C in a saturated solution of potassium permanganate acidified with sulfuric acid
3. Rinse in tap water
4. Rinse in distilled water
5. Dry in warm air

7.2.26 Polyphenylene Sulfide (PPS)

The crystalline polymer, PPS (Ryton®—Chevron Phillips Chemical Co., www.cpchem.com), has a high melting point (288 °C), outstanding chemical resistance, thermal stability, and flammability resistance. It has no known solvents below 191−204 °C. The surface may be prepared as follows:

Table 7.10 Composition of Etching Solution for Polymethylpentene

Solution Component	Parts by Weight
Sulfuric acid, concentrated	26
Potassium dichromate	3
Water	11

7.2.26.1 Solvent–Sandblast–Solvent

1. Solvent degrease in acetone[38]
2. Sandblast
3. Solvent-degrease again in acetone

7.2.26.2 Picatinny Arsenal Method

1. Wipe the faying surfaces with ethanol-soaked lint-free paper[39]
2. Sand with 120-grit sandpaper
3. Clean off the dust with a stiff, bristled brush

7.2.27 Polypropylene

This polyolefin has a similar surface to PE, and could be treated using the surface treatment method for PE. Thermal treatment, however, is somewhat more rigorous than prescribed for PE. While the treatment for PE is 60–90 min at room temperature, or 30–60 s at 71 °C, PP should be treated for 1–2 min at 71 °C.

7.2.27.1 Chromic-Acid Etch

1. Wipe with acetone, MEK, or xylene[38,40]
2. Immerse in the chromic acid solution (Table 7.11) for 1–2 min at 71 °C
3. Dissolve the potassium dichromate in clean tap water; then add the sulfuric acid in increments of about 200 g, stirring after each addition
4. Rinse in running tap water for at least 3 min
5. Rinse in distilled or deionized water
6. Dry in an air-circulating oven at 38 °C for about 1 h

Table 7.11 Composition of Etching Solution for Polypropylene

Solution Component	Parts by Weight
Sulfuric acid, concentrated	300
Potassium dichromate	24
Water	24

7.2.27.2 Oxidizing-Flame Method

Same as in PE.[26]

7.2.27.3 Gas-Plasma Method

Same as in PE.[26]

Injection-molded samples of PP were exposed to oxygen plasma and SACO (SAndblasting and COating) treatments. The pretreated surfaces were successively adhesively bonded or lacquered. The adhesion strength and failure mode of these specimens was examined. The surfaces obtained after treatments were characterized by ESCA, contact angle measurements, and scanning electron microscopy (SEM). Both micro-roughness and chemical modification of the surface led to an increase in adhesion of up to a factor of 10. The stability of the surface changes generated during the plasma and SACO pretreatments was observed by different kinds of aging experiments in air and water. The aging of SACO-treated surfaces led to no significant change on the surface. In the case of plasma-treated surfaces, hydrophobic recovery during aging in air reduced the polarity of the surface layer. During aging in water, no hydrophobic recovery on the surface was observed.[41]

7.2.28 Polystyrene

This material is ordinarily bonded to itself by solvent cementing, although conventional adhesive bonding, thermal wending, and electromagnetic bonding have been successfully tried.[26] Conventional adhesive bonding may be necessary for bonding PS to a dissimilar material. Surface preparation methods are as follows:

7.2.28.1 Abrading or Sanding

1. Degrease with methyl or isopropyl alcohol[23]
2. Abrade with 200-grit sandpaper and remove dust particles

7.2.28.2 Sodium Dichromate-Sulfuric Acid Process

1. Degrease with isopropyl or methyl alcohol[23]
2. Immerse for 3–4 min in the solution (Table 7.12) maintained at 99–104 °C

Table 7.12 Composition of Etching Solution for Polystyrene

Solution Component	Parts by Weight
Sulfuric acid, concentrated	90
Sodium dichromate	10

3. Rinse thoroughly with distilled water
4. Dry below 49 °C

Note: This is a somewhat unusual modification of typical chromic-acid etching processes. Since no water is used to dilute the acid, a much higher immersion temperature may be used without boiling off the water. The usual high-temperature immersion in the conventional chromic acid solution is about 71 °C, while 99−104 °C is used here.

7.2.28.3 Nonimmersion Etch Process

If PS parts are to be used in high-frequency electrical applications, it may be desirable that only the faying surfaces be treated as follows[23]:

1. Degrease with methyl or isopropyl alcohol
2. Apply to the faying surfaces a thixotropic paste (Table 7.13)
3. Heat parts to 82 °C and hold for a few minutes with the paste on the surface
4. Rinse thoroughly with distilled water
5. Dry below 66 °C

7.2.29 Polysulfone

Polysulfone, Udel®—Solvay Advance Polymers, www.solvayadvancedpolymers.com, is a thermoplastic resin with very high strength and has one of the highest service temperatures (171 °C) of any melt-processible thermoplastic.[26] It is highly resistant to mineral acids, alkalis, salts, detergent solutions, oils, and alcohol. On the other hand, it is attacked by polar organic solvents such as ketones, chlorinated hydrocarbons, and aromatic hydrocarbons. Polysulfone stress cracks easily and is considered notch-sensitive. It can be solvent cemented, conventionally adhesive bonded or ultrasonically welded. Air Studies have evaluated three surface-preparation techniques: (1) sandblast, (2) acid-etch, and (3) solvent-wash. The acid-etch procedure was found to give the best results. (See procedures for Polyaryl Sulfone in Section 7.2.16 for details.)

Table 7.13 Composition of Etching Paste for Polystyrene[a]

Solution Component	Parts by Weight
Sulfuric acid, concentrated	3
Powdered potassium	1

[a] *Add Cab-O-Sil (Cabot) fused silica earth as required to obtain a thixotropic paste.*

Another method using a grit-blast and ultrasonic cleaning, was used by General Electric. In this method, polysulfone parts were prepared for bonding to niobium with AF-42 epoxy-nylon film adhesive (3M Co). The procedure is as follows:[26]

1. Degrease in alcohol
2. Grit-blast with 27−50 micron aluminum oxide (Al_2O_3). Use S.S. White Airbrasive® Equipment, or equivalent, available from S.S. White Industrial Products, Piscataway, NJ
3. Clean in an ultrasonic cleaner as follows:
    a. Immerse parts in Neutra-Clean® 7 (a trademark of AMREP Inc., Marietta, Ga, www.amrep.com) (90 g/L)
    b. Rinse with tap water
    c. Rinse with distilled water
    d. Rinse with isopropyl alcohol for at least 30 s
    e. Flash with dry nitrogen
    f. Dry with warm air at 66 °C maximum

Other methods include vapor degreasing in methanol, sanding or vapor blasting, and alcohol-wipe and/or light sanding, plus vinyl, urethane, or silicone primer.

7.2.30 Polytetrafluoroethylene (PTFE)

PTFE does not melt like a true thermoplastic but "sinters".[29] As with other fluoroplastics, PTFE is relatively inert chemically. It is prepared for bonding by the techniques described in Chapter 6.

7.2.31 Polyvinyl chloride (PVC)

The procedure given here is intended for use with homopolymer rigid compounds. These compounds contain up to 5% plasticizer, making them difficult to bond with epoxy and other non-rubber types of adhesives. The homopolymer is not readily soluble, making it difficult to bond by solvent-cementing techniques. Thermal welding, especially hot-gas welding, is commonly used in joining rigid PVC. In general, a solvent is always used to remove plasticizer, grease, and dirt. Abrasion may or may not be used. If it is, sandpaper (various grits), vapor blasting, steel wool, or scouring powder is used. The following procedure is suggested.[19]

1. Wipe with solvent, such as methanol, low-boiling petroleum ether, MEK, toluene, or TCE
2. Abrade with medium-grit (200-grit) sandpaper
3. Blow off the dust
4. Repeat solvent-wipe
5. Dry
6. For maximum strength, prime with nitrile-phenolic adhesive or bond immediately

7.2.32 Polyvinyl Fluoride

Du Pont has three types of Tedlar® film, Type A, with one side treated for bonding; Type B, with both sides bondable; and Type S, which is untreated and is used as a release film (www2.dupont.com).[21] Type B is used in laminating to metals, plastics, wood, and other materials; it requires no further surface preparation for adhesive bonding. The methods for preparing the untreated film for adhesive bonding are similar to those of polyolefins and fluoropolymers (see Chapter 6).

7.2.33 Polyvinylidene Fluoride (PVDF)

PVDF is a high-performance, high-molecular-weight homopolymer.[21] It is resistant to most acids and bases, aliphatics, aromatics, alcohols, and chlorinated solvents. Strongly polar solvents, such as ketones and esters, cause partial solvation, especially at high temperatures. The methods for preparing the untreated film for adhesive bonding are similar to those of polyolefin and fluoropolymers (see Chapter 6).

7.2.34 Styrene-Acrylonitrile (SAN)

The copolymer SAN (Tyril®—Dow Chemical Co.) is usually solvent cemented with solvents similar to those used for PS, although effective solvents are more limited.[19] In applications where solvent cements cannot be used, as in bonding to metals, the procedures suggested for PS may be used.[19] TCE and gasoline have also been used, with no further treatment.[32]

7.3 Thermosets

Most thermoset plastics are relatively easy to bond. Solvent cements obviously cannot be used since these materials are not soluble. In some cases, solvent solutions can be used to join thermoplastics to thermosets. In most cases, however, conventional adhesive bonding is the only practical, non-mechanical way to join a thermoset to a thermoset or to non-plastic materials. Ultrasonic bonding can be used only with ultrasonic adhesives. Frequently, a mold-release agent is present on the surface of thermoset materials and must be removed before adhesive bonding. Mold-release agents are usually removed after a detergent wash, solvent-wash, or solvent-wipe, followed by light sanding to break the smooth surface glaze. A final solvent-wipe with clean solvent and clean lint-free cloth or paper tissue is usually effective. Solvents used include acetone, MEK, toluene, low-boiling petroleum ether, TCE, and isopropyl alcohol. Fine abrasive paper (sand, carborundum, or aluminum oxide-abrasive grit/metal, sand or oxide), or metal wool (steel, aluminum, or brass), or steel shot are frequently used for abrasion of the surface of thermosets.[26]

7.3.1 Diallyl Phthalate (DAP)

This resin has exceptional electrical insulating properties, high-temperature stability, and good resistance to most chemicals and moisture.[23] Surfaces are hard and tough and pick up very little moisture. DAP parts are ordinarily molded or laminated with glass fabric and are not easy to bond with an adhesive. Sanding or buffing appears to be the best surface treatments. Only filled resins are available. Besides glass, fillers include minerals, Orlon® (acrylic fiber, originally developed by

DuPont Co.), and asbestos. Surface preparation is as follows:

1. Wipe with acetone, MEK, toluene, low-boiling petroleum ether, TCE, or isopropyl alcohol
2. Sand-, grit-, or vapor-blast or use steel wool
3. Wipe with a clean dry cloth to remove grit and particles
4. Repeat solvent-wipe in step 1

7.3.2 Epoxies

Epoxy resins are among the workhorses of thermosetting resins.[14] They have a wide range of properties. They show good dimensional stability and good electrical properties and mechanical strength. They have good creep resistance and are useful over a wide temperature range (−73 to 427 °C). These resins are easy to bond, requiring only a clean dry surface, usually solvent-cleaned and sanded. Both filled and unfilled grades are available. Fillers include minerals, glass, and glass microballoons. Epoxy laminates should be treated as covered in Section 7.5, Reinforced Thermoplastics (laminates). A recommended surface treatment is as follows:

1. Wipe with acetone or other suitable solvent (see Section 7.3.1 diallyl phthalate) or vapor degrease
2. Abrade by scouring or other treatment suggested in Section 7.3 (Thermosets)
3. Wipe with a clean dry cloth to remove grit
4. Repeat solvent treatment as in step 1
5. Apply a silane-type primer, such as Chemlok® 607 (LORD Corporation, www.lord.com), diluted with 5−10 volumes of methanol or ethanol. This step is optional

7.3.3 Melamine-Formaldehyde (Melamines)

The amino resins, like urea-formaldehyde, are hard, rigid, and abrasion-resistant.[23] They are self-extinguishing and have superior electrical properties. They also have excellent dimensional stability and good creep resistance. They are noted for their high impact strength and resistance to water and solvents. Only filled resins are available. The fillers include cellulose, rag, and glass. A suggested surface preparation is as follows:

1. Scrub with an a abrasive household detergent
2. Rinse with tap water, then deionized water
3. Dry
4. Sand
5. Wipe with isopropyl alcohol
6. Dry
7. Prime or bond

The procedure for epoxies in Section 7.3.2 may also be used.

7.3.4 Phenol-Formaldehyde (Phenolics)

Phenolics have an excellent combination of high physical strength and high-temperature resistance, good electrical properties, and good dimensional stability.[23] Phenolics are widely bonded, not only on molded parts but also as laminates and castings. Both filled and unfilled types are available. Fillers include asbestos, cellulose, wood, flour, and glass. Methods of surface preparation given above under Epoxies are suggested.

7.3.5 Polyester

These unsaturated, non-linear resins are similar to epoxies and phenolics in their surface-preparation requirements, basically requiring only sanding for good results.[23] Polyesters have good resistance to oils and solvents. The method of surface preparation given for epoxies in Section 7.3.2 is suggested.

7.3.6 Polyimide

This is a class of polymeric materials distinguished by exceptional thermal stability.[19,42,43] They are available commercially in several forms, including fabricated parts and shapes, molding resins, films, and coatings for wire and fabrics. Some polyimides, condensation polymers, are essentially linear, with structures similar to those of thermoplastics. Others, polymers used as engineering resins in parts (moldings and laminates), are thermosetting. DuPont's Vespel® precision parts are available in graphite-PTFE, and MoS_2-filled bearing compositions, and unfilled form. These parts can withstand temperatures of up to 482 °C for short periods. A typical surface preparation method for Vespel® parts is as follows:

7.3.6.1 Vespel® Parts

1. Remove surface contamination such as dirt and oil with solvents. Clean by refluxing in perchloroethylene, or TCE, or clean ultrasonically in trichlorotrifluoroethane.
2. Mechanically abrade with a wet or dry abrasive blast. Use a light abrading (approx. 50−100 microinches) to maintain a uniform adhesive thickness. This type of abrading can be obtained with an air- or air−liquid- abrasive blast.
3. Remove residual with the solvent in step 1
4. Dry

7.3.6.2 Sodium-Hydroxide Etch

1. Degrease in acetone[18]
2. Etch for 1 min at 60−90 °C (Table 7.14)
3. Rinse in cold water
4. Dry in hot air

7.3.7 Polyurethane

This resin, like polyimides, is sometimes thermoplastic.[23] It is formed from the reaction of a polyisocyanate with compounds containing a reactive hydrogen. The plastic may be flexible or rigid, or somewhere in between, and can be obtained in different densities and forms (sheets, molding, and casting resins, etc.). Polyurethanes are unsurpassed as cryogenic materials and have excellent adhesion and skid resistance, good chemical resistance, and superior impact resistance, but are limited at elevated temperatures (to 121 °C). Polyurethanes, or urethanes as they are frequently called, also have good electrical properties. Cleaning usually involves light sanding and a dry bonding surface. A primer (urethane or silane) will usually improve adhesion. Polyurethanes are usually considered to have better cohesive than adhesive properties, which is why the interface may be the "weak link". A suggested surface preparation is as follows:

1. Wipe with acetone or methyl ethyl ketone
2. Abrade with 100-grit emery cloth, sandpaper, or steel wool
3. Wipe with a clean dry cloth to remove grit and particles
4. Wipe again with solvent as in step 1
5. Dry
6. Use urethane or silicone primer to improve adhesion

Table 7.14 Composition of Etching Solution for Polyimide

Solution Component	Parts by Weight
Sodium hydroxide	5
Water	95

7.3.8 Silicone Resins

Silicone resins are available in several forms.[17,44] They are used as thermally stable electrical insulation resins, paint vehicles, molding compounds, laminates, impregnating varnishes, encapsulating materials, and as baked-on release agents. Recommended surface preparation is as follows:

1. Wipe with acetone or other solvent listed in the general discussion for thermosets in Section 7.3
2. Sand-, grit-, or vapor-blast, or use steel wool
3. Wipe with a clean dry cloth to remove grit and particles
4. Repeat solvent wipe as in step 1

Silicone laminates should be treated according to Section 7.4, regarding Reinforced Plastics/Thermosets.

7.3.9 Urea-Formaldehyde

Like melamine-formaldehyde resins, these amino resins are hard, rigid, abrasion-resistant materials.[17,23] They have excellent dimensional stability and good solvent and creep resistance. They are self-extinguishing and have superior electrical properties. They are noted for high impact strength and resistance to water and solvents. Only cellulose-filled resins are available. The following surface preparation method is used:

1. Scrub with an abrasive household detergent
2. Rinse with tap water, then deionized water
3. Dry

4. Sand
5. Wipe with isopropyl alcohol
6. Dry
7. Prime or bond

The procedure given in Section 7.3.2 for epoxies may be used.

7.4 Reinforced Plastics/Thermosets

The reinforced thermosets of most importance are the glass-reinforced plastics (GRP).[19] The methods most often used for preparing GRP laminates for bonding involve removal of the original resin from the surface, yielding a roughened faying surface for bonding. Removal of surface gloss is usually sufficient to disposal of surface soils, exuded resin impurities, absorbed gases of vapors, and release agents used during the manufacture of the GRP. The methods of surface preparation most commonly used for laminated plastics are as follows:

7.4.1 Tear-Ply (Peel-Ply) Method

During the manufacture of the GRP laminate, either one or both outer surfaces of the laminate are made of a layer of a weakly adhering material, the outer layer of which can later be stripped or peeled off easily.[19] Nylon and Dacron® are frequently used for this purpose. This ply is cured as an integral part of the laminate. The resin used in the construction of the GRP adheres poorly to the nylon or Dacron® cloth incorporated in the outer layer or layers, permitting the nylon or Dacron® cloth to be peeled uniformly in one piece. The texture of the nylon or Dacron fabric layer is reproduced in the outer layer of the laminate. When the adhesive-bonding operation is to be performed, a thin knife is slid under a ply, and the desired distance peeled and trimmed. Loose particles are removed by brushing or blowing the surface with clean filtered air. There is very little chance of surface contamination with tear ply. The tear ply is applied only to the areas that are to be adhesively bonded. This technique is preferred over machine- or hand-sanding because of the reduced danger of surface contamination.

7.4.2 Sanding

The surface of laminated plastics may be sanded lightly with medium-grit (80−120 grit) emery paper or other abrasive paper capable of roughening the surface without substantially damaging the reinforcing fibers.[19] It is desirable to have the direction of bonding parallel to the surface fiber orientation in order to minimize damage to these fibers. The technique works best on large faying surfaces where the edges, rounded as a result of sanding, can be trimmed, or where the edge effects are negligible. Sanding dust may be removed with a short-hair stiff brush. If water-break-free surfaces are not obtained, the procedure should be repeated.

7.4.3 Grit-Blasting or Sandblasting

This method may also be used if available. A specially-trained operator is needed to produce uniformity within pieces by sandblasting. A clean, uniform-size grit is essential for proper surface preparation with sandblasting. This may be a problem when treating GRP surfaces, that is why this technique is rarely used.

After sanding or sandblasting, the surface is sometimes wiped with solvent, such as MEK, acetone, toluene, TCE, Freon® TF or Freon® TMC, depending on the known mold lubricants. In some cases, a solvent is used before and after abrading the surface. If water-break-free surfaces are not obtained, the procedure should be repeated.

Glass-reinforced plastic laminates, prepared for bonding by hand- and machine-sanding, can be stored to 30 days at 23 °C and 50% relative humidity with no adverse effect on bond strength. Machine sanding gave slightly better results than hand sanding. Tear ply and sanding gave about the same results, but the tear-ply method has less risk of surface contamination. Variations in bond strength are more likely to occur as a result of changes in sanding techniques than as a result of the difference in methods.

In general, bond quality diminished with increased surface exposure time (SET). The best overall adhesive evaluated was epoxy film adhesive, which was found to be the least sensitive to the method of surface preparation used. In general, the best result was obtained when GRP laminates were bonded within 4 h after sanding. If absolutely necessary, bonding can be carried out after periods of time of up to 14 days SET, with only moderate strength loss.

7.4.4 Manual Scouring

In this method, the faying surface is scrubbed with tap water and an abrasive household-type cleaner to remove contaminants and release agents.[45] Clean cloths or non-metallic bristle brushes will facilitate the scouring. The surface is rinsed with clean running tap water, followed by a rinse in distilled water, and then dried at 54−66 °C. The parts should exhibit a water-beak-free surface, otherwise the above procedure should be repeated.

7.4.5 Solvent-Soak and Abrading

If water-break-free surfaces cannot be obtained by tear-ply, sandblasting, or manual scouring, the plastic laminates should be treated as follows:[45]

1. Soak for 48 h in reagent-grade acetone
2. Dry for 3−4 h at 88−104 °C
3. Sand lightly with 200-grit sandpaper
4. Remove particles by air-blast or vacuum
5. Check for water-break-free condition. If achieved, the parts may be bonded. If not, resoak the laminates in acetone for an additional 24 h minimum and repeat the rest of the procedure. Parts that do not pass the water-break-free test should be rejected

7.5 Reinforced Thermoplastics (Glass-Reinforced)

Surface preparation of glass-reinforced thermoplastics is not necessarily, being similar to the technique prescribed for the base unreinforced resin.[19] In general, there is a drop of up to 50% in the expected bond strength with glass reinforcement. The reason for this drop is not fully known, although it may be the result of the finishes applied to glass during its manufacturing. In many cases, solvent cementing will be effective. Examples are aqueous phenol for glass-reinforced nylon 6 and methylene chloride for PS.

7.6 Plastic Foams

Plastic foams are generally treated by the same surface-preparation methods used for the base polymer.[17] This is particularly true for the thermoplastic “structural” foams such as PC and modified polyphenylene oxide. In some cases, these thermoplastic foams may be solvent cemented. The thermosetting foam most commonly encountered is polyurethane, which is available in rigid, semi-rigid, and flexible form. The rigid foams are obtainable in a wide range of densities. Obviously, the denser grades, with their increased surface area of actual material exposed, will be easier to prepare by the usual technique of sanding lightly and then removing the resulting dust by vacuum or by blowing-off. The cellular structure of plastic foams offers an advantage to surface preparation, in which a physical interlocking of the two faying surfaces is possible in a foam-to-foam bond. With rigid polyurethane foams, a conventional adhesive bond may not be necessary, since foam “poured-in-place” or “foamed-in-place” will adhere tenaciously to most substrates during curing.

7.7 Surface Preparation of Rubbers

Almost all types of elastomers can be bonded to a large variety of substrates by the process known as vulcanization. The strength of similar bonds by adhesive bonding, or post-vulcanization (PV) bonding, as it is also called, was originally believed to be much weaker and less resistant to environmental exposure. Published work has demonstrated that this is not true, with some exceptions. The advantages of PV bonding are:[46]

- A variety of vulcanized elastomers can be bonded
- Common elastomer surface treatments can be used
- Bonded systems possess good environmental resistance
- Bonds are comparable to vulcanization bonding
- The process is applicable to rubber-to-metal parts and to rubber-to-rubber assemblies
- Large sizes or complicated shapes may be PV bonded, which would not be economically feasible by the “bond-in-the-press” technique
- Vulcanization bonding is impractical for field repair, where the required equipment is usually not available

Table 7.15 Comparison of Vulcanization and Post-Vulcanization Bonding[a] [35]

Material	Tear Strength-Peel, N/m	
	Vulcanization	Post-Vulcanization
Natural rubber	7880	7529
Natural rubber (B)	11,132	9806
SBR	33,094	17,513
Neoprene	16,284	20,312
Butyl rubber	17,685	11,623
Nitrile rubber	16,635	2814
EPDM	22,763	4903

[a] *Adhesive used was Chemlok® 234B (LORD Corporation)*

Table 7.15 shows bond values obtained with seven elastomers, comparing the bond values obtained with both vulcanization bonding and PV (adhesive) bonding, using a 149 °C cure. In most cases, the results are comparable. Ethylene–propylene–diene terpolymer (EPDM) was the only elastomer where a significant decrease in bond strength was obtained by PV bonding.

Solvent washing and abrading are common surface treatment methods for most elastomers, but chemical treatment is often applied for maximum strength and other properties. Many synthetic and natural rubbers (NRs) require "cyclizing" with concentrated sulfuric acid until hairline cracks appear on the surface. Some rubbers require primers for optimum bonding.

Mechanical abrasion is usually accompanied by sanding or buffing the surface with 80–140 grit sandpaper or a buffing wheel. The dust from the buffing process, or other contamination, is usually removed by means of a clean cloth dipped in a suitable solvent. The solvent must be reasonably compatible with the chemical type or rubber being cleaned. If the solvent is strongly incompatible with the rubber involved, or if too much is used, the rubber may swell excessively, curl unacceptably, or be degraded. Particular care must be taken not to trap solvent in a system that is totally closed, or else the rubber may be damaged. On the other hand, a mild wipe of a somewhat aggressive solvent may help tackify the rubber surface. MEK and toluene are solvents commonly used for cleaning elastomers. If such curling occurs, a more compatible solvent, such as toluene, may be substituted. Chlorinated solvents, such as TCE, perchloroethane, and 1,1,1-trichloroethane are also common. Cyclization, mentioned above, and chlorination are other common surface-preparation methods and are described in the next section (Neoprene).

Research has shown that the bondability of elastomers is a function of polarity. The less polar EPDM and butyl elastomers, the more difficult they are to bond than are the more polar nitrile, neoprene, styrene-butadiene rubber (SBR), and NR.[46]

7.7.1 Neoprene (Polychloroprene)

Neoprene is the generic name for polymers of chloroprene (2-chloro-1,3-butadiene), first manufactured by Du Pont in 1931.[19] There are many types of solid and latex neoprene.

7.7.1.1 Abrasive Treatment

1. Scrape the surface with a sharp blade to remove gross layers of wax, sulfur, and other compounding ingredients that may have floated to the surface[17,19]
2. Solvent-wipe with ethyl, isopropyl, or methyl alcohol, MEK, or toluene
3. Uniformly abrade surfaces with 80–120 grit abrasive paper. Machine sanding with a "jitterbug" oscillating sander is preferred over hand sanding, because the machine sanding produces a more uniform surface with less effort. A buffing wheel may also be used
4. Solvent-wipe again as in step 2 to remove particles

7.7.1.2 Cyclization

This process is often applied to prepare for bonding with flexiblized epoxy adhesives.[17,47] It has been used successfully in many rubbers, in addition to neoprene. A commonly used cyclization procedure is as follows:

1. Scrape surface with a sharp blade to remove gross layers of wax, sulfur, and other

compounding ingredients that may have floated to the surface
2. Solvent-wipe with ethyl, isopropyl, or methyl alcohol, MEK, or toluene
3. Immerse rubber surface in concentrated sulfuric acid (sp. gr. 1.84) for 5−45 min. The optimum time must be determined experimentally
4. Rinse thoroughly with tap water, preferably hot
5. Rinse thoroughly with distilled water
6. Neutralize by immersing for 5−10 min in a 10−20% solution of ammonium hydroxide (sodium hydroxide is also used)
7. Rinse thoroughly with tap water
8. Rinse thoroughly with distilled water
9. Dry at temperatures up to 150 °C
10. Flex the resultant brittle surface of the rubber with clean rubber or plastic gloves so that a finely cracked appearance is produced

Cyclizing hardens and slightly oxidizes the surface, thereby permitting the necessary wetting of the adhesive bond. The finely cracked surface indicates that the rubber is ready for bonding. Light lacy lines on the surface indicate insufficient immersion time. Deep, coarse cracks, and a thick crusty surface indicate excessive immersion. If immersion is not feasible, the acid may be made up into a thick paste by the addition of barium sulfate (barytes), or Cab-O-Sil® (Cabot Corp., Boston, MA, www.cabot-corp.com), or the use of 100 parts by weight (pbw) concentrated sulfuric acid:5 pbw Santocel® C (Monsanto Co., www.monsanto.com), or equivalent. A stainless steel or other acid-resistant spatula should be used to apply the paste. After the paste is applied, the rest of the treatment (steps 4 through 8) should be carried out.

7.7.1.3 Cyclization (Boeing-Vertol Modification)

Boeing-Vertol has developed a much milder method, as follows:[48]

1. Clean in toluene
2. Force-dry 1 h at 60 °C
3. Immerse 2 min in concentrated sulfuric acid
4. Rinse in tap water
5. Force-dry 1 h at 60 °C

7.7.1.4 Chlorination

1. Scrub neoprene in 49−60 °C non-ionic detergent solution (2−3% by weight)[19]
2. Rinse thoroughly in tap water
3. Rinse thoroughly in distilled water
4. Air-dry
5. Immerse 1½ to 3 min in the solution given in Table 7.16 at room temperature (prepare solution just prior to use, adding ingredients in the order listed)
6. Rinse thoroughly with distilled water and dry at temperatures up to 66 °C

7.7.1.5 Activated Gas Plasma

This method, described in Chapter 6, has been used successfully with neoprene. The best results have been obtained with ammonia, air, and nitrogen plasmas at 30 min exposure.[49]

7.7.2 Ethylene-Propylene-Diene Terpolymer

This rubber, along with the copolymer of ethylene and propylene (EPM), forms a classification called ethylene-propylene rubbers. However, since EPDM, the terpolymer, is in much greater use than EPM, the former is frequently called ethylene-propylene rubber. Its outstanding property is high resistance to ozone and weathering. EPDM is relatively difficult to bond because of its lower polarity.[26]

7.7.2.1 Abrasive Treatment

As in neoprene, acetone or MEK are among the effective solvents.[17]

7.7.2.2 Cyclization

As in neoprene.[19]

Table 7.16 Composition of Chlorination Solution for Neoprene

Solution Component	Parts by Weight
Hydrochloric acid	0.3
Sodium hypochlorite	0.3
Water	97

7.7.3 Silicone Rubber (Polydimethylsiloxane)

These rubbers are completely synthetic materials with wide applications. They comprise two types, heat-vulcanizing and RTV. Both types have unique properties unobtainable with organic rubbers, particularly where superior endurance and extended life expectancy are required. Silicone elastomers maintain their usefulness from −101 °C to 316 °C. Resistance to oxidation, oils, and chemicals is high and stability against weathering is good.[26]

7.7.3.1 Solvent Cleaning

1. Sand with a medium-grit sandpaper[17]
2. Solvent-wipe surfaces with acetone, MEK, ethyl, methyl, or isopropyl alcohol, or toluene.

7.7.3.2 Soap-and-Water Wash

A simple washing with a mild (Ivory®) soap and water, followed by thorough rinsing, has been found to give satisfactory results.[27]

7.7.3.3 Primers

Priming the silicone rubber with Chemlok® 607 adhesive (LORD Corporation, www.lord.com) in methanol solvent has been found to give good results after cleaning with acetone or methanol.[50,51] The primer should be dried at 200 °C for 10−15 min. The Chemlok® 607 can also be used as the adhesive following the priming. Chemlok® silanol-type primers have also been developed. Other satisfactory silane-based primers can be obtained from Henkel Corp. (www.henkel.com), Dow Corning (www.dowcorning.com), GE Sealants (www.siliconeforbuilding.com), and other suppliers. This primer should be air-dried at room temperature for 15−40 min before bonding.

7.7.3.4 Activated-Gas Plasma

This method, described generally above under Activated Gas Surface Treatment of Polymers, has been used successfully with RTV vinyl-addition-type silicone rubber, using excited oxygen plasma.[52] This treatment permitted the use of an epoxy adhesive for bonding. Usually, cured RTV silicones are considered unbondable by conventional adhesives such as epoxies.

7.7.4 Butyl Rubber (BR)

BR has been commercially produced since 1942 and is a well-established specialty elastomer with a wide range of applications. It is a copolymer of isobutylene and isoprene. Its special properties are: low gas permeability, thermal stability, ozone and weathering resistance, vibration damping, and higher COF and chemical and moisture resistance.[27] Being less polar, BR is relatively difficult to bond.

7.7.4.1 Abrasive Treatment

Similarly to neoprene, toluene is used as a solvent.[12]

7.7.4.2 Cyclization

Similarly to neoprene, cyclization is not always recommended for BR.[17,47,53]

7.7.4.3 Chlorination

Similarly to neoprene, Sharpe[17,47] does not recommend chlorination for BR.

7.7.4.4 Primers—Prime

Primers−Prime with BR adhesive in an aliphatic solvent,[43] or use silicone primers.

7.7.4.5 Activated-Gas Plasma

This method has been used successfully with BR, good results that were obtained with air and nitrogen plasmas at 30 min in Picatinny Arsenal studies.

7.7.5 Chlorobutyl Rubber

This modified BR contains about 1.2 wt% of chlorine and has greater vulcanization flexibility and enhanced cure compatibility than other general-purpose elastomers.[19]

7.7.5.1 Abrasive Treatment

As in neoprene.[17]

7.7.5.2 Chlorination

As in neoprene.[17]

7.7.5.3 Other Methods

See Table 7.17 for a comparison of results obtained by a number of different surface-preparation methods.[17]

7.7.6 Chlorosulfonated Polyethylene

The synthetic rubber chlorosulfonated polyethylene—(Hypalon®—Du Pont Co., ceased operations April 20, 2010), also known as chlorosulfonyl polyethylene, introduced in 1952, is characterized by ozone resistance, light stability, heat resistance, weathering, resistance to deterioration by corrosive chemicals, and good oil resistance. Presently available types contain from 25% to 43% chlorine and 1.0% to 1.4% sulfur.[19]

7.7.6.1 Abrasive Treatment

As in neoprene, acetone or MEK is used as a solvent.[17]

7.7.6.2 Primers

1. Wipe with toluene[48]
2. Force-dry 1 h at 60 °C
3. Prime with an adhesive primer such as Scotchcast® epoxy powder coating resins (by 3M Corp., www.3m.com)

Table 7.17 Peel Strength of Epoxy—Polyamide Resin Adhesive to Chlorobutyl Rubber Pretreated by Various Methods[7]

Surface Treatment	N/m
Cyclization	3152
Solvent-clean and chlorinate	2452
Solvent-clean, abrade and chlorinate	2802
Detergent-clean and chlorinate	5254
Ethanol-wipe	1226
Abrade and ethanol-wipe	1226
MEK-wipe	1051
Abrade and MEK-wipe	1138

7.7.7 Nitrile Rubber (Butadiene-Acrylonitrile)

Nitrile rubbers (NRs), are copolymers of butadiene and acrylonitrile and are frequently referred to as Buna N. Their properties vary with the acrylonitrile content. Nitrile rubbers exhibit a high degree of resistance to attack by oils at both normal and elevated temperatures.[19]

7.7.7.1 Abrasive Treatment

As in neoprene, methanol or toluene work as solvent.[17]

7.7.7.2 Cyclization

As in neoprene, except that the exposure should be for 10−15 min.[17]

7.7.7.3 Chlorination

As in neoprene.[17]

7.7.7.4 Primers

Primers have been used successfully with Buna N rubber.[19,47,54] Those that have been particularly effective include:

Chemlok® AP-131 Primer (LORD Corporation) for bonding to steel

Chemlok® 205 adhesive (LORD Corporation) for bonding to aluminum

Chemlok® 220 adhesive (LORD Corporation) for bonding to aluminum

Scotchcast® epoxy powder coating resins (3M Co.) for bonding to aluminum

Depending on the adhesive to be used, better results may be obtained by using a toluene wipe, with or without sanding, before priming. One possible procedure is as follows:[19]

1. Wipe with toluene
2. Force-dry at 60 °C

3. Prime with an adhesive primer such as those listed above

7.7.7.5 Activated-Gas Plasma

This method has been used successfully with Buna N rubber. The best results were obtained with ammonia, air, and nitrogen plasmas at 30 min.[49]

7.7.8 Polyurethane Elastomers

This category covers thermosetting materials derived from the reaction of an isocyanate with a hydroxy compound. Their unique elastomeric properties are exceptionally high abrasion resistance, very high tear and tensile strength, and high hardness with good mechanical strength. Both polyester (AU) and polyether (EU) types are available, as are thermoplastic polyester urethane. They are usually completely soluble in strong polar solvents such as tetrahydrofuran and dimethyl formamide, and at high temperatures they can be molded, extruded, or calendered.[26] Treatments are given below.

7.7.8.1 Abrasive Treatment

As in neoprene, methanol is a solvent.

7.7.8.2 Primers

A number of primers can be used, such as Chemlok® primers AP-134, and AP-131 (LORD Corporation), or a chlorosilane supplied by GE Sealants, Rohm & Haas (www.rohmhaas.com) or Dow Corning Corp.[55] Methanol can be used as a degreasing agent prior to priming.

7.7.9 Synthetic Natural Rubber (Polyisoprene)

This rubber approximates the chemical composition of NR. Its predominant structure is *cis*-1,4-polyisoprene, the same as that of NR. In general, the synthetic polyisoprenes are lower in modulus (more flexible) and higher in elongation than the NR. Synthetic polyisoprene was first introduced commercially in 1960.[26] Suggested surface treatments are as follows:

7.7.9.1 Abrasive Treatment

As in neoprene, methanol or isopropanol are suggested as solvents.[17]

7.7.9.2 Cyclization

As in neoprene, except that exposure should be for only 5–10 min, since this is not an acid-resistant rubber.[17] Some workers suggest much shorter periods (10–45 s).

7.7.9.3 Chlorination

As in neoprene.[17]

7.7.10 Styrene Butadiene Rubber (Buna S)

This type of rubber, once called GR-S, is one of the most important synthetic rubbers. It is a copolymer of styrene and butadiene.[26] Treatments are as follows:

7.7.10.1 Abrasive Treatment

As in neoprene, toluene is recommended as a solvent.[17] Excessive toluene, however, causes the rubber to swell. A 20-min drying will restore that part to its original dimension.

7.7.10.2 Cyclization

As in neoprene, except that the exposure time should be 10–15 min.[17]

7.7.10.3 Chlorination

As in neoprene.[17]

7.7.10.4 Primers

Recommended primers include butadiene–styrene adhesive in aliphatic solvent and Chemlok® 205 adhesive (LORD Corporation) in methyl isobutyl ketone diluent.[18,55]

7.7.10.5 Activated-Gas Plasma

This method has been used with some success with Buna S rubber; best results were obtained using helium, air, and nitrogen plasmas.[49]

7.7.11 Polybutadiene (Butadiene Rubber)

Although this type of rubber was first produced in Europe in the early 1930s, it was almost unknown in the United States until 1960.[26] Treatments are as follows:

7.7.11.1 Abrasive Treatment

As is neoprene, methanol is recommended as a solvent.[17]

7.7.11.2 Cyclization

As in neoprene, except that the exposure time should be 10–15 min, since this is a non-acid resistant rubber.[17]

7.7.11.3 Chlorination

As in neoprene.[17]

7.7.11.4 Solvent Wipe

A simple solvent wipe with methanol may be used for general-purpose bonding.[18]

7.7.12 Fluorosilicone Elastomers

These rubbers have become the second largest in volume of the fluoroelastomer types. The non-silicone-containing fluoroelastomers are discussed below. Fluorosilicone rubbers retain most of the useful qualities of the regular silicone rubbers and have improved resistance to many fluids, except for ketones and phosphate esters. They are most useful when low-temperature resistance is required, in addition to fluid resistance.[26] An effective treatment is a solvent wipe with methyl, ethyl, or isopropyl alcohol, or with toluene.

7.7.13 Fluorocarbon Elastomers

These materials, also called fluoroelastomers, include Kel-F® (3M discontinued manufacturing in 1996) and Dyneon® elastomers (3M Company). Viton® (Du Pont Company, www.dupontelastomers.com) and Dyneon are copolymers of vinylidene fluoride and hexafluoropropylene. Kel-F® is a copolymer of chlorotrifluoroethylene and vinylidene fluoride and is called polychlorotrifluoroethylene. Viton® and Fluorel® are the most important members of this group today. These elastomers have excellent resistance to ozone, oxidation, weathering, heat, aliphatic and aromatic hydrocarbons, and alcohols. They are also highly impermeable to gases, and have good strength, electrical resistivity, and resistance to abrasion, water, acids, and halogenated hydrocarbons. This type usually includes the fluorosilicone elastomers, which are discussed above.[26] Treatments suggested are as follows:

7.7.13.1 Sodium Etch

For optimum bond strength, use the procedure described above under Ethylene–Chlorotrifluoroethylene Copolymer (Section 7.2.7).[56]

7.7.13.2 Dry Abrasion

For relatively low adhesion with low environmental resistance[56]:

1. Wipe or spray with, or immerse in 1,1-trichloroethane or Freon® TMC, acetone, MEK, toluene, ethyl, or isopropyl alcohol
2. Abrade lightly and uniformly with 180–320 grit abrasive paper
3. Repeat step 1

7.7.13.3 Epichlorohydrin Elastomer

This elastomer homopolymer and the copolymer combine exceptional resistance to aromatic and halogenated hydrocarbons with high resistance to ozone, weathering, gas permeability, compression set, compact and tear. These compounds have good tensile strength, resilience, and resistance to abrasion, water, acids, and alkalis. They also have good low-temperature and heat resistance.

Epichlorohydrin elastomers of both types require a simple cleaning with acetone (not MEK), alcohols, or aromatics such as toluene. No abrasion is necessary.[26]

7.7.14 Polysulfide Rubber (PTR)

The first introduction of a PTR for commercial application was in 1930, when Morton Thiokol Company Corp. developed Thiokol® (acquired by PolySpec, Corporation). Since then, a number of other types of Thiokol® have been developed (www.polyspec.com). Thiokol® resins are highly impermeable to gases, and have excellent resistance to ozone, oxidation, weathering, and aliphatic and aromatic hydrocarbons.[17] Treatments are as follows:

7.7.14.1 Abrasive Treatment

As in neoprene, methanol is used as a solvent.[17]

7.7.14.2 Chlorination

1. Degrease is methanol[18]
2. Immerse overnight in strong chlorine water
3. Wash
4. Dry

Snogren,[17] however, does not recommend chlorination for treating polysulfide.

7.7.14.3 Primers

An example of a silicone primer for use with polysulfide sealants is Chemlok® AP-131 (LORD Corporation).[55]

7.7.15 Propylene Oxide Rubber

This elastomer is a sulfur-vulcanizable copolymer of propylene oxide and allyl glycidyl ether. Its vulcanizates are particularly attractive for dynamic uses, where high resilience, excellent flex life, and flexibility at extremely low temperatures are required. It performs similarly to NR in these applications, but it also has the added advantages of (1) good resistance to aging at high temperatures, (2) good ozone resistance, and (3) moderate resistance to loss of properties in contact with fuels and/or some solvents. The surfaces of this elastomer should be prepared by solvent wiping with TCE, xylene, toluene, or other appropriate solvent.[57]

7.7.16 Polyacrylate (Polyacrylic Rubber)

Polyacrylic elastomers are noted primarily for their high resistance to heat, ozone, oxidation, weathering, aliphatic hydrocarbons, and sulfur-bearing oils. They also have good resilience and gas impermeability and moderate strength. Abrasion resistance is not as good as with nitrile rubber or SBR.[27] Surface preparation is as follows:

7.7.16.1 Dry Abrasion

As in Fluorocarbon Elastomers above, methanol has also been used as a solvent.[56]

7.8 Thermoplastic Elastomer

This class of polymers combines the end-use properties of vulcanized elastomers with the processing advantages of thermoplastics. Because of their unique molecular configurations, they may be processed with the same techniques utilized with other thermoplastics, but the mechanical properties of the final articles are essentially indistinguishable from those of similar articles fabricated from conventional vulcanized elastomers.

There are several types including polyester (Hytrel® by Du Pont Co.), polystyrene−butadiene−polystyrene block copolymers (Kraton®—KRATON Polymers U.S LLC., www.kraton.com), polystyrene−isoprene−polystyrene block copolymers (Solprene®—Dynasol Elastomers, http://dynasolelastomers.com/), polyolefin (TPR® thermoplastics rubber by Uniroyal, Inc.), and polyurethane.

Since these materials are thermoplastic and may, therefore, be soluble in a wide range of organic solvents, it is quite possible that solvent cementing is the most appropriate method of bonding the thermoplastic rubbers to themselves or to mutually-compatible plastics. Solvent cementing might work with Kraton® (KRATON Polymers U.S LLC), but not with TPR® and Hytrel® (DuPont), which do not have reactive bonding sites. In cases where the thermoplastic rubber must be bonded to metals or other non-plastic or non-rubber materials, neither solvent cementing nor fusion techniques can be considered. In such cases, conventional adhesives must be used. In the case of Hytrel® polyester elastomer, cleaning with MEK and then using commercial primers is effective. Abrasion is not recommended. Polyurethane rubber, on the other hand, has reactive sites and is cementable with solvents.

7.9 Painted Surfaces

To obtain maximum-strength bonds, paint must be removed.[17,57] Even if the bond between the adhesive and the two surfaces, paint and the other adherend, is good, the strength of the joint will be no better than the strength of the bond between the surface that has been painted and the paint. For temporary or other bonds that do not require maximum strength, clean the painted surface with a detergent solution, abrade with a medium-grit emery cloth, and wash again with detergent. Alternate procedures are as follows after loose paint has been removed:

1. Solvent cleaning[2]—Immerse, spray, or wipe in either of the solutions given in Tables 7.18 and 7.19, which degrease the surface and leave a dull finish to the paint
2. Scrub surfaces with an alkaline cleaner, such as a solution of 2–4% by weight of trisodium phosphate in hot water. Rinse with clean water

Table 7.18 Composition of Solvent Cleaning Solution for Painted Surfaces[2]

Solution Component	Volume, %
Methylene chloride	15
n-Butanol	35
Mineral spirits	48
Methyl ethyl ketone	2

Table 7.19 Composition of Solvent Cleaning Solution for Painted Surfaces[2]

Solution Component	Volume, %
Methylene chloride	20
n-Butanol	20
Isopropanol	20
Methyl acetate	20
Toluene	20

7.10 Conclusions

Thermoplastics, thermosets, and elastomers require surface treatment to remove contamination and prepare their surfaces for adhesion bonding. Both initial bond strength and bond durability are affected by the surface preparation technique. Most materials require unique methods of treatment for optimal bond strength formation. Most surface preparation treatment methods use or generate chemicals that have various serious health effects and must be used with extreme caution.

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8 Characteristics of Adhesive Materials

Sina Ebnesajjad

This chapter discusses individual adhesive types in detail. As a matter of convenience, the adhesives have been arranged in alphabetical order, without regard to classification.

Certain general categories are also listed, such as alloys, aromatic polymer, conductive, delayed-tack, elastomeric adhesives, anaerobic, film and tape adhesives, hot-melt adhesives, inorganic glues, microencapsulated adhesives, rubber-based adhesives, solvent-based systems, thermoplastic resin adhesives, thermosetting-resin adhesives, and water-based adhesives.

8.1 History of Adhesives

We begin with a brief overview of the modern history of adhesive compounds, more or less as appears in Ref. 1. The dictionary defines an adhesive as “a substance capable of holding materials together by surface attachment.” This is a simple definition for a material that is the basis for a multibillion dollar industry, with more than 750 companies competing for a share of the market.[1]

The first evidence of a substance being used as an adhesive dates back to 4000 B.C. Archaeologists studying burial sites of prehistoric tribes found foodstuffs, buried with the deceased, in broken pottery vessels that had been repaired with sticky resins from tree sap. Archaeologists have also uncovered statues from Babylonian temples that have ivory eyeballs glued into eye sockets. The tar-like glue used has held for almost 6000 years.

The first references in literature concerning glue and the art of glue appear circa 2000 B.C. Simple procedures for making and using animal glue were written.

The period of time between 1500 and 1000 B.C. gave further proof that glue had become a method of assembly. Paintings and murals showed details of wood gluing operations. A casket removed from the tomb of King Tut shows the use of glue in its construction. Museums today contain many art objects and furnishings from the tombs of Egyptian Pharaohs that are bonded or laminated with some type of animal glue.

The next period of activity is from A.D. 1 to 500 when the Romans and Greeks developed the art of veneering and marquetry, which is the bonding of thin sections or layers of wood. From this art, the making of animal and fish glues was refined, and other types of adhesives were developed, such as an adhesive from egg whites to bond gold leaf. In addition to egg whites, other natural ingredients were used to prepare glue such as blood, bones, hide, milk, cheese, vegetables, and grains. The Romans were one of the first to use tar and beeswax to caulk the planking in boats and ships.

A study of history shows that glue fell into a period of disuse that lasted until about A.D. 1500–1700, when adhesives were used in the building of furniture. Some of the greatest furniture and cabinet makers of all time used adhesives in their products—names you will still recognize today like Chippendale and Duncan Phyfe.

The secret of violins made by Antonio Stradivari was the adhesive process used to laminate his specially treated woods. His methods have been lost in antiquity and have not been rediscovered, even with today’s sophisticated analytical methods.

Around 1700, the widespread use of glue brought about some rapid changes in the history of adhesives. The first commercial glue factory was started in Holland to manufacture animal glue from hides.

About 1750, the first glue patent was issued in Britain for a fish glue. Patents were then rapidly issued for adhesives using natural rubber, animal bones, fish, starch, and milk protein (casein). By 1900, the United States had a number of factories producing glue from the aforementioned bases.

The Industrial Revolution caused an explosion in technical breakthroughs that resulted in new materials becoming available for use in formulating adhesives. The first plastic polymer to be synthesized was cellulose nitrate, a thermoplastic material derived from the cellulose of wood. Its first use was in the manufacture of billiard balls, which had been

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made of ivory. The era of plastics began with the introduction of Bakelite phenolic, a thermoset plastic, in 1910. Within a year, adhesives using phenolic resin were put on the market. The 1920s, 1930s, and 1940s saw many new plastics and rubbers synthetically produced and many—out of an urgent necessity—were developed during World War II. Although adhesives have existed for about 6000 years, most of the technology relating to adhesives has been developed during the last 100 years.

The development of plastics and elastomers has rapidly advanced the development of adhesives and has given formulators a wide variety of products that can change and improve various properties of adhesives, such as flexibility, toughness, curing or setting time, temperature, and chemical resistance.

Adhesives touch our lives every day. They are never more than an arm's length away, even though we may not be aware of their presence. Descriptions, as follows, of some of the more common types of adhesives and their uses should make you more aware of how adhesives touch your life.

Animal glues—made from the protein extracted from the bones, hide, hoofs, and horns of animals by boiling. The extract is cooked to form a gelatin material. The gelatin can then be reliquified with heat, which gives it quick setting properties. Its major use has been in the wood and furniture industry. If you have seen a heated glue pot with a brush in it, it was probably an animal glue. Animal by-products from meat processing have been the source of supply for this type of glue.

Fish glue is a similar protein-based glue made from the skins and bones of fish. An exceptionally clear adhesive can be made from fish and was the first adhesive used for photographic emulsions for photo film and photo resist coatings for photoengraving processes.

Casein glue is made from a protein isolated from milk. The extraction process creates an adhesive that is waterproof. Its first use was in bonding the seam of cigarette paper. It provides a fast setting bond that requires very little adhesive; 1 g of adhesive can bond 2000 cigarettes.

Starch—a carbohydrate extracted from vegetable plants such as corn, rice, wheat, and potatoes, probably better known as paste. Major use area is in bonding paper and paper products such as bookbinding, corrugated boxes, paper bags, wallpaper paste (nonremovable); also used as a sizing in textiles. The laundry uses starch on your shirt collars to stiffen and give shape to your shirt.

Cellulose adhesive is made from a natural polymer found in trees and woody plants. It is the adhesive used on the cellophane wrapper on cigarette packs, the adhesive on decals we put on windows and, interestingly enough, the adhesive used on the strippable wallpaper we have in our homes that allows us to remove the paper easily.

Rubber-based solvent cements are adhesives made by combining one or more rubbers or elastomers in a solvent. These solutions are further modified with additives to improve the tack or stickiness and the degree of peel strength, flexibility, and the viscosity, or body. Rubber-based adhesive is used in a wide variety of applications, such as contact adhesive from plastic laminates used for counter tops, cabinets, desks, and tables. Adhesive is used on pressure-sensitive tapes as floor tile adhesive and carpeting adhesive. Self-sealing envelopes and shipping containers use rubber cements. Solvent-based rubber adhesives have been the mainstay of the shoe and leather industry.

Epoxies are adhesive systems made by a complex chemical reaction. Various resins are made synthetically by reacting two or more chemicals. The resultant resin can then be reacted or cured by the addition of another chemical called a hardener or catalyst. The basic epoxy resin systems are further modified to change their physical properties by the addition of such things as flexibilizers for impact resistance and flexibility, diluents or solvents to reduce the viscosity fillers, and reinforcements like glass fiber, alumina, silica sand, clay, metal powders, and flakes to change properties such as heat and electrical resistance, fire retardance, strength, and adhesion to certain substrates or materials.

Epoxy adhesives can bond a wide variety of substrates with high strength, particularly metals. They have been used to replace some traditional metalworking methods of joining like nuts and bolts, rivets, welding, crimping, brazing, and soldering. High-strength epoxies are used to construct rotor blades of helicopters, and to attach aluminum skins to the struts of aircraft wings and tail sections. Those of you who ski may know that your skis are laminates of plastics, wood, and metal joined with an epoxy. If you are a golfer, the heads of your clubs are bonded with an epoxy.

Hot melt adhesives are thermoplastic polymers that are tough and solid at room temperature but are very liquid at elevated temperatures. The origin of hot melts probably started with the use of sealing wax used to seal documents and letters with a signature ring or stamp, but the art of hot melts was not pursued until the 1960s.

Other adhesives that you may have heard of that represent higher technology and/or complicated chemical processes include the following:

RTV silicone adhesive is a rubberlike polymer called polydimethsiloxane. RTV stands for “room temperature vulcanizing,” or simply a rubber that cures at room temperature. Silicone rubber adhesives are made using a complicated process that turns elemental silicon metal made from sand (silica) into a rubbery polymer. When cured, silicone rubber adhesives/sealants have excellent resistance to heat (500−600 °F) and moisture that makes them exceptionally suited for outdoor weathering applications such as sealant and caulking compounds in the construction industry. Because of its exceptional properties, silicone adhesive has been used in some exotic applications such as the soles of the boots worn by the first astronauts to walk on the moon. Silicone adhesive/sealants are used to seal windows, doors, and portholes on the space shuttle and many satellite missiles. A special silicone adhesive is used to bond the heat shield tiles on space shuttles.

Anaerobic adhesives are derived from methacrylates, a monomer related to acrylic, or more commonly known as Plexiglas. The word anaerobic really applies to microbes that become active or live in the absence of oxygen. Although anaerobic sealants do not contain microbes, they become active and cure or polymerize in the absence of oxygen. These adhesives were developed by Professor Vernon Krieble, the founder of American Sealants Company, now known as Loctite Corporation.

The basic ingredient in anaerobic adhesives is a monomer from the acrylic family, a special liquid of small molecules that can combine chemically to form a polymer or a group of molecules. The molecules of an anaerobic monomer contain two carbon atoms that are double bonded to each other. The “active” ingredient in this monomer is called a free radical. This is a molecule that has an affinity for carbon but prefers to react with oxygen. As this free radical reacts with oxygen molecules, it forms a stable liquid like the original monomer.

A special ingredient in this chemical composition continually produces free radicals as they react with the oxygen and are used up. As you can see, there is an unlimited supply of catalyst being produced.

If no oxygen is present, the free radical then reacts with the carbon of the double bonded atom of the monomer molecule. A reaction is caused, which makes that molecule react with another molecule and spurs a chain reaction that produces a solid polymer chain.

Metals have a place in this reaction process. The presence of metal speeds the polymerization process by causing the production of free radical catalysts to increase greatly. The increased amount of catalyst in the monomer causes polymerization to occur more quickly.

This anaerobic reaction has been stated in a fairly simple manner, but it is really a very complex chemical reaction using certain ingredients in a parts-per-million basis. Other reactions can occur at the same time as curing occurs such as cross-linking of the polymer chains that makes the resultant solid resin insoluble in a solvent or by the use of heat.

Anaerobic adhesives are very versatile and are used in a wide variety of applications. The very first application of an anaerobic adhesive was to lock and seal a screw in the carburettor of an automobile engine. Today, anaerobic adhesives are not only used to lock all types of threaded fasteners. They are also used to seal pipe fittings, retain bearings, pulleys, and gears to shafts as well as to seal flanged surfaces to replace cut gaskets. The major users of these adhesives are automotive, truck, construction, and farming equipment companies. The actual market for these adhesives is anywhere that fasteners, gaskets, bearings, or any mechanical device that needs to be secured or sealed is used.

Cyanoacrylates are extremely rapid curing adhesives known as instant adhesive or Super glue. These adhesives were discovered by accident by Dr Harry Coover’s group at Eastman Chemical Company while doing some basic research on characterizing certain polymers derived from a chemical called ethylene.

Prior to the twentieth century, practically all adhesives were derived from plant or animal sources. The main classes included glue from animal bones, fish glue, and vegetable adhesives. Progress in organic chemistry and an increase in demand for adhesives led to the development of synthetic compounds, beginning with phenol-formaldehydes and casein adhesives. Developments in polymerization and adhesive chemistry proceeded in a near parallel fashion.

8.1.1 Chronology of Developments

An approximate chronological list of adhesive development is given below:

1920s: Cellulose ester, alkyd resin, cyclized rubber in adhesives, polychloroprene (neoprene), soybean adhesives

1930s: Urea-formaldehyde, pressure-sensitive tapes, phenolic resin adhesive films, polyvinyl acetate wood glues

1940s: Nitrile-phenolic, chlorinated rubber, melamine-formaldehyde, vinyl-phenolic, acrylic polyurethanes

1950s: Epoxies, cyanoacrylates, anaerobics, epoxy alloys

1960s: Polyimide, polybenzimidazole, polyquinoxaline

1970s: Second-generation acrylic, acrylic pressure-sensitive, structural polyurethanes

1980s: Tougheners for thermoset resins, water-borne epoxies, water-borne contact adhesives, formable and foamed hot melts

1990s: Polyurethane-modified epoxy, curable hot melts, UV and light cure systems

2000s: Water-borne adhesives, reduced volatile organic compounds (VOCs), solvent-free one- and two-part adhesives

8.2 Acrylics

A number of acrylic resins are used for bonding cloth, plastics, leather and, in some cases, metal foils. The acrylic monomers most commonly used in adhesives are ethyl acrylate, methyl acrylate, methacrylic acid, acrylic acid, acrylamide, and acrylonitrile. The polymers or copolymers are soluble in common organic solvents and can be supplied in much the same manner as other solvent-based systems. In addition, the polymers are soluble in the monomers. When a catalyst is added, monomers polymerize, thus providing good bonding to glass and to plastic surfaces of similar composition (e.g., polymethylmethacrylate).[2–4]

A variety of acrylic copolymers are prepared by emulsion polymerization. A number of acrylic adhesives, called “reactive adhesives,” “modified acrylics,” “second-generation acrylics,” or “reactive-fluid adhesives,” have become available over the years. These formulations polymerize in the glue line and become an integral part of an adhesive assembly.

The “first-generation acrylic adhesives” cover adhesives that used solutions of polymers, usually rubber, in methacrylate monomers and involved polymerization of these monomers in the presence of a reinforcing resin. The newer compounds are based on a combination of different modifying polymers for acrylics and a surface activator. A modifying polymer reinforces and toughens the bond and provides a reactive chemical site, which acts as a catalyst in the presence of special activators. Adhesion happens when the monomers and activators graft polymerize in modifying the polymer in the glue line.

In commercial form, these acrylic adhesive systems consist of two components, each being a 100% solids composition in fluid form, reacting to form an adhesive film. Curing takes place by a free-radical reaction scheme. As a result, these materials do not require careful metering and accurate mixing for full performance. Other advantages include as follows:[3–5]

- Tolerance for oily and otherwise poorly prepared surfaces
- Rapid bonding at room temperature, which can be further accelerated by an increase in the temperature or the use of accelerators
- Low shrinkage during cure
- High peel and impact strength, combined with excellent shear strength
- Good environmental resistance and elevated-temperature properties (up to 177 °C)

Excellent bonds to a wide variety of substrates can be obtained. Aluminum, brass, copper, stainless steel, and carbon steel are easily bonded to similar or dissimilar metals. Most plastics, including glass-reinforced grades, can also be bonded, along with wood, glass, cement-asbestos board, and hardboard.

Some adhesives will bond cured elastomers. Typically, a thin layer (0.0025-mm thickness) of the activator is applied to one of the adherends and a layer of the adhesive (0.026–0.26 mm) is placed on the other adherend. The two substrates are then pressed together and secured until adequate handling strength develops. Most acrylic adhesives cure to this point in 2–20 min, but some cure in as little as 10 s. In all cases, cure is completed within 24 h. These adhesives provide excellent shear, peel, and impact strengths at temperatures ranging from −107 °C to +121 °C. These adhesives can withstand short exposures of up to 177 °C.[3–5]

Bonds made with acrylics typically resist immersion in isooctane, motor oil, aircraft hydraulic fluid, 10% sodium chloride solution, distilled water, ethyl alcohol, and dilute mineral acids and alkalis. However, they are not resistant to concentrated acids and alkaline solutions or acetone. Weathering resistance, including salt spray environments, is also excellent.

Acrylic adhesives can be used to replace spot welding where immediate handling of the joined metal parts is required. Another broad area of application is for bonding dissimilar substrates, including metals and other materials, with different coefficients of expansion.[3–5]

8.3 Allyl Diglycol Carbonate (CR-39)

See Section 8.35 on polyester adhesives.

8.4 Alloyed or Modified (Two-Polymer) Adhesives

These adhesives are important as *structural* adhesives, especially in metal bonding. They are comprised of a thermosetting and a thermoplastic polymer, including certain elastomers. Although each component has adhesive properties by itself, on the whole, the conjoint system forms a stronger and more versatile adhesive. The two-polymer systems have been particularly successful as film and tape adhesives, with applications ranging from building construction to aerospace.[6]

The physical properties of each component polymer are modified by the addition of the other, possibly increasing heat resistance of one component, while reducing that of the other. Similarly, the toughness of one may be increased by sacrificing the flexibility of the other. Therefore, it is possible to formulate a variety of adhesives with a wide range of characteristics by simply varying the ratio of one polymer to the other.

In most widely used two-polymer adhesives, the thermosetting component is phenolic. Phenolic resins are generally compatible, although not easily miscible, with a number of thermoplastic polymers. Particularly good compatibility is demonstrated between conventional alcohol-soluble phenolic resins and polyvinyl esters and acetals. Epoxies are important in two-polymer adhesive systems. The most important thermoplastic components are the polyvinyl acetals (polyvinyl formal and butyral) and synthetic rubber, particularly nitrile rubber. Soluble nylons are also an important class.[7]

Five of the most important two-polymer adhesives used in films and tapes include vinyl-phenolics, epoxy-phenolics, nitrile-phenolics, nylon-epoxies, and elastomer-epoxies. Neoprene-phenolics are available in organic solutions and in supported and unsupported films. These adhesives are used to bond a variety of substrates. Curing takes place under heat and pressure at 150−260 °C and 0.3−1.75 MPa for 15−30 min for film and at 90 °C and contact to 0.7 MPa of pressure for 15−30 min for the liquid, after drying at 90 °C. Because of their high resistance to creep and most service environments, neoprene-phenolic joints can withstand prolonged stress. Fatigue and impact strengths are excellent, but shear strength is lower than that of other modified phenolic adhesives.[5,8,9]

The geometrical factors defining an adhesive joint are of great importance, as the design of the adhesive joint greatly conditions the performance of the bonding. One of the most relevant geometrical factors is the thickness of the structural adhesive, as it decisively influences the mechanical properties of the bonding and has a clear economic impact on the manufacturing processes or long runs. Structural adhesive joints are only selected in industrial applications, demanding mechanical requirements and adverse environmental conditions if the suitable reliability (the same or higher than the mechanical joints) is guaranteed. A study[10] published in 2010 has analyzed the influence of the adhesive thickness on the mechanical behavior of the joint and, by means of a statistical analysis based on Weibull Distribution, proposes the optimum thickness for the adhesive, combining the best mechanical performance and high reliability. The procedure, which is applicable without a great deal of difficulty to other joints and adhesives, provides a general use for more reliable adhesive bonding and, therefore, for better and wider use in industrial manufacturing processes.

Epoxy polysulfides[11] are available as two-part liquids or pastes that cure at room temperature or higher to rubbery solids that provide bonds with excellent flexibility and chemical resistance. These adhesives bond well to a number of substrates. Shear strengths and elevated-temperature properties are low, but resistance to peel and low-temperature properties are quite high.

Of the five alloy-tape adhesives, vinyl-phenolic is also available in solvent-based solution and emulsion, liquid, and co-reating powder. Epoxy-phenolic is also available as a two-part paste. Solvent blends of this material are usually force-dried at 80−90 °C for 20 min before assembly of adherends. Curing is generally for 30 min at 95 °C with contact pressure, followed by 30 min to 2 h at about 165 °C and 0.07−0.4 MPa of pressure. Postcuring provides optimum strength at elevated temperatures.

Nitrile-phenolic and nylon-epoxy adhesives are also available as solvent solutions, as well as in film form. The nitrile-phenolic film is cured at 150–260 °C for 15–30 min, with bonding pressures from 0.12 to 1.8 MPa. The liquid alloy is dried at 80 °C and cured for 15–30 min at 90 °C and contact at 0.7 MPa of pressure. The nylon-epoxy paste is cured for 3 days at 20 °C to 1 day at 150 °C under bonding pressure from 0.11 to 0.32 MPa. Cure temperatures for some formulations can be increased to 200 °C with corresponding reduction in cure time (4 h). No volatiles are released during cure, so large areas can be bonded without venting.[5,8,9]

8.5 Anaerobic Adhesives/Sealants

This adhesive group has been promoted for use as sealant. The adhesives used are acrylate acid diesters (polyester-acrylic). They are essentially monomeric thin liquids that polymerize to form a tough plastic bond when confined between closely fitting metal joints. Contact with air before use keeps the monomeric adhesive liquid. Metal surfaces accelerate the polymerization in the absence of air (anaerobic conditions). These materials will bond all common metals, glass, ceramics, and thermosetting plastics to each other. Phenolic plastics and some plated metals, such as cadmium and zinc, require a primer such as ferric chloride. Polymerization is essentially a free-radical-type addition polymerization.[12–14]

The most important application of anaerobic adhesives/sealants is as liquid lock washers for screws and bolts. Because of their strong penetrating ability, they can be applied either before or after assembly. The prevailing torque for the strongest grades is many times greater than that of locknuts and lock screws. Cure speed is largely dependent on the parts being joined. There are three basic cure-speed types—fast (5 min to 2 h), medium (2–6 h), and slow (6–24 h)—all at room temperature without primer. Addition of heat will speed up the cure. As a rule, these adhesives will cure outside the connection if the temperature exceeds 93 °C, despite the presence of inhibiting air. Heat cures of up to 149 °C are practical. Anaerobic adhesives can be cured faster with accelerators or primers, especially on inactive surfaces (nonmetals). The recommended primers are degreasing solvents, which, on evaporation, leave a light deposit of a catalyst to speed up curing.

These anaerobic adhesives fill all surface irregularities and tolerance gaps and effectively seal clearances of up to 0.76 mm. They can be applied by high-speed applications in moving production lines. The cured film has excellent chemical resistance to most liquids and gases within an operating temperature range of −54 °C to 232 °C.

Anaerobic structural adhesives combining urethane-modified acrylic technology have been developed for more exacting applications. These adhesives can be formulated to meet the requirements of Federal Specification MMM-A-132. Anaerobic sealants and thread-locking products are designed to withstand normal tensile and shear loading. The applications of these products often subject them to shear loading. Generally, anaerobic adhesives are recommended for use on metal surfaces. Some materials are more active than others and depending on the types of materials used curing may be faster or slower. Active and inactive materials are classified as follows:[15]

Very Active	Active	Inactive	Very Inactive
Brass	Aluminum	Anodize aluminum	Ceramics
Copper	Bronze	Cadmium	Composites
Manganese	Iron	Chrome finishes	Glass
	Kovar	Gold	Plastics
	Monel®	Inconel	Paint-coated parts
	Nickel	Magnesium	Paint-coated parts
	Steel	Plated parts	Rubber
		Galvanized steel	
		Stainless steel	
		Titanium	
		Zinc	

Anaerobic adhesives can now withstand continuous aging at 232 °C. Resistance to salt-spray is also excellent.[12–14]

An excellent, although perhaps outdated, source of information is a chapter on anaerobic adhesives by Burnham et al.[16]

8.6 Aromatic Polymer Adhesives (Polyaromatics)

Considerable progress has been made in improving the thermal and oxidative stabilities of organic resins at high temperatures. Heat-resistant resins and polymers have been developed as adhesives to meet the needs of the aircraft industry (supersonic aircraft) and space vehicles (missiles, satellites, and rockets), where resistance to temperatures approaching 316 °C is required throughout the life of bonded assemblies based on metals and reinforced plastic composites. The oxidative stability of organic polymers is improved by the incorporation of aromatic and heterocyclic rings (such as imide, imidazole, and thiazole) into the molecules of the polymer.

The most important resins available for use as adhesives in high-temperature structural applications are polybenzimidazoles (PBIs) and polyimides (PIs), both of which are described later (see Sections 8.34 and 8.36). These resins are supplied as prepolymers containing open heterocyclic rings, which are soluble and fusible. At elevated temperatures, the prepolymers undergo condensation reactions that lead to ring closure and formation of insoluble and infusible cured resins.[8]

The high-temperature adhesives are available in film and tape form. They show better bond strengths above 260 °C in air than epoxy-phenolic, although the latter gives better strength retention after exposure to water or other polar liquids at lower temperatures. The major disadvantages are their high cost, generally 10 or more times that of epoxy-based adhesives, the difficulty in handling or curing, and the problems involved in the elimination of volatiles during cure to obtain a void-free bond. A long and careful series of cure and postcure steps at progressively increasing temperatures of up to the 316–371 °C range, coupled with intermittent application and release of high-clamping pressure, is required to obtain optimum results. Currently, only PIs can be used in the 260–427 °C service temperature range.[17–19]

Glass transition temperature of aromatic adhesives can be tailored by blending them with polymers such as ethylene vinyl acetate (EVA) copolymers. These blends have been studied[20] and showed a glass transition temperature at about −25 °C and a melting peak between 30 °C and 100 °C. The peaks of loss modulus increased with increasing softening point of the aromatic hydrocarbon resin. The melt viscosity of the blends decreased with increasing temperature. Also, the melt viscosity increased with increasing softening point but decreased with increasing aromatic hydrocarbon resin and vinyl acetate content. Increasing the softening point of the aromatic hydrocarbon resins, in cases of the same blend ratio, increased the crystallinity, whereas the addition of aromatic hydrocarbon resin decreased the crystallinity. Also, increasing the vinyl acetate content decreased the crystallinity of the blend because of a decrease in the crystalline region of ethylene. The lap-shear strength increased with increasing softening point of the aromatic hydrocarbon resin. The lap-shear strength also increases with increasing concentration of aromatic hydrocarbon resin, until it reached a maximum value.

8.7 Asphalt

Asphalt is a low-cost thermoplastic material, which is highly temperature dependent. The addition of a thermoplastic rubber at 1–5% by weight greatly reduces the dependence of viscosity on temperature. Useful operating temperature ranges can often be doubled in this manner. The addition of a thermoplastic rubber, such as butyl rubber or polyisobutylene, at 10–30% by weight, produces a truly thermoplastic product with elasticity, resilience, and high cohesive strength. Such mixtures are useful as sealants. Asphalt emulsions are used to increase solid content, improve water resistance, and lower the cost of laminating adhesives. Such adhesives are used in laminating paper and other packing materials where a water-barrier layer is required. Another important application is in roofing and flooring adhesives.[2,21,22]

8.8 Butyl Rubber Adhesives

Butyl rubber is an elastomeric polymer used widely in adhesives and sealants, both as primary binders and as tackifiers and modifiers. Butyl rubber is a copolymer of isobutylene with a small amount of isoprene.[23] These materials have relatively low strength and tend to exhibit creep under load. They are useful in packaging applications where their low permeability to gases, vapors, and moisture can be exploited. Butyl rubber is also used as an adhesive sealant. It is generally applied from a solvent-based solution.[2,7] Table 8.1 summarizes some of the important properties of butyl rubber adhesives.

8.9 Cellulose Ester Adhesives

These include cellulose acetate, cellulose acetate butyrate, cellulose cap-rate, and cellulose nitrate (nitrocellulose or pyroxylin). Cellulose esters are used for bonding leather, paper, and wood. Although not generally used with metals, specific nonporous substrates such as cellophane (regenerated cellulose) and glass are sometimes bonded with cellulose nitrate or other cellulose esters applied from solution.[2,8]

Cellulose acetate and cellulose acetate butyrate are water clear and more heat resistant, but less water resistant, than cellulose nitrate. Cellulose acetate butyrate has better heat and water resistance than cellulose acetate and is compatible with a wide range of plasticizers. Cellulose nitrate is tough, develops strength rapidly, is water resistant, bonds to many surfaces, and discolors in sunlight. The dried adhesive (nitrocellulose) is highly flammable.[7,24]

8.10 Cellulose Ether Adhesives

These include ethyl cellulose, hydroxy ethyl cellulose, methyl cellulose, sodium carboxy methyl cellulose, and benzyl cellulose. Ethyl and benzyl cellulose can be used as hot-melt adhesives. Methyl cellulose is a tough material, completely nontoxic, tasteless, and odorless, which makes it a suitable adhesive for food packages. It is capable of forming high-viscosity solutions at very low concentrations, so it is useful as a thickening agent in water-soluble adhesives. Hydroxy ethyl cellulose and sodium carboxy methyl cellulose can also be used as thickeners. The cellulose ethers have fair to good resistance to dry heat. Water resistance varies from excellent for benzyl cellulose to poor for methyl cellulose.[7,8,24]

8.11 Conductive Adhesives

Appropriate fillers have been used to produce adhesives with high thermal or electrical conductivity for specialized applications. The basic resins used include epoxies, urethanes, silicones, and polysulfones. Epoxies, however, are the most widely used resins.[25–27]

Tin–lead solder alloys are widely used in the electronics industry.[28] They serve as interconnects that provide the conductive path required to achieve connection from one circuit element to another. There are increasing concerns with the use of tin–lead alloy solders in recognition of hazards of using lead. Lead-free solders and electrically conductive adhesives (ECAs) have been considered as the most promising alternatives of tin–lead solder. ECAs consist of a polymeric resin (such as an epoxy, a silicone, or a polyimide) that provides physical and mechanical properties such as adhesion, mechanical strength, and impact strength, and a metal filler (such as silver, gold, nickel or copper) that conducts electricity. ECAs offer numerous advantages over conventional solder technology, such as environmental friendliness, mild processing conditions (enabling the use of heat-sensitive and low-cost components and substrates), fewer processing steps (reducing processing cost), low stress on the substrates, and fine pitch interconnect capability (enabling the miniaturization of electronic devices). Therefore, conductive adhesives have been used in liquid crystal display and smart card applications as an interconnect material and in flip–chip assembly, chip scale package, and ball grid array applications in replacement of solder. However, no currently commercialized ECAs can replace tin–lead metal solders in all applications because of some challenging issues such as lower electrical conductivity, conductivity fatigue (decreased conductivity at elevated temperature and humidity aging in normal use conditions) in reliability testing, limited current-carrying capability, and poor impact strength. Considerable research has been conducted recently to study and optimize the performance of ECAs, such as electrical, mechanical, and thermal behaviors improvement, as well as reliability enhancement under various conditions. This review article will discuss the materials, applications, and recent advances of ECAs as an environmental friendly solder replacement in the electronics packaging industry.

Table 8.1 Properties of Elastomeric Polymers in Nonstructural Applications[7]

	Adhesives			
	Natural Rubber (Polyisoprene)	**Reclaimed Rubber**	**Butyl Rubber**	**Polyisobutylene**
Description	Solvent solutions, latexes, and vulcanizing type	Solvent solutions, some water dispersions; most are black, some gray and red	Solvent system, latex	Solvent solution
Curing method	Solvent evaporation, vulcanizing type by heat press RT (two-part)	Evaporation of solvent	Solvent evaporation, chemical cross-linking with curing agents and heat	Evaporation of solvent
Usual adherends	Natural rubber, masonite, wood, felt, fabric, paper, metal	Rubber, sponge rubber, fabric, leather, wood, metal, painted metal, building materials	Rubber, metals	Plastic film, rubber, metal foil, paper
Advantages	Excellent resilience, moisture, and water resistance	Low cost, applied very easily with roller coating, spraying, dipping, or brushing; gains strength rapidly after joining; excellent moisture and water resistance	Excellent aging characteristics; chemically cross-linked materials have good thermal properties	Good aging characteristics; used as tackifiers in other adhesives; also provide softness and flexibility and improve adhesion by "wetting out" substrates
Limitations	Becomes quite brittle with age; poor resistance to organic solvents; does not bond well to metals	Becomes quite brittle with age; poor resistance to organic solvents	Metals should be treated with an appropriate primer before bonding; attacked by hydrocarbons	Attacked by hydrocarbons; poor thermal resistance
Special characteristics	Excellent tack, good strength, shear strength 0.21–1.23 MPa; peel strength 98.1 N/m; surface can be tack-free to touch and yet bonds to similarly coated surface	Low cost, widely used; peel strength higher than natural rubber; failure occurs under relatively low constant loads	Low permeability to gases, good resistance to water and chemicals, poor resistance to oils, low strength	Sticky, low-strength bonds; copolymers can be cured to improve adhesion, environmental resistance, and elasticity; good aging resistance; poor thermal resistance; attacked by solvents

	Adhesives		
	Nitrile Rubber	**Styrene-Butadiene Rubber (SBR)**	**Polyurethane**
Description	Latexes, solvent solutions compounded with resins, metallic oxides, fillers, etc.	Solvent solutions and latexes; because tack is low, rubber resin is compounded with tackifiers and plasticizing oils	Two-part liquid or paste
Curing method	Evaporation of solvents and/or heat pressure	Evaporation of solvent	RT or higher
Usual adherends	Rubber (particularly nitrile), metal, vinyl plastics	Fabrics, foils, plastic film laminate, rubber and sponge rubber, wood	Plastics, metals, rubber
Advantages	Most stable synthetic rubber adhesive, excellent oil resistance, easily modified by addition of thermosetting resins	Good heat aging and water resistance; uniform appearance, non-staining light color, disperses easily in hydrocarbon solvents; low cost	Excellent adhesion at cryogenic temperatures and excellent retention of elasticity and shock resistance at these temperatures
Limitations	Does not bond well to natural rubber or butyl rubber	Strength characteristics poor; tendency to creep, lack of tack requires a tackifier for use in adhesives	Poor resistance to hydrolytic degradation (reversion), even in the polyether type
Special characteristics	Most versatile rubber adhesive; superior resistance to oil and hydrocarbon solvents; inferior in tack range, but most dry tack-free, an advantage in precoated assemblies; shear strengths of 1.03–13.8 MPa, higher than neoprene, if cured	Usually better aging properties than natural or reclaimed rubber; low dead-load strength similar to reclaimed rubber; useful temperature range from –40 °C to 71 °C	Excellent tensile shear strength from –240 °C to 93 °C; poor resistance to moisture before and after cure; good adhesion to plastics

(*Continued*)

	Adhesives		
	Polysulfide (Thiokols)	**Silicone**	**Neoprene (Chloroprene)**
Description	Two-part liquid or paste	Solvent solution: heat or RT-curing and pressure sensitive; RT-vulcanizing solvent-free pastes	Latexes and solvent solutions, often compounded with resins, metallic oxides, fillers, etc.
Curing method	RT or higher	Solvent evaporation, RT or elevated temperature	Evaporation of solvent
Usual adherends	Metals, wood, plastics	Metals, glass, paper, plastics, rubber (including silicone and butyl rubber), and fluorocarbons	Metals, leather, fabric, plastics, rubber (particularly neoprene), wood-building materials
Advantages	Resistance to water, organic solvents, greases, oils, salt water; excellent aging and weathering resistance; superior low-temperature flexibility (flexible down to –62 °C)	Retain flexibility (peel) over a wide temperature range; resistant to moisture, hot water, oxidation, corona discharge, and weathering	Good resistance to water, salt spray, biodeterioration, aliphatic hydrocarbons, acetone and ethyl alcohol, lubricants, weak acids and alkalis; shows good shear and peel strengths
Limitations	Poor high-temperature resistance; usually softens at 70–94 °C, with little strength retention above 120 °C	Some forms (acid-curing) may corrode electrical equipment	Unsuitable for contact with aromatic and chlorinated hydrocarbons, certain ketones, and strong oxidizing agents; cold flow at shear strengths >2.9 MPa
Special characteristics	Resistant to a wide range of solvents, oils, and greases, good gas impermeability; resistant to water, sunlight, ozone; retains flexibility over a wide temperature range; not suitable for permanent load-bearing applications	Of primary interest in pressure-sensitive type used for tape; high strengths for other forms are reported from –73 °C to 260 °C; limited service to 371 °C; excellent dielectric properties	Superior to other rubber adhesives in most respects—strength, quick-setting; maximum temperature to 93 °C, sometimes 177 °C; good aging resistance; resistant to light, weather, mild acids, and oils

8.11.1 Electrically Conductive Adhesives (Chip-Bonding Adhesives)

Synthetic resins are made electrically conductive by the addition of either metallic fillers or conductive carbons. The carbon can be either an amorphous carbon, such as acetylene black, or finely divided graphite. Usually finely divided silver flake is used in conductive epoxies and conductive coatings. An advantage of silver is that it has moderately conductive salts and oxides, so that slight oxidation or tarnishing can be tolerated. The resistivity techniques give much lower values than methods involving thin glue lines, such as ASTM D2739-97(2004), where interfacial resistance plays an important role.[25]

Silver is preferable to gold as filler, because it is less costly and has lower resistivity. Under conditions of high humidity and DC voltage, however, silver is reported to undergo electrolytic migration to the surface of the adhesive. Microspheres of silver-coated copper do not migrate, nor does gold. The highest silver loading possible is about 85% by weight. Silver loadings lower than about 65% by weight cause sharp drops in conductivity but offer higher adhesive strengths. Carbon (graphite) gives fairly low conductivities.

Aside from silver and gold, other common metallic fillers include nickel, aluminum, and copper. Each of these metals presents particular compounding problems. Silver is often used in flake form, therefore making it more difficult to achieve particle-to-particle contact than with spherical metal particles. A stearate coating is applied to the silver flake to improve its dispersibility. The stearate tends to outgas at elevated temperatures. The out-gassing may contaminate critical parts, such as those in microelectronic applications. Some silver products are uncoated and do not evolve out-gassing products. Copper and aluminum form oxide films, which reduce electrical conductivity by hampering particle-to-particle contact.[25]

Electrically conductive adhesives are used in microelectronic assemblies.[29] These applications include attachment to fine lead wires to printed circuits, electroplating bases, metallization on ceramic substrates, grounding metal chassis, bonding wire leads to header pins, bonding components to plated-through holes on printed circuits, wave-guide tuning, and hole-patching. Conductive adhesives are applied as substitutes for spot welding when welding temperatures build up excess resistance at the weld because of oxide formation.

Another application is in ferroelectric devices used to bond electrode terminals to the crystals in stacks. These adhesives replace solders and welds where crystals tend to be deposited by soldering and welding temperatures. Bonding of battery terminals is another application when soldering temperatures may be harmful. Conductive adhesives form joints with sufficient strength, so they can be used as structural adhesives where electrical continuity, in addition to bond strength, is required, as in shielded assemblies.[30] Sharpe et al.[31] have published an excellent comprehensive review of ECAs.

8.11.2 Thermally Conductive Adhesives

The use of thermally conductive adhesives in electrical/electronic assemblies has been described.[29,31] In these applications, temperature rising due to evolution of heat from tubes, resistors, transformers, and so on in high-density circuits is often critical and a cause for concern. Design considerations for these applications must include thermally conductive parts for removing heat from the circuitry involved. This circuitry may or may not be encapsulated. In confined circuitry, as on a printed-circuit board, nonencapsulated heat sinks bonded in place is one solution. In this case, aluminum is usually the preferred heat-sink material because of its lightweight and high thermal conductivity. If good dielectric properties are required, a high concentration of inorganic or mineral fillers can be used.

A typical thermally conductive epoxy system used as an adhesive, as well as for other purposes, has a thermal conductivity of 0.0026 cal/cm/sec/°C and a volume resistivity of 1.5×10^{15} ohm.cm (1.5×10^{13} ohm.m). Fillers include alumina (aluminum oxide), beryllia (beryllium oxide), other unspecified inorganic oxides, boron nitride, and silica. Boron nitride is an excellent choice as a thermally conductive filler, except that its content reaches a maximum at about 40% by weight in epoxy resins. The resultant products are always thixotropic pastes. Beryllia powder has excellent thermal conductivity by itself, but when mixed with a resin binder, its conductivity drops drastically. It is also highly toxic and high in cost. Alumina is a commonly used filler to impart thermal conductivity in resins.[25]

8.12 Cyanoacrylate Adhesives

These so-called "wonder" adhesives are marginally thermosetting materials and were first introduced commercially by Eastman Chemicals. They form strong thermosetting bonds between many materials without heat or an added catalyst. They are particularly useful in bonding metal to nonmetal. Lap-shear strengths of 13.7 MPa have been reported. However, the resistance of these adhesives to moisture is still somewhat low.[2] These materials set very quickly when squeezed out to thin film between many types of adherends.

A cyanoacrylate adhesive is a very rapid curing adhesive, also from the acrylic family tree but having a completely different cure system. Cyanoacrylate monomer is made from a complex chemical process. The monomer produces a very reactive polymerization. The reaction or polymerization process is stabilized and the monomer kept in the liquid state by the addition of a small amount of an acid stabilizer material.[1]

When a drop of cyanoacrylate adhesive is put on the surface of a part, the acid stabilizer molecules react with the water molecules present on the surface of the part from the relative humidity in the air. The reaction of the water and acid causes the acid stabilizer to be neutralized. The cyanoacrylate molecules then react with each other and form polymer chains without cross-linking.[1]

The amount of stabilizer molecules in cyanoacrylate is very small—measured in parts per million—and very little moisture molecules are required to cause rapid polymerization. Cyanoacrylates begin to form polymer chains immediately on contact with the water vapor on the surface of the part. If parts are moved during initial contact, the polymerization process and polymer chains are stopped. The process must start again at a new catalyzed site.[1]

Cyanoacrylates are very rapid curing and provide high bond strengths on plastic and rubber materials. The versatility of these adhesives makes them highly useful in all industries. Some of the larger application areas are in electronics for printed circuit board wires and components and in medical technology for disposable plastic medical devices. Other applications include toy, small and large appliance, automotive, and cosmetic packaging. Applications exist in all industries for repair of all rubber and plastic parts, as well as some metal parts. The consumer market is a large volume user of cyanoacrylate adhesives for repairing everything in the home from wallpaper tears to broken toys to torn and false fingernails.

Cyanoacrylate adhesive can be made from different acrylate monomers such as methyl, ethyl, butyl, isopropyl, and so on. These molecules differ in size and adhesives and exhibit different physical properties. Methyls are the smallest molecule and seem to work best on metal and rubber parts while ethyls work best on plastic parts. Many modifications can be made to the monomers to alter or improve their properties as adhesives. They can be toughened with rubber or formulated to have low odor, resistance to thermal cycling, or less sensitivity to surface conditions which tend to stabilize the adhesive and slow down the cure.[1]

As with other acrylics, the monomers are liquids of low viscosity that polymerize very easily in the presence of a slightly basic surface containing adsorbed water. Polymerization is ionic. The resulting polymers have different properties, depending on the alkyl group. The methyl ester (methyl-2-cyanoacrylate) is the most commonly used compound. This material is formulated with a thickener (to prevent *starved* joints from being formed) and a plasticizer to make it more resistant to shock loading. The thickener can be a polymer of the same monomer. An essential feature is a *stabilizer* to prevent polymerization in the adhesive container, which is usually made of polyethylene.[32]

The polymerization of cyanoacrylates is inhibited by low pH (high acidity); thus it does not proceed satisfactorily on acid surfaces such as wood. The suggested incorporation of poly-*N*-vinyl pyridine or polyethyleneamine, or even simple amines, presumably serves the dual purpose of thickening the liquid and increasing the pH.

Adhesives based on higher homologs than the methyl form have been in use for a number of years. These include the ethyl, propyl, and butyl esters of cyanoacrylic acid. Moisture resistance of the methyl-2-cyanoacrylate is only fair. Ethyl cyanoacrylate has been shown to form stronger bonds than the methyl form between several different types of plastic surfaces. The higher homologs, however, generally do not form bonds as strongly as the methyl form.[33]

The most important step in the successful application of a cyanoacrylate adhesive is the application of a thin adhesive film between two well-mated surfaces. The thinner the film is, the faster the rate of bond formation, and the higher the bond strength. Bond strength is dependent on proper surface preparation.

In general, aging properties of the cyanoacrylates are good. Rubber-to-rubber and rubber-to-metal bonds typically have endured outdoor weathering for more than 7 years. These bonds have also passed stringent water-immersion and salt-spray tests. Plastic-to-plastic and plastic-to-rubber bonds have aged satisfactorily for 3−5 years. Metal-to-metal bonds generally age rather poorly, except under special conditions whereby the minimal glue line is exposed to moisture. Solvent resistance is also generally satisfactory. Dilute alkaline solutions weaken the bond considerably, whereas dilute acid solutions weaken it to a lesser degree. Impact resistance is generally poor because of the thin, inflexible bond.

This is especially true with two rigid substrates, such as metals. The methyl cyanoacrylate bond melts at approximately 165 °C. Prolonged exposure to temperatures in this range results in a gradual but permanent breakdown of the bond. Generally, the upper temperature limit for continuous exposure is about 77 °C. At low temperatures, bonds remain intact at least down to −54 °C. Grades of cyanoacrylates with specialized improved properties are available. For example, one grade has improved heat resistance to 246 °C, high viscosity, and very fast setting ability.[33]

Among the advantages of the cyanoacrylates are the following:

- Very fast bond formation
- High bond strength with thin glue line
- No added catalyst or mixing needed
- No solvent to evaporate during bond formation
- Contact pressure is usually sufficient
- Very low shrinkage
- Economical because of minute quantities needed, although relatively expensive

The Loctite Corporation offers a rubber-toughened cyanoacrylate adhesive, dubbed 380 *Black Max*®, that is reported to achieve improved strength, resiliency, and fast fixturing at the expense of a rather limited shelf life (about 4 months).[34] This adhesive cures to *fixturing* strength in 2 min in the case of most substrates. It reaches 80% strength in 24 h and full strength in 72 h (Table 8.2). On aluminum, its average strength is 16.6 MPa after full room temperature cure, versus 6.2 MPa for a typical epoxy

Table 8.2 Typical Performance of Cured Loctite 380 Cyanoacrylate Adhesive[34]

Adhesive properties	**N/mm^2 (psi)**
After 24 h at 22 °C	
Lap-shear strength, ISO 4587	
Steel (grit-blasted)	26 (3770)
Aluminum (etched)	18 (2610)
ABS	>6 (>870)
PVC	>4 (>580)
Polycarbonate	>5 (>725)
Phenolic	10 (1450)
Neoprene	>10 (>1450)
Nitrile	>10 (>1450)
Tensile strength, ISO 6922	
Steel (grit-blasted)	18.5 (2700)
After 48 h at 22 °C	
Lap-shear strength, ISO 4587	
Steel (grit-blasted)	$\geq 17.2^{\mathrm{LMS}}$ (≥ 2495)
Cured for 24 h at 22 °C, followed by 24 h at 121 °C, tested at 121 °C	
Lap-shear strength, ISO 4587	
Steel (grit-blasted)	$\geq 6.9^{\mathrm{LMS}}$ (≥ 1000)
Cured for 24 h at 22 °C, followed by 24 h at 121 °C, tested at 22 °C	
Lap-shear strength, ISO 4587	
Steel (grit-blasted)	$\geq 19.3^{\mathrm{LMS}}$ (≥ 2800)

adhesive and 3.8 MPa for "instant" adhesives. After 240 h of tensile-shear thermal-cycling tests, this adhesive improved its strength to 21.3 MPa for "instant" adhesive. Loctite claims that this adhesive is consistently 20 times stronger than epoxies on aluminum, 10 times stronger on neoprene, 4 times stronger on steel, and 2 times stronger on epoxy/glass after the tests. This adhesive is designed for assembly-line cure.[35]

8.13 Delayed-Tack Adhesives

In the packaging field, acrylics are often used for delayed-tack adhesive coatings for labels. Copolymer dispersions of acrylic ester with vinyl acetate, vinyl chloride, or styrene are usually employed for these applications. The backing material, usually paper, is coated after the dispersion has been modified accordingly. The coated papers are tack-free under normal conditions, so the sheets and cuttings can be rolled up or stacked. These adhesives consist primarily of one or a mixture of polymer film formers in dispersion form and one or several crystalline plasticizers. The plasticizer is usually employed in dispersion form with small particle size. Resin solutions or dispersions are added as additives for obtaining certain adhesive effects. The adhesive coating must be dried at a temperature below the melting point of the plasticizer to obtain a tack-free product.[36]

Labels produced in this manner are applied according to the following procedure. The adhesive coat is heated directly by infrared radiation or hot air, or by hot plates from the reverse side, to a temperature above the melting point of the plasticizer. The polymer is plasticized (i.e., the coating is tackified by the molten plasticizer, which is present in excess). Under this condition, the label can be bonded to the substrate by applying a slight pressure. Adhesion to glass, metals, polyvinyl chloride (PVC), wood, and so on, is durable even after the plasticizer has recrystallized.[36]

Other polymers that can provide delayed-tack adhesives include styrene-butadiene copolymers, polyvinyl acetate, polystyrene, and polyamides. Solid (crystalline) plasticizers for these adhesives include dicyclohexyl phthalate, diphenyl phthalate, *N*-cyclohexyl-*p*-toluene sulfonamide, and *o*/*p*-toluene sulfonamide. Adhesives with different heat-activation temperatures could be obtained because of the range of melting points available. Delayed-tack adhesives have a large number of uses, such as coating paper for labels on bread packages, cans, and so on.

More recently, adhesives and sealants have been developed[37] from novel anionic block copolymers of mono alkenyl arenes and conjugated dienes, and to blends of such block copolymers with other polymers. The block copolymers were selectively hydrogenated and have mono alkenyl arene end blocks and controlled distribution blocks of mono alkenyl arenes and conjugated dienes. The block copolymer could also be combined with tackifying resins, oils, and other components to form the adhesives and sealants for various applications.

In another development,[38] a delayed-tack adhesive composition exhibiting a high tack strength even for adherends made of nonpolar materials such as polyethylene and polypropylene, which comprises a (co) polymer, was prepared by the use of a radical-polymerizable monomer having a straight-chain or branched alkyl group having 9−18 carbon atoms and a plasticizer being solid at ordinary temperatures.

Another reported invention[39,40] was concerned with a thermal delayed tack composition that is nonadhesive at ordinary temperatures but could be activated and tackified when heated, and would maintain its tackiness for a long period of time even after separation from a heat source; and thermal delayed tack sheets were prepared by coating basic sheets with this thermal delayed tack composition and then drying the same. The thermal delayed tack sheets had the features that even when wound into a roll or superimposed upon each other, no blocking or sticking occurred, and the tackiness thereof was maintained for a long period of time even upon a plastic material (polyethylene, for example) having low polarity. The aforesaid thermal delayed tack composition comprised an aqueous resin dispersion containing, as fundamental components, solid components of (a) 100 parts by weight of a polymer resin containing 1% by weight or more of carboxylic acid-modified polyethylene, (b) 10−120 parts by weight of a tackifier, and (c) 50−300 parts by weight of a solid plasticizer. The thermal delayed tack sheets could also be prepared by aqueously coating the basic sheets with the above-mentioned composition and then drying the same.

8.14 Elastomeric Adhesives

Most of these adhesives are natural or synthetic rubber-based materials, usually with excellent peel strength but low shear strength. Their resiliency provides good fatigue and impact properties. Except for silicone, which has high temperature resistance, their uses are generally restricted to temperatures in the range of 66−93 °C. A significant amount of creep (flow-under-load) occurs at room temperature. The basic types of elastomeric adhesives used for nonstructural applications are shown in Table 8.1. These systems are generally supplied as solvent-based solutions, latex, cements, and pressure-sensitive tapes.

Solvent solutions and latex cements require the removal of the solvent from the adhesive before bonding can take place. This is accomplished by simple or heat-assisted evaporation. Some of the stronger or more environmentally resistant rubber-based adhesives require an elevated-temperature cure. Only slight pressure is usually required for pressure-sensitive adhesives (PSAs) to obtain a satisfactory bond. These adhesives are permanently tacky and flow under pressure; thus, they provide intimate contact with the adherend surface.

In addition to PSAs, elastomers are used in the construction industry for mastic compounds. Neoprene and reclaimed rubber mastics are used to bond gypsum board and plywood flooring to wood framing members. The mastic systems cure by evaporation of solvent through the porous substrates. Elastomer-adhesive formulation is particularly complex because of the need for antioxidants and tackifiers.[7]

Table 8.1 summarizes the properties and characteristics of elastomeric adhesives for nonstructural applications. Individual elastomeric adhesive types are discussed in this chapter under separate headings.

8.15 Epoxy Adhesives

In the unhardened state, the chemical structure for an epoxy resin is characterized by the epoxide group, shown in Fig. 8.1.

All epoxy compounds contain two or more of these groups. Epoxy resins may vary from low-viscosity liquids to high-melting point solids. More than two dozen types are known. Tens of curing agents, including commonly available compounds such as amines, primary and secondary amines, and anhydrides, are used. Only a few of these are used widely in adhesive formulations.[30]

Of all the thermosetting plastics, epoxies are more widely used than any other plastic, in a variety of applications. There are resin/hardener systems (two-part) that cure at room temperature, as well as one-part systems that require extreme heat cures to develop optimum properties (e.g., 121 °C and

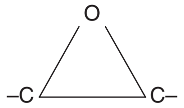

Figure 8.1 Chemical structure of epoxide group.

177 °C). Proper selection of various hardeners, resins, modifiers, and fillers allows the development of desired properties for a particular application. Because of the wide versatility and basic adhesive qualities, epoxies make excellent structural adhesives that can be engineered to widely different specifications. Essentially no shrinkage occurs during polymerization because epoxies are completely reactive, producing no volatiles during cure. Epoxy adhesives can be formulated to meet a wide variety of bonding requirements. Systems can be designed to perform satisfactorily at a temperature of −157 °C or at 204 °C.[41]

Epoxy adhesives form strong bonds to most materials, in addition to excellent cohesive strength (good attraction to itself). Epoxy adhesives also have excellent chemical resistance and good elevated-temperature capabilities. As with many other structural adhesives, to obtain maximum strength, particularly under adverse conditions, substrate surfaces must be prepared carefully. Epoxies yield good to excellent bonds to steel, aluminum, brass, copper, and most other metals. Similar results are obtained with thermosetting and thermoplastic plastics, as well as with glass, wood, concrete, paper, cloth, and ceramics. The adherends to which epoxy is being bonded usually determine the adhesive formulation. Epoxy adhesives have relatively low peel strengths.[41]

One-part epoxy adhesives include solvent-free liquid resins, solutions in solvent, liquid resin pastes, fusible powders, sticks, pellets and paste, supported and unsupported films, and preformed shapes to fit a particular joint. Two-part epoxy adhesives are usually composed of the resin and the curing agent, which are mixed just prior to use. The components may be liquids, putties, or liquid and hardener powder. They may also contain plasticizers, reactive diluents, fillers, and resinous modifiers. The processing conditions are determined by the curing agent employed. In general, two-part systems are mixed, applied within the recommended pot life (a few minutes to several hours), and cured at room temperature for up to 24 h or at elevated temperatures to reduce the cure time. Typical cure conditions range from 3 h at 60 °C to 20 min at 100 °C.[8]

With an aliphatic amine (e.g., diethylenetriamine) as curing agent at room temperature, the resin is cured in 4−12 h to an extent sufficient to permit handling of the bonded assembly. Full strength develops over several days. A compromise between cure rate and pot life must be made. Too rapid a cure at room temperature results in the formation of an unspreadable mixture in the mixing pot. Heat buildup (exothermic reaction) can be restricted by lowering the temperature of the mixture, limiting the size of the batch, or using shallow mixing containers. Actions such as these will extend the pot life of the adhesive. Contact bonding pressures usually suffice but small pressures from 0.016 to 0.02 MPa result in more uniform joints with maximum strength. One-part systems incorporate a hardening agent that requires heat to activate curing. A period of 30 min at 100 °C is typical.[8]

8.15.1 Hardening Agents for Epoxy Adhesives

Hardeners used in curing bisphenol-A epoxy resins, the type most commonly used in adhesives, include the following:[24]

- *Aliphatic polyamine hardeners:* These are used in adhesive systems capable of curing at normal or slightly elevated temperatures. The most important examples are diethylenetriamine, triethylenetetramine, and diethylenepropylamine
- *Fatty polyamides:* These are condensation products of polyamines and unsaturated fatty acids. They are high-melting linear polyamides of the nylon type, containing carboxyl end groups and amide groups along the chain. The amount of hardener required for curing is large and the proportion is not critical. These materials are used to impart flexibility, as well as for curing. Fatty polyamides are probably the most widely used epoxy curing agents
- *Aromatic polyamine hardeners:* These mostly solid hardeners include metaphenylenediamine, diaminodiphenylmethane, and diaminodiphenyl sulfone. In general, these hardeners provide poorer bond strengths and are more sensitive to temperature cycling than the aliphatic amines. Shrinkage is also high
- *Anhydride hardeners:* These materials are organic polycarboxylic anhydrides. Most require severe curing cycles. They provide thermal stability superior to that of the amines. Anhydride-cured epoxies are often brittle and require a flexibilizer, which results in reduced heat and chemical resistance

- *Boron trifluoride hardeners:* Boron trifluoride monoethylamine melts at 95 °C and is used in one-part adhesives
- *Miscellaneous curing agents:* The most important is dicyandiamide, used frequently in metal bonding. This material melts at about 200 °C and is nonreactive at room temperature, and so it is convenient for use in a one-package adhesive in the form of a powder or rod

8.16 Epoxy-Phenolic Adhesives

These relatively expensive adhesives account for only a small fraction of the current usage of structural adhesives. They are used primarily for military applications designed for service between 149 °C and 260 °C. Epoxy-phenolics are blends of thermosetting phenolic and epoxy resins. They are supplied as viscous liquids, which may contain solvents, or as glass-cloth or fabric-supported films or tapes. They are often modified with fillers and thermal stabilizers.[17−19]

Solvent blends are usually force-dried at 80−90 °C for 20 min before assembly of adherends. Curing generally lasts for 30 min at 95 °C at contact pressure, followed by 30 min to 2 h at 165 °C and 0.07−0.4 MPa pressure. Postcuring is used to obtain optimum curing at elevated temperatures.[8]

Applications are for high-temperature structural bonding of metals including copper and its alloys, titanium, galvanized iron and magnesium, glass and ceramics, and phenolic composites. Epoxy-phenolics are also applied in bonding honeycomb sandwich composites. Liquid forms are often used as primers for tapes. These materials display excellent shear and tensile strength over a wide temperature range. Films give better strengths than liquid systems. Peel and impact strengths are usually poor.

Epoxy-phenolic film and tape adhesives have good resistance to weathering, aging, water, weak acids, aromatic fuels, glycols, and hydrocarbon solvents. The service-temperature range is from −60 °C to 200 °C, but special formulations are suitable for end uses at cryogenic temperatures down to −260 °C.[8]

8.17 Epoxy-Polysulfide Adhesives

These adhesives are products of reaction between an epoxy resin and liquid polysulfide polymer, usually catalyzed by an additional tertiary amine.[7] They are available as two-part liquids or pastes that are usually cured at room or higher temperatures to rubbery solids that provide bonds with excellent flexibility and chemical resistance. Epoxy-polysulfide adhesive forms satisfactory bonds to different substrates. Shear strength and elevated-temperature properties are low, but resistance to peel and low temperature is acceptable.[7,8]

Curing is usually for 24 h at 20 °C, or up to 20 min at 100 °C. Bonding pressures are low, in the range of 0.07−0.16 MPa. A disagreeable sulfur odor forms during processing, rendering ventilation necessary. Resistance to water, salt spray, hydrocarbon fuels, alcohols, and ketones is acceptable. Resistance to weathering properties is excellent.

Epoxy-polysulfide adhesives are suitable for use as low as to −100 °C and even lower temperatures. Some blends have been used down to liquid nitrogen temperatures of −198.5 °C. The maximum service temperature is about 50 °C to 71−82 °C.[42,43] The resistance of bonds to moisture is quite high but may deteriorate if the bonds are stressed. Some formulations will corrode copper adherends.

Applications of epoxy-polysulfide adhesives primarily include structural assemblies requiring some degree of resilience. Epoxy-polysulfides are used in bonding concrete for floors, airport runways, bridges, and other concrete structures, metals, glass and ceramics, wood, rubber, and some plastics. They are particularly durable in outdoor applications where temperature extremes (freeze−thaw cycles) will be encountered.[8] Epoxy-polysulfides can be heavily filled without adversely affecting their properties.[42,43]

8.18 Film and Tape Adhesives

A number of high-strength structural adhesives are currently supplied in film and tape form. Although the bond strengths provided by both film and tape and one-component pastes are generally similar, there are several advantages of using film and tape:[2]

- Provide uniform, controlled glue line thickness
- Speed and ease of application (a clean, solvent-free operation is facilitated)
- Two-sided films can be prepared for use in lightweight sandwich constructions. The honeycomb side will provide good filleting, while the skin

side will provide high peel strength. If one side of the film is tacky, it is easier to align the assembly to be bonded

In some film adhesives, a cover or knitted fabric is used to support the polymer film. It will also carry a part of the load and will provide improved bond strength by more efficient distribution of the applied forces. Film adhesives are produced in two forms: unsupported or, alternatively, supported on a flexible carrier such as glass, cloth, nylon, or paper. The carrier will usually have little effect on adhesive properties.[2] The adhesive polymer is usually elastomeric, blended with curing agents, fillers, and other ingredients and is usually extruded, calendered, or cast into 0.1–0.4-mm-thick unsupported films. This type is called *film* adhesive. When the mixture is cast or calendered onto a mesh support, such as woven or nonwoven mesh of glass or other fibers, the resulting product is called *tape* adhesive.

Films and tapes may be either soft and tacky or stiff and dry. They may be room-temperature storable or may require refrigeration between manufacture and the time of use. Most film and tape adhesives are cured at elevated temperatures and pressures. Film and tape adhesives differ from paste and liquid adhesives in that the former contains a high proportion of high-molecular-weight polymer. The 100% solid paste and liquid adhesives contain only low-molecular-weight resins in order to permit them to remain fluid and usable. The film and tape adhesives contain components that permit them to be much tougher and more resilient than paste adhesives. Figures 8.2 and 8.3 compare typical tensile shear data for a number of adhesive types. It should be noted that the best film and tape types have higher peak values and broader service temperatures than the best 100% solids adhesives.[44]

The handling and reliability advantages of tape and film adhesive include that they are ready to use, and there is no need for mixing, no degassing, and no possibility for error in adding catalyst. Tapes permit a variety of lay-up techniques, which facilitate the production of virtually defect-free structures. The use of a mesh support helps to control the bond-line thickness with tape adhesives, avoiding thin, adhesive-starved areas where curvature or external pressure is the greatest.

Tape and film adhesives are generally composed of three components:[17–19]

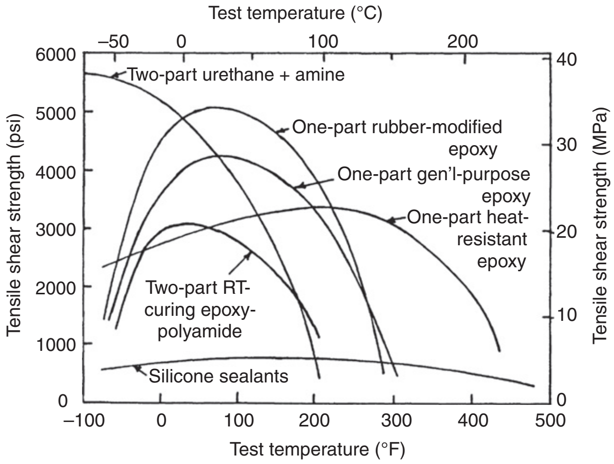

Figure 8.2 Typical tensile-shear strength data for paste and liquid adhesives.[18–20]

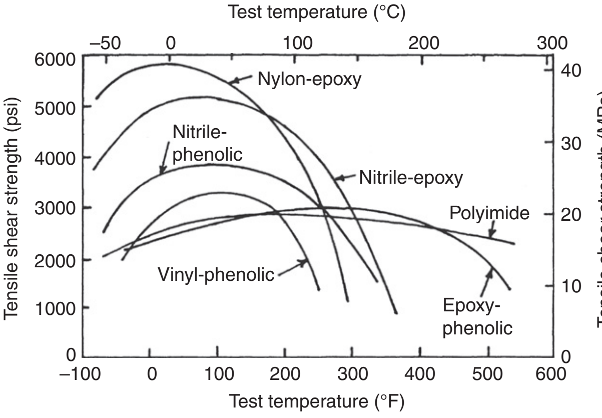

Figure 8.3 Typical tensile-shear strength data for tape-, film-, and solvent-based adhesives.[18–20]

- A high-molecular-weight *backbone* polymer providing the elongation, toughness, and peel. This is the thermoplastic or elastomeric component
- A low-molecular-weight cross-linking resin, invariably either an epoxy or a phenolic (thermosetting types)
- A curing agent for the cross-linking resin

Exceptions to this generalization are the epoxy-phenolic adhesives, which are composed of two thermosetting adhesives.

Film and tape adhesives are also frequently called "two-polymer" or "alloyed adhesives." With few exceptions, all successful film and tape adhesive are, or have been, one of the types shown in Tables 8.3 and 8.4. The adhesive types based on phenolic cross-linking resins liberate volatiles during cure,

Table 8.3 Most Important Tape and Film Adhesives[18–20]

Adhesive type	Backbone polymer	Cross-linking resin	Catalyst	High-pressure cure
Nylon-epoxy	Soluble nylon	Liquid epoxy	DICY-type	No
Elastomer-epoxy	Nitrile rubber	Liquid epoxy	DICY-type	No
Nitrile-phenolic	Nitrile rubber	Phenolic novalac	Hexa, sulfur	Yes
Vinyl-phenolic	PVB or PVF	Resol phenolic	Acid	Yes
Epoxy-phenolic	Solid epoxy	Resol phenolic	Acid	Yes

DICY: dicyandiamide; PVB: polyvinyl butyral; PVF: polyvinyl fluoride.

whereas the types based on epoxies only need sufficient pressure to maintain alignment and compensate for cure shrinkage.[17–19] (See also Section 8.4).

8.19 Furane Adhesives

These are dark-colored synthetic thermosetting resins containing the chemical group known as the furane ring (Fig. 8.4).

These compounds include the condensation polymers of furfuraldehyde (furfural) and furfuryl alcohol. On addition of an acid, these furane compounds polymerize, passing through a liquid resinous state, and have adhesive properties. Volatile loss during cure is low; thus, bonding pressure need not be high. Resistance to boiling water, organic solvents, oils, and weak acids and alkalis is good. However, strong oxidizing agents attack these materials. High-temperature resistance depends on the type and quantity of catalyst. For continuous exposure, service temperatures up to 150 °C are acceptable.

Furane resin adhesives are used as bonding agents or modifiers of other adhesive materials. Applications include surfacing and bonding agents for flooring compositions and acid-resistant tiles, chemically resistant cements for tank linings, phenolic laminates (shear strengths up to 40 MPa), binder resins for explosives, and ablative materials used in rockets and missiles at 1250 °C service temperatures, foundry core boxes, and binder resins for carbon and graphite products.[8,24]

Furane adhesives are suitable for gap-filling applications, because their strength is maintained with thick glue lines. For this reason, the resins are used as modifiers for urea-formaldehyde adhesive to improve gap-filling and craze resistance. As furanes are compatible with a variety of other resins, they are used in mixtures with silicates and carbonaceous materials for chemically resistant grouting compositions.[8]

8.20 Hot-Melt Adhesives

Hot-melt adhesives are thermoplastic bonding materials applied as melts that achieve a solid state and resultant strength on cooling. These thermoplastics of 100% solid materials melt in the temperature range from 65 °C to 180 °C. Theoretically, any thermoplastic can be a hot-melt adhesive, however, preferred materials are usually solid up to 79.4 °C or higher. They melt sharply to give a low-viscosity

Table 8.4 Range of Bond Strengths of Tape and Film Adhesives at Room Temperature[18–20]

Adhesive type	Tensile-shear strength (MPa)	T-peel strength (N/m)
Nylon-epoxy	34–49	14,000–22,750
Elastomer-epoxy	26–41	3,850–15,750
Nitrile-phenolic	21–31	2,625–10,500
Vinyl-phenolic	21–31	2,625–6,065
Epoxy-phenolic	14–22	1,050–2,100

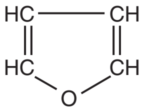

Figure 8.4 Chemical structure of furane.

fluid that is easily applied and is capable of wetting the substrate to be bonded, followed by rapid setting upon cooling. When hot-melt adhesives are used, factors such as softening point, melt viscosity, melt index, crystallinity, tack, heat capacity, and heat stability must be considered, in addition to the usual physical and strength properties being considered.[2,8]

The plastics used in hot-melt applications are generally not newly developed materials. However, the combination of properly formulated resins and application equipment to handle these resins has contributed much to the success of hot-melt technology.[2] Although most hot-melt adhesives melt at about 79.4 °C, they are usually applied at much higher temperatures, from 149 °C to 288 °C. In addition to the thermoplastic polymers, other ingredients are incorporated to improve processing characteristics, bonding characteristics, or service properties. Stabilizers retard oxidation, tackifiers improve bond strength, waxes reduce viscosity and alter surface characteristics, and various fillers increase viscosity, melting point, and bond strength. Hot melts are sold only by a manufacturer's number or name designation, with no generic identification, as is common in most other adhesives. This is why comparison of competing brands of similar hot-melt adhesives is not easy.[45]

One of the most important characteristics of hot-melt adhesives is service temperature. Service temperatures of hot melts are low because of their low melting temperatures, which is a disadvantage. These materials also flow under load over extended time. Thermoplastics have some of the characteristics of viscous liquids and, with a few exceptions, are not dimensionally stable under load. This is why hot melts are recommended primarily for hold-in-place operations with negligible load requirements. The main disadvantages of hot melts are limited strength and heat resistance. Unlike other adhesives, the setup process is reversible, and at about 77 °C most hot melts begin to lose strength. The maximum shear load capacity is usually about 3.4 MPa.[46] Lap-shear strengths up to 4.3 MPa have been reached with hot-melt adhesives used to bond untreated high-density polyethylene to high-density polyethylene.[47]

8.20.1 Foamable Hot-Melt Adhesives

These materials were introduced in 1981. The process involves introducing a gas, normally N_2 or O_2, into the hot-melt adhesive in a volumetrically metered fashion using a two-stage gear pump. Typically, the volume of the adhesive is increased by 20−70%. Although all adhesives foam under these conditions, the quality of the foam depends on the individual adhesives. Foamed hot-melt adhesives can be used on the same substrates on which standard hot melts are used. A superior bond can often be obtained on metal, plastics, and paper products, as well as on heat-sensitive and porous substrates. This is because of the characteristics resulting from foaming including increased spreading ability, larger open time, shorter set time, increased penetration, and reduced thermal distortion over traditional hot melts. Polyethylene, in particular, gives excellent results. Typical applications include gasketing and sealants.[48]

8.20.2 EVA and Polyolefin Resins

These are the least costly resin materials used in hot melts. Their applications include bonding paper, cardboard, wood, fabric, and so on for use in the range of −34 °C to 49 °C. Compounded versions can be used for nonload-bearing applications of up to about 71 °C. EVAs and polyethylenes represent the highest volume of hot-melt adhesives used, primarily in packaging and wood-assembly applications.[45]

8.20.3 Polyamide (Nylon) and Polyester Resins

These compounds are the next step up in strength and general service in hot-melt adhesives. These so-called "high-performance" hot melts are used to assemble products made from glass, hardboard, wood, fabric, foam, leather, hard rubber, and some metals. Service temperatures range from −40 °C to about 82 °C. A number of formulations are available that can be used at >93 °C. Some are capable of being used in nonload-bearing applications at >149 °C.[45]

Polyester-based hot melts are generally stronger and more rigid than the nylon compounds. Polyesters have sharp melting points because of their high crystallinity, a decided advantage in high-speed hot-melt bonding. Frequently, they have a combination of high tensile strength and elongation. Both nylon and polyester adhesives are sensitive to moisture during application. Nylons combine good strength with flexibility. If nylon compounds are not stored in a dry area, they may pick up moisture, which may cause foaming in the heated adhesive. This problem, in turn, may produce voids in the applied adhesive layer, reducing bond strength. Moisture affects polyesters in a somewhat different manner by hydrolysis of the molecular structure of the resin, thereby lowering the molecular weight and viscosity. This is precisely why polyester hot melts should not be used in reservoir-type application systems.[35]

8.20.4 Other Hot-Melt Adhesives

Other materials include polyester-amides and those formulated from thermoplastic elastomers. The former are said to have the desirable properties of polyesters but with improved application characteristics. The principal base polymers in thermoplastic elastomers are used mostly in pressure-sensitive applications, replacing other adhesives, such as contact cements, to eliminate solvent emission problems. These materials are used for applications such as tape products and labels, which require relatively low strength.[45] One particular thermoplastic rubber formulation provides paper tear in the range of −23 °C to 60 °C. This adhesive may also be applied by a gun for attaching items, such as plastic molding, to wooden cabinet doors.[49]

Thermoplastic elastomer hot melts are not as strong as the polyesters but are stronger than conventional thermosetting rubbers. They provide good flexibility and toughness for applications requiring endurance and vibration resistance, and have good wetting properties. These compounds are quite viscous, even at 232 °C, because of their high molecular weights. This characteristic renders them more difficult to apply than the nonelastomeric materials, unless they are formulated with other ingredients.[49]

An example of a 100% solid, nonflammable, heat-activated hot-melt adhesive recommended for structural bonding of aluminum, steel, copper, brass, titanium, fabric, and some plastics is 3M Company's Scotch®-Weld Thermoplastic Adhesive Film 4060. Strength data are shown in Table 8.5.[50] Bonding using this clear, amber, unsupported film adhesive takes place rapidly. The speed of bonding is limited only by the heat-up time required to reach the optimum bonding temperature of 149 °C at a pressure sufficient to maintain contact between the surfaces to be bonded. The adhesive can also be preapplied to parts for days or months in advance of the actual bonding operation. When parts are ready to be bonded, heat is applied to the previously applied adhesive to quickly activate the material for bonding. Typical applications include nonload-bearing honeycomb panels, application of decorative trim, and installation of electronic parts.[50,51]

8.21 Inorganic Adhesives (Cements)

These materials are widely used because they are durable, fire-resistant, and inexpensive when compared with organic materials. Inorganic adhesives are based on compounds such as sodium silicate, magnesium oxychloride, lead oxide (litharge), sulfur, and various metallic phosphates. The characteristics of some of the more important commercial materials are summarized.

Table 8.5 Strength Characteristics of Thermo-Bond Thermoplastic Adhesive Film Used to Bond to Etched Aluminum* [52]

Temperature (°C)	Overlap-shear strength (psi)	T-peel strength (per inch width)
23	1160	16.5
38	1090	17.5
52	990	19.2
66	910	18.0
79	590	15.0

**(1) Overlap shear (OLS) made by bonding 20-mil etched aluminum to 63-mil etched aluminum using 160 °C bond-line temperature, 2-s dwell, 14-lb gauge pressure. (2) Peel bonds made by bonding 4.5-mil aluminum foil to test substrates using 320 °F (160 °C) bond-line temperature, 2 s-dwell, 14-lb gauge pressure. (3) Adhesion tests done at 2 in./min for peel and 2 in./min for OLS.*

8.21.1 Soluble Silicates (Potassium and Sodium Silicate)

Sodium silicate is the most important of the soluble silicates. This material is often called "water glass" and is ordinarily supplied as a colorless, viscous water solution displaying little tack. Positive pressure must be used to hold the substrates together. This material will withstand temperatures of up to 1100 °C. The main applications of sodium silicate adhesives are in bonding paper and making corrugated boxboard, boxes, and cartons. They are also used in wood bonding and in bonding metal sheets to various substrates; in bonding glass to glass, porcelain, leather, textiles, stoneware, and so on; bonding glass-fiber assemblies; optical glass applications; manufacture of shatter-proof glass; bonding insulation materials; refractory cements for tanks, boilers, ovens, furnaces; acid-proof cements; fabrication of foundry molds; briquettes; and abrasive polishing wheel cements. Soluble silicates may also be reacted with silicon fluorides or silica to produce acid-resistant cements with low shrinkage and a thermal expansion approaching that of steel.[8,52]

8.21.2 Phosphate Cements

These cements are based on the reaction product of phosphoric acid with other materials, such as sodium silicate, metal oxides and hydroxides, and the salts of the basic elements. Zinc phosphate is the most important phosphate cement and is widely used as "permanent" dental cement. It is also modified with silicones to produce dental-filling materials. Compressive strengths of up to 200 MPa are typical of these materials, which are formulated to have good resistance to water. Copper phosphates are used for similar applications, but they have a shorter useful life and are used primarily for their antiseptic qualities. Magnesium, aluminum, chromium, and zirconium phosphates are also used.[8]

8.21.3 Basic Salts (Sorel Cements)

These are basic salts of heavy metals, usually manganese or magnesium cement or magnesium oxychloride cement. They are suitable for dry locations where 2−8 h of hardening will permit their immediate use for bonding many refractory materials, ceramics, and glass. The final strength will be in the range of 48−69 MPa. Magnesium oxychloride is an inorganic adhesive notable for its heat and chemical resistance. It is usually supplied as a two-part product (magnesium oxide and magnesium chloride) that is mixed at the time of use. Copper is added to overcome the tendency to dissolve in water. These cements resist damage by cooking fats and greases, repelling vermin, and preventing the growth of molds and bacteria. They also conduct static electricity from flooring and similar materials.[8,52]

8.21.4 Litharge Cements

Mixtures of glycerin and litharge (lead oxide or PbO) are used as adhesives in the repair of tubs and sinks, pipe valves, glass, stoneware, and common gas conduits. A mixture of one part slightly diluted glycerin with two to three parts of lead oxide requires approximately 1 day to form a crystalline compound. The resulting cement resists weak acids and nitric acid but reacts with sulfuric acid. These materials have also been used as ceramic seals in potting electronic equipment.[8,52]

8.21.5 Sulfur Cements

Liquid sulfur (melting point 388 °C) can really be considered an inorganic hot-melt adhesive. This material should not be exposed to temperatures higher than 93 °C because of a marked change in the coefficient of expansion at 96 °C as a result of a phase change. The addition of carbon black and polysulfides improves its physical properties. Tensile strength values of about 4.0 MPa were reported, which decreased to 3.0 MPa after 2 years of exposure to water at 70 °C. The principal use of sulfur cements is for acid tank construction, where high resistance to oxidizing acids, such as nitric and hydrofluoric acid mixtures at 70 °C is required. Resistance to oleic acid, oxidizing agents, and strong bases or lime is poor. Adhesion to metals, particularly copper, is satisfactory.[8]

8.21.6 Sauereisen's Adhesives

Sauereisen's adhesives[53] and potting compounds are inorganic, ceramic-based materials. These specialty cements are composed of high-purity, inert fillers such as silica, alumina, or zircon. The nature of these materials, when formulated in a dense matrix with an appropriate binder, is to exhibit high thermal conductivity and electrical insulation. When dispensed, Sauereisen cements exhibit the consistency of a thick cream until they harden and fully cure. Sauereisen products bond to ceramics, metals, and glass, which makes them ideal for many electrical instruments that operate at high temperatures. Some end-use components that require technical cements include heating elements, resistors, halogen lamps, igniters, and thermocouples. The original Sauereisen adhesive, formulated in 1899, is still in demand today.

8.22 Melamine-Formaldehyde Adhesives (Melamines)

These synthetic thermosetting resins are condensation products of unsubstituted melamines and formaldehyde. They are equivalent in durability and water resistance to phenolics and resorcinols. Melamines are often combined with ureas to reduce cost. Melamines have higher service temperatures than those of ureas.[7,8,24]

Savia[54] has discussed amino resins, including melamines, in considerable detail. Other comprehensive discussions are by Pizzi.[55,56]

8.23 Microencapsulated Adhesives

Microencapsulation is a method for separating an activating solvent or a reactive catalyst from the adhesive base. The materials, whether solid or liquid, are packaged in very small "microscopic" capsules. When adhesion is desired, the encapsulated solvent is released by breaking the capsules by heat or pressure, and a tacky adhesive with instant "grab" is produced. In addition to solvents, small quantities of plasticizers or tackifiers may be contained in the capsules. The capsules are made of gelatin and are insoluble in water and neutral to the solvents. Heat-activated adhesives are another form of microencapsulation. A blowing agent is mixed with the solvent in the capsule. Upon application of heat, the blowing agent vaporizes and ruptures the capsule, releasing either the entire adhesive or the solvent needed to make the adhesive tacky. A third form of encapsulation involves two-part adhesives, such as epoxy or polyurethanes. In this type, both the base resin and the catalyst are stored in the same container. The catalyst can be released by pressure, or by other means, to cure the adhesive.[44]

8.24 Natural Glues

These adhesives include vegetable- and animal-based materials and have been replaced by synthetic resin adhesives. Their occasional uses are usually limited to paper, paperboard, wood, and metal foil. Hide glue forms a strong and long-lasting bond and was the most common woodworking glue for thousands of years until its replacement with man-made adhesives. Hoof glue is still used today in cabinetry and other fine woodworking projects where the joints must be extremely fine, if not invisible.

Shear strengths range from 0.034 to 6.9 MPa. Few natural glues retain their strengths at temperatures above 100 °C. Most of these materials have poor resistance to moisture, vermin, and fungus, but they do have good resistance to organic solvents. Common natural glues are discussed below.

8.24.1 Vegetable Glues

These adhesives are soluble or dispersible in water and are produced or extracted from natural sources. Other adhesives, such as rubber cements, nitrocellulose, and ethyl cellulose lacquer cements, are also produced from plant sources but are not water soluble or water dispersible and are therefore not classified as vegetable glues.[57]

Starch adhesives are derived primarily from the cassava plant, although other starch sources may be used. Starch is usually heated in alkaline solutions, such as NaOH, followed by cooling to room temperature to prepare the dispersions. After cooling, they are applied as cold-press adhesives. They develop their strength by loss of water into a wood substrate. Tack is developed rapidly; normal wood processing takes 1–2 days at room temperature and 0.5–0.7 MPa. Starch adhesives are also used for paper cartons, bottle labeling, and stationery applications. Joint strengths are low compared with other vegetable adhesive types. These adhesives are resistant to water and biodeterioration, and their resistance to these environments is improved by adding preservatives.[8] An example of starch adhesive application is found in Military Specification MIL-A-17682E, "Adhesive, Starch," for use in mounting paper targets to target cloth. In this specification, the starch source must be wheat. Readers may recall using "flour and water" to make a simple paste for school and home use. It should be noted that this source of starch is not subjected to heating in alkaline solution and, therefore, does not have the strength of the commercial material.

Dextrins are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch. They have the same general formula as carbohydrates but are of shorter chain length. Industrial production is generally performed by acidic hydrolysis of potato starch. Other catalytic agents used include enzymes, alkali, and oxidizing agents. Dextrins are water soluble, white to slightly yellow solids that are optically active. These adhesives can be used in formulations for many different substrates. Their applications are primarily for paper and paperboard. Laminating adhesives are usually made from highly soluble white dextrins and contain fillers such as clay, as well as alkalis or borax. Blends of white dextrins and gums are common. Urea-formaldehyde is often added to produce water resistance.[57] Military Specification MIL-A-13374D, "Adhesive, Dextrin, for Use in Ammunition Containers," covers four classes of dextrin adhesives for use in making spirally wound containers and chipboard spacers.

Soybean glue (nitrogenous protein soybean) is the most common plant protein adhesive derived from seeds and nuts, hemp, and Zein. These adhesives are inexpensive and can be applied in making semiwater-resistant plywood, and can be used for coating some types of paper. The protein from the soybean is separated out mechanically and used much like casein protein, with the addition of calcium salts to improve water resistance. The soybean glues are used as room-temperature-setting glues to produce interior-type softwood plywood, where only limited moisture resistance is needed. Soybean glues have been largely replaced by protein-blend glues, such as combinations of soybean and blood proteins, and by phenolics for plywood bonding. Cold-press bonding of plywood with soybean adhesives requires 4−12 h at 0.70−1.0 MPa. Hot-press bonding requires 3−10 min at 100−140 °C and 1.0−1.5 MPa pressure. Water resistance of soybean glues is limited, although they become stronger up on drying, similar to casein glues.

These materials will biodeteriorate under humid conditions unless inhibitors are used. Their resistance to heat and weathering is poor; therefore, they are restricted to indoor applications. Soybean glues are filled for paper and paperboard lamination, cardboard and box fabrication, and particle binders.[8]

Rosin family's most common form of adhesive is colophony, a hard amorphous substance derived from the oleoresin of the pine tree. This material is applied in solvent solution form as a hot-melt mastic. It has poor resistance to water, is subject to oxidation, and has poor aging properties. Plasticizers are usually added to reduce its brittleness. Bond strengths are moderate and develop rapidly. These materials are used as temporary adhesives in bonding paper and as label varnishes. They are also used as components of PSAs based on styrene-butadiene copolymers and in hot-melt adhesives and tackifiers. These materials have been largely replaced by synthetic-resin adhesives.[12] One specialized form of rosin adhesive is Canada Balsam, covered by the obsolete Military Specification MIL-C-3469C, titled "Canada Balsam." This material was intended for cementing optical elements.

8.24.2 Glues of Animal Origin

The term animal glue usually is confined to glues prepared from mammalian collagen, the principal protein constituent of skin, bone, and muscle. When treated with acids, alkalis, or hot water, the normally insoluble collagen slowly becomes soluble. These glues are categorized into those derived directly and indirectly from animals, including mammals, insects, and fish, as well as milk products. The category should not be called "animal glues," as that term is a specialized form.

Casein glue is the protein of (skim) milk, from which it is obtained by precipitation. Dry-mix casein glues are simply mixed with water before use. Casein glues are used at room temperature and set or hardened by loss of water (to the wood substrate) and by a degree of chemical conversion of the protein to the more insoluble calcium derivative. Applications include packaging, where the adhesives are used to apply paper labels to glass bottles. In woodworking, they are applied in laminating large structural timbers for interior applications. They are also used for general interior woodworking applications, including furniture. They cannot be used outdoors, although they are more resistant to temperature changes and moisture than are other water-based adhesives. Casein adhesives will tolerate dry heat of up to 70 °C, but under damp conditions the adhesives lose strength and are prone to biodeterioration. Chlorinated phenols can be used to reduce this tendency to deteriorate. These glues are often compounded with materials such as latex and dialdehyde starch to improve durability. They have generally good resistance to organic solvents.[7,58]

Blood albumen (blood glues) are used in much the same manner as casein glues. The proteins from animal blood in slaughtering are precipitated out, dried, and sold as powders, which are then mixed with water, hydrated lime, or sodium hydroxide. The blood proteins undergo some heat coagulation so that they can be hardened by hot-pressing and by losing of water. Processing usually takes 10−30 min at 70−230 °C for plywood, with bonding pressures of 0.5−0.7 MPa. Porous materials require only several min at 80 °C. Cold-press applications are also possible. Blood glues are used to a limited degree in making softwood plywood, sometimes in combination with casein or soybean proteins. They have also been used as extenders for phenolic-resin glues for interior-type softwood plywood. Another application is for bonding porous materials such as cork, leather, textiles, and paper, and for packaging, such as in bonding cork to metal in bottle caps.

Animal glues (bone and hide glues): The term "animal glues" is normally reserved for glues prepared from mammalian collagen, the principal constituent of skin, bone, and sinew. Other types of glues obtained from animal sources are usually referred according to the material from which they are derived (casein, blood, fish, and shellac). Bone glues are made from animal bones, whereas hide glues are made from tannery waste. These glues are supplied as liquid, jelly, or solid in the form of flake, cube, granule, powder, cake, slab, and so on, for reconstitution with water. They are used primarily not only for furniture woodworking but also for leather, paper, and textiles, and as adhesive binders for abrasive paper and wheels. Liquid hide glues are normally supplied with a gel depressant added to the molten-glue mixture. This is done to assure that the dispersion leaves liquid when cooled to room temperature, so that it can be bottled. These glues harden only by the loss of water to the adherend, which must be relatively porous.[59−61]

The processing conditions for animal glues are dependent on the type of glue. These glues set at temperatures in the range of 80−90 °C, or they may set at room temperature. Bonding pressures range from contact pressure to 1−1.4 MPa for hardwoods and 0.35−0.70 MPa for softwoods. Application periods range from 5 min to several hours. Hide glues are stronger than bone glues. The bond strengths of these glues usually exceed the strengths of wood and fibrous adherends. High-strength joints are obtained when the bonds are kept under dry conditions. Structural applications are limited to interior uses. These glues are gap-filling, which makes them useful when close-fit joints are not feasible and filler products are not required.[6]

Animal glue is the primary adhesive component in gummed tapes used in sealing commercial solid fiber and corrugated shipping uses, as well as the more common lightweight types used in retail packaging.[62]

Fish glues are by-products of desalted fish skins, usually cod, and have properties similar to animal skin and hide glues, which have largely replaced them in woodworking applications. Fish glues were the forerunners of all household glues. Many of the original industrial applications developed because fish glue was liquid and had an advantage over animal glues, which required a heated glue pot. Fish glue has been in use for more than 100 years. Even with the many synthetic adhesives available today, there are applications that require the unique properties of fish glue.[8,63]

Fish glues are available in cold-setting liquid form that does not gel at room temperature. Solvents such as ethanol, acetone, or dimethyl formamide may be added to facilitate the penetration of the glue into substrates that may be coated or finished (e.g., paper, leather, and fabrics). These glues may be exposed to repeated freezing and thawing cycles without adverse effects. Initial tack is excellent on remoistening dry fish-glue films with cold water. The water resistance of dried glue films can be improved by exposure to formaldehyde vapors, which renders the fish gelatin component insoluble. Fish glues bond well to glass, ceramics, metals, wood, cork, paper, and leather. The main uses are in the preparation of gummed tapes with animal/fish glue compositions and in the bonding of stationery materials. Latex, animal glues, dextrins, and polyvinyl acetate adhesives are sometimes modified with fish glues to improve wet-tack properties. High-purity fish glues are important photoengraving reagents. Service temperature ranges from −1 °C to 260 °C and shear strength (ASTM D905-08e1) is 22 MPa with 50% wood failure.[8,63]

Shellacs are thermoplastic resins derived from insects. They are used in alcoholic solutions or as hot-melt mastics. They have good electrical insulating properties but are brittle unless compounded with other materials.

Shellacs are resistant to water, oils, and grease. Bond strengths are moderate. Shellacs are used to bond porous materials, metals, ceramics, cork, and mica. They are also used as adhesive primers for metal and mica, for insulating sealing waxes, and as components of hot-melt adhesives. Shellacs are the basic components of de Khotinsky cement. Their application has declined over time because of their high cost.[8]

Shellac is used as an alternative to alkyd resins in binding mica splitting to produce mica board. This is pressed into shapes used as insulation in electric motors, generators, and transformers. Mica tape, used as insulators in motors and generator coil slots, is fabricated by bonding mica flakes to glass cloth and tissue paper with shellac or silicones.[64]

8.25 Neoprene (Polychloroprene) Adhesives

This type of synthetic rubber has been used extensively to bond aluminum. Its characteristics are summarized in Table 8.1. Neoprene is ordinarily used in organic solvents for convenient application. Although properties of neoprene and natural rubber are similar, neoprene generally forms stronger bonds and has better resistance to aging and heat. Solvent-based neoprene cements are also used extensively as shoe adhesives. For structural applications, neoprene is usually combined with a phenolic resin plus a number of other additives for curing and stabilizing the mixture (neoprene-phenolic). Both cold-setting and heat-curing formulations can be prepared.[2]

Neoprene is a general-purpose adhesive used for bonding a wide range of materials. Gap-filling properties are satisfactory. Neoprene joints may require several weeks of conditioning to yield maximum strength. The unalloyed adhesives should not be used for structural applications requiring shear strengths of >2 MPa, because they are likely to creep under relatively light loads. Tack retention is generally inferior to natural rubber. Loads of 0.2–0.7 MPa can be sustained for extended periods soon after bonding.[8,65]

8.26 Neoprene-Phenolic Adhesives

These alloy adhesives are thermosetting phenolic resins blended with neoprene (polychloroprene) rubber. They are available in solvent solutions in toluene, ketones, or solvent mixtures, or as unsupported or supported films. The supporting medium may be glass or nylon cloth. Neoprene-phenolic adhesive may be used to bond a variety of substrates such as aluminum, magnesium, stainless steel, metal honeycombs and facings, plastic laminates, glass, and ceramics. Wood-to-metal bonds are often primed with neoprene-phenolic adhesives.

Compounding with neoprene rubber increases flexibility and peel strength of phenolic resins and extends the high-temperature resistance. The film form is preferred for applications where solvent removal is problematic. The higher curing temperatures provide the highest strengths. Curing takes place under heat and pressure. The film is ordinarily cured at 150–260 °C for 15–30 min at 0.35–1.8 MPa bonding pressure. The liquid adhesives are ordinarily dried at 80 °C and then cured for 15–30 min at 90 °C and contact pressure of 0.7 MPa. The bond may be removed from the hot press while still hot. The liquid adhesive may be used as a metal primer for film adhesives.[7,8]

The normal service temperatures of these adhesives range from −57 °C to 93 °C. Because of their high resistance to creep and most severe environments, neoprene-phenolic joints can withstand prolonged stress. Fatigue and impact strengths are excellent. However, shear strength is lower than that of other modified phenolic adhesives.[7]

8.27 Nitrile-Epoxy (Elastomer-Epoxy) Adhesives

The term *nitrile-epoxy* is frequently used to signify elastomer-epoxy, even though this is not the only elastomer-epoxy available. Tables 8.2 and 8.3 summarize some of the important properties of this important adhesive. The maximum bond strength of these adhesives is generally below the maximum attainable, with nylon-epoxies at room temperature. A major advantage of these adhesives, however, is that their peel strength does not decrease as abruptly at subzero temperatures as do the peel values of the nylon-epoxies. Bond durability of these high-peel elastomer-epoxies is satisfactory, as measured by most long-term moisture tests, but it does not match the durability of the vinyl-phenolic or nitrile-phenolic systems.[17–19] Nitrile-epoxies should not be used in applications involving exposure to marine environments or under continuous immersion in water.[66]

8.28 Nitrile-Phenolic Adhesives

These adhesives are usually made by blending a nitrile rubber with a phenolic novalac resin, along with other compounding ingredients. Usage in tape, film, or solution form is very high. The major uses include bonding brake shoes and clutch disks in the automotive industry. They are also used in aircraft assembly and in many other smaller applications thanks to their low cost, high bond strengths at temperatures of up to 121 °C, and exceptional bond durability on steel and aluminum. Nitrile-phenolics exhibit exceptionally high durability after extended exposure to salt spray, water immersion, and other corrosive environments. They constitute the most important tape adhesives (see Tables 8.3 and 8.4). Their important disadvantages include the need for cure under high pressure (1.38 MPa), while the trend is toward reduced cure pressures, and the need for high temperature (149 °C), and long dwell cures, the trend being toward adhesives that cure rapidly at or below 121 °C.[7]

The liquid nitrile-phenolic adhesives are dried at 80 °C and cured for 15−30 min at 90 °C at contact to 0.70 MPa pressure.[8]

8.29 Nitrile Rubber Adhesive

This is one of the most important synthetic thermoplastic elastomers. Nitrile rubber is a copolymer of butadiene and acrylonitrile. The copolymer usually contains enough acrylonitrile (>25%) such that good resistance to oil and grease can be obtained. Adhesive properties also increase with increasing nitrile content. These adhesives are used to bond vinyls, other elastomers, and fabrics where good wear, oil, and water resistance are important. Compatibility with additives, fillers, and other resins is another advantage of this material.[2,67] Table 8.1 summarizes the properties of nitrile rubber.

8.30 Nylon Adhesives

Nylons are synthetic thermoplastic polyamides of relatively high molecular weight that have been used as the basis for several types of adhesive systems. They are used as solution adhesives, as hot-melt adhesives, and as components of other adhesive-alloy types (nylon-epoxy and phenolic-nylon). The high-molecular-weight products are generally referred to as *modified* nylons. Low- and intermediate-molecular-weight materials are also available. The latter two are more commonly used in hot-melt formulations, and the modified nylons are often blended with small amounts of a phenolic resin to improve surface wetting (hence nylon-phenolic).

Solution systems of low- and intermediate-molecular-weight nylon resins can be coated on paper, metal foil, or plastics, and when heat activated will act as adhesives for these substrates. Modified nylons have fair adhesion to metals, good low- and high-temperature properties, and good resistance to oils and greases but poor resistance to solvents.[2,8]

Certain specialty nylon resins with low melting temperatures have been used quite successfully with extrusion techniques. Both nylon and high-molecular-weight polyamide resins that are chemically related to dimer acid-based polyamides are used in high-strength metal-to-metal adhesives; they are applied by extrusion.[2]

8.31 Nylon-Epoxy Adhesives

These are possibly the best film-and-tape structural adhesives available. Their tensile strength of >48 MPa and climbing-drum peel strengths of >26,265 N/m are the highest available in structural adhesives. These adhesives also have exceptional fatigue and impact strengths. Low-temperature performance is good down to the cryogenic range, except that brittleness occurs at cryogenic temperatures (−240 °C). Other disadvantages include poor creep resistance and extreme sensitivity to moisture.[2,17−19] Properties data on these adhesives are shown in Tables 8.3 and 8.4.

Nylon-epoxy film adhesives have the tendency of picking up substantial amounts of water before use. They also tend to lose bond strength rapidly after use on exposure to water or moist air. After 18 months of exposure to 95% RH, conventional nitrile-phenolic adhesive loses only a fraction of its initial strength, going from 21 to 18 MPa in tensile shear. On the other hand, one of the best nylon-epoxy adhesives available degraded from about 34 to 6.8 MPa in just 2 months under the same test conditions.[68] A considerable effort has been made to solve this moisture problem, but nitrile-epoxy or acetal-toughened epoxy film adhesives are still superior in durability.[17−19]

8.32 Phenolic Adhesives

These adhesives, more properly called *phenol-formaldehyde* adhesives, are condensation products of formaldehyde and a monohydric phenol.[24]

They dominate the field of wood adhesives and represent one of the largest volumes of any synthetic adhesive. Phenolics are also among the lowest-cost adhesives and may be formulated as water dispersions, to allow penetration into the cell structure of wood that is important for the formation of permanent bonds. Beyond the wood and wood products area, unmodified phenolics are used mainly as primers, to prepare metal surfaces for bonding, and as binders, for such varied products as glass wool insulation mats, foundry sand, abrasive wheels, and brake lining composites. Phenolics are supplied either as one-component, heat-curable liquid solution, as powder, or as liquid solution to which catalysts must be added. The curing mechanisms are different for these two groups.[2]

8.32.1 Acid-Catalyzed Phenolics

The acid-catalyzed phenolics form wood joints requiring from 1 to 7 days conditioning, depending on the end use. Metals bonded with these adhesives require priming with a vinyl-phenolic or rubber-resin adhesive before bonding. These adhesives have good gap-filling properties, but they are not recommended as structural adhesives unless their glue line pH is higher than 2.5. Glass or plastic mixing vessels are required because of the acidic nature of these adhesives. The mixed adhesive is exothermic (gives off heat) and temperature sensitive. These adhesives are cured under the conditions listed in Table 8.6.

Curing time is reduced by increasing the curing temperature. Resistance to weather, boiling water, and biodeterioration is satisfactory. Resistance to elevated temperatures is also satisfactory but inferior to that of heat-cured phenolic and resorcinol adhesives. Excess acidity due to poor control of the acid catalyst content often leads to wood being damage on exposure to warm humid air. The durability of joints at high and low temperatures for extended periods is usually acceptable. These adhesives are used for woodwork assemblies, where the service temperature does not exceed 40 °C. Applications include furniture construction and, to a minor extent, plywood fabrication. This adhesive is also used to join metal to wood for exterior use.[8]

Table 8.6 Cure Conditions of Acid-Catalyzed Phenolics[8]

General purpose	3–6 h at 20 °C
Timber (hardwood)	15 h at 15 °C and 1.2 MPa
Timber (softwood)	15 h at 15 °C and 0.7 MPa

8.32.2 Hot-Setting Phenolics

The hot-setting form of phenol-formaldehyde adhesive is supplied in spray-dried powder to be mixed with water as alcohol, acetone as water-solvent solutions, or as glue films.[57,69,70] It may be compounded with fillers and extenders. The gap-filling properties of this type of phenolic adhesive are poor and inferior to those of the acid-catalyzed phenolic adhesives. Joints require conditioning of up to 2 days. Although durable and resistant to many solvents, the bonds are brittle and prone to fracture under vibration and sudden impact. These adhesives are used as additives to other materials to form adhesives for glass and metals, or modifying agents for thermoplastic elastomer adhesives, or as components of thermoplastic resin-elastomer adhesives for metal bonding.[8]

Hot-setting phenolic adhesives are processed for up to 15 min at 100–150 °C and at 0.7–1.7 MPa bonding pressure. The film form is processed for up to 15 min at 120–150 °C and at 0.7–1.4 MPa. This type of phenolic is resistant to weather, boiling water, and biodeterioration. It has superior temperature stability to that of the acid-catalyzed form. Applications of this adhesive include fabrication of exterior-grade weather- and boil-proof plywood, as well as bonding glass to metal for electric light bulbs.[8]

8.33 Phenoxy Adhesives

These materials are synthetic thermoplastics in the form of polyhydroxy ethers. Phenoxy adhesives are supplied as one-component systems in powder, pellet, or film forms. They may be dissolved in solvents or supplied as special shapes. Phenoxies act as hot melts and set upon cooling. The liquid forms require removal of the solvent by drying before bonding. Time and temperature are important factors in obtaining maximum strength: bonding pressure is not critical. Typical conditions include bonding for 30 min at 192 °C, 2–3 min at 260 °C, or 10 s at 300–350 °C, and pressure from contact to 0.17 MPa. Phenoxies are used as structural adhesives for rapid assembly of metals and rigid materials, for continuous lamination of metal to metal (cladding) or wood and flexible substrates, paper, cloth, metal foil, and plastic laminations. Other applications include pipe jointing (with fiber type), assembly of automotive components, and bonding polymeric materials such as polyester film, polyurethane foam, acrylics, and phenolic composites. They are also used as components of hot-melt adhesives for conventional applications.[8]

Phenoxy adhesives withstand weathering and resist biodeterioration. They have excellent resistance to inorganic acids, alkalies, alcohols, salt spray, cold water, and aliphatic hydrocarbons, but they swell in aromatic solvents and ketones. Thermal stability is adequate, with a service temperature range of −62 °C to 82 °C. Resistance to cold flow and creep is high, even at 80 °C. These adhesives provide rigid, tough glue lines with high adhesive strength. Shear strengths are similar to epoxies, and for metals generally exceed 17 MPa, possibly approaching 27.5 MPa. Film thickness is not critical and can be as little as 0.012 mm.

Liquid adhesives do not usually provide maximum bond strengths, as complete solvent removal may be difficult. Hot-melt adhesive systems may also present difficulties. Thermal degradation can occur before the resin is completely melted, unless plasticizers are used.[7] Plasticizers used are diphenyl phthalate, tricresyl phosphate, and dicyclohexyl phosphate (DCHP), which are used in hot-melt formulations. Unplasticized phenoxies give peel strengths of 3152−5253 N/m in bonding Neolite to Neolite. Formulations with 60% DCHP raise the peel strength to 5078−5213 N/m.[44,71,72] Good adhesion has been obtained with substrates such as copper, brass, steel, aluminum, wood, and many other nonmetallic substances.[2]

8.34 Polybenzimidazole Adhesives

These adhesives are supplied in film form on glass cloth. Normally, filler (usually aluminum) and antioxidants are among the components. PBIs are thermoplastics, although their thermoplastic nature is not evident below 371 °C. These materials were developed specifically for use in high-temperature applications. They are relatively stable in air: up to 288 °C in short-term exposures. PIs are superior for long-term strength retention. PBIs are expensive and are limited to the bonding of high-temperature metals (stainless steel, beryllium, and titanium). PBIs are of greatest interest to aerospace engineers for use in the adhesive assembly of lightweight honeycomb structures for supersonic aircrafts, missiles, and other space systems. They are somewhat sensitive to moisture at room temperature; lap-shear strength drops gradually on heating to 316 °C, then more rapidly at higher temperatures. Figure 8.5 shows the effect of heat aging at 371 °C, compared with PIs.[2]

Processing is normally carried out in a preheated press at 370 °C with pressure maintained at 0.03 MPa for 30 s. The pressure is then increased to 0.6−1.4 MPa, and the glue line temperature is maintained at 370 °C for 3 h. The temperature is then reduced to 260 °C or less, and the assembly is removed from the press. Autoclave techniques can also be employed. For improved mechanical properties, postcuring in an inert atmosphere (nitrogen, helium, or vacuum oven) is recommended. The desirable conditions are 24 h each at 316 °C, 345 °C, 370 °C, and 400 °C followed by 8 h at 427 °C in air to achieve maximum properties.[8] Obviously, these "literature" recommendations should be checked against manufacturers' recommendations, but they provide a starting point for PBI processing.

PBI adhesives have good resistance to salt spray, 100% humidity, aromatic fuels, hydrocarbons, and hydraulic oils. About 30% loss of strength occurs after exposure to boiling water for 2 h. Electrical properties are fairly constant throughout the temperature range, up to 200 °C. Thermal stability at high temperatures for short periods is satisfactory, such as exposure at 540 °C for 10 min or at 260 °C for 1000 h. The useful service-temperature range as adhesives

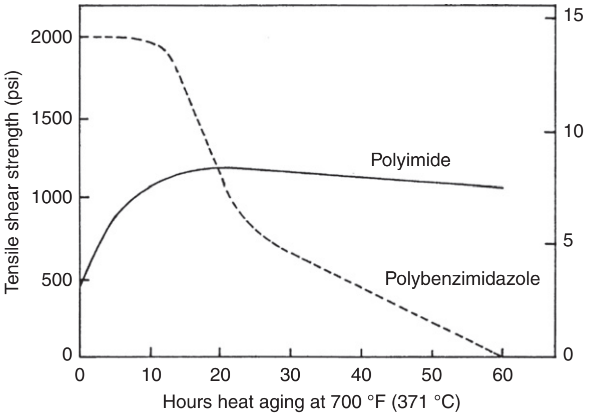

Figure 8.5 Performance of high-temperature adhesives (polybenzimidazole and polyimide) at 371 °C.[2]

is −250 °C to 300 °C.[9] Note that this includes the cryogenic temperature range.

8.35 Polyester Adhesives

Polyester adhesives may be divided into two distinct groups: saturated (thermoplastic) and unsaturated (thermosetting). The saturated polyesters are reaction products of difunctional acids and difunctional alcohols or glycols. Their adhesive applications are minor, except in hot melts (high performance). The unsaturated (thermosetting) polyesters, which require a catalytic cure, have a few uses as adhesives. These usually involve bonding of polyester substrates. Polyester adhesives are also used in patching kits for repair of fiberglass boats, automobile bodies, and concrete flooring.

Other minor uses include bonding polyester laminates to polyester or to metal, and as adhesives for optical equipment. CR-39 allyl diglycol carbonate is an example of the latter. This material, in the cured condition, exhibits improved abrasion and chemical resistance over other transparent adhesive resins and displays the good heat resistance and dimensional stability associated with thermosetting systems. These properties are retained on prolonged exposure to severe environmental conditions. CR-39, which stands for Columbia Resin 39, is an allyl resin, a special type of unsaturated polyester.[2,8,45]

8.36 Polyimide Adhesives

For a general discussion of these high-temperature adhesives, compared with PBI, see Section 8.6. These adhesives are synthetic thermosetting resins formed by the reaction of a diamine and a dianhydride. As with PBIs, they were developed specifically for high-temperature aerospace applications. PI adhesives are superior to PBIs for long-term strength retention, as shown in Fig. 8.3.[8]

PI adhesives are supplied as solutions of the PI prepolymer in solvent, or in film form, usually containing fillers, such as aluminum powder, on a glass-cloth interliner. Processing is as follows: liquid form—removal of solvent by heat or under reduced pressure and by precuring the resin to the desired degree (B-staging), usually at 100−150 °C. The volatile content may range from 8% to 18% w/w after B-staging. Final cure (C-staging) is carried out in stages over the range 150−300 °C or higher. The film form may require B-staging. Their typical cure schedule involves heating to 250 °C over a 90-min period and maintaining at this temperature for 90 min. Postcuring at higher temperatures, up to 300 °C and beyond, is recommended when maximum mechanical properties are required. Bonding pressures should be in the range of 0.26−0.65 MPa. Like PBIs, the adhesives require tedious processing, compared with other adhesives.

PI adhesives have good hydrolytic stability and salt-spray resistance and excellent resistance to organic solvents, fuels, and oils. They are resistant to strong acids but are attacked slowly by weak alkalies. Ozone causes the deterioration of the adhesive bond. Service temperature range is from −196 °C to 260 °C for long-term exposure, but these materials will withstand short exposures (200 h) of up to 250 °C and for 10 min at 377 °C. PIs are exceptionally good high-temperature electrical insulation materials. They also have exceptional resistance to atomic radiation (electrons and neutrons). PI materials are used as structural adhesives for high- and low-temperature applications, down to the cryogenic range, for bonding metals such as stainless steel, titanium, and aluminum, and generally in aircraft applications. They are also used in preparing glass-cloth-reinforced composites for electrical insulation and in bonding ceramics.[8]

PI adhesives require higher cure temperatures than epoxy-phenolic adhesives. Curing at 250 °C is usually adequate when service temperatures do not exceed the cure temperature. Volatiles are released during the cure of PI adhesives. The best results are, therefore, obtained when the volatiles can freely escape (e.g., honeycomb or perforated-core structures). For long-term aging at temperatures in the range of 204−316 °C, PIs are superior to PBI and epoxy-phenolic adhesives.

According to Edson,[73] PI adhesives are capable of withstanding temperatures of up to 316 °C for hundreds of hours and up to 204 °C for thousands of hours. Thermal "spikes" of 538−816 °C can be accommodated. PIs are several times more expensive than epoxies. According to Alvarez,[74] PI adhesives can be processed at 177 °C and postcured at 232 °C to produce bonds capable of 316 °C service. The "exchange" grade of PI polymers has a processing range of 177−288 °C at a pressure of 0.10 MPa. These materials will withstand 316 °C with normal 232 °C postcuring. PIs are useful for bonding high-temperature metals like titanium and graphite/PI composite for use at 260−316 °C.[75,76]

8.37 Polyisobutylene Adhesives

These thermoplastic elastomers are covered briefly in Table 8.1. Polyisobutylene is a homopolymer.[23]

8.38 Polystyrene Adhesives

Polystyrene is a transparent, colorless thermoplastic resin available in solvent-solution or aqueous-emulsion form. In both forms, applications are limited to conditions where at least one of the adherends is porous. An example is sticking polystyrene tiles onto a plaster wall. Polystyrene adheres well to wood but not to plastics, except to itself. For bonding polystyrene, a low-molecular-weight styrene polymer with a peroxide catalyst is used. This adhesive polymerizes in the glue line.[24]

With some woods, shear strengths of up to 13 MPa can be obtained. Polystyrene is used as a modifier for other adhesives such as unsaturated polyesters, hot-melt materials, and in optical cements. Resistance to high temperatures is limited. The heat-distortion temperature is about 77 °C. Electrical insulating properties are excellent. Polyester adhesives have good resistance to water, nuclear radiation, and biodeterioration. However, they generally have poor resistance to chemicals. Other undesirable properties include high flammability and a tendency to brittleness and crazing. Copolymers of styrene and butadiene (SBR), also described in Table 8.1, are much less brittle and more valuable as adhesives. These materials are commonly used in footwear for bonding leather and rubber soles.[8,24]

8.39 Polysulfides (Thiokols)

Polysulfides are flexible materials belonging to the synthetic rubber family. Some of the more important characteristics of polysulfide adhesive/sealants are tabulated in Table 8.1. Although polysulfides are primarily used as sealants for automotive, construction, and marine uses, they are used to some extent as flexibilizing hardeners for epoxy adhesives. Their sulfur linkages combine good strength with the ability to rotate freely, resulting in a strong, flexible polymer. Polysulfides utilize atmospheric moisture to accelerate cure. A two-component system is usually used, consisting of formulated polysulfide and formulated lead dioxide catalyst. Moisture converts a portion of the lead dioxide catalyst to a faster-reacting form.[2]

Polysulfides cure at room temperature and reach maximum strength in 3−7 days. Polysulfides and epoxies are mutually soluble in all proportions. Polysulfides are also alloyed with phenolics.[8]

Curing agents may be furnished in powder, paste, or liquid form. The activity of the metallic curing agents is a function of surface area, thus increasing the importance of particle size. As it is necessary to obtain a fairly complete dispersion throughout the polymer in order to achieve complete cure, combining lead oxide with a plasticizing agent to form a paste is generally more effective. A finished polysulfide adhesive/sealant will generally contain the following ingredients as a minimum:

1. Liquid polymer
2. Reinforcing filler to increase strength and reduce cost
3. Plasticizer to modify modulus and hardness
4. Retarder to control set time
5. Oxidizing agent

Heat, humidity, and sulfur will accelerate the cure.[77,78]

8.40 Polysulfone Adhesives

These are temperature-resistant thermoplastic adhesives that require fairly high temperatures for heat activation after solvents have been removed.[4] Polysulfones are a family of tough, high-strength thermoplastics that maintain their properties over a temperature range from −101 °C to >149 °C. Bakelite's UDEL Polysulfone P-1700 has the following properties: tensile strength 70 MPa; flexural strength 106 MPa; heat-distortion temperature 174 °C; second-order glass transition temperature 191 °C. The flexural modulus is maintained over a wide temperature range. At 149 °C, more than 80% of the room-temperature stiffness is retained. Resistance to creep is excellent. Polysulfone adhesives are resistant to strong acids and alkalis but attacked and/or dissolved by polar organic solvents and aromatic hydrocarbons.[79]

These adhesives maintain their structural integrity up to 191 °C. More than 60% of their room-temperature shear strength, as well as excellent creep resistance, is retained at 149 °C. Cure cycles only need to be long enough to introduce enough heat to wet the substrate with the P-1700 polysulfone. For unprimed aluminum, a temperature of 371 °C should be used after drying the adhesive film for 2–4 h at 121 °C to remove the equilibrium moisture. With a platen temperature of 371 °C and a pressure of 0.55 MPa, joints with tensile lap-shear strengths of >21 MPa are developed in 5 min. Higher temperatures at shorter dwell times may be used whenever the metal will tolerate such temperatures. Tensile-shear strengths of >27.5 MPa have been obtained with stainless steel after pressing at 371 °C.[79]

Polysulfone adhesives have good gap-filling properties. In general, polysulfone adhesives combine the high strength, heat resistance, and creep resistance of a thermosetting-type adhesive with the processing characteristics and toughness of a high-molecular-weight thermoplastic.[79]

8.41 Polyurethane Adhesives

Urethane polymers[80] have been used in flexible and rigid foams, cryogenic sealants, and abrasion-resistant coatings. Their application as adhesive has been expanding.

The principal use of polyurethanes is in bonding plastics that are difficult to bond, usually to a dissimilar material or to metals. Cured urethanes are lightly cross-linked thermoset resins, almost thermoplastic. This gives them a flexible rubbery characteristic. A brief description of their characteristics is given in Table 8.1. Their flexibility, combined with good adhesion, ensures good bonding to flexible plastics, where peel strength is important. The outstanding feature of urethanes is strength at cryogenic temperatures. Table 8.7 compares the strength of urethane, epoxy-nylons, and epoxy-polyamides at −240 °C.[2]

Polyurethanes are one-component thermoplastic systems in solvents (ketones, hydrocarbons), often containing catalysts in small amounts to introduce a degree of thermosetting properties. They are also available as two-part thermosetting products in liquid form, with or without solvents. The second part is a catalyst. The one-part solvent type is used for contact bonding of tacky adherends, following solvent release or heat-solvent reactivation of dried adhesive coating. The two-part thermosetting products are mixed and fully cured at 20 °C in 6 days. They may also be heat cured in 3 h at 90 °C or in 1 h at 180 °C. Bonding pressures range from contact to 0.35 MPa.[8]

A one-component urethane prepolymer adhesive, Accuthane® (available from H.B. Fuller Co., www.HBFuller.com), is designed for bonding various substrates, including plastic to plastic, plastic to metal, and metal to metal.[81] This adhesive can be used to bond imperfectly matched substrates and can

Table 8.7 Comparison of Typical Urethane Adhesive With Other Adhesives on Aluminum at −240 °C[2]

Adhesive	Lap-shear strength (MPa)	Peel strength (N/m)
Urethane	55.2	4550
Epoxy-nylon	31.7	Brittle
Epoxy-polyamide	11.0	Brittle

Table 8.8 Average Tensile Properties of Cured One-component Polyurethane Adhesive According to ASTM D638-10

Temperature (°C)	Tensile strength (MPa)	Elongation (%)
−40	54	8.7
22	16.6	32
82	4	22
127	2.2	16

be used for tack welding. No priming of the substrate surface is required, except for a solvent wipe. Average tensile strength and elongation, according to ASTM D638-10 and after 30 min cure at 127 °C, have been listed in Table 8.8.

Another urethane one-part adhesive (urethane bond) developed by Dow Corning is cured by moisture in the air at room temperature. This material requires a thin glue line and clamping to produce the strongest joints. The resultant bonds are moisture resistant and are claimed to work well on polystyrene, PVC, and acrylics, and fairly well on polyethylene.[82] There are excellent references for additional study of this adhesive family.[56,83,84]

8.42 Polyvinyl Acetal Adhesives

Polyvinyl acetal[85] is the generic name for a group of polymers that are products of the reaction of polyvinyl alcohol and an aldehyde. In preparing these acetals, polyvinyl acetate is partially hydrolyzed to an alcohol. As adhesives, the most common acetals are those from formaldehyde, namely the *formal,* and from butyraldehyde, the *butyral.* The properties of these polymers are largely dependent on the molecular weight and on the degree of hydrolysis of the acetate. As an adhesive, the butyral (polyvinyl butyral) is much more important than the formal (polyvinyl formal). This is because of its more ready solubility and lower melt viscosity, and because it is softer and more flexible, thus yielding better peel strength and higher apparent adhesion with thin adhesives. In the two-polymer adhesive system, the formal is at least as important as the butyral.[24]

Polyvinyl butyral is commonly used in safety-glass laminates. Polyvinyl acetals are used in making thermoset resins more flexible to obtain structural adhesives for metals.

8.43 Polyvinyl Acetate Adhesives

The most widely used resin in water-dispersion form is polyvinyl acetate in homopolymer and copolymer variety. Polyvinyl acetate latex is the basis for the common household "white glue," of which Elmer's® (www.elmers.com) is probably the most well known. Products of this type are good adhesives for paper, plastics, metal foil, leather, and cloth. Their major use is in packaging for flexible substrates. This material is also used as a lagging adhesive to bond insulating fabric to pipe and duct work in steam plants and ships. It is also used in frozen-food packaging where low-temperature flexibility is important. Polyvinyl acetates are used in hot-melt adhesive formulations. Other uses include bookbinding and the lamination of foils. Organic solvent solution and water dispersion are two common forms of polyvinyl acetate adhesives.

For wood bonding, 10 min to 3 h at 20 °C and contact to 1 MPa pressure is recommended. These adhesives have low resistance to weather and moisture. Resistance to most solvents is poor, although they withstand contact with grease, oils, and petroleum fluids and are not subject to biodeterioration. The cured films are light stable but tend to soften at temperatures approaching 45 °C. Polyvinyl acetates are low-cost adhesives with high initial-tack properties. They set quickly to provide almost invisible glue lines. Curing for 1−7 days is recommended before handling the bonded assemblies. Maximum bond strength of up to 14 MPa can be reached by baking the adhesive films, followed by solvent reactivation and assembly. Polyvinyl acetates tend to creep under substantial load. They have satisfactory gap-filling properties.[8]

Polyvinyl acetate adhesives are used in the construction of mobile homes. The purpose is to provide temporary bonds during construction until the units are supported on foundations. They provide strong initial bonds that develop strength quickly. Immediate strength and stiffness are needed to resist stress induced by flexing and racking of long mobile homes as they are moved within the factory and during hauling and lifting at the construction site.[86]

Polyvinyl acetate glues should be applied at 16−32 °C working temperatures. They soften when sanded.[87]

8.44 Polyvinyl Alcohol Adhesives

This is a water-soluble thermoplastic synthetic resin with limited application as an adhesive.[88] The chief uses are in bonding porous materials such as leather, cork, and paper in food packaging, and as a remoistenable adhesive. It is available as a water solution with good wet-tack properties. It sets by losing water to give a flexible transparent bond with good resistance to oils, solvents, and mold growth, but has poor resistance to water. It is nontoxic and odorless. Cured films are impermeable to most gases. The maximum service temperature is about 66 °C. Polyvinyl alcohol is also used as a modifier for other aqueous adhesive systems, to improve film-forming properties or to promote adhesion. These materials are used with dextrins and starches to provide low-cost laminating adhesives. They are also used for envelopes and stamps.[8]

8.45 Polyvinyl Butyral Adhesives

See the discussion of these adhesives under Polyvinyl Acetal Adhesives (Section 8.42).

8.46 Premixed Frozen Adhesives

Ablestik Laboratories (now part of Henkel Corp.) in Gardena, California,[89] has available frozen reactive adhesives, such as epoxies, in disposable tubes or syringes ranging upward in size from 1 cm^3. These adhesives are packed in dry ice and shipped in insulated cartoons. Included in each carton is a safety indicator that is formulated to melt and lose shape when exposed to temperatures unsafe for adhesive storage. Storage life at −40 °C before use is usually from 2 to 6 months. In use, the frozen adhesive is thawed to room temperature and applied within 2 h after thawing. These adhesives eliminate production-line delays caused by on-the-job mixing of messy two-part adhesives, saving valuable assembly time. They also guarantee accurate formulation of components. Another advantage is the reduction in the possibility of workers contracting dermatitis from handling irritating amine curing agents.[90]

8.47 Pressure-Sensitive Adhesives

The most common application of PSAs is in tape form. In the dry state, PSAs are aggressively and permanently tacky at room temperature and firmly adhere to a variety of dissimilar surfaces, without the need for more than finger or hand pressure.[91,92] They require no activation by water, solvent, or heat to exert a strong adhesive holding force.

Most PSAs are based on natural rubber. Rubber by itself has very low tack and adhesion to surfaces thus requires addition of tackifying resins based on rosins, petroleum, or terpenes. Hydrogenated resins are added to enhance PSAs' long-term aging. Adhesives based on acrylic polymers and natural rubbers are the leading PSAs. These acrylics have good ultraviolet (UV) stability, are resistant to hydrolysis, and are water-white with good resistance to yellowing or aging. Acrylic-based PSAs have poor creep properties compared with natural rubber. Blends of natural rubber and SBR also produce excellent PSAs. Other less desirable adhesives include polyisobutylene and butyl.

The adhesives discussed above are all applied in the solution and hot-melt forms. These are pressure-sensitive at room temperature. These materials may be based on EVA copolymers tackified with various resins and softeners. They produce rather soft adhesives, with poor cohesive strength. Their use is minor, mostly on label stock. Of wider interest are hot-melt adhesives based on the block copolymers of styrene with butadiene or isoprene. Vinyl ether polymers are also used, particularly in medicinal self-adhering plasters or dressings.[93]

Silicone adhesives are, to a small degree, used in PSAs. These products are based on silicone rubber and synthetic silicone resins. They have excellent chemical and solvent resistance, excellent elevated-temperature resistance, excellent cold-temperature performance, and high resistance to thermal and oxidative degradation. Their disadvantages include lack of aggressive tack and high cost (three to five times as much as acrylic systems).[94]

PSAs are often supplied to the final consumer coated onto a substrate such as cellophane tape or insulating tapes based on plasticized PVC film. These consist of the backing film, a primer or key coat, and the adhesive. If the product is to be rolled up in tape form, a release coat may be applied to the back of the film to reduce unwind tension when the tape is applied; otherwise it is omitted. The adhesive, generally of the types discussed here, is usually applied from an organic solvent. Aqueous dispersions and hot-melt forms, however, can be used. The coating weights range from 10 g/m^2 upward but are generally around 20−50 g/m^2. The primer is applied at a coating weight of 2−5 g/m^2 from solvent or aqueous dispersion. Nitrite rubber, chlorinated rubbers, and acrylates are common primers.

A graft copolymer of methyl methacrylate and natural rubber can be used as a primer coat for plasticized PVC. The release coat is also applied to a lightweight coating at 1−5 g/m^2. Acrylic acid esters of long-chain fatty alcohols, polyurethanes incorporating long aliphatic chains, and cellulose esters have also been used as release coats. Almost any material that can also be put through a coating process can also be used as adhesive backing.[93]

8.48 Resorcinol-Formaldehyde Adhesives

These adhesives cure by the addition of formaldehyde, compared with phenolics, which cure upon addition of strong acids.[8,56,70] Commercially, these adhesives are supplied as two-part systems. A liquid portion, the "A" part, is the resinous constituent. The resinous constituent is, generally, a solution of the preformed formaldehyde-deficient resin within a mixture of alcohol and water, and it has a solid content of about 0%. This resin is stable if kept in closed containers at or below room temperature. The pH at which the liquid is buffered controls the reactivity of the glue. The solid portion, or "B" part, is a solid, powdered mixture of para-formaldehyde, or "para" and fillers. The para is selected for control of glue-mix working life and curing efficiency. Once the A and B portions are mixed, the pot life of the mixture is limited. Many of these glue mixtures are exothermic (upon mixing), increasing the mix temperature and thus accelerating the cross-linking reaction. Consequently, the pot life is reduced considerably. In these cases, removing the heat by stirring and cooling as rapidly as the heat is generated is important. Actual gluing may take place anywhere in the range of 21−43 °C, with clamping at moderate pressures.[95]

These adhesives are suitable for exterior use and are unaffected by water (even boiling water), molds, grease, oil, and most solvents. Their applications primarily include wood, plywood, plastics, paper, and fiberboard.[7] Resorcinol-formaldehydes are excellent marine-plywood adhesives. Curing at room temperature normally takes 8−12 h, whereas phenolic wood adhesives require a high-temperature cure. The adhesives are also used for indoor applications because of their high reliability.[2,95]

8.49 Rubber-Based Adhesives

See Elastomeric Adhesives (Section 8.14).

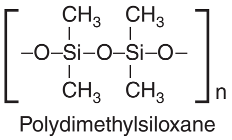

Figure 8.6 Chemical structure of polydimethylsiloxane.

8.49.1 Silicone Adhesives

Silicones are semi-inorganic polymers (polyorganosiloxanes) that may be fluid, elastomeric, or resinous, depending on the types or organic groups on the silicone atoms and the extent of cross-linkage between polymer chains.[8,96,97] An example of silicone resin structure is exhibited in Fig. 8.6.

The silicone resins owe their high heat stability to the strong silicon−oxygen−silicon bonds. The resin systems vary significantly in their physical properties as a result of the degree of cross-linkage and the type of radical (R) within the monomer molecule. In this regard, the chief radicals are methyl, phenyl, or vinyl groups.[98]

These polymers have unusual properties and are used both to promote and to prevent adhesion. Silicones have good heat stability, chemical inertness, and surface-active properties. Applications of silicone adhesive fall into four types:[2]

- Primers or coupling agents
- Adhesives and sealants (adhesive/sealants)
- PSAs
- Heat-cured adhesives

Silicones have not found broad use as adhesives, relative to the total consumption volume, because of their high cost. Their applications are numerous and varied. Silicones are applied where organic materials (based on carbon) cannot withstand exposure to the environmental conditions, superior reliability is required, or their durability gives them economic advantages. As coupling agents, silicones are widely used for surface treatment of fiberglass fabric for glass-reinforced laminates. The adhesion of epoxy or polyester to glass cloth is improved both in strength and in moisture resistance of the cured bond by the use of silicone-coupling agents. The retention of flexibility and a fraction of strength at a temperature range from cryogenic to >260 °C is an advantage of silicones. Generally, the room-temperature mechanical properties of silicone adhesives are quite low compared with typical polymers.[2]

Table 8.9 Examples of Peel and Lap-Shear Strength of Silicone Adhesives[2]

Adherends	Peel strength
Rubber to aluminum	2975–3500 N/m
Urethane sealant to aluminum	
Without primer	612 N/m
With silicone-coupling agent	2450 N/m
Lap-shear strength	
Metal to metal	1.7–3.4 MPa

The excellent peel strength properties of silicones are more important in joint designs than the tensile or lap-shear properties. Examples of peel and lap-shear strengths with silicones are presented in Table 8.9.

Silicone applications in adhesives include the following:

- Two-part adhesive for bonding insulating tapes to magnet wire (Class M performance)
- One- or two-part adhesives for pressure-sensitive tapes, used in the temperature range of −62 °C to 260 °C. End uses of these tapes include some in electronics and aerospace industries

Silicone use in primers includes the following:

- Bond promoters with phenolic binders for foundry sand on abrasive wheels
- Filler treatment in filled polyester or epoxy coatings (epoxy concrete patching formulations)
- Improved bonding of polysulfide or urethane sealants to metal substrates or glass

In some cases, silicone is as effective when blended into an adhesive formulation as when it is applied separately as a primer. For silicone-coupling agents, moisture adsorbed on the substrate plays an important role in attaching the silicone molecule through hydrolysis. The opposite end of the molecule contains a chemical group, such as a vinyl or amine, which is reactive with the epoxy, polyester, or another resin that is to be adhered to the substrate. In this manner, a single layer of silicone molecules "couples" the resin to the substrate. In addition to bond strength, moisture resistance also improves.[2]

Silicone adhesives cure without the application of heat or pressure to form permanently flexible silicone rubber. The rubber remains flexible despite the exposure to high or low temperatures, weather, moisture, oxygen, ozone, or UV radiation. This flexibility means that they are useful for joining and sealing joints in which considerable movement can be expected, such as intermediate layers between plastics and other materials of construction (e.g., acrylic glazing). Several types of silicone adhesives/sealants are available, including one-part and two-part systems.

One-part silicone systems are ready to use, require no mixing, present no pot-life problem, and are generally the least expensive. Conventional one-part adhesive/sealants are available with two different types of cure systems: acid and nonacid cure. Both require moisture from the atmosphere to cure. The acid-curing type has the greatest unprimed adhesion and the longest shelf life. The nonacid-curing type is effective when the acetic acid released by the cure reaction may cause corrosion or be otherwise objectionable.[99]

The two-part silicone adhesive/sealants do not require moisture to cure and produce a superior deep-section cure. Two types are available: addition-cure and condensation-cure. Addition of curing produces no by-products, can be heat accelerated, produces negligible shrinkage, and provides the best high-temperature resistance of all silicone adhesives. Condensation-cure silicones are not easily inhibited and can be used on a greater variety of materials.[101]

Dow Corning Corp. offers an improved silicone adhesive/sealant for high-temperature use. This is a one-part, non-slumping paste that cures to a tough, rubber solid at room temperature on exposure to water vapor in the air. This material is said to perform at temperatures ranging from −65 °C to 260 °C for continuous operation and to 316 °C for intermittent exposure. This material will meet the requirements of MIL-A-46106A (2), Type 1 (see http://mil-spec-industries.com). The adhesive/sealant is acid cured and acetic acid is evolved during cure.[89] Table 8.1 summarizes some of the characteristics of silicone adhesives.

GE Silicones reported[100] that silicone PSAs have been prepared from a newly developed, high solids silicone technology. The platinum-catalyzed silicone compositions consist of siloxane resin and hydrosilylation-reactive silicone fluids containing silicon-bonded vinyl and hydride functionalities. These high solids silicone compositions exhibit a manageable viscosity profile and cure at a rate proportional to the platinum level, at temperatures as low as 100 °C. The effect of the SiH to Si-vinyl stoichiometry ratio, the molar ratio of MH to DH, hydride cross-linker type and structure, and the chain length of the silicone oligomer on the peel and tack adhesive properties, as well as the chain extension and branching hydrosilylation reactions, were investigated.

Another report[101] reveals the preparation of silicone PSAs from platinum-catalyzed, high solids silicone composition. The adhesive compositions consist of an MQ siloxane resin, vinyl- and hydride-terminated silicone fluids, and a multifunctional vinyl silicone cross-linker. In this investigation, multifunctional vinyl silicone cross-linkers of various structures, including linear polymers, T, TQ, and Q resins, were prepared and evaluated for their effect on the adhesive properties of cured silicone PSAs. The siloxane resins of the type produced in this study are frequently designated "MQ" resins.[102] MQ resins are macromolecular polymers consisting essentially of $R_3SiO_1/2$ and $SiO_4/2$ units (the M and Q units, respectively), wherein R is a functional or nonfunctional organic group. These resins may also include a limited number of $R_2SiO_2/2$ and $RSiO_3/2$ units, respectively, referred to as D and T units. As used herein, the term "MQ resin" means that, on average, no more than about 20 mole percent of the resin molecules are composed of D and T units.

8.50 Solvent-Based Systems

Natural and synthetic rubber and synthetic resins are soluble in organic solvents, resulting in cements, resin solutions, or lacquers. In addition, there are many cellulose derivatives, such as nitrocellulose, ethyl cellulose, and cellulose acetate butyrate, used in preparing solvent-based adhesives. Solvent-based adhesives are also prepared from cyclized rubber, polyamide, and polyisobutylene. Low-molecular-weight polyurethane and epoxy compounds can be used with or without solvent. On the other hand, high-molecular-weight types or prepolymers require solvent to make application possible.[22]

Table 8.10 Principal Polymers Used for Solvent-Based Adhesives and Solvent- or Water-Based Adhesives[22]

Solvent-based	
Nitrocellulose	Cyclized rubber
Cellulose acetate butyrate	Polyisobutylene
Solvent- or water-based	
Natural rubber	Polyvinyl ether
SBR	Polyvinylidene chloride and copolymers
Butyl rubbers	Polyacrylate and polymethacrylate
Neoprene rubbers	Polyamide
Nitrile rubbers	Asphalt
Reclaim rubbers	Urea-formaldehyde
Polyvinyl acetate and copolymer	Phenol-formaldehyde
Polyvinyl chloride copolymer	Resorcinol-formaldehyde
	Resin esters

Solvents, or solvents containing small amounts of bodying resin, are used for bonding thermoplastic resins and film adhesives. An example is *toluol*, which can be used to soften and dissolve polystyrene molded articles to allow joining the softened pieces. Ketones can be used to bond PVC films in a similar manner. A small amount of resin can be used to thicken the solvent, so that a sufficient amount stays in place to dissolve the substrate. However, that solvent welding of molded plastics can cause stress cracking and weakening of the structure as the parts age should be noted.[22]

Another class of solvent-based dispersion is the organosols. In this case, vinyl chloride copolymer resins are dispersed in suitable nonvolatile plasticizers and solvent. The solvent is evaporated and the remaining film is heated to approximately 177 °C. The heat helps dissolve the resin in the plasticizer, and a tough, flexible film is obtained upon cooling to room temperature. The major polymers used for solvent-based adhesives are listed in Table 8.10.

Solvent-based adhesives are more expensive than water-based products. They usually make bonds that are more water resistant and have higher tack and earlier strength than do water-based adhesives. Solvent-based adhesives also wet oily surfaces and some plastics considerably better than do water-based adhesives. Organic solvents must be handled in explosion-proof equipment and precautions must be taken during application. Ventilation to remove toxic hazards must also be provided in order to avoid exposure of personnel to solvent vapors.[22]

8.51 Thermoplastic Resin Adhesives

A thermoplastic resin adhesive is one that melts or softens on heating and rehardens on cooling without (within certain temperature limits) undergoing chemical change. At temperatures above the melting point, an irreversible chemical change, such as depolymerization or oxidative degradation, could take place. When used as adhesives, thermoplastic resins are applied in the form of solutions, dispersions in water, or solids. They are usually set by solidification, which is a purely physical means. When applied as solution or dispersion, adhesion follows evaporation or absorption of the liquid phase, as in solvent activation. When applied by melting and cooling the solids, the terms "hot-melt" or "melt-freeze" are used to describe the method of application. Although the terms "setting" and "curing" are frequently used synonymously for both thermoplastic and thermosetting adhesives, the term setting is more common with thermoplastic adhesives. When a chemical reaction such as polymerization occurs, the term curing is more appropriate.

Although thermoplastic adhesives fall into many different chemical classes, they are all composed predominantly of linear macromolecules. Most thermoplastic resins are capable of bonding a wide variety of substrates such as paper, wood, and leather. Some are capable of bonding rubbers, metals, and some plastics, without special surface treatment. The most notable exceptions are the silicone and fluorocarbon plastics.[24]

8.52 Thermoplastic Rubber (for Use in Adhesives)

Thermoplastic rubber is a relatively new class of polymer. It has the solubility and thermoplasticity of polystyrene, whereas at ambient temperatures, it has the toughness and resilience of vulcanized natural rubber or polybutadiene. These rubbers are actually block copolymers. The simplest form consists of a rubbery mid-block with two plastic end blocks (A-B-A), as shown in Fig. 8.7. Examples of commercial products are Kraton® (www.kraton.com) and Solprene® (http://dynasolelastomers.com).[103] These materials are often compounded with plasticizers in order to decrease hardness and modulus, eliminate drawing, enhance pressure-sensitive tack, improve low-temperature flexibility, reduce melt and solution viscosity, decrease cohesive strength or increase plasticity if desired, and substantially lower material costs. Low levels of thermoplastic rubbers are sometimes added to other rubber adhesives. These materials are used as components in the following applications: PSAs, hot-melt adhesives, heat-activated-assembly adhesives, contact adhesives, reactive contact adhesives, building construction adhesives, sealants, and binders. Two common varieties of thermoplastic rubber adhesives are styrene-butadiene-styrene (S-B-S) and styrene-isoprene-styrene (S-I-S).[21]

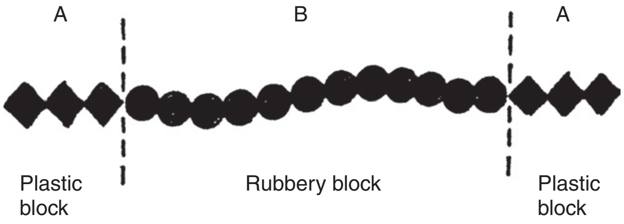

Figure 8.7 Simplified representation of a thermoplastic rubber molecule.[21]

8.53 Thermosetting Resin Adhesives

A thermosetting synthetic resin is one that undergoes an irreversible chemical and physical change during curing to become substantially infusible and insoluble. The term thermosetting is applied to the resin both before and after curing. Some thermosetting adhesives are condensation polymers and some are addition polymers. The important thermosetting resin adhesives are urea-formaldehydes, melamine-formaldehydes, phenol-formaldehydes, resorcinol-formaldehydes, epoxies, polyiso cyanates, and polyesters.[24]

8.54 UV-Curing Adhesives

UV-curable adhesives, and, in general, radiation-curable adhesives, use UV light or other radiation sources to initiate curing. A permanent bond forms without application of heat by means of free-radical chemistry. The advantages of UV curing include lower application temperature (120−140 °C), solvent-free, improved shear resistance at a higher temperature, improved chemical resistance, and lower equipment installation costs. A disadvantage of UV-curing adhesives is that one substrate is usually required to be transparent to UV light. Some UV resin systems utilize a secondary cure mechanism to complete the curing of the adhesive regions that are shielded from UV rays. The electron beam, in contrast, does not have this advantage and penetrates through most materials.

UV-curing adhesives are available in a number of chemical systems, most of which are polymer based. These systems include acrylics and acrylates, epoxies, polyurethanes, polyesters, silicones, and vinyl and vinyl esters. The most common UV-curable adhesive is the acrylics. Specially modified acrylic and epoxy adhesives can be cured rapidly by UV radiation. In the case of epoxy adhesives, the adhesives can be pre-irradiated after application to the substrate and before closing the bond line. These adhesive systems are offered by most major suppliers.[104]

The cure time of different UV-curable adhesives varies, ranging from instantaneously to several hours. Typically, UV exposure starts the process, which begins with tackiness of the adhesive and requires a given length of time to set fully. Longer cure times are required at lower curing temperatures.

There are a wide variety of UV-curing materials available for a broad range of applications. UV-curing resins are used to protect laminated flooring or to coat the “peel and stick” labels you use. We will look at two types of high-performance engineering adhesives that are typically used in product assembly.[105]

Firstly is an epoxy-based material adhesive. Although some people use the term epoxy as a generic reference to all high-performance engineering adhesives, it has a specific meaning within the adhesive world. It is also different from other adhesive types, particularly the acrylic-based adhesives.

Epoxy adhesives use a catalytic cure mechanism. The catalyst is a byproduct from the reaction of the photoinitiator to UV light. By definition, a catalyst is a substance that promotes a chemical reaction but is not consumed in the reaction. One consequence of this is that UV-curing epoxy adhesives can exhibit a shadow curing capability—material that is not directly exposed to UV light will cure, sooner or later.

Epoxy adhesives are also easy to modify for special purposes. For example, they can be filled with carbon, silver, or gold to provide electrical conductivity. Other additives can enhance thermal conductivity while maintaining electrical insulation. Additional performance properties of epoxy-based adhesives that can be modified include impact resistance, shrinkage, glass transition temperature, high-temperature strength, surface specific adhesion characteristics, and chemical or moisture resistance.

Acrylic adhesives result from an entirely different chemistry and a different type of photoinitiator. Curing of acrylic adhesives results from a free radical mechanism. The free radicals are produced by the photoinitiator when it is exposed to UV light. However, the free radicals are consumed in the adhesive cure process, so acrylic adhesives can cure only where UV light is delivered. At least one of the components being bonded must be UV transparent to some degree. Another consequence of this cure mechanism is that no shadow cure capability is evident.

Modification of properties in acrylic adhesives is more often conducted at the chemical level through changes in formulation or by combining with other base resins. Wide-ranging properties can include impact resistance, surface insensitivity, environmental resistance, and so on. The emergence of urethane acrylate adhesives, as well as of acrylated epoxies, begins to make simplistic adhesive classifications more challenging.

8.55 Urea-Formaldehyde Adhesives (Ureas)

These adhesives are commonly called urea glues.[54−56] They are the condensation products of unsubstituted urea and formaldehyde. They are usually two-part systems, consisting of the resin and the hardening agent (liquid or powder). They are also available as spray-dried powders with incorporated hardener. The latter is activated by mixing with water. Fillers are also added. Curing is normally accomplished under pressure without heat. For general purposes, curing is carried out for 2−4 h at 20 °C and 0.35−0.70 MPa bonding pressure. In manufacturing of plywood, adhesion is accelerated by heat assist. Typical conditions include a 5–10-min dwell at 120 °C and up to 1.6 MPa of pressure. Timber (hardwood) is cured for 15–24 h at 20 °C and 0.14 MPa. Softwood curing conditions are a dwell of 15–24 h at 20 °C and 0.70 MPa. Bonding pressure depends on the type of wood, shape of parts, and similar factors.

The most common application of urea-formaldehyde adhesives is in plywood. Urea glues are not as durable as other types but are suitable for a wide range of service applications. When glue line thickness ranges from 0.05 to 0.10 mm, the bond strength usually exceeds the strength of the wood. However, when glue line thickness exceeds 0.37 mm, the gap-filling properties are poor. Thick glue lines craze and weaken the joints unless special modifiers, such as furfural alcohol resin, are incorporated. These adhesives are not suitable for outdoor applications or extreme temperatures.[7,8,24]

8.56 Vinyl-Epoxy Adhesives

These structural adhesive alloys are polyvinyl acetals.

8.57 Vinyl-Phenolic Adhesives

These structural adhesive alloys are also polyvinyl acetals. They may be phenolic-vinyl butyral or phenolic-vinyl formal.[8] “Vinyl” in vinyl-phenolic adhesive is a somewhat misleading term referring either to polyvinyl formal or to polyvinyl butyral. Vinyl phenolics generally have excellent durability, both in water and in other adverse environments. Cure takes place at 177 °C for the polyvinyl formal-phenolic and at 150 °C for the polyvinyl butyral-phenolic. These adhesives provide excellent performance, primarily as film adhesives. Grades that cure at lower temperatures and pressures yield higher hot strength, and higher peel strength, and have other performance advantages.[8,17–19] Tables 8.3 and 8.4 and Section 8.4 provide useful information on these adhesives and their strength properties.

Cure conditions for the polyvinyl formal-phenolic film consist of 177 °C for 5 min or 150 °C for 30 min at 0.35–3.5 MPa bonding pressure.

Curing of polyvinyl butyral-phenolic film requires a temperature of 150 °C at 0.10–0.20 MPa pressure. Polyvinyl formal-phenolic film, the most common form, retains adequate strength when exposed to weather, mold growth, salt spray, humidity, and chemical agents such as water, oils, and aromatic fuels. These adhesives generally have good resistance to creep, although temperatures up to 90 °C produce creep and softening of some formulations. Fatigue resistance is excellent, with failure generally occurring in the adherends rather than in the adhesive, which has a service temperature range of −60 °C to 100 °C.[8]

8.58 Polyvinyl Formal-Phenolics

These structural adhesives are used to bond metal to metal in aircraft assemblies, metal honeycomb panels, and wood-to-metal sandwich construction. Other applications include bonding cyclized rubber and, in some cases, vulcanized and unvulcanized rubbers and copper foil to plastic laminates for printed circuits. They are also applied as a primer for metal-to-wood bonding with resorcinol or phenolic adhesives. Polyvinyl formal-phenolics are among the best thermosetting adhesives for metal-honeycomb and wood–metal structures. These adhesives are generally equivalent to nitrile-phenolics for strength, but they have slightly better self-filleting properties for honeycomb assembly. They are superior to epoxy types where strength in sandwich construction is desirable.[8]

8.59 Polyvinyl Butyral-Phenolics

These are used in bonding metal or reinforced plastic facings to paper (resin impregnated) honeycomb structures, cork and rubber compositions, cyclized and unvulcanized rubbers, steel to vulcanized rubber, and electrical applications. They are also used as primer for metals to be bonded to wood with phenolics. Polyvinyl butyral-phenolics lack the shear strength and toughness of the polyvinyl formal-phenolic type.[8]

8.60 Vinyl-Resin Adhesives

Several vinyl monomers are used to prepare thermoplastics that are useful in certain adhesive applications. The most important vinyl resins for adhesives are polyvinyl acetate, polyvinyl acetals (butyral and formal), and polyvinyl alkyl ethers. PVC and copolymers of both vinyl chloride and vinyl acetate with other monomers, such as maleic acid esters, alkyl acrylates, maleic anhydride, and ethylene, are also used to produce solvent-based adhesives.[2]

Table 8.11 Principal Polymers Used Exclusively for Water-Based Adhesives[22]

Starch and dextrin	Casein
Gums	Sodium carboxymethylcellulose
Glue (animal)	Lignin
Albumen	Polyvinyl alcohol
Sodium silicate	

8.61 Water-Based Adhesives

These adhesives are prepared from materials that can be dispersed or dissolved only in water. Some of these materials are the basis of solvent-based adhesives and are the principal materials used for liquid-adhesive formulations given in Table 8.11.

Table 8.10 lists polymers used for both water- and solvent-based adhesives. Water-based adhesives cost less than the equivalent solvent-based compounds. Even inexpensive organic solvents are costly when compared with water. The use of water eliminates problems of flammability, emission, and toxicity associated with organic solvents. However, in most cases, water-based adhesives must be kept from freezing during shipment and storage because of possible permanent damage to both the container and the contents.[22]

There are two general types of water-based adhesives: solutions and latexes.[106] Solutions are made from materials that are soluble only in water or in alkaline water. There are two sources for the soluble substances: natural and synthetic polymers (Table 8.12).

Water-based (more commonly referred to as *waterborne*) adhesives are typically formulated:[107]

Natural polymers—from vegetable sources (e.g., dextrins, starches), protein sources (e.g., casein, blood, fish, soybean, milk albumen), and animal (e.g., hides, bones), or

Soluble synthetic polymers—from polymers including polyvinyl alcohol, cellulose ethers, methylcellulose, carboxymethylcellulose, and polyvinylpyrrolidone

These adhesives may be supplied as solutions or formulated as dry powders that must be mixed with water prior to application. The strength of the adhesive is attained when water is lost from the glue line by evaporation or absorption by the substrate. Because of this requirement, use of these adhesives requires that at least one substrate is permeable. Where neither substrate is permeable, applying a thin coat of adhesive, allowing it to dry, and activating the adhesive by lightly wiping with a wet brush or roller, or by spraying, is possible. This procedure gives the system "quick tack," and the amount of water in the glue line is so small that a porous substrate is not required. Considering that the polymers are water soluble, bonds made using these adhesives have limited resistance to moisture and water. Some plant glues, and casein glues, have the special feature of base raw materials being insoluble in room temperature water and having to be dissolved in alkaline media (sodium hydroxide solution or ammonia). These adhesives have improved moisture resistance compared with adhesives that are directly soluble in

Table 8.12 Commonly Used Water-Based Adhesives[110]

Type of adhesive	Origin of the base raw material	Area of application
Glutin Adhesives		
Skin Adhesives	Raw skin waste and tissue	Bonding paper
Fish Adhesive	Fish skin	Gummed adhesive strips
Based on natural plant products		
Starch adhesive	Maize, potatoes, and rice	Bonding paper
Methyl cellulose	Casein: cellulose and wood	Wallpaper paste
Casein adhesive	Protein component of milk	Bottle labeling
Polyvinyl acetate (PVAc) adhesives	Saponification product of polyvinyl acetate or other polyvinvyl esters	Bonding paper, cardboard, wood, base material for moisture-activated bonding

Table 8.13 Dispersion Adhesives[111]

Polyvinyl acetate	Good adhesion to cellulose-containing substrates such as wood and paper. Primarily used for wood adhesives
Vinyl acetate copolymers	Good adhesion to many polar plastics
Polyacrylates	Good aging properties and resistance to media. Primarily used for pressure sensitive adhesives (labels, adhesive tapes), permanent adhesives (e.g., for tiles and floor and wall coverings) and laminating adhesives (e.g., glossy films)
Polyvinylidene chloride	Physiologically harmless and hence preferred for laminating adhesives used for food packaging applications
Styrene-butadiene copolymers	Laminating adhesives (e.g., aluminum foil on paper)
Polyurethanes	Usually very good adhesion to many substrates and high adhesion strengths. Applications in the shoe-making industry and for film lamination
Polychloroprene	High elasticity and adhesion strength. Primarily used in the shoe-making industry
Rubber Latexes	For example, chloroprene latex. Alternative to solvent-containing contact adhesives

water. Many water-based solution adhesives are perishable and so extended storage is not possible.

Latex is a stable dispersion of a polymeric material (Table 8.13) in an essentially aqueous medium. An *emulsion* is a stable dispersion of two or more immiscible liquids held in suspension by small percentages of substances called emulsifiers. In the adhesives industry, the terms latex and emulsion are sometimes used interchangeably. There are three types of latex: natural, synthetic, and artificial. Natural latex refers to the material obtained primarily from the rubber tree. Synthetic latexes are aqueous dispersions of polymers obtained by emulsion polymerization. These include polymers of chloroprene, butadiene-styrene, butadiene-acrylonitrile, vinyl acetate, acrylate, methacrylate, vinyl chloride, styrene, and vinylidene chloride. Artificial latexes are made by dispersing solid polymers. These include dispersions of reclaimed rubber, butyl rubber, rosin, rosin derivatives, asphalt, coal tar, and a large number of synthetic resins derived from coal tar and petroleum.[108]

Latex adhesives replace solvent-based adhesives more easily than do solution adhesives. Most latex adhesives are produced from polymers that were not designed for use as adhesives. This is why they require extensive formulation: to obtain the proper application and performance properties. Application methods for latex adhesives include brush, spray, roll coat, curtain coat, flow, and knife coat. The bonding techniques used for latex adhesives are similar to those used for solvent adhesives. The following techniques are popular:[106,109]

- *Wet bonding:* Used when at least one of the bonded materials is porous. The adhesive is usually applied to one surface only. Bonding takes place while the adhesive is still wet or tacky
- *Open-time bonding:* In this method, the adhesive is applied to both surfaces and allowed to stand "open" until suitable tack is achieved. At least one of the adherends should be porous
- *Contact bonding:* In this method, both surfaces are coated and the adhesive is permitted to become dry to the touch. Within a given time, these surfaces are pressed together and near-ultimate bond strength is immediately achieved. In this method, both surfaces may be nonporous. Neoprene latex adhesives are commonly utilized in contact bonding
- *Solvent reactivation:* In this method, the adhesive is applied to the surface of the part and allowed to dry. To prepare for bonding, the adhesive is reactivated by wiping with solvent or placing the part in a solvent-impregnated pad. The surface of the adhesive tackifies and the parts to be bonded are pressed together. This method is suitable only for relatively small parts

- *Heat reactivation:* In this method, a thermoplastic adhesive is applied to one or both surfaces and is allowed to dry. To bond, the part is heated until the adhesive becomes soft and tacky. The bond is made under pressure while hot. After cooling, a strong bond is obtained. This method is common for nonporous heat-resistant materials. It can also be used in a continuous in-line operation. The adhesive is applied in liquid form to a film or sheet, force-dried with heat to remove the water and then laminated to a second surface while still hot. Temperatures are usually in the range of 121−177 °C

Solid contents of latex adhesives are in the 40−50% range compared with about 20−30% for solvent-based adhesives. The main disadvantage of latex adhesives is the longer drying time required before tack or strength develops. On the other hand, latex adhesives have good brushability and usually require less pressure to pump or spray than solvent-based adhesives. Prior to drying, they can be cleaned up with water.

8.62 Green Adhesives and Sealants

Green adhesives and sealants are products that reduce harm to the environment and are either being developed or have only recently been introduced to the market. Green adhesives and sealants include those with any of the following characteristics:[110]

1. Manufactured from sustainable raw materials, generally taken to mean materials based on renewable feedstock
2. Manufactured through an environment-friendly process (one that conserves materials and energy) and are safe, and harmless to the environment
3. Have low VOCs
4. Provide finished assemblies that are more environment-friendly (e.g., adhesives reduce the weight of automobiles that in turn improves fuel efficiency)

As such, bioderived adhesives (based on natural origins) have been there for over a century, with multipronged benefits such as their relatively low cost, easy clean-up process (using detergent and water rather than organic solvents needed for synthetic petroleum-based adhesives), and minimal environmental impact. It is expected that there will be coexistence of renewable plant resources with conventional, hydrocarbon-based ones.

Primarily based on starch, soy, and vegetable oils, naturally occurring adhesives have had a history of commercial use and are being further developed to compete with petroleum-based adhesives. Bioderived polyols from agricultural feedstock such as soybeans can be effectively used in polyurethane adhesive and sealant formulations. These offer properties comparable with traditional adhesives, with several products now being commercially available. Other adhesive polymers generated from vegetable oil derived building blocks include epoxies, polyamides, and polyisoprene. Significantly, several new polymers capable of being used in adhesive formulations are produced by way of fermentation or microbial processes.

According to IntertechPira,[110] green additives are being developed at an increasing rate, as having adhesive formulation components derived from renewable sources is advantageous. These include biosolvents, nonhazardous plasticisers, waxes from vegetable oil, cellulose fibres, and rheology modifiers. Many additives are also being developed in order to provide biopolymers with enhanced properties that compete effectively with their petroleum-based counterparts.

Key environmental initiatives examined in this study include the development of adhesives directly based on naturally-occurring high volume-based resources, new raw materials based on renewable and naturally occurring feedstock, development of adhesives and processes that improve end products environmentally to which they are applied, and all the potential industry end-use sectors.

Indirect environmental effects mainly pertain to the impact that adhesives have on waste streams (with biodegradable or compostable adhesives developed to address this issue), environmentally acceptable design opportunities offered by adhesives relative to other methods of fastening, weight reduction in transportation vehicles (with the resulting savings in fuel cost), and the manufacture of alternative energy products such as wind turbine blades, solar panels, and fuel cells.

The major value propositions supporting the development of green adhesives are primarily related to the prevention of pollution and to energy consumption, efficient use of resources, and regulations and standards.

According to the study, usage of green adhesives technology accords the following advantages to business, namely:

1. Lower insurance costs as a result of reduced risk
2. Lower permit and disposal fees as a result of reduced generation of hazardous waste
3. Reduced regulatory burden through elimination of stack and fugitive air emissions
4. Elimination of solvent capture, recovery and incineration equipment, and avoided costs of emission control systems
5. Lower health and safety regulation costs (e.g., monitoring VOC concentration levels)

Acknowledging the significant role of the end-use sector in greening the adhesive industry, InterTechPira states that green activity is mainly prevalent in heavily regulated industries. Typically these are industries whose products come in contact with the public and have the largest volume use of adhesives. Thus, sectors such as packaging (laminating, hot-melt and tape-and-label adhesives), building and construction (green building standards for adhesives and sealants), woodworking (manufacture of wood composites as well as joining), transportation, shoe making, paper products, and general assembly are likely to show maximum green adhesive activity.

Synthetic, petroleum-based adhesive products that are supposed to be "green" are based on either solventless liquid, waterborne, or 100% solid adhesive systems. The study adds that over the last few years, green adhesives have experienced a positive growth rate at the expense of solvent-based adhesive systems.

Looking ahead on the technology front, InterTechPira expects the continuing advancement of conventional, petroleum-based green adhesives, with a key focus area being the improvements made in the moisture resistance of waterborne adhesive systems through additives and surfactant technology. Further development in reactive hot-melt adhesives is expected to lead to adhesives that can be applied via hot-melt processes, and also result in performance properties that are equivalent to conventional thermosetting adhesives.

Research priorities for biopolymer-based adhesives will be strongly influenced by the evolution of their product markets. In years to come, scientists will also make significant advances in refining crops and in converting them into commercial products via green chemistry technology and biorefineries, with the main research thrust focused on the development of economical, cost-effective production processes.

The formulation of adhesives, using the raw materials produced by biopolymer manufacturers, is also expected to be a key research area in the future. Thus, adhesive manufacturers must work with raw materials suppliers and end users to ensure optimal performance levels, while offering more ecologically sound products that appeal to customers.

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9 Heat-Resistant Adhesives

Guy Rabilloud

9.1 Introduction

In contrast with inorganic materials such as metals, alloys, or ceramics, which can work at high temperatures for years, the thermal stability of organic polymers is a time−temperature dependent parameter. Accordingly, heat resistance is defined as the time during which an organic material can be subjected to a given temperature. Typically, a thermally stable polymer must be safely utilized for 30,000 h at 200 °C, 10,000 h at 250 °C, 1000 h at 300 °C, 10 h at 400 °C, or for a few minutes at 500 °C. Depending on the application, the safety margin is either an acceptable weight loss (5−10%) resulting from pyrolysis or oxidation or a decrease of the initial mechanical properties. It will be seen later on that below the onset of thermal degradation the tensile modulus of films, the flexural modulus of composite materials, or the lap-shear strength of adhesives remains relatively stable for a long time. Then, their value rapidly drops within a few hours.

From a theoretical point of view, the highest achievable thermal stability of organic polymers should be attained with poly(1,4-phenylene). Its macromolecular backbone, represented in Fig. 9.1(**I**), contains only carbocyclic aromatic rings connected at the 1,4-carbon atoms. However, there is no chemical method to prepare this polymer because it does not exhibit any melting point and solubility as soon as the degree of polymerization *n* exceeds 5−6. This observation was the key factor in developing the "polyheterocyclization" concept, involving alternate aromatic carbocyclic and heterocyclic rings. The former are carried out by the "monomers," whereas the latter are formed during either the polycondensation reaction or the processing stage. Some examples of heterocycles incorporated in polymer repeating units are provided in Fig. 9.1 to illustrate the versatility of the chemistry explored over the past few decades.

Many thermally stable heterocyclic polymers have been studied for more than 30 years, but few of them have achieved commercial development. The main reason is not the nonavailability of the starting reagents or monomers but the extreme conditions required to process these materials, generally related to the insolubility of most polymers in any solvent, except sometimes strong inorganic acids. Examples are the fully aromatic polybenzimidazoles (PBIs), polybenzothiazoles, poly(imidazoquinazolinediones), and "ladder" polymers made of highly rigid fused polycyclic structures. In the literature, these polymers are described as "brick dust" materials, because they are obtained only in the form of nonfusible orange, red, or even black powders.

Obviously, heterocyclic polymers synthesized at high temperatures (350−450 °C) exhibit an outstanding thermal stability, up to 500 °C, when they are subjected to dynamic thermogravimetric analysis (TGA). This, however, can be misleading, because the stringent conditions of polycondensation in solid or semisolid phases are sometimes over the actual onset of thermal decomposition. This has been demonstrated with carborane-containing macromolecules considered to be the most thermally resistant polymers, because they do not exhibit any weight loss below 700 °C. The apparent high thermal stability of poly(carboranylene-azomethines)[1] and poly(carboranylene-dihydrobenzothiazoles)[2] is an artifact because the weight loss due to the degradation of the organic moieties is hidden by the gain in mass resulting from oxidation of the carborane cage into boron oxide and boric acid.

During 1960−1970, an impressive number of heterocycles were engaged in macromolecules without taking into account their processability. At the present time, a few heterocyclic polymers have found general acceptance in the industry as heat-resistant adhesives, dielectric and insulating films, high-modulus fibers, protecting overcoats, and matrices for composites. The

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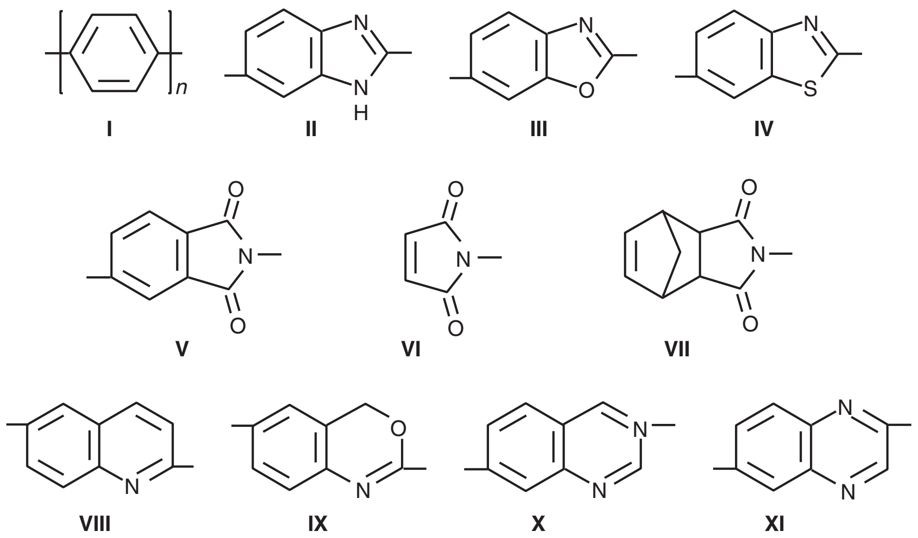


Figure 9.1 Examples of carbocyclic and heterocyclic repeating units used to build the macromolecular backbone of heat-resistant polymers: **I** poly (1,4-phenylene) or poly(*para*-phenylene), **II** benzimidazole, **III** benzoxazole, **IV** benzothiazole, **V** isoindoledione (imide), **VI** pyrroledione or maleimide, **VII** bicycloheptylpyrroledione or nadimide, **VIII** quinoline, **IX** benzoxazine, **X** quinazoline, and **XI** quinoxaline.

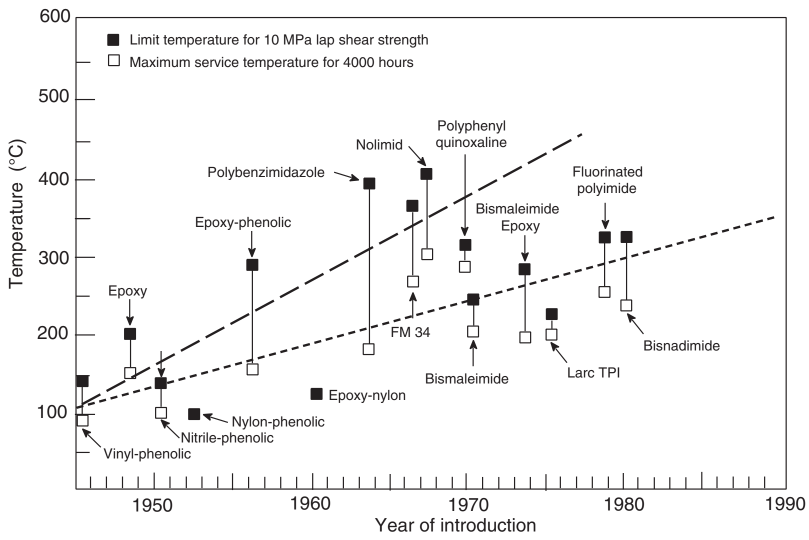


Figure 9.2 Thermal stability of structural adhesives as a function of their year of introduction in the technical literature or on the market place.

data plotted in Fig. 9.2 extend those published by Schwartz[3] and Keimel[4] and show the progressive increase in thermal stability of the most important classes of polymers used to make structural adhesives. The upper line, joining the early vinyl-phenolic resins to the CYTEC FM 34 and old Rhône-Poulenc Nolimid 380 (both are condensation polyimide precursors), represents the search for the highest thermal stability. The adhesives close to the lower line are significantly less heat resistant but often easier to process. As previously stated, the thermal stability is expressed either as a time–temperature dependence or as an adhesive strength–temperature relationship.

The basic chemistry of aromatic polyimides was first disclosed in patents filed by DuPont de Nemours[5] for polypyromellitimides and later on by Edwards[6,7] for polyimides prepared with various aromatic dianhydrides and diamines. They comprise certainly the family of heat-resistant polymers that provide most of the existing high-performance organic materials. They are now available from many manufacturers in the form of both polyimide precursors, such as polyamic acids and polyamic esters, and as precyclized soluble and meltable polyimides. Far behind this series are the commercially available PBIs, produced by Hoechst-Celanese[8] to make heat-resistant fibers and fabrics, and polyphenylquinoxaline was developed at IFP in the early 1980s. Extensive reviews of the chemistry and applications of heterocyclic polymers, particularly polyimides, can be found elsewhere.[9–14]

Heat-resistant polymers were initially developed for aerospace uses requiring a continuous service temperature of approximately 260 °C. However, legislation on energy efficiency and safety requirements continues to expand the market potential, in particular for polyimides, in the ground and aerospace transportation industries. The development of commercial polyimides that are melt processable on conventional molding equipment boosted the use of these materials. Because of their high flexural modulus and compressive strength, polyimides are now widely used in load-bearing applications in automotive and aircraft structures. New under-the-hood parts made of thermoplastic or thermosetting polyimides have been developed based on the high heat stability and resistance of these polymers to automotive lubricants, fuels, and coolants. Thermoplastic polyimides are tough and exhibit good impact strength, whereas thermosetting oligomers display inherent brittleness. High-molecular-weight linear polyimides are stiff with tensile modulus in the range of 2–6 GPa for films and 3–5 GPa for molded materials. Tensile, flexural, and compressive strengths are excellent below the glass transition temperature (T_g). The T_g determines the method of processing and the maximum temperature at which a polymer can be used in any given application.

9.2 Polymer Properties

9.2.1 Molecular Weight Determination

Oligomers and polymers are characterized by measuring their inherent viscosity (η_{inh}), which is obtained by using an Ubbelhode viscometer. Inherent viscosity is calculated by the relation $\eta_{inh} = (t_1/t_0)/C$, where t_1 and t_0 are the flow times of the polymer solution and pure solvent, respectively, and C is the polymer concentration generally expressed in gram per deciliter. Both relative and inherent viscosity values, determined at various concentrations, are then plotted as a function of C, and the intrinsic viscosity $[\eta]$ is calculated by extrapolation to zero concentration by using Huggins and Kraemer's relationships. Detailed information on the relationship between viscosity data and polymer molecular weight of polyphenylquinoxalines can be found in a previous book.[15] It was demonstrated that these polymers do follow Huggins' law $\eta_{red} = [\eta] + k'[\eta]^2 C$ with, however, quite high and variable values for the k' constant. Two techniques have been used to measure the molecular weight of heterocyclic polymers in solution: light scattering analysis and gel permeation chromatography (GPC). They are illustrated here by experiments conducted using two polymers that are reported in Section 9.3 (Polymer Chemistry).

9.2.1.1 Light Scattering Analysis

Light scattering analysis was employed to determine the molecular weight of long-chain precyclized polyphenylquinoxaline **15** (Fig. 9.10), whereas size exclusion chromatography (SEC) was found to be most suited to separate the components of low-molecular-weight polyimide oligomers **31** obtained by thermal polycondensation of the mixture of monomers **30a** and **30b** (Fig. 9.15). Weight average molecular weights are often calculated from low angle light scattering analysis according to the relation $KC/\Delta R_\theta = 1/M_w + 2A_2C$, where A_2 is the second virial coefficient, K the polymer optical constant, and ΔR_θ the excess Rayleigh's ratio. The general relationship between the weight average molecular weight and the intrinsic viscosity is generally expressed by Mark–Houwink's equation $[\eta] = KM_w{}^a$, whereas the translational diffusion coefficient D_t is also coherently related to the molecular weight by the following power law function: $D_t = KM_w{}^{-b}$. As an example, Fig. 9.3 displays the dependence of $[\eta]$ [line (a)] and D_t [line (b)] on the molecular weight M_w for polyphenylquinoxaline solutions in chloroform.

9.2.1.2 Size Exclusion Chromatography

Size exclusion chromatography (SEC), also known as GPC, separates the molecules according to their effective size in solution using a stationary phase in the form of either cross-linked polymers that swell in contact with a solvent or a microporous polymer of

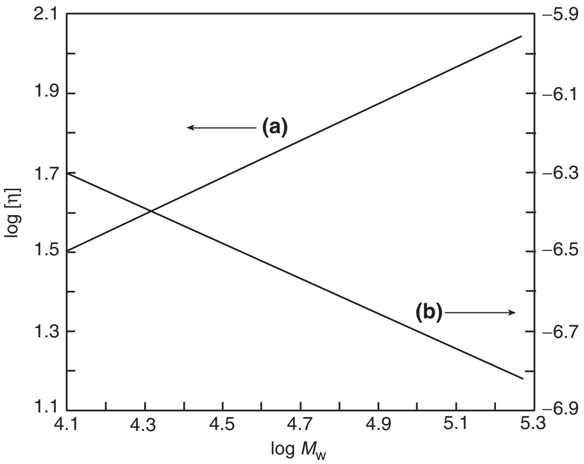


Figure 9.3 Dependence of (a) intrinsic viscosity $[\eta]$ and (b) diffusion coefficient D_t on the molecular weight M_w of the polyphenylquinoxaline **15** shown in Fig. 9.10.

rigid structure. The small molecules diffuse into the pores of the gel, where they are temporarily retained, so that they move more slowly through the column. Conversely, the large molecules cannot enter the pores, are excluded, and freely move through the column, appearing first in the chromatogram. Molecules of intermediate size are retained to a lesser extent than the smaller species and move through the column at speeds dependent on their size.

Because the effective size in solution is closely related to the weight average molecular weight (M_w), the accurate measurement of M_w requires the availability of a series of standards of known molecular weights close to monodisperse ($M_w/M_n < 1.1$). By plotting the logarithm of M_w versus the elution volume or retention time, a calibration curve is drawn. Samples of the polymer under study are then chromatographed on the same column and the elution volumes of the peaks are compared with the calibration curve to estimate the molecular weight.

This means that unavoidable errors result when the calibration made with narrow polystyrene standards is used to characterize polymers of other types. Estimations of M_w obtained with this method are often referred to as polystyrene equivalent molecular weights and their actual values can be in error by a factor of 2 or 3.

In the case of polyimides, it is worth noting that the self-condensable monomer **30 a–b** (Fig. 9.15) is a particularly interesting material, because the early stages of its thermal polycondensation can be easily monitored by using SEC. The spectra drawn in Fig. 9.4 were recorded at various time intervals during the polycondensation of the monomer in solution in benzyl alcohol at 105 °C. The experimental conditions of SEC analysis are reported in another book.[15] The first chromatogram shows that the starting material comprises 84% of monomer **30**, 15.2% of dimer, and 0.8% of trimer. The digits (0–7) plotted on the top of the peaks correspond to the number of monomer units minus one (m in formula **31**), which are clearly separated on the SEC curves. Additional computer calculation provides data up to a degree of polycondensation DP) of 12 (13 monomer units). The molecular weight peak of high intensity progressively shifts from 300 to 3690 g mol^{-1} as the inherent viscosity of the oligomer mixture increases from 0.05 to 0.22 dL g^{-1}. This makes it possible to draw an internal standard or self-calibration curve, the linear regression coefficients of which are a slope of −0.14, a Y-intercept of 6.48, and a determination coefficient of 0.9997. It is obvious that, in this case, the molecular weight accuracy is excellent in the early stage of the polycondensation reaction because the oligomers used as internal standards have the same chemical structure at any stage of the polymerization. In this particular case, SEC analysis has proved to be the most accurate method for checking the batch-to-batch consistency in the production of polyimide oligomers.

9.2.2 Thermal Properties

9.2.2.1 Dynamic TGA

The thermal and thermal-oxidative stabilities of polymers are determined by dynamic TGA using a temperature ramp of 10 C min^{-1}. The curves representing the change in polymer weight versus temperature in flowing air and in argon, respectively, are reported in Fig. 9.5 for polyphenylquinoxaline **15**. The onset of thermal decomposition in an inert atmosphere is approximately located at 560 °C, whereas polymer oxidation in air begins at 500 °C. However, even if TGA can be considered as the most useful tool for determining the thermal stability, the results must be taken only as a crude indication of the thermal resistance.

An impressive amount of data published in the literature indicates, based on TGA, that many heterocyclic polymers can be used at temperatures more than 350–400 °C. All experiments conducted later with these polymers, in actual long-term thermal operations, showed that heat-resistant polymers exhibit only a very short-term thermal stability at the onset of degradation revealed by TGA. In actual use, the thermal stability of a given polymer is approximately 150 to 200 °C less than the value provided by dynamic TGA. However, it is worth noting that significant differences exist between materials such as films and adhesives. In the former case, the surface area subjected to pyrolysis or oxidation is far greater than the periphery of an adhesive joint.

9.2.2.2 Isothermal Aging

As stated in the previous paragraph, dynamic TGA cannot provide useful information on the behavior of polymers subjected to high temperature stressing during long periods of time. Using the same analytical apparatus, isothermal thermogravimetric analysis (ITGA) can be considered as more representative of the actual thermal stability of polymers. Isothermal

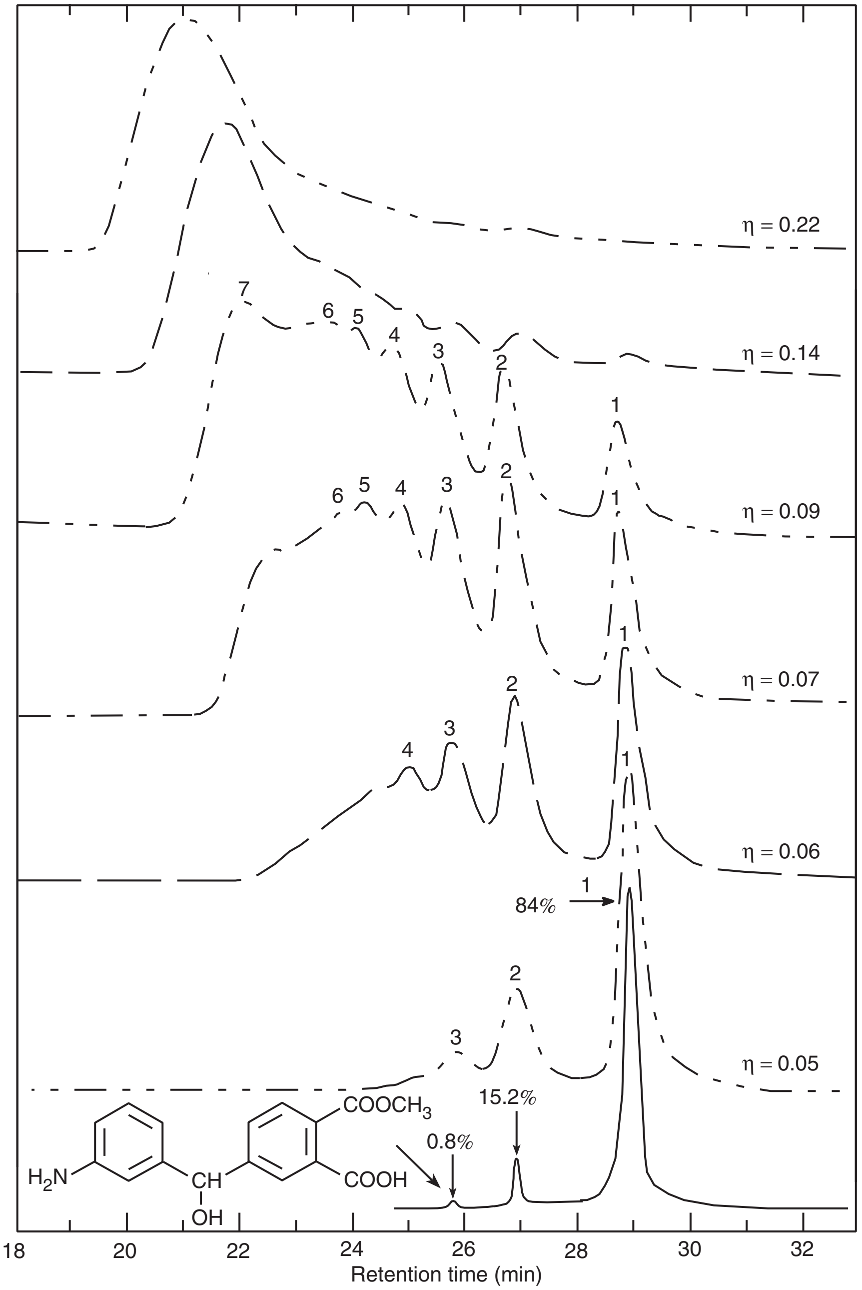


Figure 9.4 Size exclusion chromatographic analysis of the mixture of oligoimides **31** (Fig. 9.15) at various degrees of polycondensation in solution at 105 °C in benzyl alcohol.

aging in flowing air over a wide temperature range, from 250 to 550 °C, was used to determine the thermal-oxidative stability of polyphenylquinoxaline films on the basis of the results presented in Fig. 9.6. Because mechanical and electrical properties show significant variations when the polymer weight loss is more than 5%, a first estimate of the useful lifetime would be roughly 10,000 h at 250 °C, 1500 h at 300 °C, 20 h at 400 °C, 45 min at 500 °C, and 3 min at 600 °C.

To support this assumption, the variation of the mechanical properties of polyphenylquinoxaline films during isothermal aging in air at 250, 300, and 350 °C was studied and reported by Verdet et al.[16] At 250 °C, the initial values are very stable over an aging time of 1000 h and the mechanical properties remain unaffected by air oxidation. After 1000 h at 300 °C, the tensile modulus increases from 2.3 to 2.65 GPa and the tensile strength from 132 to 153 MPa. Finally, at 350 °C, both the modulus and ultimate strength significantly change within the first 200 h, thus indicating material degradation due to air oxidation. These results correlate very well with the thermal stability data determined by the isothermal aging

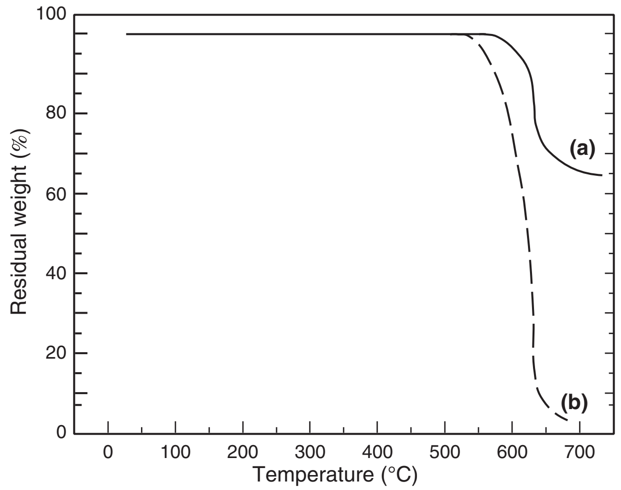


Figure 9.5 Dynamic thermogravimetric analysis of polyphenylquinoxaline **15** in argon (a) and in air (b) at a heating rate of 10 °C min^{-1}.

curves of Fig. 9.6, which demonstrates that the polymer is unaffected after 1000 h aging at 250 °C but loses approximately 2% of its initial weight when heated for the same time at 300 °C and 9% after 200 h at 350 °C. In addition, the elongation at break decreases from 8 to 1% after 200 h at 350 °C, whereas the glass transition temperature increases from 340–350 to 415 °C within 400 h at that temperature. These results have been explained[15,17] as the consequence of thermal cross-linking at high temperatures.

9.2.2.3 Thermomechanical Analysis

As adhesive compositions are most often obtained by mixing an organic binder with inorganic fillers and various additives, thermomechanical analysis is generally conducted with an expansion probe. The output of the thermal analyzer is a curve plotting the variation of adhesive thickness as a function of the temperature, which is increased at a rate of 10 °C min^{-1}. Figure 9.7 illustrates the typical behavior of polyimide **32** loaded with silver flakes and cured for 30 min at 275 °C.

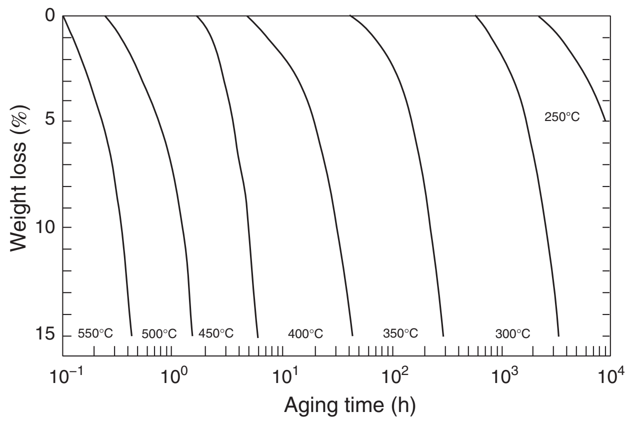


Figure 9.6 Isothermal thermogravimetric analysis of polyphenylquinoxaline **15** in flowing air in the temperature range of 250–550 °C.

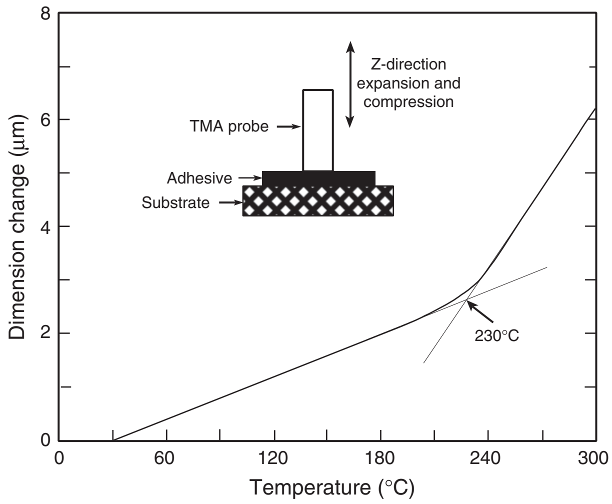


Figure 9.7 Thermomechanical analysis (TMA) of polyimide **32** loaded with 70% by weight of silver flakes.

The first linear region with a slope of 4.5×10^{-5} K^{-1} is associated with the glassy state, followed at about 230 °C by a change to a second linear region of higher slope of the order of 1.2×10^{-4} K^{-1}. This change in slope is caused by a second-order thermodynamic transition of the organic material from the glassy to the rubbery state, which is one definition of the glass transition temperature (T_g).

Thus, thermomechanical analysis provides both the T_g value and the coefficients of linear thermal expansion (CTE) before and after T_g.

9.3 Polymer Chemistry

As shown in Fig. 9.2, only some epoxy-phenolic compositions and a limited number of heterocyclic polymers exhibit long-term thermal stability at 200 °C and higher temperatures. In the heterocyclic series, only PBIs, polyimides, and polyphenylquinoxalines have been subjected to extensive testing at high temperature. Several classification schemes are commonly used in the literature to represent these polymers. In the following discussion, the polymer chemistry is presented in the form of four general classes: linear polymer precursors, precyclized thermoplastic polymers, condensation oligomers, and thermosetting resins. PBIs belong to the third category, whereas polyphenylquinoxalines are fully cyclized thermoplastic materials. Only polyimides have representative polymers in the four series.

9.3.1 Linear Polymer Precursors

The method used to prepare aromatic polyimides is illustrated in Fig. 9.8 with the reaction of 1,2,4,5-benzenetetracarboxylic acid dianhydride (pyromellitic acid dianhydride, PMDA) **1** and 4,4′-oxybisbenzeneamine (oxydianiline, ODA) **2**.[5] After a charge transfer complex between compounds **1** and **2** is initially formed, propagation occurs through the amine nucleophilic attack at the carbonyl groups of the cyclic anhydride. The reaction is actually a step polycondensation, but it looks like a polyaddition or polymerization, because the condensation by-product remains chemically bonded to the aromatic ring. It has been demonstrated that the propagation reaction is reversible however, with, equilibrium constants more than 10^5 L mol^{-1} in polar aprotic solvents that form stable complexes with the free carboxyl groups. Basic solvents thus decrease the reverse reaction and favor the formation of high-molecular-weight polyamic acids at ambient temperature. Thus, dianhydride **1** and diamine **2** lead to the intermediate PMDA–ODA polyamic acid **3**.

One point that deserves to be mentioned is that the synthesis of polyamic acids is a solid–liquid interfacial polymerization because of the low solubility of aromatic dianhydrides in organic solvents. This is also the predominant mechanism when polyphenylquinoxalines are prepared from poorly soluble aromatic tetramines (see Section 9.3.2.1). In both cases, very-high-molecular-weight macromolecules are formed almost immediately along with low-molecular-weight polymers in regions of unbalanced stoichiometry. The net result is that polyamic acids and polyphenylquinoxalines generally exhibit a broad molecular weight distribution with a number average molecular weight M_n close to that predicted by step-growth theory and M_w several times higher than the theoretical value. However, there exists a significant difference between these two families of polymers because the reversibility of the former reaction makes solutions of polyamic acids prone to equilibration during storage at temperatures higher than −10 to 0 °C. As an example, M_n reaches a value of 11,000 within 1.5 h after all PMDAs have been added and remains constant for the following few hours of storage at 31 °C. In contrast, the value of M_w is approximately 90,000 after 30 min and decreases to less than 60,000 in 5.5 h. It has been demonstrated that the polyamic acid re-equilibration is predominantly governed by the reversion of amic acids to anhydride and amine, which subsequently react with other antagonistic groups to reach the equilibrium.[18]

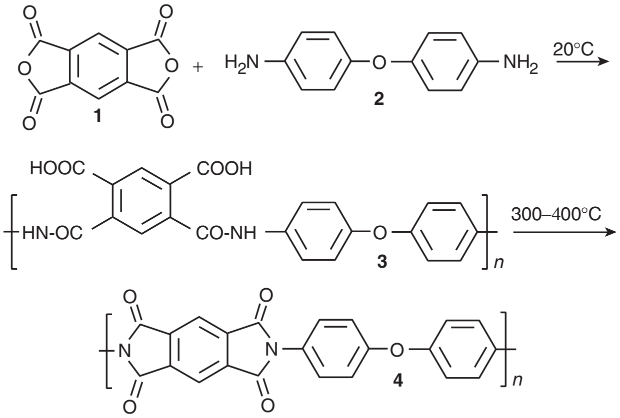


Figure 9.8 Reaction of 1,2,4,5-benzenetetracarboxylic acid dianhydride (PMDA) **1** with 4,4′-oxybisbenzene-amine (ODA) **2** providing the intermediate high-molecular-weight polyamic acid **3**, which is subsequently cyclodehydrated into aromatic polyimide **4.**

Polyamic acid **3** is the soluble precursor of PMDA–ODA polyimide **4**, which was the first commercially available aromatic polyimide film (Kapton®, www2.dupont.com) from DuPont de Nemours.[19] Solutions of polyamic acid **3** in *N*-methylpyrrolidone (NMP) typically contain 13–15% solids by weight and can be deposited onto the surface of various substrates to produce films with thicknesses in the range of 0.5–500 μm. After solvent evaporation, polymer **3** is subjected to thermal imidization (cyclodehydration) by a multistage heating culminating at 300–400 °C to produce films of polyimide **4**. One typical heating cycle is 1 h each at 100, 200, and 300 °C. When cured on inorganic substrates, polyamic acid **3** provides films of polypyromellitimide **4** exhibiting good adhesion to metals and ceramics. However, the very high glass transition temperature (385 °C) of this polyimide does not allow its use to bond two metallic parts. To produce polyimides with lower T_g while maintaining high thermal stability, in 1972, DuPont introduced a series of fluorinated polyimides whose formulae are displayed in Fig. 9.9.[20]

The chemistry of these polymers is based on the dianhydride of 4,4′-[2,2,2-trifluoro(1-trifluoro methyl)ethylidene]bis(1,2-benzenedicarboxylic acid)

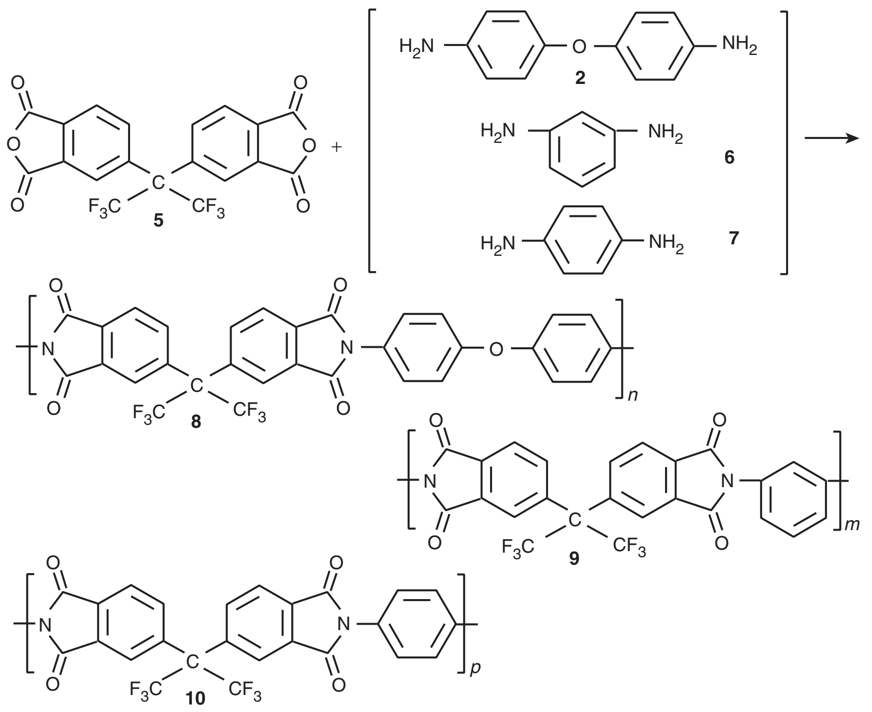


Figure 9.9 Synthesis of fluorinated polyimides marketed by DuPont. NR 150 A2® is polyimide **8** prepared from 4,4′-[2,2,2-trifluoro(1-trifluoromethyl) ethylidene]bis(1,2-benzenedicarboxylic acid) dianhydride (6FDA) **5** and ODA **2**. NR 150 B2® is a copolyimide synthesized by reacting dianhydride **5** with diamines **2**, **6**, and **7**. The macromolecule is formed of randomly distributed repeating units **8**, **9**, and **10**. NR 056X® is a copolyimide comprising recurring units **10** (75%) and **8** (25%).

5 (6FDA) that is reacted with ODA **2** to produce polyimide **8** (DuPont NR 150 A2®). The other polymers in this series are copolyimide NR 150 B2® consisting of repeating units **8**, **9**, and **10** obtained by reacting dianhydride **5**, with ODA **2**, 1,3-benzenediamine **6** (*meta*-phenylenediamine, MPDA), and 1,4-benzenediamine **7** (*para*-phenylenediamine, PPDA). The last copolymer, NR 056X®, contains recurring units **8** (25%) and **10** (75%). These polymers are tailored to cover a broad range of glass transition temperatures by using diamines **2**, **6**, and **7** providing flexible, semi-rigid, and rigid repeating units. Primarily developed as resin binders for the fabrication of composite materials, other versions were then marketed by DuPont to fulfill the requirements of high-performance adhesives.

9.3.2 Precyclized Polymers

Polymers discussed in the previous section consist of linear polyimide precursors (polyamic acids) that are transformed into polyimides during the processing stage. This means that water molecules evolve within the adhesive layer and must be removed to avoid the formation of large voided areas. To circumvent this drawback, research was focused on the synthesis of fully cyclized heterocyclic polymers, which are intrinsically thermoplastic, even though the T_g can be extremely high. Polyphenylquinoxalines, poly(isoimides), and poly(ether-imides) have been extensively studied to prepare structural adhesive films and pastes.

9.3.2.1 Polyphenylquinoxalines

A significant breakthrough was made in 1967 when Hergenrother and Levine[21,22] reported the synthesis of phenyl-substituted quinoxalines by reacting aromatic tetramines with bis(α-diketones) in *meta*-cresol solvent. The reaction occurs at room temperature within a few hours, producing high-molecular-weight precyclized polyphenylquinoxalines. The three polymers **15**, **16**, and **17** shown in Fig. 9.10 are prepared by reacting [1,1′-biphenyl]-3,3′,4,4′-tetramine **11** with (1,4-phenylene)-1,1′-bis [2-phenyl-1,2-ethanedione] **12**, (1,3-phenylene)-1,1′-bis [2-phenyl-1,2-ethanedione] **13**, and 1,1′-(oxydi-4,1-phenylene)bis[2-phenyl-1,2-ethanedione] **14**, respectively.

Most polyphenylquinoxalines show no crystallinity in wide-angle X-ray diffraction studies. Their amorphous nature is primarily due to the configurational disorder carried out in the backbone of the polymer chains by the presence of different isomers.[15] Glass transition temperature values decrease from 360 °C for polymer **15** to 320 °C for **16** and 290 °C for **17**. However, the T_g significantly increases when the polymers are heated at

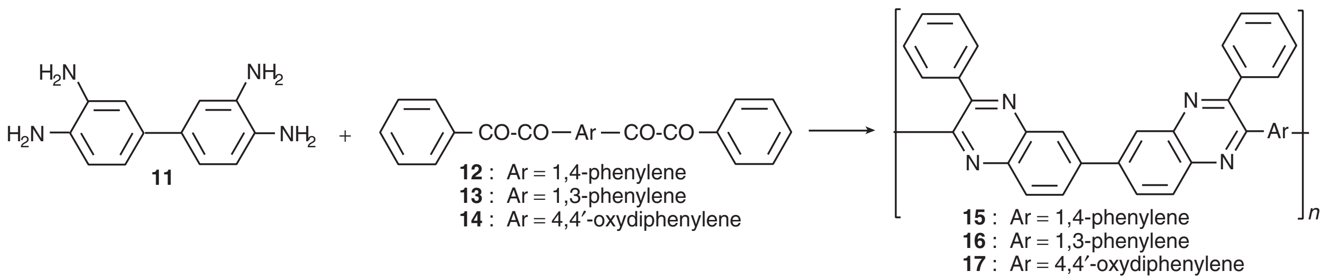


Figure 9.10 Synthesis of polyphenylquinoxalines **15**, **16**, and **17** by reaction of [1,1′-biphenyl]-3,3′,4,4′-tetramine **11** with (1,4-phenylene)-1,1′-bis[2-phenyl-1,2-ethanedione] **12**, (1,3-phenylene)-1,1′-bis[2-phenyl-1,2-ethanedione] **13**, and 1,1′-(oxydi-4,1-phenylene)bis[2-phenyl-1,2-ethanedione] **14.**

temperatures below the onset of fast oxidative degradation. Becker and Raubach[23] showed that some dephenylation and dehydrogenation reactions occurred at high temperature producing macroradicals. The subsequent recombination of closely spaced radical pairs then led to interchain crosslinking. This thermal reaction is commonly applied to the polyphenylquinoxaline adhesives used to bond metallic substrates. For example, when polymer **15** is heated in a vacuum bag for 1 h at 400 °C, its glass transition temperature increases from 350 to 415 °C.

9.3.2.2 Poly(isoimides)

If thermal imidization of polyamic acids remains the predominant technique to make polyimide films, the main drawback of this method is the production of water molecules during the processing stage. This, obviously, increases the probability of including voids and structural defects in the bulk of the final material. Because imidization is an intramolecular dehydration reaction, water can also be taken off by using chemical reagents. A particular case of chemical cyclodehydration is observed when dicyclohexylcarbodiimide or trifluoroacetic anhydride are used as dehydrating agents.[24] Instead of producing polyimides, these chemical compounds give polyheterocycles that are cyclic isomers of the imide rings, that is, polyisoimides or polyiminolactones.

Chow et al.[25] investigated the isoimide to imide conversion process with commercial Larc-TPI samples. As illustrated in Fig. 9.11, the reaction of 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride **18** and 3,3′-carbonylbisbenzeneamine **19** leads to polyamic acid **20**. Dehydrocyclization to polyisoimide **21** is then performed in solution by adding

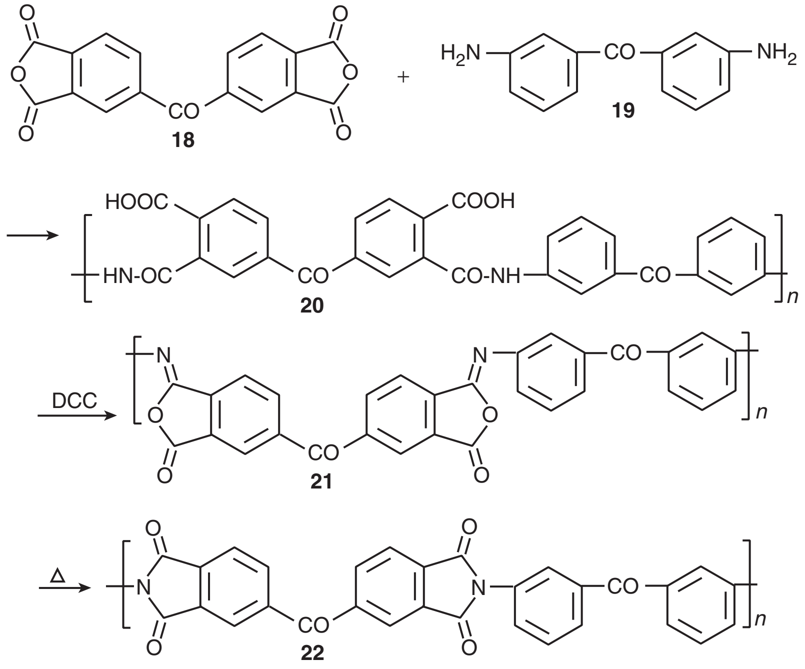


Figure 9.11 Reaction of 3,3′,4′,4′-benzophenonetetracarboxylic acid dianhydride (BTDA) **18** with 3,3′-carbonylbisbenzeneamine **19** in the presence of dicyclohexylcarbodiimide (DCC) leading to polyisoimide (polyiminolactone) **21** via the intermediate polyamic acid **20.** Isoimide-imide conversion predominantly occurs by heating polymer **21** at 300 °C, followed by a final excursion at 350–400 °C.

dicyclohexylcarbodiimide (DCC) or trifluoroacetic acid anhydride. Polymer **21** is generally processed from its solutions in polar organic solvents, dried, and converted to the polyimide **22** by thermal isomerization.

Using a Rheometrics mechanical spectrometer and powdered polymer samples, the authors compared the rheological behavior of two polymers with similar chemical compositions but different structures. The rheological profiles of polymers **21** and **22** were determined between 140 and 400 °C by increasing the temperature at 10 °C min^{-1} from 140 to 190 °C and from 300 to 400 °C. In the predominant region of isoimide−imide conversion (190−300 °C), the temperature was raised by 2 or 5 °C increments, the dynamic viscosity η being measured at each temperature step. At 190 °C, the viscosity of poly(isoimide) **21** was approximately 5×10^4 Pas and decreased to a minimum value of 10 Pas at 243 °C as the polymer softened and melted. Thermal conversion to polyimide **22** concurrently induced an increase in dynamic viscosity to 10^6 Pas at 27 °C. The rheological response of polyimide **22** was studied in a separate experiment that showed a large drop in viscosity from 2×10^7 Pas at 250 °C to 10^5 Pas at 275 °C, in the region of the glass transition temperature. This work demonstrates that the isoimide form enhances the processability of polyimides, because the melt viscosity can be reduced by several orders of magnitude. In addition to Larc TPI **22**, structural adhesives have been prepared at the Langley NASA research center from other polyisoimides leading to the three polyimides represented in Fig. 9.12.

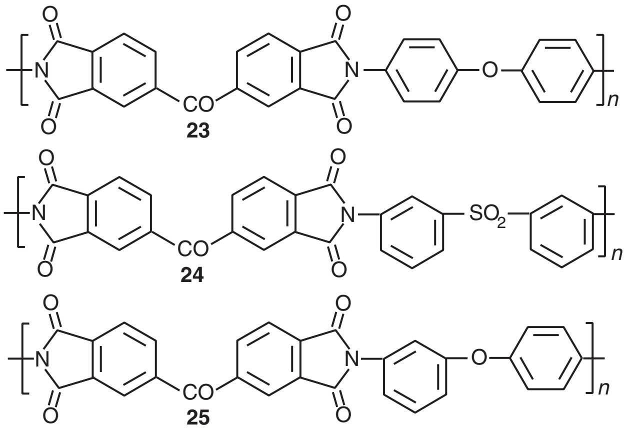


Figure 9.12 Chemical formulae of polyimides belonging to the Larc TPI series: Larc TPI-ODA **23**, Larc TPI-SO_2 **24**, and Larc TPI-IA **25**.

Larc TPI-ODA **23** is a copolyimide containing repeating units **22** (95 mol%) and **23** (5 mol%) with a T_g of 250 °C and a processability better than that of the homopolymer **22**.[26] Larc TPI-SO_2 **24**, prepared from BTDA and 3,3′-sulfonylbisbenzeneamine, has a T_g in the range of 220−250 °C according to the cure cycle.[27] Larc TPI-IA **25**, synthesized by reacting 4,4′-oxydiphthalic anhydride with 3,4′-oxybisbenzeneamine, exhibits a T_g of 243 °C.[28]

9.3.2.3 Poly(ether-imides)

Ultem 1000® (www.sabic-ip.com) **26** (Fig. 9.13) marketed by SABIC is a poly(ether-imide) representative of a series of thermoplastic polyimides that can be used as adhesives or molding materials for applications at moderate temperatures ($T_g = 220$ °C).

9.3.3 Condensation Oligomers

The long-chain semirigid polymers described in the previous sections are thermoplastic materials with glass transition temperatures ranging from 220 to 350 °C. This means that they must be heated at temperatures at least 100 °C higher than the T_g for the adhesive to flow and wet the substrate during the bonding process. One of the ways explored to do that is the synthesis of low-molecular-weight oligomers prepared by a controlled step polycondensation at moderate temperatures. Figure 9.2 indicates that the so-called "condensation oligomers" were the first high-temperature structural adhesives marketed by Narmco for PBIs and Rhône-Poulenc for polyimides. Studying the synthesis of PBIs, Vogel and Marvel[29] reported the melt polycondensation process shown in Fig. 9.14.

Equimolecular amounts of powdered 1,3-benzenedicarboxylic acid diphenyl ester **27** and [1,1-biphenyl]-3,3′,4,4′-tetramine **11** are heated in a special apparatus at 260 °C for 30 min. The polycondensation proceeds and generates molecules of phenol and water by-products. At this stage, low-molecular-weight oligomers, generally represented by the simplified formula **28**, are produced. In the actual process, the mixture still contains large amounts of monomers **27** and **11** and uncyclized *ortho*-amino-amide structures. When the blend becomes solid, it can be used to prepare adhesive pastes after it has been crushed to produce a fine tan-colored powder. High-molecular-weight polymer **29**, which is the raw material to fabricate PBI fibers, is

Figure 9.13 Chemical formula of SABIC Ultem 1000® thermoplastic poly(ether-imide) **26** with a macromolecular backbone comprising two oxygen bridges and one methylethylidene linking unit between the aromatic rings.

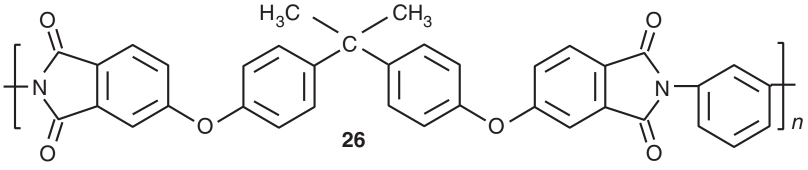
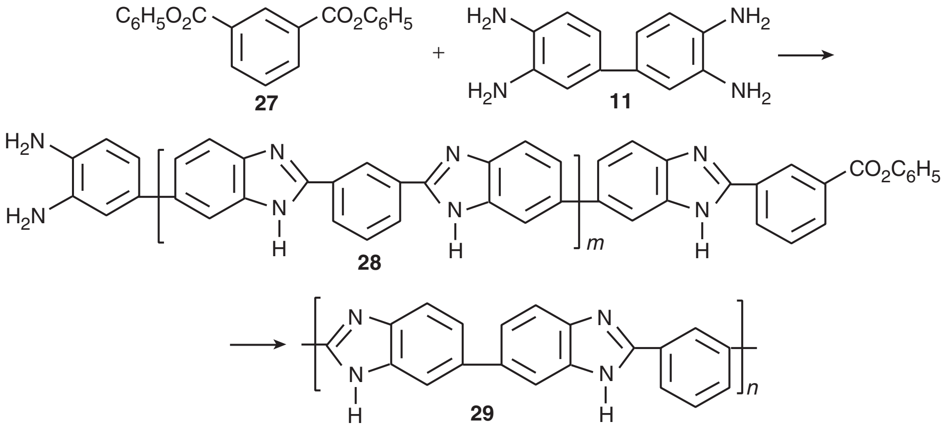


Figure 9.14 Step polycondensation of 1,3-benzenedicarboxylic acid diphenyl ester **27** with [1,1′-biphenyl]-3,3′,4,4′-tetramine **11** leading to intermediate oligomers **28**. When heated at high temperature, the oligomer mixture provides high-molecular-weight polybenzimidazole **29**.

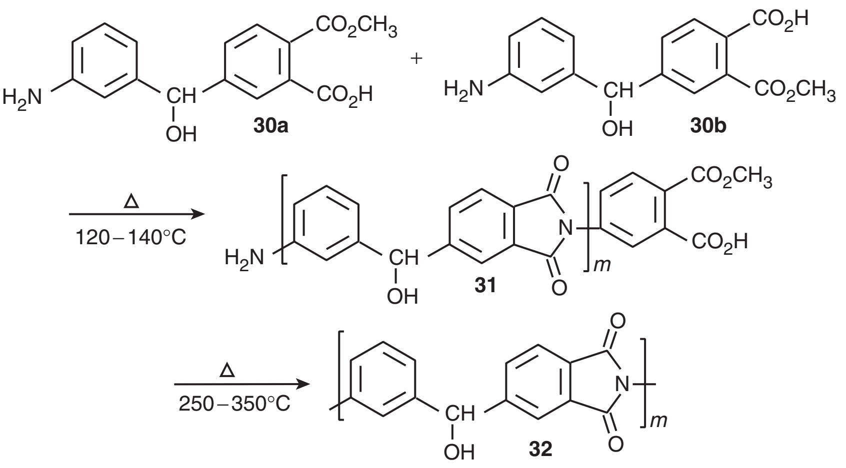


obtained by evacuating the system to 0.025 mm Hg, whereas the temperature is raised to 340 °C. The polymer is soluble in formic acid and concentrated sulfuric acid, producing stable solutions that are used to cast stiff and tough films or solution spun fibers. In the case of structural adhesives, prepolymer **28** is cured under pressure at 316 °C, followed by a post-cure treatment at 370 °C for 3 h.

The concept of "self-condensable reactive monomers," shown in Fig. 9.15, was developed to produce heat-resistant structural adhesives with a high level of dry matter content.[30] The method of synthesis generates two isomers **30a** and **30b** whose molecules carry an amine group and an antagonistic *ortho-acid* ester center. Compounds **30a** and **30b** differ only in the position of the carboxylic acid group relative to the secondary alcohol (−CHOH−) linking unit.

The thermal polycondensation in solution of these monomers is controlled to provide low-molecular-weight oligomers **31** with a DP *m* in formula **31** of approximately 10. Solutions of the oligomers in NMP at 35−40% by weight exhibit the viscosity required to prepare adhesive compositions loaded with metallic particles. Films or pastes of oligomers **31** are then cured at high temperature (300−350 °C) to increase the DP. Once completed, this reaction produces the high-molecular-weight polyimide **32**.

Figure 9.15 Synthesis of oligoimide **31** precursor of polyimide **32** by thermal polycondensation of self-condensable monomers **30a** and **30b** carrying amine and *ortho*-acid-ester groups on the same molecule.



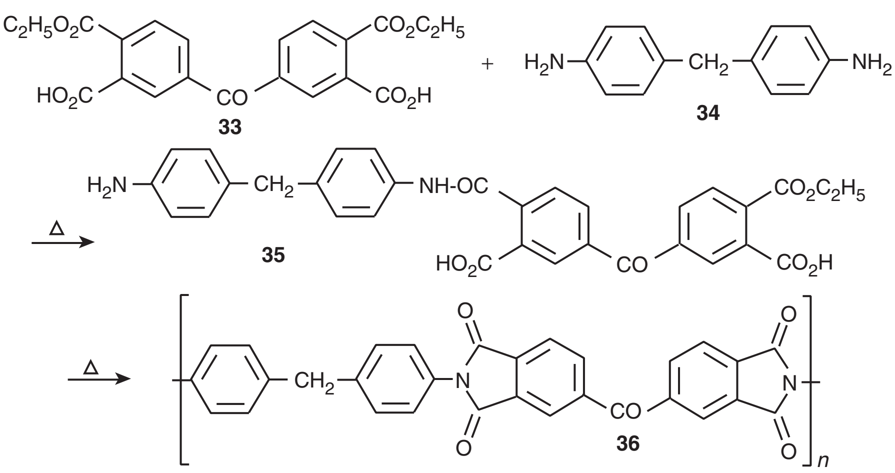


Figure 9.16 Synthesis of polyimide precursor **35** by the controlled polycondensation in solution of the bis-*ortho*-acid ester **33** and 4,4′-methylenebisbenzeneamine **34**. The reaction initially gives short-chain amide-acid such as **35** that is transformed into polyimide **36** when the adhesive is processed at high temperature.

Compared with other polyimides, the adhesive strength is significantly enhanced because of the thermal reflow that occurs during the cure cycle. When cured at temperatures lower than 300 °C, polyimide **32** has a glass transition temperature of 230 °C, sufficiently high for the electronics industry. By contrast, the structural adhesives intended to be used in aerospace applications are prepared by blending the oligomer mixture **31** with aromatic diamines to increase the formation of a cross-linked network.

Structural adhesive FM 34® marketed by CYTEC is based on a similar chemistry using the reactants shown in Fig. 9.16. The bis(*ortho*-acid ester) **33** is prepared in situ by the reaction of BTDA with ethyl alcohol in polar aprotic solvents. After 4,4′-methylenebisbenzeneamine (MDA) **34** has been added in stoichiometric amount, the solution is heated to 130−150 °C. The reaction mechanism leading to high-molecular-weight polyimides when ODA is opposed to the diethyl esters of different tetracarboxylic acids has been published.[31]

The authors suggest that the most probable scheme is an initial intramolecular cyclization of the *ortho-acid* ester centers generating the corresponding anhydrides that then react as usual to produce polyamic acids, finally subjected to thermal imidization. The intermediate compound **35** in Fig. 9.16 would be the first step of polyamic acid formation when one anhydride group has been produced and immediately opened by one amine function. The reaction is thermally controlled to produce oligomers that are marketed in the form of adhesive films, pastes, or solid powders. Polycondensation and imidization are completed on processing at high temperature, followed by a postcure at 316 °C.

9.3.4 Thermosetting Resins

High-molecular-weight linear polyimide precursors and precyclized polymers are best suited for the fabrication of self-standing films and protective coatings, requiring good mechanical properties at elevated temperature. However, these polymers are not convenient for making adhesive compositions or composite materials. Even a thermoplastic polyimide such as SABIC's Ultem® 1000 with a T_g of 223 °C must be extruded at a temperature significantly higher than 300 °C. In addition, when the linear polymers are dissolved in organic solvents, the concentration is limited to about 15% by weight. This means that the drying schedule must be carefully conducted to evaporate a large amount of solvents mainly by diffusion through relatively thick layers. In "open to air" conditions—films, varnishes, and coatings—adequate cure cycles provide homogeneous films without structural defects. In the case of adhesives, where evaporation is often limited to small peripheral areas, entrapped bubbles or voids can be the source of delamination because of the high stresses concentrated in these local defects.

To circumvent solvent-related problems, researchers developed the concept of polymerizable heterocyclic telechelic oligomers. Low-molecular-weight polyheterocycles are synthesized with respective quantities of the two monomers far from the stoichiometry. The average molecular weight generally falls in the range of 1000 to 3000 g mol^{-1}, and the terminal functions of the oligomers are then end-capped with compounds containing unsaturated double (ethylenic) or triple (acetylenic) carbon−carbon bonds. Theoretically, all thermosetting polyimides should have melting points lower than the polymerization temperature to ensure adequate flow and good wetting properties during processing. In practice, this ideal behavior is rarely encountered in the three main families of oligomers reported in the following sections. Excellent reviews on the chemistry, processing, and properties of oligoimides terminated by maleimide, nadimide, and acetylene groups can be found elsewhere.[32] Most of these materials have been used as organic binders to make adhesives and composites for the aerospace industry. The general requirements for these types of oligomers is a combination of opposite properties such as high T_g and good processability (low viscosity before cross-linking), long-term resistance to oxidation and radical cross-linking, low moisture uptake and high content of aromatic and heterocyclic rings, good mechanical properties, and so on. Most of the end-capped telechelic oligomers polymerize following complex kinetic laws depending on the conversion rate. This is because, in many cases, gelation and vitrification occur at a low degree of conversion. Recent studies on the polymerization mechanisms and chemical behavior of the main families of heat-resistant oligomers are briefly discussed in the following sections.

9.3.4.1 Maleimide-Terminated Resins

Oligomers end-capped with maleimide rings, which are known as bismaleimide (BMI) resins, exhibit thermal stability intermediate between epoxies and polyimides.[86] BMI systems are mainly used to fabricate structural composites capable of sustaining temperatures up to 230 °C. Specific versions, such as CYTEC FM 32 and Ciba-Geigy Kerimid 601, have been developed to prepare adhesive compositions. Figure 9.17 displays a typical constitutive unit of various commercial BMI resins based on BMI **38**, prepared from maleic anhydride **37** and 4,4′-methylenebisbenzeneamine (MDA) **34**.

However, a number of other aromatic diamines, in particular the alkyl-substituted MDA derivatives, have been converted into the corresponding BMIs to study the effect of the chemical structure on both the melting and curing temperatures. Most of these BMIs are crystalline materials with high melting points in the range of 150−250 °C. The chemical reactivity of these resins is a consequence of the electron-deficient carbon−carbon double bond that can be subjected to different reactions such as nucleophilic attack of amines or thiols, radical polymerization, and ene-, diene-, and cycloadditions. Polymers known as poly (amino-BMIs) or polyaspartimides are prepared by

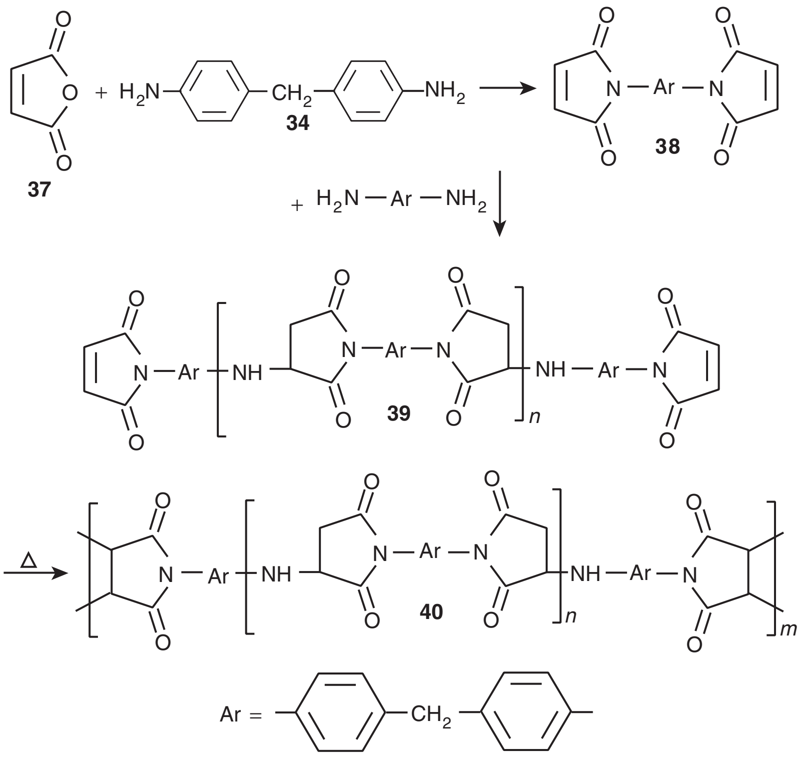


Figure 9.17 Examples of BMI monomer **38** and maleimide-terminated resin **39** prepared by Michael-type addition of 4,4′-methylenebisbenzeneamine **34** to the carbon−carbon double bond of BMI **38**. Thermal polymerization of oligoimide **39** generates the cross-linked network **40**.

Michael's reaction, which is a controlled addition of amine functions to the ethylenic double bond. This is illustrated in Fig. 9.17 with BMI **38** and MDA **34** whose respective proportions are calculated to produce oligomers **39**. This reaction has been used to increase the distance between the cross-linking sites with, however, two opposite effects. The fracture toughness increases with the degree of polymerization *n*, whereas the glass transition temperature decreases. Kerimid® 601 developed by Rhône-Poulenc,[33,34] and now produced by Ciba-Geigy, is a typical example of this type of oligomer prepared by Michael's addition. BMI is also the base material of commercial resins such as Compimid® 353 developed by Stenzenberger.[35] Addition polymerization occurs at 150−250 °C without evolution of volatile by-products.

Thermal polymerization of short-chain BMI resins occurs through radical polymerization of the maleimide double bond, producing highly cross-linked and brittle networks. A number of experimental results have been published that allow one to correlate the chemical structure of BMIs with the "processability windows $T_p - T_m$," where T_p is the onset of polymerization exotherm and T_m is the maximum of the melting temperature curve determined by differential scanning calorimetry. A study by Stenzenberger reports data of Technochemie GmbH comparing the melting point, maximum of exotherm peak, and heat of polymerization of various BMI resins in relation to their chemical structure.[32] For similar chemical formulas, *meta*-isomers melt at lower temperatures than those with *para*-catenation but exhibit higher heat of polymerization. This behavior suggests that monomer conversion is more complete before vitrification for compounds with flexible chains. In addition, it was shown that the glass transition temperature of polymerized BMIs decreases with the increase in distance between the cross-links. Radical polymerization is the most commonly used method for this category of thermosetting polyimides.

The thermal stability of cured BMI formulations during long-term aging experiments was found to be intermediate between the heat resistance of epoxy-novolacs and that of norbornene-terminated polyimides or nadimide resins discussed in the following paragraph. Composite materials made with BMI resins can be safely used for about 10,000 h at 200 °C and approximately 100−200 h at 240 °C. For long-term applications at 300 °C, that is, 2000−3000 h, other resins are more effective.

9.3.4.2 Nadimide-Terminated Resins

Historically, norbornene-terminated imide oligomers were developed at TRW Inc. by reacting 4,4′-methylenebisbenzeneamine with 3,3′,4,′4′-benzophenonetetracarboxylic acid dianhydride and (3aα, 4β,7β,7aα)-tetrahydro-4,7-methanoiso-benzofuran-1, 3-dione, also known as 5-norbornene-2,3-dicarboxylic acid or nadic anhydride.[36,37] The relative quantities of the two anhydrides are calculated to produce short-chain polyamic acid oligomer with, for example, a molecular weight of 1300 ($n = 1.67$) for the commercially available Ciba-Geigy P13N® material. Imidization first occurs to produce oligoimides terminated by reactive norbornene groups that polymerize at temperatures in the range of 280−350 °C. However, materials made with P13N solution or molding powder encountered many processing problems and this class of oligomers achieved little commercial success.

The concept of norbornene-terminated oligoimides was further studied at the NASA Lewis Research Center by researchers who developed the "polymerization of monomeric reactants (PMR)" approach.[38] The method, represented in Fig. 9.18, involves a blend of both the dimethyl ester of 3,3′-benzophenonetetracarboxylic acid **42** and the monomethylester of 5-norbornene-2,3-dicarboxylic acid **41** with 4,4′-methylenebisbenzeneamine **34** in solution in methanol.

Fibers or fabrics are impregnated with the low viscosity solution, and the solvent is removed at a relatively low temperature to provide tacky prepregs containing the three monomer reactants and 5−10% by weight of residual methanol. To prevent any reaction of the monomers, prepreg rolls protected with polyethylene films are stored at low temperature (−18 °C).

At temperatures between 120 and 230 °C, polycondensation and imidization occur in situ to form nadimide end-capped oligoimides **43** with significant evaporation of methanol and water that must be eliminated before final curing. This obviously implies that a complicated curing schedule, alternating partial vacuum and applied pressure, has to be implemented to prepare void-free composites. Up to now, the most widely known PMR resin is PMR-15, optimized to exhibit the best overall performance. An impressive number of experiments were conducted to achieve a chemical composition containing diester **42**, monoester **41**, and diamine **34** in a molar ratio of

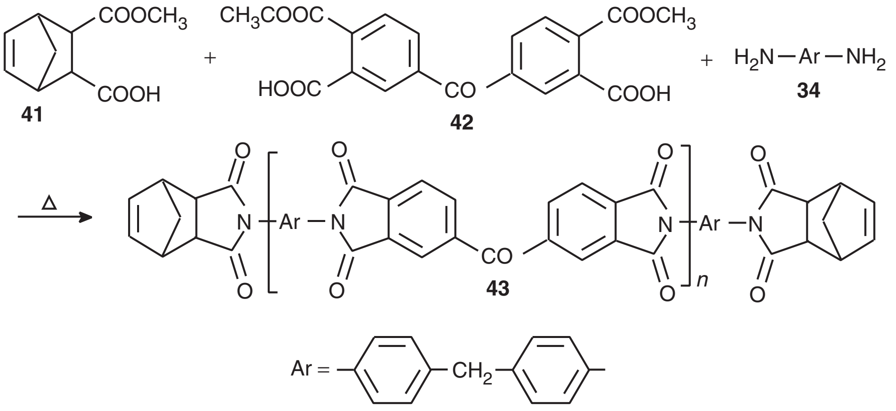


Figure 9.18 Chemical sequences involved in the polymerization of monomer reactants (PMR) process. The average molecular weight of intermediate oligomer **43** is controlled by the relative amounts of monoester **41**, diester **42**, and diamine **34**. Chain extension of bisnadimide **43** occurs at high temperature by the reverse Diels-Alder polymerization process.

2.087:3.087:2, corresponding to a formulated molecular weight of the imidized oligomer **43** of 1500 g mol^{-1}. The final cure is performed between 280 and 320 °C via complex reaction sequences involving the liberation of cyclopentadiene. Thermal polymerization of nadimide resins obviously depends on the experimental conditions that can impede (high pressure) or allow cyclopentadiene evaporation. As with other highly cross-linked systems, the reaction mechanism can be studied only in the first few polymerization steps. It seems now established that the *endo*–*exo* nadimide isomerization takes place below 200 °C, whereas cyclopentadiene is released above 250 °C.[39,40] Studies with model compounds show that dienophile exchange and *endo-exo* isomerization occur via Diels-Alder/retro Diels-Alder equilibrium at relatively low temperature, that is, 160 °C, both reactions being easier with the *endo* isomer. Comparing the mechanical properties and heat resistance of composites prepared with PMR-polyimides made with different aromatic diamines, Alston demonstrated[41] that 4,4′-methylenebis-benzeneamine **34** was essential to obtain the optimum results. In addition, Vannucci[42] provided evidence that the nadimide end-caps contribute most to the thermal degradation of the cross-linked resins.

9.3.4.3 Acetylene-Terminated Resins

In 1868, Berthelot discovered the method of synthesis of benzene by the cyclotrimerization of three molecules of acetylene. Applied to telechelic oligomers terminated by acetylenic groups, this method could provide the most thermally stable networks. This concept was applied in 1974 to synthesize the new thermosetting resins displayed in Fig. 9.19.[43,44] They are prepared by reacting BTDA **18** with 3,3′-(1,3-phenylenedioxy)bisbenzeneamine **44** and 3-ethynylbenzeneamine **45**. Figure 9.19 shows the expected formation of amide acid **46**, which is soluble in acetone and other low-boiling polar solvents, whereas polyimide oligomer **48** is soluble only in NMP. Three types of oligomers became commercially available through National Starch Chemical Company: Thermid AL 600® for the amide acid structure **46** (or more probably the corresponding amide ester), Thermid 600® for imide **48,** and Thermid IP 600® for the isoimide form **47**. This latter material is obtained when the amide acid **46** is chemically cyclodehydrated with dicyclohexylcarbodiimide.[45]

As a general class of polymers, polyisoimides are less symmetric than the corresponding polyimides with, therefore, better flow (lower T_g) and solubility. The processing window of preimidized Thermid 600® **48** is very narrow, because the resin has a melting point of 195–200 °C and polymerization starts in this temperature range. Thermid FA-700®, prepared from 6FDA dianhydride **5**, exhibits better characteristics with a melting temperature of approximately 170 °C and a good solubility in solvents such as γ-butyrolactone, *N,N*-dimethylformamide and tetrahydrofuran.

Even though other classes of ethynyl-terminated oligomers have been reported in the literature, only the Thermid® series is produced in commercial quantities. If formation of benzene rings from acetylene triple bonds was expected in the earlier studies, later works demonstrated a more complex chemistry during the cure cycle with only 30% of the ethynyl groups undergoing cyclotrimerization.[46] Polymerization starts at approximately 150 °C with a heat of polymerization in the range of 100–160 kJ mol^{-1}, these values being far from the 200 kJ mol^{-1} measured for the trimerization of acetylene into benzene. Electron spin resonance spectroscopy shows an intense signal

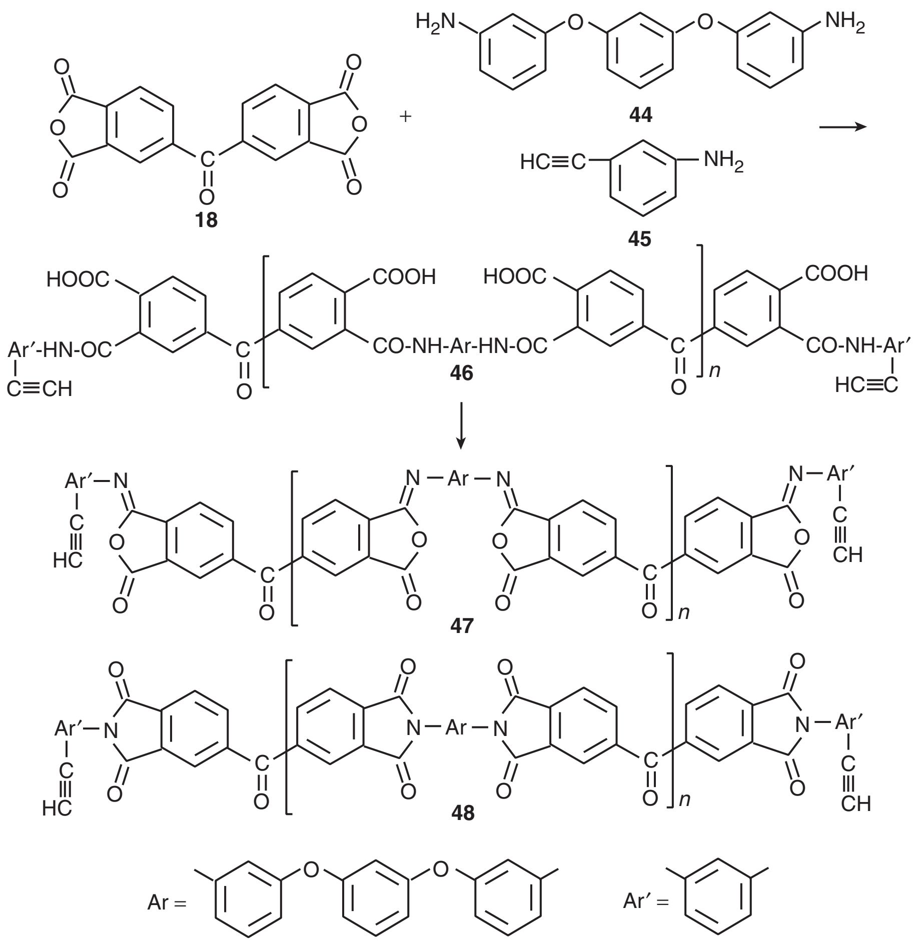


Figure 9.19 Acetylene-terminated polyimide precursors synthesized by reacting BTDA **18** with less than the stoichiometric balance of 3,3′-(1,3-phenylenedioxy) bisbenzeneamine **44** and the complement to stoichiometry of 3-ethynylbenzeneamine **45** as end-capping agent. Low-molecular-weight polyamic acid **46** is then chemically cyclized to poly (isoimide) **47** or thermally cyclodehydrated to give polyimide **48**.

corresponding to free radical species during the thermal polymerization of ethynyl-terminated oligomers.[47] Studies with model compounds indicate the formation of low-molecular-weight oligomers containing aromatic rings and polyene structures.

The formation of aromatic rings has been observed by ^{13}C-NMR spectroscopy,[46] whereas benzene and naphthalene derivatives can be separated by high-performance liquid chromatography (HPLC).[48] 1,7- and 2,7-disubstituted naphthalene dimers and 1,2,3-, 1,2,4-, and 1,3,5-trisubstituted benzenes have been isolated and identified. At the end of the thermal polymerization, the weight ratio (dimers + trimers)/oligomers is approximately 30/70. It seems conclusively established that ethynyl-terminated polyimides form only low-molecular-weight oligomers with highly conjugated polyene and aromatic structures.

9.4 Resin Characterization

As discussed in Section 9.2, polymers are initially characterized by their molecular properties in solution, that is, inherent and intrinsic viscosities, molecular weight, and molecular weight distribution. As polycondensation is generally performed in solution, measurements are often conducted directly in the polymerization solvent. However, it is sometimes necessary to precipitate polymer molecules in nonsolvent, such as alcohol, diethyl ether, or chlorinated hydrocarbons. Then, the thermal properties are determined with either polymer films or precipitated powder by TGA, isothermal aging, and thermo-mechanical analysis. Additional information is obtained by means of other techniques including infrared and sometimes UV–visible spectroscopies, nuclear magnetic resonance (NMR) and HPLC.

9.4.1 Infrared Spectroscopy

Before the advent of Fourier transform infrared spectroscopy (FTIR), IR analysis had been only used to obtain qualitative information on the polycondensation process because of the low polymer concentration versus large amounts of organic solvents. With FTIR, the situation changed with computer programs allowing one to subtract solvent absorption peaks from the global spectra. Then, infrared spectroscopy became a powerful analytical tool to monitor the formation of polyamic acids by observing the intensity changes of anhydride absorption peaks. But more often, IR spectroscopy has been extensively used to study, by transmission or reflection, the thermal imidization of very thin films. This is done by following the intensity changes of imide absorptions at 1780 cm^{-1} ($\nu_{C=O}$ symmetrical stretch), 1380 cm^{-1} (ν_{C-N} stretch), and 720−725 cm^{-1} ($\delta_{C=O}$ bending). Intensities are either compared with those of films assumed to be completely imidized[49,50] or normalized[51,52] against internal absorption bands of the aromatic rings at about 1500 and 1015 cm^{-1}.

Thus, FTIR has been used to determine the imidization kinetics by plotting the degree of imidization as a function of the temperature in the range of 150−350 °C.[53] At any temperature, the curves clearly show an initial fast imidization reaction followed by a second slow step. The slopes of the linear parts of the curves provide the two reaction rates k_1 and k_2 characterizing the imidization process. For example, at 200, 250, and 300 °C, the values of k_1 are 6.9×10^{-2}, 2.96×10^{-1}, and 1.18 min^{-1}, whereas k_2 values are approximately 5.5×10^{-3}, 4.2×10^{-2}, and 1.4×10^{-2}. Drawing the linear function $k = f(1/T)$ for k_1 and k_2 allows the calculation of the activation energies of the two consecutive dehydration processes.

Although infrared spectroscopy provides valuable information on the cyclization process, there is a general lack of agreement over the degree of imidization actually achieved. In particular, it was shown that the dielectric properties are more sensitive to the final cure temperature with a continuous decrease of the dielectric dissipation factor (tan δ) between 300 and 400 °C.[53] However, it is not clear whether this phenomenon is due to completion of the imidization process or to enhanced chain packing. Curves of Fig. 9.20 illustrate the results obtained with capacitors made of metal−insulator−semiconductor structures in the range of 200−400 °C. It is obvious that tan δ decreases with increasing cure temperature to reach a minimum when cure is achieved at 350−400 °C.

9.4.2 NMR

In the analysis of pure organic compounds, virtually all hydrogen and carbon atoms can be identified by using high resolution ^{1}H and ^{13}C NMR spectrometers. ^{1}H NMR spectra of epoxy and epoxy-novolac resins have been published in a previous publication.[17] Solid-state NMR has been used to study the chemical and physical structure of polymers, as well as the diffusion processes in solid polymer matrices.[54] Figure 9.21 provides the spectra of imide monomer **30a,b** and polyimide **32** (Fig. 9.15) in solution in dimethylsulfoxide-d_6.

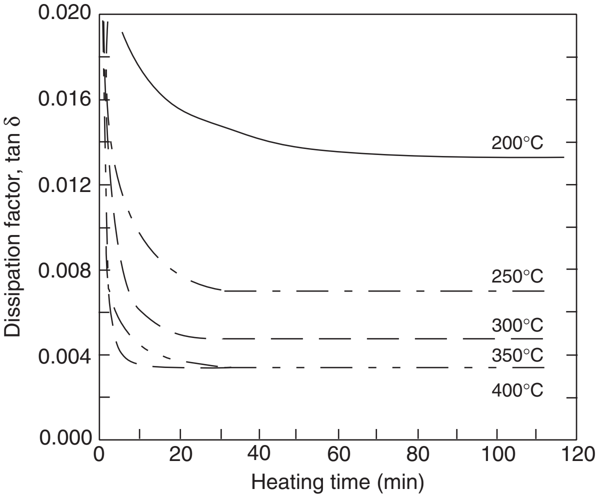


Figure 9.20 Degree of imidization of polyamic acids determined by the variation of the dielectric dissipation factor (tan δ) versus heating time at different temperatures between 200 and 400 °C. Experiments are performed at 100 kHz with metal-insulator-semiconductor capacitors built by microlithography on silicon wafers.

It can be seen that all carbon atoms are recognized by using additive increments that are calculated from the chemical shift data observed on various model molecules of increasing complexity. It is worth noting that many changes occur during the polycondensation of the monomer mixture, in particular, the disappearance of the methyl ester at 53.1 ppm and the deshielding of the 3-, 4-, and 5-carbon atoms at the *ortho*- and *para*-positions of the primary amine group, which shift from 115.7, 116.3, and 118.9 ppm to 126.3, 129.0, and 124.5 ppm, respectively. The formation of the imide ring also has a strong influence on the resonance of the quaternary 15-carbon atom at 147.6 ppm, which is deshielded to 153 ppm in the imide molecule.

9.4.3 High-Performance Liquid Chromatography

In liquid−solid or adsorption chromatography, the chemical components are adsorbed on the hydroxyl

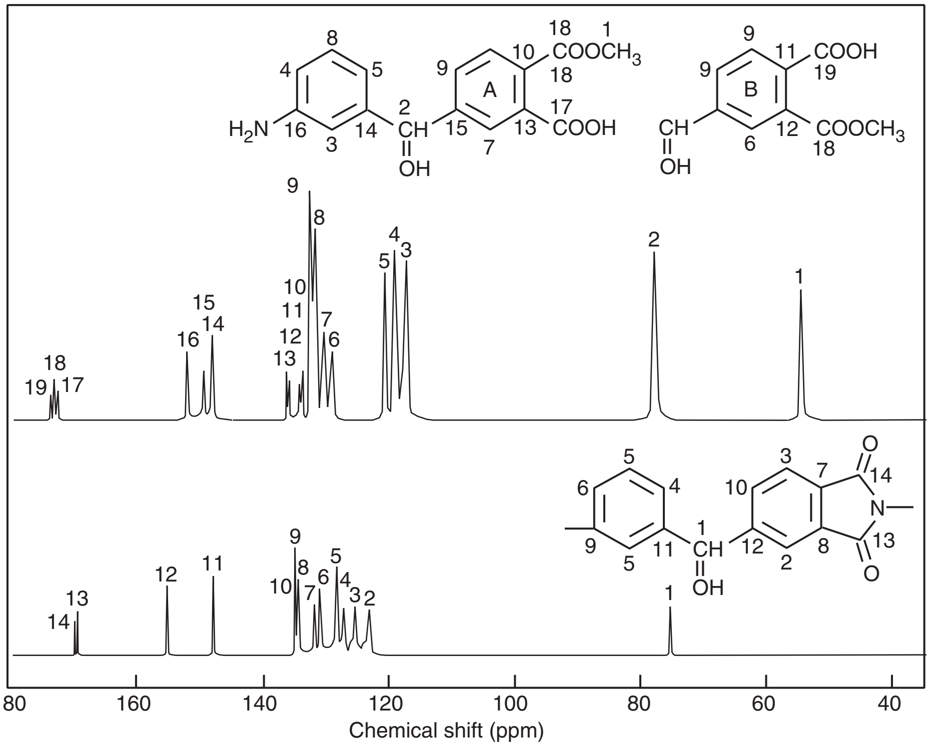


Figure 9.21 ^{13}C NMR spectra of the mixture of monomers **30a,b** and polyimide **32** (Fig. 9.15) in dimethylsulfoxide-*d*$_6$. Polyimide **32** is obtained by heating the monomers at 275 °C for 30 min.

sites of polar adsorbents such as powdered silica and alumina packed in the column, and elution is performed with solvents of increasing polarity.[55] HPLC is a variant incorporating high pressure pumps and automated metering units to change the gradient of the mobile phase, providing a fast and high-resolution separation. The separation mechanism depends on the differential distribution of the organic components between the liquid mobile phase and the solid stationary phase and the time spent in each phase. The most difficult aspect of HPLC is the selection of the solvent system and of the column, because the separating power depends on the interactions between the components and the two phases. With a careful adjustment of the chromatographic conditions, HPLC has the ability to separate isomeric mixtures if the polar groups of the organic compounds are appropriately matched with the more polar sites of the stationary phase. The technique is generally applicable to organic materials of molecular weight ranging from 100 to 1000 g mol^{-1}.

In general, HPLC gives accurate results with nonionic materials, but it can also be used to separate ionic compounds by using the reversed-phase method employing a nonpolar stationary phase and a mobile phase consisting of water as the base solvent, to which a miscible organic solvent such as methanol is added to adjust the solvent strength. This separation technique is illustrated in Fig. 9.22 with the polyimide monomers **30a,b** (Fig. 9.15), which are prepared by the catalytic hydrogenation of the corresponding benzophenone derivatives.

This reaction leads to two isomers: 4-(3-aminobenzoyl)-1,2-benzenedicarboxylic acid 1-monomethyl ester **c** in the headline X=CO and 4-(3-aminobenzoyl)-1,2-benzenedicarboxylic acid 2-monomethyl ester **d**. Hydrogenation of the benzophenone carbonyl group of compounds **c** and **d** with palladium on charcoal catalyst is not selective and the final material is a mixture of the six isomeric monomers containing the carbonyl (−CO−), hydroxymethylene (−CHOH−) **a,b**, and methylene (−CH$_2$−) **e,f** linking units between the two aromatic rings. The quantitative determination of all compounds was performed by reverse phase HPLC of monomer **30a,b**. Figure 9.22 shows that the chromatogram, recorded with a UV detector at a wavelength of 254 nm, exhibits all the expected peaks, which were identified by separately analyzing samples of each couple of isomers. Carbonyl-linked compounds **c** and **d** (X=CO) are the starting materials before hydrogenation, whereas methylene-linked monomers **e** and **f** (X=CH$_2$) were obtained after hydrogenation had been completed.

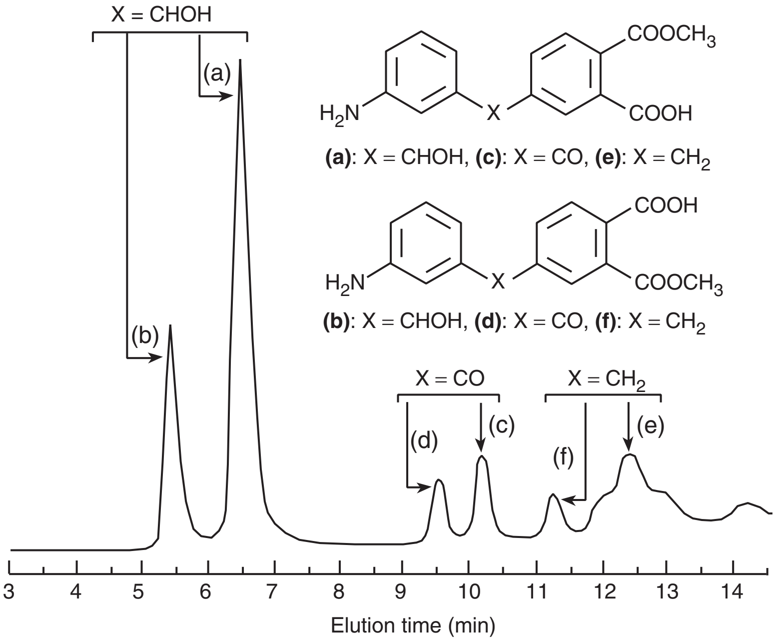


Figure 9.22 HPLC analysis of self-condensable monomers **30a,b** (X = CHOH) prepared by hydrogenation of the carbonyl groups of the corresponding benzophenone derivatives **c** and **d** (X = CO). HPLC reveals the presence of fully hydrogenated linking units **e** and **f** (X = CH_2).

9.5 Adhesive Properties

According to the final use, there exist different methods to measure the adhesive strength of polymeric materials. The island blister test and 90° peel test are particularly suited to determine the level of adhesion of very thin films in electronic applications. In the case of structural adhesives, the lap-shear strength of three- or multiple-layer structures is a typical standard.

9.5.1 Lap-Shear Strength Measurement

The mechanical properties of adhesive joints are primarily determined by applying an in-plane shear stress to the assemblies. Figure 9.23 shows the single lap shear configuration recommended in ASTM D 1002, Federal Specification MMM-A 132, and Federal Test Method Standard No. 175.

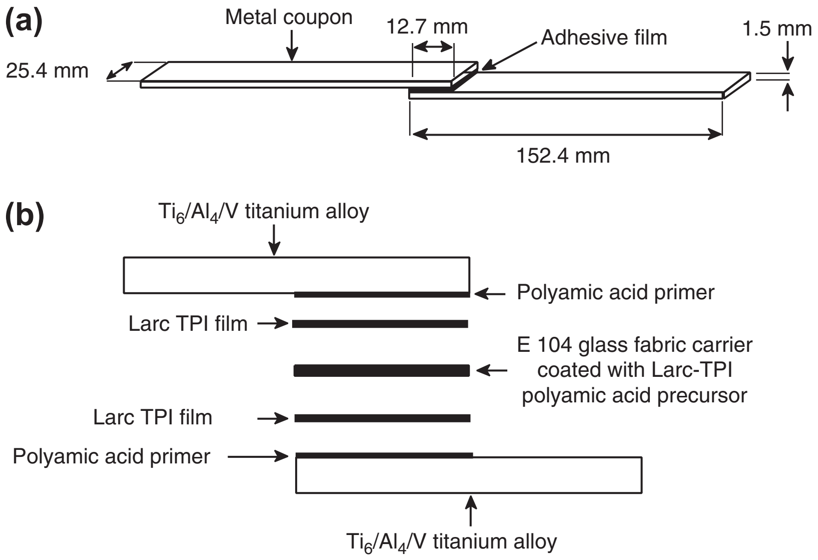


Figure 9.23 Lap-shear strength determination: (a) test specimen recommended in ASTM D1002 standard; (b) multilayer process used to bond titanium alloy coupons with thermoplastic Larc TPI polyimide adhesive.

The adhesive layer is applied between two aluminum coupons (2024-T3 alloy), etched with chromic acid prior to bonding, typical dimensions of which are 15.24 cm length, 2.54 cm width, and 0.15 cm thickness, with an overlap length of 1.27 cm, leading to a bonding area of 3.226 cm^2. The assembly is maintained with one or two clamps exerting a slight pressure and cured in an air-circulating oven according to the appropriate thermal schedule. The lap-shear strength is then measured with a tensile machine at a pull rate of 1−2 mm min^{-1} and expressed in MPa on an average of five specimens. Obviously, this lap shear configuration combines a predominant shear stress with significant peel and cleavage stresses arising from the adhered bending. The lap-shear strength method is of universal use in the adhesives industry because of its ease in specimen preparation and testing alike. In addition, the variation of the lap-shear strength as a function of the test temperature can be easily determined by using a heating chamber. The adhesive strength values discussed in the following sections have been obtained by this standard method.

9.5.2 Precyclized and Linear Polymers

9.5.2.1 Polyphenylquinoxalines

As reported in Section 9.3.2.1, polyphenylquinoxalines are amorphous thermoplastic polymers that can be processed above their glass transition temperature. However, if not subsequently subjected to cross-linking reactions, the T_g constitutes the upper operating temperature of the bonded assembly. Another point to take into consideration with heat-resistant adhesives is that void-free bond lines can be obtained only if the solvents are completely evaporated before processing. This means that the T_g-lowering effect of solvents cannot be used to conduct the bonding operation in less drastic conditions. There is, therefore, a need to find a compromise in selecting the most convenient polymer for a given application, because the higher the glass transition temperature, the better the adhesive strength at temperatures above 250 °C but the harsher the process parameters.

This can be illustrated by the first adhesive reported by Hergenrother and prepared by coating a solution of polyphenylquinoxaline **16** (T_g = 318 °C) on a fiber-glass fabric to achieve, after drying, a 0.28-mm-thick adhesive film containing 0.2% residual solvent.[56] This film was used to bond titanium alloy coupons with an applied pressure of 0.34 MPa and increasing the temperature from the ambient to either 316 °C for 1 h or to 400, 427, and 455 °C for 1 h each. In the first case, the initial lap-shear strength was 33.7 MPa at 20 °C and 25.5 MPa at 232 °C, dropping slightly to 24.8 MPa after 5000 h at 232 °C. However, thermoplastic failure (4.8 MPa) was observed when the specimen was heated to 316 °C. Conversely, the specimens cured up to 455 °C exhibited initial strengths of 24.1 and 13.8 MPa at 20 and 316 °C, respectively, decreasing to 10.3 MPa after 500 h at the latter temperature.

Hergenrother published additional results to compare the adhesive properties of polyphenylquinoxalines **16**, **17** (T_g = 290 °C) and a polymer (T_g = 285 °C) synthesized by reacting 4,4′-carbonylbis(1,2-benzenediamine) with (1,4-phenylene)-1,1′-bis[2-phenyl-1,2-ethanedione] **12** for bonding both stainless steel and titanium coupons.[57] When cured at 371 or 399 °C, the three polymers exhibited similar adhesive strengths of 31−34 MPa at 22 °C and 23−25 MPa at 232 °C, virtually unchanged after 8000 h at that temperature. All but adhesive **16** heated to 455 °C exhibited thermoplastic failure at 316 °C. Hergenrother and Progar[58] also reported the results obtained with polyphenylquinoxaline **16** for bonding both titanium alloy specimens and carbon-fiber composite materials. This study showed that a cure cycle ending at 399 °C provided a very good lap-shear strength at 316 °C for the composite/composite assemblies but not for the Ti/Ti structure.

9.5.2.2 Linear Polyimide Precursors

Polyimide **22** (Fig. 9.11), commonly referred to as Larc-TPI®, has been extensively evaluated as a structural adhesive by Progar and St. Clair.[59,60] As for polyimide NR 056X® (Fig. 9.9), early work demonstrated that diglyme was a good solvent for the intermediate polyamic acid **20** and diglyme solutions provided the highest level of adhesive strength. Different variants of this polymer are produced by Mitsui Toatsu, which provides the polyamic acid either in diglyme solution at 29% concentration or in the form of adhesive films with a thickness of 46 μm. These films exhibit the following properties: T_g 250 °C, specific mass 1.33 g cm^{-3}, fracture energy (G_{1c}) 2.6 kJ m^{-2}, tensile modulus 3.72 GPa, elongation at break 4.8%, and tensile strength 136 MPa.[61] The most effective and reliable technique for bonding large areas is that shown in Fig. 9.23. Test specimens made of Ti_6Al_4V titanium alloy, subjected to surface treatment with Pasa-Jell 107, are coated with a thin layer of Larc TPI polyamic acid **20** and dried. The adhesive joint consists of two Larc-TPI polyimide films in contact with the metal surfaces and a central E-104 glass fabric carrier impregnated with Larc-TPI polyamic acid. The cure cycle is carried out under a pressure of 2.1 MPa by heating the assembly from the ambient to 343 °C at a rate of 8 °C min^{-1}, followed by 1 h at that temperature. A postcure treatment at 343 °C for 4–6 h is applied to the assemblies, which are subsequently tested at temperatures higher than the T_g.

The 25 °C Ti/Ti lap-shear strength values reported in the literature are scattered between 32 and 43 MPa, with 37 MPa being more common. Figure 9.24 shows the change in lap-shear strength observed with Ti/Ti specimens subjected to long-term aging at 232 °C.[62] The initial value of 13.8 MPa progressively increases to 15.2 MPa after 1000 h and to about 24 MPa after 10,000 h. As shown in Fig. 9.24, this latter value remains constant over a long period of time, that is, it was 40,000 h when the test was completed.

The high melt viscosity of Larc-TPI at 350 °C (10^6 Pas) prohibits its use as an adhesive for bonding metallic or laminate skins on core honeycombs to make high-strength sandwich structures. The work of Chow et al.[25] discussed in Section 9.3.2.2 demonstrates that the melt viscosity of the poly(isoimide) form **21** of Larc-TPI is of the order of 10 Pas at 240–250 °C, compared with 2×10^7 Pas for polyimide **22**. A semicrystalline form of Larc-TPI has been obtained by chemical imidization of the polyamic acid with acetic anhydride and triethylamine.[63] The differential scanning calorimetric curve exhibits an endotherm at 274 °C because of melting of the crystalline sites. The value of the initial inherent viscosity (0.22 dL g^{-1}) indicates, however, that the lower melt viscosity also results from low-molecular-weight polymer.

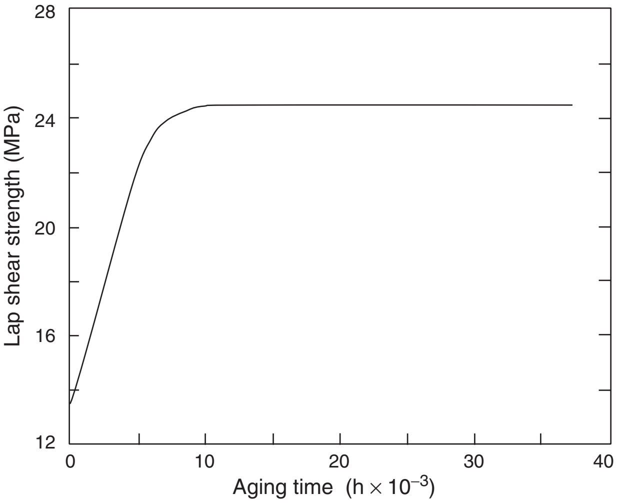


Figure 9.24 Lap-shear strength values determined with Ti/Ti assemblies bonded with Larc TPI adhesive during long-term thermal aging in air at 232 °C.

Various copolyimides including the chemical structure of Larc-TPI were evaluated in the late 1980s. A paper reports that the polymer Larc TPI-ODA made from the reaction of BTDA with 95 mol% of 3,3′-carbonylbisbenzeneamine and 5 mol% of 4,4′-oxybisbenzeneamine copolyimide containing the repeating units **22** and **23** (Figs 9.11 and 9.12) has a T_g similar to that of Larc-TPI (250 °C) but exhibits better processability.[26] Ti/Ti bonding provides lap-shear strength values of 32.4 and 21.1 MPa at 25 and 232 °C, respectively. Other copolymers have been prepared by incorporating various amounts of 3,3′-(1,3-phenylenedioxy)bisbenzeneamine into the macromolecular backbone of Larc-TPI.[64] Figure 9.12 displays the chemical formulae of polyimides evaluated as thermoplastic adhesives for high temperature uses. The polyamic acid form of polymer **24** (Larc-PI-SO_2) is synthesized from BTDA and 3,3′-sulphonylbisbenzeneamine, whereas polyimide **25**, referred to as Larc-TPI-IA, is produced by reacting 4,4′-oxybis(1,2-benzene-dicarboxylic acid) dianhydride with 3,4′-oxybisbenzeneamine.[27,28] The glass transition temperature of polyimide **24** varies from 220 to 250 °C according to the cure cycle applied, whereas polymer **25** has a T_g of 243 °C.

Table 9.1 lists the lap-shear strength values measured with Ti/Ti test specimens bonded with these thermoplastic polymers: Larc-TPI, Larc-TPI-ODA, Larc-IA, and Larc-PI-SO_2. The heat resistance of the four polymers in oxidative conditions was determined in an air circulating oven at 204 °C for 1000 and 5000 h.

Table 9.2 provides the lap-shear strength properties of a water-soluble version of Larc-TPI obtained using a two-step synthesis. In the first stage, the polyamic acid form of this polymer is prepared as usual in diglyme solution and then precipitated in water as a fine powder.[65] Once dried, the solid is dissolved in an aqueous solution of *N,N*-dimethylethanolamine to form the corresponding polyamic

Table 9.1 Comparison of the Lap-Shear Strength Values Measured With Ti/Ti Assemblies Bonded with Larc-TPI, Larc-TPI-ODA, Larc-IA, and Larc-PI-SO_2

	Lap-shear strength (MPa)			
***T*[a] (°C)**	**TPI**	**ODA[b]**	**IA**	**SO_2**
25	33.0	28.3	44.2	32.1
177	29.5	21.9	36.6	–
204	25.2	15.4	28.4	–
232	17.5	–	9.3	24.5

[a] Test temperature. [b] 32.4 and 21.1 MPa at 25 and 232 °C, respectively, after a postcure treatment.

Table 9.2 Lap-Shear Strength Values of Ti/Ti Test Specimens Bonded With a Commercial Grade of Larc-TPI Compared With the Data Obtained With the Water-Soluble Version Larc-TPI (H_2O)

	Lap-shear strength (MPa)	
***T*[a] (°C)**	**Larc-TPI**	**TPI (H_2O)**
25	33.5	28
232	19.7	20
25[b]	26.9	23

[a] Test temperature. [b] After 5000 h aging in air at 232 °C.

acid quaternary salt. The experimental data reported in Table 9.2 compare the adhesive properties of this water-soluble polymer, referred to as Larc-TPI (H_2O), with those measured from a commercial grade of Larc-TPI. The last row of the table indicates the lap-shear strength determined after the specimens have been subjected to thermal aging in air at 232 °C for 5000 h.

The lap-shear strength values listed in Table 9.3 show that Larc-IA exhibits the best adhesive properties up to 204 °C before and after thermal aging at that temperature but Larc-TPI remains better when adhesion is measured at 232 °C.

To date, no high-molecular-weight condensation polyimide combines excellent adhesive properties, easy processability without volatile evolution and low melt viscosity. The results discussed in Section 9.5.4.1 show that condensation oligomers, such as Nolimid 380 and FM 34B, are the most effective adhesives for long-term uses at temperatures of more than 250 °C. They have, however, a major drawback, which is also encountered with high-molecular-weight polyamic acids. A large amount of volatile compounds—solvents and by-products from cyclodehydration—evolves during the cure cycle. This results in severe processing problems, particularly for large area parts that exhibit a high degree of porosity. Larc-TPI and its associated modifications were

Table 9.3 Lap-Shear Strength of Ti/Ti Test Specimens Bonded With Polyimides of the Larc-TPI Series as a Function of the Test Temperature Before and After Thermal Aging in Air at 204 °C

		Lap-shear strength (MPa) at °C			
Polyimide	**Time (h)**	**25**	**177**	**204**	**232**
Larc-TPI	0	33.0	29.5	24.5	17.5
	1000	32.9	29.9	27.8	23.3
	5000	27.1	25.7	26.0	23.7
Larc-TPI-ODA	0	28.9	22.3	20.8	18.1
	500	25.0	22.5	22.1	17.0
	1000	28.3	18.4	17.5	15.3
Larc-IA	0	44.2	36.6	28.4	9.3
	1000	35.0	33.4	30.4	9.7
	5000	29.0	30.9	30.4	7.9
Larc-IA + 50% Al	0	43.8	33.2	28.7	13.6
	1000	42.9	34.3	31.3	12.9
	5000	34.1	28.3	24.5	7.7

tailored to reduce the melt viscosity by significantly decreasing the molecular weight, using unbalanced stoichiometry, and blocking the terminal functions with end-capping agents.

9.5.3 Thermosetting Resins

Addition-type polyimides, which are thermosetting resins, were developed to improve the processability of polyimides, but their thermal stability is severely degraded by the presence of aliphatic bonds in place of the aromatic nuclei. However, the adhesive strength has been evaluated for the BMI- (Section 9.3.4.1), bisnadimide- (Section 9.3.4.2), and acetylene-terminated (Section 9.3.4.3) imide oligomers.

9.5.3.1 Maleimide-Terminated Adhesives

As previously stated, BMIs are crystalline compounds with melting points in the range of 100−210 °C. A few examples are given in Table 9.4, which provides the melting temperatures T_m, the maximum temperatures of the exothermic peak T_{max} and the polymerization enthalpies ΔH. Diamines based on 4,4′-methylenebisbenzeneamine carrying

Table 9.4 Melting Temperature T_m, Temperature at the Maximum of the Exothermic Peak T_{max}, and Polymerization Enthalpy $\triangle H$ for Some BMIs

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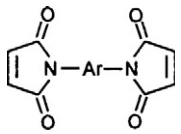
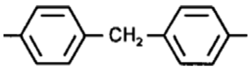
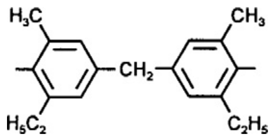
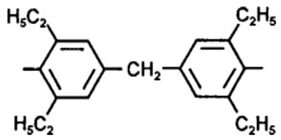
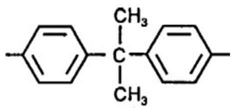
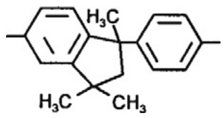
<tr><td colspan="4"> </td></tr>
<tr><th>Ar</th><th>T_m (°C)</th><th>T_{max} (°C)</th><th>ΔH (J g^{-1})</th></tr>
<tr><td> </td><td>155−157</td><td>235</td><td>198</td></tr>
<tr><td> </td><td>150−154</td><td>298</td><td>187</td></tr>
<tr><td> </td><td>149−151</td><td>328</td><td>206</td></tr>
<tr><td> </td><td>235</td><td>290</td><td>216</td></tr>
<tr><td> </td><td>90−100</td><td>203</td><td>89</td></tr>
</table>

methyl and ethyl substituents exhibit melting points around 250 °C, whereas the only BMI melting at about 100 °C is the compound obtained from the reaction of maleic anhydride with 6-amino-1-(4-phenyl)-1,3,3-trimethylindane.

The chemistry of BMIs has been briefly discussed in Section 9.3.4.1, which outlines that neat BMI resins form brittle networks. The values characterizing the shock resistance and crack propagation of a given material are the stress intensity factor, K_{1C}, and the fracture energy, G_{1C}, which indicates the relaxation of the strain energy. In highly cross-linked networks, such as those formed by tetrafunctional epoxy resins, K_{1C} *is* of the order of 0.5 MPa $m^{0.5}$ and G_{1C} values are around 60 J m^{-2}, whereas the data obtained for a thermoplastic polyimide are 2.8 MPa $m^{0.5}$ and 3.5 kJ m^{-2}, respectively. The fracture toughness of cured BMIs is approximately 100 J m^{-2}, increasing by a factor of two on chain extension between the two terminal double bonds. For example, the fracture energy of polymer **40** (Fig. 9.17) is enhanced when the molecular ratio of BMI **38** to 4,4′-methylenebisbenzeneamine **34** is increased.

Several methods have been investigated to improve the fracture toughness of BMI resins, the most used technique being the incorporation of a second phase formed by the dispersion of rubber particles into the cross-linked matrix. Carboxyl-terminated butadiene-acrylonitrile elastomers (CTBN), which are very effective with epoxy resins, are also frequently added to BMI adhesives. The general formula of CTBN rubbers is

$$HO_2C-[-(CH_2-CH=CH-CH2-)_m-(CH_2CH(CN)-)_n]-CO_2H$$

where the number average molecular weight is in the range of 1300−3500 g mol^{-1} with, in this latter case, typical values of 5 and 10 for *m* and *n,* respectively. Starting from a homogeneous mixture, three steps characterize the cure cycle: phase segregation, gelation, and vitrification. The final material is composed of rubber particles with average diameters between 1 and 5 μm dispersed within the continuous BMI matrix. The maximum fracture resistance is obtained for 15−20% CTBN, resulting in fracture energy values multiplied by a factor of 20−30. It has been demonstrated that mixtures of CTBN Hycar 1300-X8 and BMI Compimide 353 could be copolymerized at 170−200 °C to provide two-phase materials containing dispersed rubber microspheres.[66] Figure 9.25 shows that the fracture energy increases with the quantity of CTBN rubber, which can be as high as 50%. The flexural modulus at high temperature (250 °C), however, rapidly decreases to become close to zero at 50% CTBN concentration.

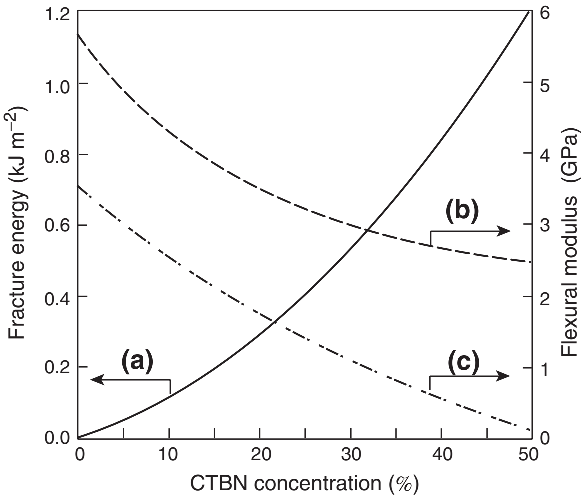


Figure 9.25 Changes of the fracture energy (a) and flexural modulus at 25 °C (b) and 250 °C (c) for CTBN-BMI adhesives as a function of the CTBN-rubber content.[66]

Another method used to improve the fracture energy of BMI resins consists in mixing the thermosetting material with linear thermoplastic polymers. This can be illustrated by the behavior of mixtures containing Compimide® 796 and TM 123 BMI resins with SABIC Ultem 1000®, poly(etherimide) **26** (Fig. 9.13).[67] The critical stress intensity factor K_{1C} of the linear polymer is six times higher than that of the BMI matrix and does follow the mixture law for all BMI/Ultem combinations. The linear polyimide can also be added as 20−40 μm spherical particles to the BMI resin before it is polymerized. In another example, particles of a soluble precyclized polyimide (Ciba Geigy XU 218®) are dispersed in BMI monomer, which is subsequently melted at 177 °C and cured at 232 °C.[68] The two-phase material obtained by this means exhibits a glass transition temperature of 348 °C compared with only 260 °C for the BMI resin without polyimide additive.

The fracture energy values published in the literature have been generally determined with either neat resins or composite materials and exceptionally with adhesives. The actual fracture energies of

Table 9.5 Fracture Energies G_{1C} of Commercially Available High-Performance Adhesives, Measured at Ambient Temperature[69]

Adhesive trade mark	Type of material	G_{1C} (J m^{-2})
Narmco SR 5208	Modified epoxy resin	82
Hexcel HX 976	Condensation polyimide	94
Cyanamid FM-300K	Modified epoxy resin	191
Upjohn 2080	Thermoplastic copolyimide	310
Cyanamid FM 34B-18	Condensation oligoimide	385
Larc 13/AATR	CTBN-modified bisnadimide	387
Torlon 4000 T	Poly(amide-imide)	480
DuPont NR 056X	6FDA-based polyamic acid	620
Hughes HR 602	Ethynyl-terminated oligoimide	815
Plastilock 650	Nitrile rubber modified phenolic	1037
Plastilock 655	Nitrile rubber modified phenolic	1513
Udel PI 700	Thermoplastic polysulfone	1620
Cyanamid FM 73	Modified epoxy resin	2107

thermoplastic and thermosetting adhesives are, in fact, considerably lower than those measured with molded resins.[69] This discrepancy can be explained by the pressure–temperature conditions used in the bonding techniques. They would not allow the melted resins to flow and wet the metal surfaces. Moreover, the small thickness of the adhesive joint limits the level of plastic deformation in contact with the propagating cracks. Table 9.5 summarizes, by order of increasing energy, the fracture energy values measured at room temperature for some commercial adhesives.

Melt processable thermoplastic adhesives, such as Udel P1700® ($G_{1C} = 306$ J m^{-2}), Upjohn 2080®, and Torlon 4000T® have fracture energies similar to that of the modified nadimide-terminated polyimide Larc 13/AATR® containing 20% of acrylonitrile-butadiene rubber. Compared with the melted form, adhesive films of Udel P1 700® exhibit a fracture energy close to 1.7 kJ m^{-2}. In the group of thermosetting adhesives, Cyanamid FM 73® and Plastilock 650–655® possess the best properties of fracture resistance, surprisingly followed by the ethynyl-terminated HR 602. These data show that judiciously formulated thermosetting polymers can provide excellent adhesives.

Commercial BMI adhesives are generally blends of BMI resin, various nucleophilic co-reactants, and toughening compounds. A number of chemical systems were studied and developed by Rhône-Poulenc, SABIC, CYTEC, and many other companies, but the thermal stability of BMI-based adhesives does not exceed 230 °C for long-term uses. Figure 9.26 illustrates some data published by CYTEC for Al/Al assemblies bonded with FM 32 BMI adhesive cured at 177 °C for 4 h under 0.28 MPa.[70] The two other curves refer to BMIs from Dexter-Hysol Corporation (www.scottsales.com/hysol.html).[71] Aluminum coupons were bonded

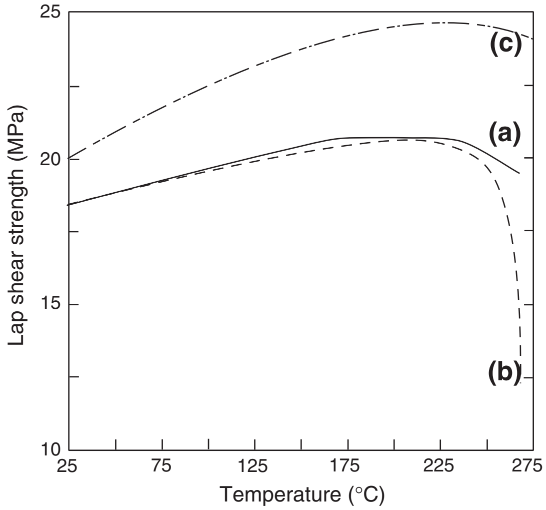


Figure 9.26 Lap-shear strength versus temperature measured on Al/Al assemblies bonded with: (a) CYTEC FM 32,[70] (b) Dexter-Hysol EA 9655, and (c) Dexter-Hysol LR100–774[71] BMI adhesives.

with EA 9655 under 0.17 MPa at 177 °C for 1 h, followed by 2 h at 232 °C, whereas the bonding conditions for LR 100-774 were 0.2 MPa, 1 h at 177 °C and 2 h at 246 °C. The resistance to humidity for Al/FM 32/Al structures was tested after 72 h in boiling water, providing lap-shear strengths of 20.3, 20 and 19 MPa at 25, 177, and 203 °C, respectively.

9.5.3.2 Nadimide-Terminated Adhesives

The chemistry of norbornene-terminated polyimide oligomers, also referred to as nadimide-terminated resins, is discussed in Section 9.3.4.2. A paper by St. Clair and Progar[72] reports the first experiments made using nadimide resins as structural adhesives. The polyimide Larc-13, used in this study, belongs to the PMR category with 3,3′-methylenebisbenzeneamine replacing the 4,4′-isomer employed as the diamine of the PMR 15 formulation. The *meta*-catenation provides excellent melt-flow properties allowing bonding in an autoclave. Titanium specimens bonded under 0.34 MPa with a final cure temperature at 329 °C followed by a postcure at 343 °C exhibit lap-shear strength values of 22.8 and 19.3 MPa at 25 and 260 °C, respectively. Another study indicates that the adhesion strength of the Ti/Ti assemblies drops to 8.3 MPa after aging in air for 2000 h at 232 °C.[73] Even though certain types of assemblies with the Larc-13 resin have demonstrated good mechanical properties, the fracture resistance has had to be improved by adding either rubbery materials or linear thermoplastic poly(amide-imides).[74]

The Larc-13 adhesive has been tested for bonding ceramics to titanium alloys as parts of cruise missiles requiring short-term resistance at 600 °C, as well as for pieces implemented in the space-shuttle and YF-12 aircraft. Even if the global performance is satisfactory, the brittleness inherent to the Larc-13 system is a limiting factor. The addition of various rubbery materials significantly improves the shock resistance, elongation to rupture, and toughness but to the detriment of the tensile strength, elastic modulus, and other thermomechanical properties. The Larc-13 adhesive is no longer commercialized because of the high cost of the diamine, which was replaced by 3,3′-sulphonylbisbenzeneamine in a modified version.

With PMR resins, the mixture of the three monomers is applied to a glass fabric as either a methanol solution or after addition of different wetting and flow control agents and eventually fillers (aluminum and silica powders). The melt process provides excellent quality films that have been tested by Rockwell International for the space shuttle. The adhesive, used to bond metal parts or sandwich honeycombs, presents excellent resistance to 315 °C.[75] The CYTEC commercial adhesive FM 35 is based on PMR 15 resin chemistry. Bonding tests made with aluminum specimens give lap-shear strength values of 35.8, 21.4, and 21.7 MPa at 25, 260, and 288 °C, respectively.[76] Titanium alloy coupons bonded at 288 °C with this adhesive under 0.28 MPa pressure exhibit lap-shear strengths of 21.7, 17.2, and 13.8 MPa at the same test temperatures. When the final cure temperature is increased to 329 °C, the adhesive joint becomes more brittle and the lap-shear strength decreases significantly. Within the framework of the studies intended to make high-performance adhesives for the space shuttle, Stenersen and Wyke[75] compared the properties of the nadimide-terminated oligoimides in development.

Table 9.6 Lap-Shear Strength Values Obtained With Nadimide-Terminated Adhesives Used to Bond Titanium, Stainless Steel, and Composite Materials

Substrate	T^a(°C)	Lap-shear strength (MPa)		
		Larc-13	Larc-160	PMR 15
Titanium	25	17.9	16.3	17.4
	316	14.2	14.1	12.3
Steel	25	16.2	18.8	19.8
	316	13.8	14.5	14.3
Composite	25	18.9	19.5	15.7
	316	15.1	15.1	14.0

[a] *Test temperature.*

Table 9.6 lists some of the results obtained with Larc-13, Larc-160, and PMR 15 used to bond different substrates.

The authors outlined that certain parameters had to be optimized to achieve valuable mechanical properties with adhesives based on the PMR concept. In particular, they investigated the effects of the treatments applied to the surfaces prior to bonding, the nature of the glass cloth carrier, and the partial drying of the adhesive film intended to eliminate the maximum amount of solvent and to partially convert the polyamic acids into polyimides. This can be considered as the most critical point because the residual solvent plays an important role during the bonding process. Its presence offers the tackiness and drapability required by large area substrates. It also increases both the surface wetting and low melt viscosity necessary to achieve optimum adhesion strength.

All heat-resistant high-performance adhesives, either thermoplastic or thermosetting, impose very constraining operating conditions. If relatively high values of the room temperature lap-shear strength are easily achieved, the assemblies must be subjected to postcure treatments to obtain maximum adhesive strength at high temperatures. As a rule of thumb, the assembly has to be postcured at a temperature at least equal to or more than the test temperature. The data in Table 9.7 show the lap-shear strength changes observed with assemblies made of stainless steel coupons bonded with Larc-13 and Larc-160 nadimide-terminated PMR resins and exposed to 316 °C postcure for 2−125 h.

When heat-resistant adhesives are applied by using the temperature and pressure recommended by the manufacturers, the adhesive properties at room temperature are generally very good, but the lap-shear strength at high temperature is significantly lower. This results from the compromise imposed by the existing production tools. In these conditions, the degree of polymerization (or cross-linking) does not reach a value high enough to obtain the optimum mechanical properties at 300 °C or more. The lap-shear strength values listed in Table 9.7 show that an adequate postcure treatment slightly decreases the adhesion strength at room temperature but significantly enhances the adhesion at 316 °C. It is worth noting that the adhesive strengths measured after 20 h at 316 °C are similar to the values obtained with condensation polyimides such as Nolimid 380® and DuPont NR 056X®.

9.5.3.3 Acetylene-Terminated Adhesives

Polymers **46**, **47**, and **48** (Fig. 9.19) were all evaluated as heat-resistant structural adhesives for bonding titanium alloys, copper, and composite materials. The thermal polymerization of the ethynyl end-groups starts at about 200 °C with so narrow a processing window that the reaction must be completed by postcuring the assemblies for 16 h at 315 °C or 4 h at 370 °C. Typical lap-shear strength values measured for Ti/Ti bonding are 22.1 MPa at 25 °C and 13.1 and 8.3 MPa at 232 and 260 °C after 1000 h aging at these two temperatures, respectively. The main problem lies in the very fast reaction rate of the ethynyl groups just below the glass transition temperature, resulting in poor substrate wetting in the early stages of the bonding process. A paper by Kuhbander and Aponyi[77] shows that hydroquinone can retard to some extent the polymerization of the acetylenic triple bonds and thus offers better processing conditions. Titanium specimens bonded under 0.34 MPa at 316 °C, followed by a postcure at 343 °C, exhibit lap-shear strengths of 26.2 MPa at

Table 9.7 Effect of a Postcure Treatment at 316 °C on the Lap-Shear Strength of Stainless Steel Coupons Bonded With Larc-13 and Larc-160 Adhesives Based on Nadimide-terminated Polyimide Oligomers

	Lap-shear strength (MPa)			
	Larc-13		**Larc-160**	
Postcure time at 316 °C (h)	**25 °C**	**316 °C**	**25 °C**	**316 °C**
2	20.7	13.1	22.4	12.4
10	18.6	14.5	18.6	13.1
20	17.9	15.2	17.2	13.1
125	17.2	14.5	16.5	12.4

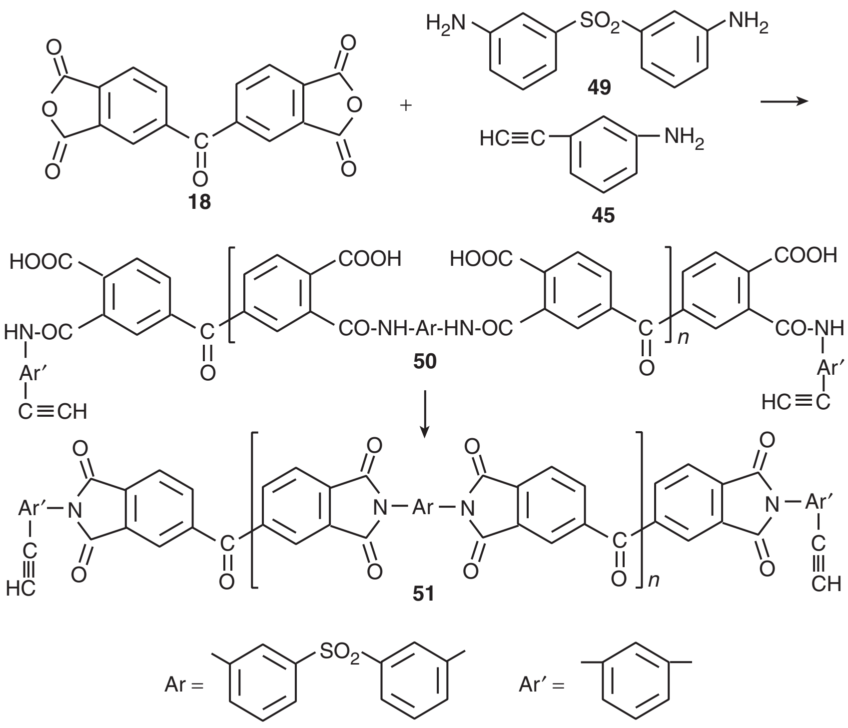


Figure 9.27 Chemical formulae of the polyamic acid **50** and polyimide **51** oligomers prepared from BTDA, 3,3′-sulphonylbisbenzeneamine **49**, and 3-ethynylbenzeneamine **45**.

25 °C, 14.5 MPa at 288 °C, and 17.6 MPa at 288 °C after aging at that temperature for 500 h.

Hanky and St. Clair[78] evaluated a series of imide oligomers end-capped with ethynyl groups. Polyamic acid **50** and polyimide **51** in Fig. 9.27 were prepared from BTDA **70**, 3,3′-sulphonylbisbenzeneamine **49**, and 3-ethynylbenzeneamine **45** with a DP *n* varying between 1 and 3.

The authors prepared other oligomers with 3,3′-methylenebisbenzeneamine and 3,3′-carbonylbisbenzeneamine as diamine components. The results of differential scanning calorimetry measurements listed in Table 9.8 indicate the thermal range of polymer flow for polyimide **51** as a function of its molecular weight. T_s is the temperature where the polyimide starts to flow, T_{min} represents the temperature corresponding to the minimum of the endothermic peak, and T_{max} is the maximum of the exothermic polymerization peak. Note that endothermic and exothermic reactions succeed one another over a few degrees without clear separation between the two phenomena. The last column of the table provides the glass transition temperature achieved with fully cured polymers. As expected, the T_g decreases when the molecular weight of the oligomers is increased.

Table 9.8 Thermal Characteristics of the Imide Oligomers **51** Determined by Differential Scanning Calorimetry

n	T_s (°C)	T_{min} (°C)	T_{max} (°C)	T_g (°C)
1	165	195	271	305
2	168	198	284	284
3	181	211	298	253

Titanium alloy (Ti_6Al_4V) test samples were bonded with acetylene-terminated polyimide oligomers **51**, with DP *n* = 1, 2, and 3, under 0.34 MPa pressure at 300 °C without postcure. The variation of the lap-shear strength values measured at 25 and 177 °C during thermal aging in air at 177 °C is illustrated by the curves of Fig. 9.28. They clearly demonstrate that the higher the molecular weight of the oligomers, the better the resistance to degradation in long-term thermal-oxidative conditions.

The results presented in this section show that polyimide adhesives are far from having the versatility offered by epoxy resins, which can be processed as solventless resin–hardener combinations without volatile evolution during the curing step. Even though several polyimides exhibit good adhesive properties at high temperature, in long-term aging tests and in humid conditions, the shortcomings inherent to the chemistry of heterocyclic polymers have not yet been solved.

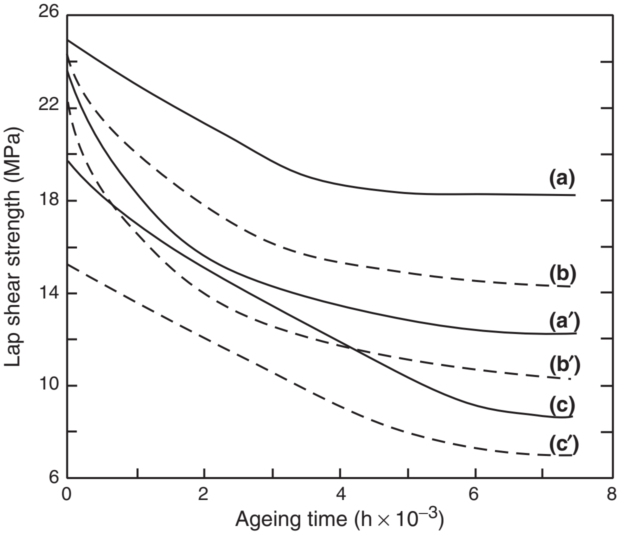


Figure 9.28 Lap-shear strength versus aging time in air at 177 °C for Ti/Ti specimens bonded with polyimide oligomers **51**. Curves (a–c) are lap-shear strength values measured at 25 °C for oligomers with n = 3, 2, and 1, respectively, whereas curves (a′–c′) refer to lap-shear strengths measured at 177 °C in the same order of molecular weights.

9.5.4 Condensation Prepolymers

9.5.4.1 Polyimides

Historically, the adhesives based on reactive condensation prepolymers were the first materials to be extensively studied, developed, and introduced to the market. One of the best performing polyimides in this category is Nolimid® 380, produced by Rhône-Poulenc after an extensive series of tests.[79] The resin binder is the mixture of monomers **30a** and **30b**, as well as the low-molecular-weight (oligoimide) polyimide **31** of Fig. 9.15. Typical compositions are prepared as previously reported by mixing the two monomers and 4,4′-oxybisbenzeneamine in NMP and methanol.[15] To this solution, introduced into a roll-mill, are added aluminum powder (400 mesh) and El Monte Chemicals Arsenone® as antioxidant. Nolimid 380/glass tapes are made by depositing the adhesive composition on both sides of E-112 glass fabric carriers and then drying at 90 °C for 10 min in an air circulating oven. Other adhesive layers are coated and dried to obtain a final weight of 650 g m^{-2}, the weight of residual solvent accounting for approximately 15%.

Once cleaned, the metal surfaces are coated with a primer prepared by roll-milling 200 g of adhesive composition and 500 g of methanol. A first layer of primer is applied to the metal parts, dried for 10 min at 90 °C, covered with a second layer of primer and finally dried at 90 °C for 1 h in an air-circulating oven. The adhesive film is inserted between the two primed metal surfaces and the assembly is placed between the platens of a hydraulic press preheated to 316 °C. A pressure of 0.3–0.5 MPa is applied and the test specimens are cured at 316 °C for 1.5 h, before cooling down to 100 °C under pressure. The assemblies are removed from the press and postcured in an air-circulating oven as follows: the temperature is raised from 20 to 300 °C in 1 h, then from 300 to 350 °C in 5 h, and left at 350 °C for 5 h. The lap-shear strength values determined at different temperatures are plotted in Fig. 9.29 for TU-2 Ti/Ti assemblies [curve (a)] and Z10 CNT 1810 stainless steel coupons [curve (b)].

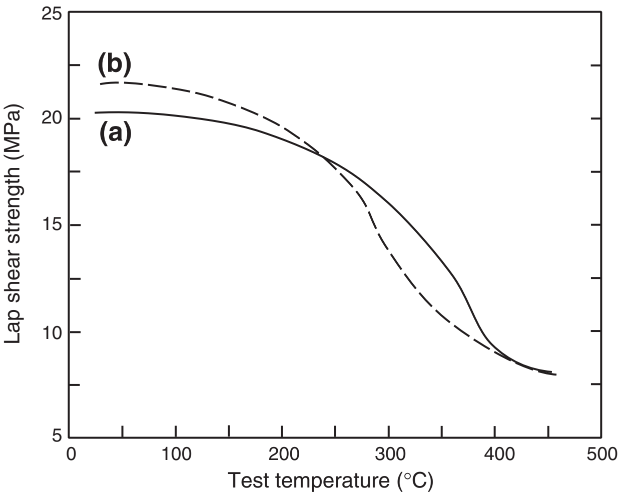


Figure 9.29 Variation of the lap-shear strength as a function of the test temperature between 25 and 450 °C. Assemblies made by bonding: (a) TU-2 titanium alloy and (b) Z10 CNT 1810 stainless steel with adhesive films prepared from condensation oligomers **31**.

Ti/Ti test specimens were subjected to long-term aging in flowing air at 260 and 300 °C, the adhesive strength being measured every 500 h. The curves fitting the lap-shear strength data are plotted in Fig. 9.30 in which curves (a) and (b) provide the adhesive strength determined at 23 and 260 °C, respectively for specimens aged at 260 °C. The initial increase in adhesion, generally observed with most condensation polyimide adhesives, is commonly attributed to additional curing reactions. These two curves demonstrate the excellent stability of the adhesive joint after 12,000 h of air-aging at 260 °C. Curves (c) and (d) are drawn from the lap-shear

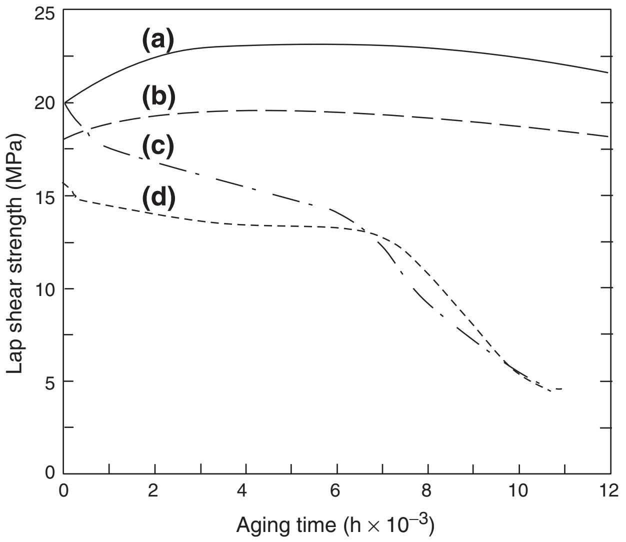


Figure 9.30 Variation of the lap-shear strength as a function of the aging time in flowing air for TU-2 titanium alloy bonded with polyimide precursors **30**. Assemblies aged at 260 °C: lap-shear strength measured at room temperature (a) and at 260 °C (b). Assemblies aged at 300 °C: lap-shear strength measured at room temperature (c) and at 300 °C (d).

strength values measured at 25 and 300 °C, respectively, during isothermal aging in air at 300 °C. The threshold value of 15 MPa is preserved for 5000 h at that temperature, but the rate of degradation increases significantly after 7000 h to reach a final adhesion strength of 5.9 MPa after 10,000 h at 300 °C. Thermal aging at 275 °C, not shown in the figure, results in lap-shear strength values lying between these two boundaries.

Aging tests were also performed with stainless steel specimens subjected to thermal-oxidative stressing at 300 °C for 2000 h. The experimental results are plotted in Fig. 9.31 in which curves (a), (b), and (c) show the variation of the lap-shear strength values measured at 25, 300, and 350 °C, respectively.

The resistance of the TU-2 titanium assemblies to shorter term exposure at high temperature was determined at 340, 377, 400, and 450 °C. The lap-shear strength data plotted in Fig. 9.32 were determined at the corresponding aging temperature.

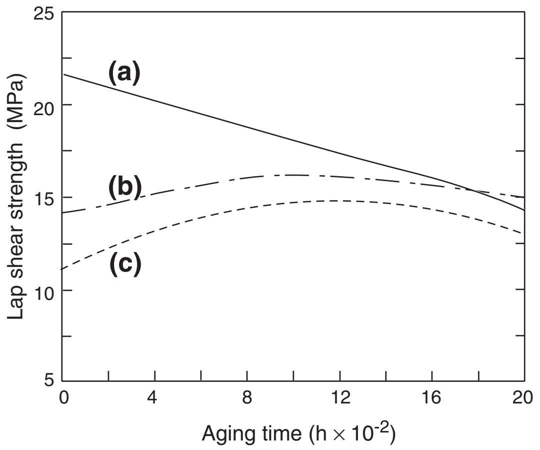


Figure 9.31 Variation of the lap-shear strength as a function of the aging time in flowing air at 300 °C for Z10 CNT 1810 stainless steel coupons bonded with Nolimid 380 polyimide precursor. Curves (a), (b), and (c) fit the lap-shear strength values measured at 25, 300, and 350 °C, respectively.

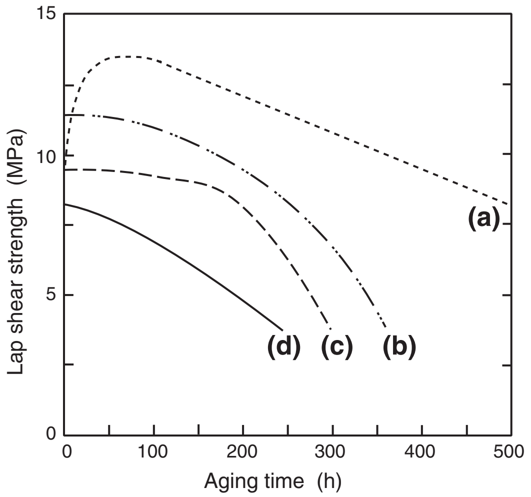


Figure 9.32 Variation of the lap-shear strength as a function of the aging time in flowing air for TU-2 titanium alloy bonded with Nolimid 380 polyimide precursors. The strength of adhesion is measured at the aging temperatures: (a) 340, (b) 377, (c) 400, and (d) 450 °C.

Specimens of both TU-2 and 6Al4V titanium alloys were also subjected to the so-called "Mach 3 Fighter" test, which consists of 500 h of aging at 300 °C, followed by 24 h at 340 °C and 1 h at 350 °C. At the end of the test, the lap-shear strength was measured at 25, 300, and 350 °C. Before aging, the initial strengths were 20, 15.5, and 12.5 MPa at these temperatures, respectively. Lap-shear strengths of the aged specimens slightly decreased from 20 to 18 and 16 MPa for TU-2 and 6Al4V alloys when measured at 25 °C. By contrast, they increased by 10−15% for the measurements made at 300 and 350 °C. Finally, the resistance of the polyimide joints to humidity was determined with assemblies exposed to water immersion at room temperature and to 100% relative humidity at 50 °C for 1 month each. The lap-shear strength of wet specimens was 13−15 MPa increasing to 15−18 MPa for the same samples dried at 100 °C. FM 34® of CYTEC presents some analogy with the previous class of condensation prepolymer. Even though its composition is not clearly displayed, it seems to be prepared from the reaction of 4,4′-carbonylbis(1,2-benzenedicarboxylic acid) dimethyl ester **33** with 4,4′-methylenebisbenzeneamine **34** (Fig. 9.16) in NMP solution. The FM 34 brand, which contained arsenic derivatives, was withdrawn from the market and replaced by FM 34B-18 without arsenic pentasulfide.

As for all the other adhesives retaining relatively large amounts of solvents and other potential volatile materials, the best processing technique is to place the assembly in a bag allowing one to apply a partial vacuum, whereas the adhesive is cured in an autoclave. The results of Table 9.9, published by the manufacturer, were obtained with stainless steel specimens bonded at 371 °C under 0.28 MPa.[80] Compared with Nolimid 380®, the initial adhesive strength is improved by about 26%, but the resistance to air oxidation at 260 and 315 °C is not as good.

High-performance adhesives based on the in situ polycondensation of monomer precursors of polyimides were developed by Gibbs using the chemistry evolved from the NR 150® series of polyimides where 4,4′-[2,2,2-trifluoro(1-trifluoromethyl)ethylidene]bis(1,2-benzenedicarboxylic acid) dianhydride is opposed to various aromatic diamines in NMP.[81,82] The chemical formula of the NR 150-A2 polyimide **8** is shown in Fig. 9.9 with, however, a fabrication process involving the tetracarboxylic acid (6FTA) instead of the dianhydride **5**. NR 150-B2, also known as Avimid® N, is synthesized by reacting the same fluorinated tetracarboxylic acid with 1,4-benzenediamine **7** (95 mol%) and 1,3-benzenediamine **6** (5 mol%) in a mixture of NMP and ethanol. The last brand, DuPont NR 056X®, is a composition of oligomers whose thermal polycondensation provides a polyimide comprising the recurring units **8** and **10** in Fig. 9.9. This material is prepared by dissolving in diglyme the fluorinated acid, 75 mol% of 1,4-benzenediamine **7**, and 25 mol% of 4,4′-oxybisbenzeneamine **2**. A paper by Blatz[83] reports that replacing NMP by the less polar diglyme, which has a lower boiling point, results in better adhesion. This adhesive composition containing 65 phr of aluminum powder was employed to bond Ti/Ti specimens at 316 °C under 1.38 MPa. A postcure of 16 h at 316 °C was required to achieve lap-shear strength values above the NASA goal of 20.7 MPa at room temperature and 13.8 MPa at 316 °C. In these conditions, the adhesive strength was 24.1 and 15.1 MPa at 25 and 316 °C, respectively, and 13.8 MPa at 232 °C after aging for 5000 h at that temperature. Table 9.10 lists a few examples of polyimide materials that have been extensively tested as structural adhesives. This series includes virtually all categories of polymers such as condensation oligomers, high-molecular-weight polyimide precursors, precyclized thermoplastic polyimides, and thermosetting telechelic addition polyimides.

Table 9.9 Lap-Shear Strength of Stainless Steel Coupons Bonded with FM 34B-18 Adhesive Cured at 371 °C Under 0.28 MPa Pressure

Aging conditions	LSS[a] (MPa) at 24 °C	LSS[a] (MPa) at 260 °C
Before aging	27.9	16.1
After 750 h at 260 °C	23.2	15.5
After 2000 h at 260 °C	18.7	9.7
After 192 h at 316 °C	10.9	8.8

[a] *LSS: lap-shear strength.*

Figure 9.33 summarizes the typical data discussed in the present section to compare the best performing polyimide adhesives at temperatures exceeding 200 °C. It can be seen that condensation polyimides (Nolimid 380® and FM 34B®) seem to work better in aging tests between 260 and 300 °C. The thermoplastic polyimides, Larc-IA and Larc-TPI, exhibit excellent adhesive properties between 200 and 232 °C, whereas the BMI FM 32 can be used up to 200−230 °C.

The best epoxy or epoxy-phenolic adhesives employed in the aerospace industry show initial lap-shear strength values often higher than those of the polyimides, but the maximum operating temperatures are in the range of 150−170 °C. For example, the adhesion strength of Al/Al assemblies bonded with a high-temperature epoxy resin is of the order of 30 MPa at 150 °C and remains virtually constant when aged at that temperature for 5000 h. The adhesive film 3M Scotch-Weld AF 131, based on epoxy-phenolic resins, provides Al/Al bonds with lap-shear strengths of 25.5, 20, and 10.3 MPa at 180, 200, and 260 °C, respectively. Solventless epoxy and epoxy-phenolic adhesives provide bond lines with a low level of porosity. This is also the case with poly(ether-imide) Ultem® 1000 and poly(imide-siloxanes), which are generally processed at temperatures

Table 9.10 Examples of Polyimide Structural Adhesives Including the Main Families of Linear Polyimide Precursors as Well as Oligomers Terminated by Ethylenic Double Bonds and Acetylenic Groups

Trade mark	Chemistry	Presentation
Nolimid 380[a]	Monomer **30** and prepolymer **31** (Fig. 9.15) + Al	Glass fiber tape
FM 34[b]	Prepolymer **35** in solution (Fig. 9.16) + Al	Glass fiber tape
FM 36[b]	Condensation prepolymer	Glass fiber tape, Adhesive paste
NR 150 A2[c]	Linear fluorinated polyimide precursor **8** (Fig. 9.9) + Al	Adhesive paste
NR 150 B2[c]	Linear copolyimide precursors **9** and **10** (Fig. 9.9)	Solution in NMP
NR 05X[c]	Linear copolyimide precursors **8** and **10** (Fig. 9.9)	Solution in diglyme
Ultem 1000[d]	Thermoplastic poly(ether-imide) **26** (Fig. 9.13)	Solid powder
Larc TPI[e]	Thermoplastic polyamic acid **20** and polyimide **22** (Fig. 9.11)	Adhesive film
Nolibond 1[a]	Thermosetting poly(amide-imide)	Solution in NMP
Kerimid 601[f]	Thermosetting BMI **39** + diamine **34** (Fig. 9.17)	Solid powder
PMR 15[g]	Mixture of unreacted monomers **41**, **42**, and **34** (Fig. 9.18)	Solution in methanol
Larc 160[h]	Mixture of unreacted monomers **41**, **42** and Jeffamine	Solution in methanol
Thermid 600[i]	Ethynyl-terminated imide oligomers **48** (Fig. 9.19)	Solid powder
Thermid IP 600[i]	Ethynyl-terminated isoimide oligomers **47** (Fig. 9.19)	Solid powder

Manufacturers:[a]*Rhône-Poulenc,* [b]*CYTEC Industries,* [c]*DuPont de Nemours,* [d]*SABIC,* [e]*Gulf Oil/Mitsui Toatsu,* [f]*Ciba Geigy,* [g]*NASA/Ferro/Fiberite,* [h]*NASA/US Polymeric,* [i]*National Starch.*

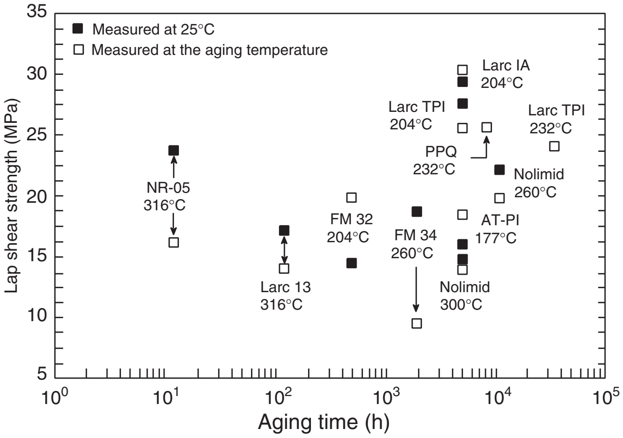


Figure 9.33 Comparative evaluation of the different polyimide structural adhesives from the experimental data published in the literature or provided in manufacturers' technical bulletins.

50–100 °C above their T_g. In contrast, high porosity is observed with most condensation polyimides and PBIs even if a partial vacuum is applied to help the removal of volatile by-products and organic solvents. Addition polyimides fall in between with average porosity values in the range of 4–6%.

9.5.4.2 Polybenzimidazoles

The general process used to synthesize aromatic PBIs is presented in Section 9.3.3. Detailed information can be found in previously published books.[84,85] During 1960–1970, a number of publications, comparable with those on polyimides, reported the synthesis and properties of all aromatic and aryl-aliphatic PBIs. Most of these polymers were prepared by the two-step process illustrated in Fig. 9.14 with the reaction of 1,3-benzenedicarboxylic acid diphenyl ester **27** and [1,1′-biphenyl]-3,3′,4,4′-tetramine **11** yielding ultimately PBI **29**. All the applications—laminates and filament winding resins, adhesives, fibers, and foams—used polymer **29**, which was produced in semicommercial quantities by the Whittaker Corporation (Narmco Division)

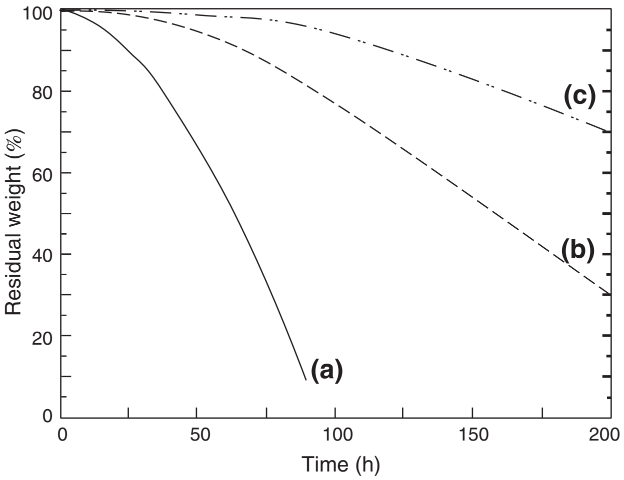


Figure 9.34 Isothermal aging in air at 371 °C of heat-resistant heterocyclic polymers: (a) polybenzimidazole **29**, (b) poly(*N*-phenylbenzimidazole), (c) polyimide **4** and polyphenylquinoxaline **15**.

under the generic trade mark Imidite®. Currently, 40 years later, this polymer is manufactured by Hoechst-Celanese and its only commercial success is in the area of heat-resistant fibers and fabrics. However, it is worth noting the adhesive properties of this polymer and the reasons explaining the major obstacles to the development of PBIs as heat-resistant adhesives.

Although original work demonstrated that PBI **29** shows no significant change on heating at 550 °C and less than 5% weight loss after several hours at 600 °C, the polymer exhibits appreciably lower stability in an oxidizing atmosphere. The source of this instability has been attributed to the N—H group of the imidazole ring, this assumption being supported by the isothermal weight loss curves of Fig. 9.34.

Thermal aging in air at 371 °C shows that PBI **29** is completely degraded after 100 h at that temperature [curve (a)]. Poly(*N*-phenylbenzimidazole) in which all N—H groups are replaced by N—C_6H_5 substituents exhibits better resistance to air oxidation with 70% weight loss after 200 h at 371 °C [curve (b)], whereas both polyimide **4** and polyphenylquinoxaline **15** [curve (c)] are more stable with only 30% weight loss under the same time—temperature conditions.

Despite the copious evolution of phenol and water during processing, Narmco's commercial adhesive system (Imidite® 850) was based on prepolymer **28** mixed with aluminum powder, inorganic arsenic compounds such as arsenic thioarsenate or arsenic pentasulfide, and sterically hindered polyphenol antioxidant. Adhesive tapes were manufactured by hot-melt deposition of this mixture on a 112-type glass cloth carrier used in conjunction with a heat-resistant primer (PBI or polyimide). As with all other heat-resistant polymers, surface preparation of flat and honeycomb metal surfaces is an important factor in long-term aging. Sand blasting, solvent degreasing, and acid etching are sequentially used before primer deposition. Imidite® 850 requires a curing schedule of 1 h at 220 °C followed by 1 h at 315 °C under 1.4 MPa pressure. A postcure treatment of 1 h at 371 or 400 °C is then applied to improve the adhesive properties at high temperature. PBI adhesives exhibit high-shear strength values for short periods at elevated temperatures, but the curves of Fig. 9.35 shows that the adhesive properties fall off rapidly on prolonged aging. Although the strength retention of PBI adhesives at high temperature is superior to that of epoxy-phenolics, it is significantly inferior to that of condensation polyimides at 260 and 316 °C. To conclude this brief overview of the polybenzimidazole adhesives, it is quite clear from the number of test results that PBI cannot compete with polyimides. The major obstacle to the development of Imidite® 850 has been its poor thermal-oxidative stability at temperatures of more than 250 °C. In addition, the dependence on the use of aromatic tetramines has introduced two other negative parameters, that is, the cost of these comonomers and their carcinogenic properties. Furthermore, arsenic derivatives have been forbidden in adhesive composition and unsuccessfully replaced by boron powder which

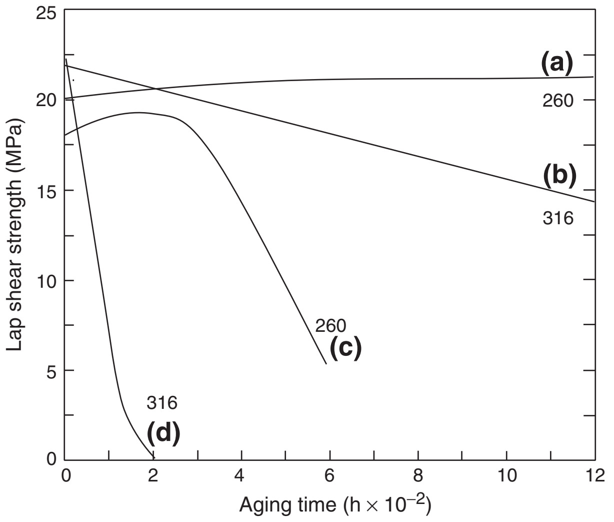


Figure 9.35 Variation of the lap-shear strength as a function of the aging time in flowing air for TU-2 titanium alloy coupons: Nolimid 380 at (a) 260 °C and (b) 316 °C; Imidite® 850 at (c) 260 °C and (d) 316 °C.

Table 9.11 Processing Conditions—Pressure, Temperatura, and Postcure—For Typical High-Performance Adhesives Developed for the Aerospace Industries

Adhesives	Pressure (MPa)	Curing (°C)	Postcure (time, h/temperature, °C)	Voids (vol%)
Epoxy-phenolics	0.4	180	–	<2
HT-epoxies[a]	0.4	220	–	<1
PBI oligomers[b]	1.4	316	3/370	>10
Nolimid 380[c]	0.3	316	5/350	5–10
FM 34[c]	0.4[d]	180	2/316	13.8
NR 150 PAA[e]	0.5[d]	370	1/370	11
PPQ[f]	1.4[d]	400	1/425	1.4
Ultem 1000[g]	0.4	380	–	<1
Poly (imide-siloxane)	0.1	250	–	<2
Poly (amide-imide)	0.8	200	8/250	<2
Larc TPI[h]	2.1	343	2/316	8.3
FM 32 BMI	0.3	177	4/204	0.5
EA 9373[i]	0.2	232	2/232	<1
Larc 13 bisnadimide	1.4[d]	316	4/316	5–8
FM 35 bisnadimide	1.4	290	10/316	5
Larc 160 PMR resin	0.7[d]	290	10/316	4–5
Thermid 600[j]	1.4[d]	290	4/316	6
Thermid IP 600[j]	1.4[d]	290	4/316	<3
Diethynyl-PPQ	0.35	370	4/370	<1

[a] *High temperature epoxies.* [b] *Polybenzimidazole oligomers.* [c] *Polyimide oligomers.* [d] *Specimens bonded in vacuum bags (625 mm Hg) placed in autoclave at the indicated pressure.* [e] *Polyamic acid.* [f] *Polyphenylquinoxaline.* [g] *Poly(ether-imide).* [h] *Thermoplastic polyimide.* [i] *Epoxy-BMI.* [j] *Acetylene-terminated oligomers.*

is not as good at preventing air oxidation of joined stainless steel alloys. Table 9.11 provides some key data to compare the processing conditions of different high-performance commercial adhesives tested for the fabrication of structural parts.

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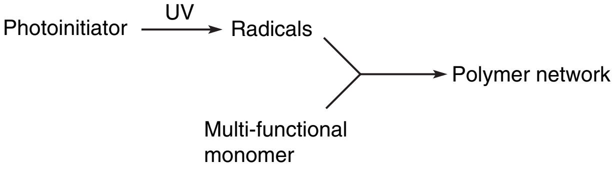
10 UV-Radiation Curing of Adhesives

Christian Decker

10.1 Introduction

There is a growing trend in the adhesives industry to develop fast-setting solvent-free resins because of ever more stringent regulations regarding the emission of volatile organic compounds. In this respect, UV-curable adhesives appear to be ideal candidates because such liquid formulations contain no organic solvents and are readily transformed into solids by a short exposure to UV-radiation at ambient temperature. This feature, together with the resulting low consumption of energy and the high performance of the UV-cured materials, explains the increasing use of this environment-friendly technology in the adhesives industry. The subject has been extensively investigated over the past two decades and covered in several comprehensive articles and textbooks.[1−10]

UV-radiation curing consists basically of a photoinitiated polymerization of multifunctional monomers that are converted into a tridimensional polymer network according to the following reaction scheme:[11]



A photoinitiator is used to absorb the UV-radiation and generate upon cleavage the reactive species, free radicals, or protonic acid that will initiate the cross-linking polymerization reaction according to a radical or cationic mechanism, respectively. Once initiating radicals or ions have been produced, the following steps (chain propagation and termination) will essentially be the same as in a conventional polymerization, except for the much larger rate of initiation caused by the intense illumination. A liquid resin can thus be transformed into a solid polymer within a fraction of a second.[12]

A unique advantage of the UV-curing technology is to provide precise temporal and spatial control of the setting process that will occur on order, selectively in the illuminated areas. Such performance, together with cost and environmental consideration, is the main reasons why UV-curable adhesives are being increasingly used and continue to attract attention in various industrial sectors, as shown by the numerous patents taken recently on novel applications of this technology.[13−19]

A crucial factor in developing high performance UV-curable adhesives is obviously to ensure an excellent adhesion onto the various types of supports (plastics, glass, metals, and paper). In this respect, the absence of a solvent in the resin formulation is certainly a disadvantage, compared with solvent-based adhesives in which the bonding onto organic materials is enhanced through the solvent-driven softening effect of the substrate surface. Moreover, a high strain builds up in the polymer during the ultrafast curing reaction and its concomitant volume contraction, which leads usually to a poor adhesion.[20] One way to offset this detrimental effect is by promoting the formation of van der Waals or hydrogen bonds between the UV-cured polymer and the substrate or even covalent bonds by photografting.

Another limitation of the UV technology in adhesive applications results from the fact that curing of the resin occurs only in the illuminated areas, so that at least one part of the assembly needs to be transparent to UV light. Moreover, for complex-shaped tridimensional objects, it will be difficult to harden the resin located in the shadowed areas. Both of these issues need to be addressed to widen the field of application of UV-curable adhesives.

In this review article, the progress recently made in the development of UV-curable adhesives will be outlined, with respect to both the resin formulation and the characteristics of the photopolymer obtained. Special attention will be given to the basic chemistry

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involved in photocross-linking polymerization and its kinetic analysis, because the final properties of UV-cured adhesives will depend on a good understanding and control of the manifold reactions occurring during such ultrafast molecule to material transformations. The main applications of UV-curable adhesives will be discussed afterward in consideration of the growing development of such systems in a large variety of industrial sectors where they are used as structural adhesives to bond metals, glass, and plastic components, as sealants or encapsulation compounds, and as pressure-sensitive and hot-melt adhesives.

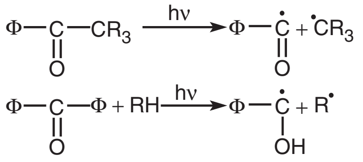
10.2 Different Types of UV-Curable Adhesive Resins

The light-induced hardening of adhesives is generally achieved by a polymerization reaction proceeding either by a radical mechanism (e.g., for acrylic resins) or a cationic mechanism (e.g., for epoxides). Dual-cure systems, where the UV-exposure is followed by a thermal treatment, have to achieve an effective curing of the insufficiently illuminated areas.[21] Typical formulations of UV-curable adhesives consist of a photoinitiator, a functionalized oligomer or prepolymer that will constitute the backbone of the tridimensional polymer network, and a monomer used as reactive diluent or plasticizer to adjust the formulation viscosity or rheology. Dual-cure systems contain some additional functionalities, usually isocyanate and hydroxy groups, to ensure an effective cross-linking in the dark areas upon heating.

The photoinitiator plays a key role by controlling both the rate of initiation and the penetration of the incident light and, therefore, the depth of cure. The rate of polymerization depends on the reactivity of the functional group, its concentration, and on the viscosity of the resin, as well as on the intensity of the UV radiation. The chemical structure and functionality of both the functionalized oligomer and the monomer are critical factors that determine the cross-linking density and the viscoelastic properties of the UV-cured polymer. Better adhesion is usually achieved with low-modulus elastomers showing a great affinity toward the substrate through hydrogen bonding or grafting. The different types of UV-curable resins commonly employed in adhesive applications will now be described by focusing on the chemical and kinetic aspects of the curing process, in relation to their adhesion performance.

10.2.1 Photoinitiated Radical Polymerization

Most of the radical-type photoinitiators used in UV-curable adhesives consist of aromatic ketones that are known to generate free radicals upon UV-exposure, either by homolytical cleavage of C−C bonds or by hydrogen abstraction from a H-donor molecule.[11]



$$\Phi-\underset{\underset{O}{\|}}{C}-CR_3 \xrightarrow{h\nu} \Phi-\underset{\underset{O}{\|}}{\dot{C}}+\dot{C}R_3$$

$$\Phi-\underset{\underset{O}{\|}}{C}-\Phi+RH \xrightarrow{h\nu} \Phi-\underset{\underset{OH}{|}}{\dot{C}}+R^{\bullet}$$

Both the benzoyl and alkyl radicals initiate the polymerization by the addition to the monomer double bond. By contrast, the ketyl radical is inactive toward vinyl double bonds, so that initiation occurs through the H-donor radical. To be efficient, a photoinitiator must effectively absorb the radiation emitted by the light source and generate initiating radicals with high yields. There are a large number of commercially available photoinitiators that have recently been surveyed by Dietliker in a comprehensive compilation[22] and an excellent textbook.[23] The chemical formulae of some typical radical photoinitiators are given in Chart 10.1. Their absorption needs to overlap the emission spectrum of the UV source, usually a mercury lamp, as photochemical reactions can only occur if light has been absorbed.

10.2.1.1 UV-Curable Acrylate Resins

Acrylates are known to be among the most reactive monomers polymerizing by a free-radical mechanism. This feature, together with the tailor-made properties of the photopolymer obtained, account for the wide use of acrylate-based UV-curable adhesives. There are a large variety of acrylate-functionalized oligomers that are commercially available.[24] They differ in their chemical structures, which can be polyurethanes, polyesters, polyethers, and polysiloxannes, and by their molecular weight that ranges typically between 500 and 2000 g. The photoinitiated cross-linking polymerization of an acrylated oligomer is represented schematically in Chart 10.2. The final properties of UV-cured acrylate polymers depend primarily on the chemical structure of the functionalized oligomer, the degree of cure and

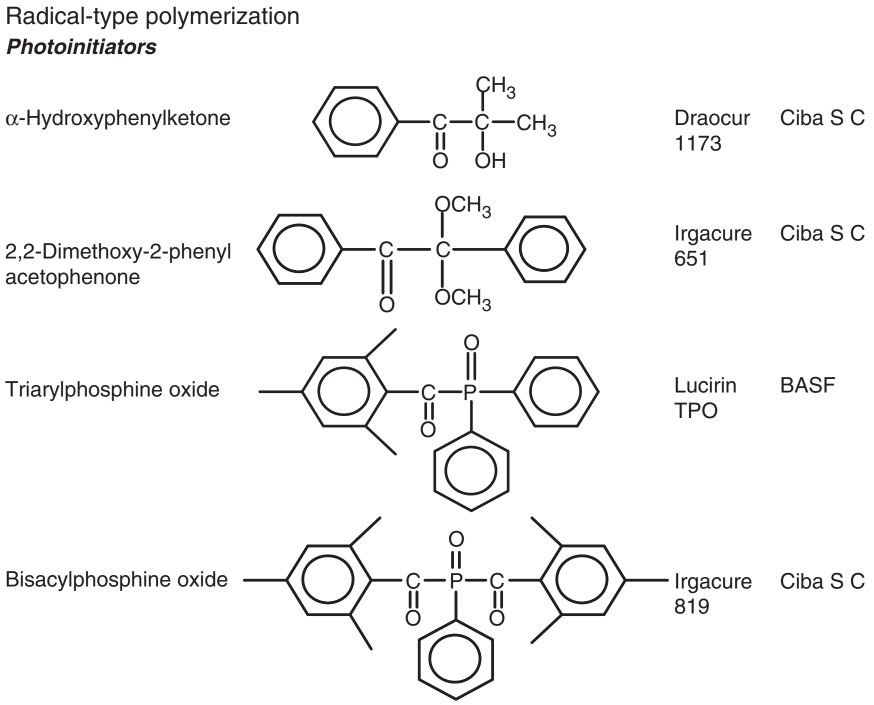
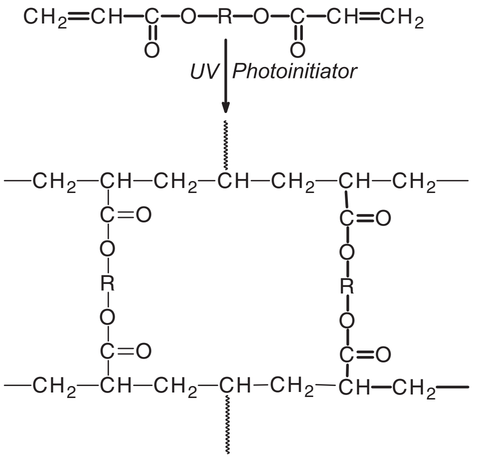


Chart 10.1 Chemical formula of radical-type photoinitiators.

the cross-linking density. Low-modulus elastomers are generally obtained with aliphatic compounds having soft segments, whereas hard and glassy materials are formed when aromatic structures are present in the polymer chain.[25]

Because of growing molecular mobility restrictions during the light-induced liquid to solid phase change, polymerization stops when vitrification occurs, which leads to an incompletely cured glassy material. High degrees of polymerization (close to 100% conversion) are reached with aliphatic polyurethane-acrylates (PUAs) that give elastomeric materials upon UV curing at ambient temperature, well suited for adhesive applications. Figure 10.1 shows some typical polymerization profiles recorded by real-time infrared (RTIR) spectroscopy[26,27] for an



with R: polyester, polyether, polyurethane, polysiloxane, polybutadiene

Chart 10.2 UV curing of an acrylated oligomer.

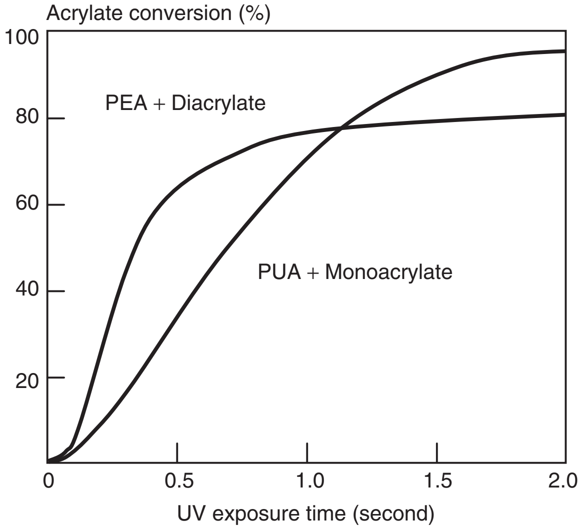
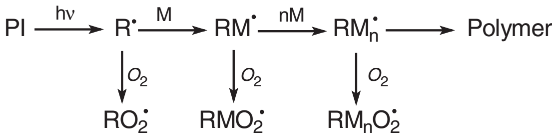


Figure 10.1 Polymerization profiles recorded by RTIR spectroscopy upon UV exposure of an aliphatic polyurethane-acrylate (PUA) or an aromatic polyether-acrylate (PEA) in the presence of a monoacrylate or a diacrylate reactive diluent (25 wt%), respectively. Light intensity: 40 mW cm^{-2}. Laminated film.

aromatic polyether-acrylate (glassy material) and an aliphatic PUA (elastomeric material) by using diacrylate and monoacrylate reactive diluents, respectively. The monomer used to lower the formulation viscosity plays a key role by controlling not only the polymerization kinetics but also the properties of the cross-linked polymer formed. Increasing the monomer functionality was found not only to accelerate the curing reaction but also to reduce the final degree of polymerization because of early gelation and vitrification of the irradiated sample. The greater cross-link density leads to glassy polymer materials that are hard but brittle and, therefore, ill suited for adhesive applications.

UV-curable adhesives contain usually monoacrylates as reactive diluents (such as carbamate-acrylates or isobornyl acrylate[28]) that produce soft and flexible elastomers showing a strong adhesion on various substrates. Excellent adhesion to plastics has been achieved with phenoxyethyl acrylate (Ebecryl 114 from UCB Chemicals) and to nonpolar substrates with octyl-decyl monoacrylate (ODA-N from UCB), when such monomers were associated with an aliphatic urethane diacrylate oligomer (Ebecryl 230 or 270).[29] In systems when good adhesion is difficult to achieve, chlorinated polyester resins diluted with diacrylate monomers such as hexanediol diacrylate (Ebecryl 524) or tripropyleneglycol diacrylate (Ebecryl 525) proved to be very effective and are recommended for UV-curable laminating adhesives. In the case of metallic substrates, polyester acrylates associated with monomers bearing carboxylic groups (acrylic acid or its dimer) were shown to improve substantially the adhesion on metal foils.[30] Novel urethane-acrylate oligomers have been recently developed to be used as UV-curable adhesives to bond clear films to various substrates (paper, plastics, and foils) and achieve superior peel adhesion,[31] the best performance being reached by using a bisacylphosphine oxide photoinitiator.[32] With the tackifying compounds CN-3000 and CN-3001, high peel strength (8 lb-in.) has been reached, which makes these oligomers well suited for pressure-sensitive adhesive (PSA) applications. In UV-curable laminating adhesives, the bond strength increases as expected with the degree of cure and thus with the UV dose received by the sample. For a typical PUA resin, it was found to level off at a UV dose of 0.4 J cm^{-2}.[33]

One of the problems encountered in photoinitiated radical polymerization is the inhibitory effect of atmospheric oxygen that is known to react readily with free radicals to give inactive peroxyl radicals.



To cure thin coatings in contact with air, it is, therefore, necessary to work under intense illumination to consume rapidly the O_2 dissolved in the sample and shorten the exposure time during which atmospheric oxygen diffuses into the coating. This is not a problem anymore in adhesive applications that are performed under oxygen diffusion-free conditions (laminates). After a short induction period during which the dissolved O_2 is consumed by the initiator radicals, the polymerization of the acrylate double bond proceeds as fast in the laminated sample as in an inert atmosphere and much faster than for a coating, as shown in Fig. 10.2 for a PUA resin.

It is well known that adhesives need to be low-modulus elastomers, so that the resin formulation has to be designed to give, after UV curing, a soft material with a low glass transition temperature (T_g). Figure 10.3 shows some typical elastic modulus (E) and tan δ profiles recorded by dynamic mechanical analysis for a UV-cured PUA that is suitable for adhesives applications, based on its E and T_g values. It is quite soft, as shown by its Persoz hardness value of 50 s, on a scale that goes up to 400 s for glassy materials.

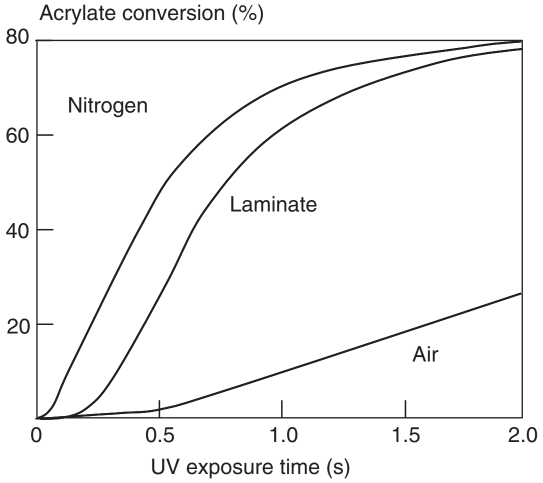


Figure 10.2 Inhibitory effect of oxygen on the photopolymerization of a polyurethane-acrylate + diacrylate resin exposed to UV radiation ($I = 20$ mW cm^{-2}). Film thickness: 10 μm.

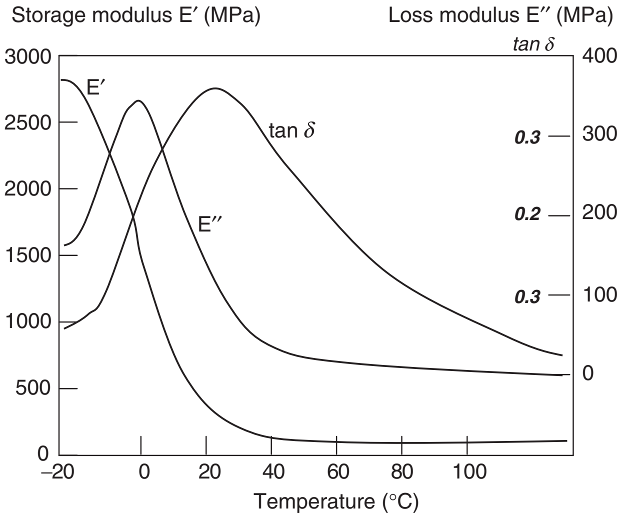


Figure 10.3 DMA recording of the storage modulus (*E*′) loss modulus (*E*″) and tan δ for a UV-cured acrylate elastomer.

To ensure good adhesion, the acrylate double bond content of the UV-glue has to be kept as low as possible (≤3 mol/kg) to minimize shrinkage. This is achieved by using relatively high-molecular-weight oligomers, such as the aliphatic polyester urethane acrylate SR-966 from Sarkomer that provides superior adhesion onto polyethylene and polycarbonate substrates.[33] A triacrylate oligomer having a tris (2-hydroxyethyl) isocyanurate structure (SR-368 from Sarkomer) was found to promote adhesion on this type of substrate because of its highly polar character.[33]

Low shrinkage and good adhesion was also achieved by using water-based UV-curable acrylate resins, such as Laromer PE-55W from BASF, associated with Irgacure 2959 from Ciba SC as photoinitiator. After drying at 80 °C, the tacky film obtained proved to be an excellent adhesive to assemble glass plates or transparent films by a short exposure to UV radiation, which transforms the tacky resin into a low-modulus elastomer. The multistep processing can be represented as follows:

$$\begin{array}{c}\text{Spraying}\\\text{Waterborne resin}\end{array} \xrightarrow{\text{Drying}} \begin{array}{c}\text{Lamination}\\\text{Tacky film}\end{array} \xrightarrow{h\nu} \begin{array}{c}\text{UV-irradiation}\\\text{Elastomer}\end{array}$$

Another important requirement for achieving excellent adhesion is to ensure a perfect wetting of the substrate by the liquid resin. It can only be achieved if the surface energy of the resin is lower than the surface energy of the substrate. This explains why it is so difficult to get strong adhesion on plastics such as polyolefins or fluorinated polymers that have a low surface energy. In this case, chemical bonding of the acrylic resin through photografting proved to be the most effective way to assemble this type of materials.[34] The photoinitiator radicals may abstract hydrogen atoms from the polymeric substrate and generate reactive sites at its surface. The latter can then initiate the polymerization of the monomer, thus ensuring a strong chemical bonding of the UV-cured resin to the organic substrate.

An effective way to improve the wetting on low-energy substrates is by adding to the UV-curable formulation small amounts (<1 wt%) of fluorinated surfactants or silicones which lower its surface energy, thus increasing the adhesion of the UV-cured material onto polyethylene and polycarbonate.[35] Fluoro- or silicone-functionalized acrylic monomers have been successfully used to modify the surface properties of UV-cured PUA networks.[36] Adhesion on organic substrates was also enhanced by using UV-curable resins capable of establishing hydrogen bonds, for example, PUA-functionalized polymers, as well as polymers such as poly(vinyl chloride) or aliphatic polyurethanes. Acrylate functionalized polymers, plasticized with a multifunctional acrylate monomer, were found to have a good adhesion on glass after photocross-linking and were successfully used as intercalates to rapidly produce safety glasses at room temperature.[37]

10.2.1.2 Thiol-Polyene System

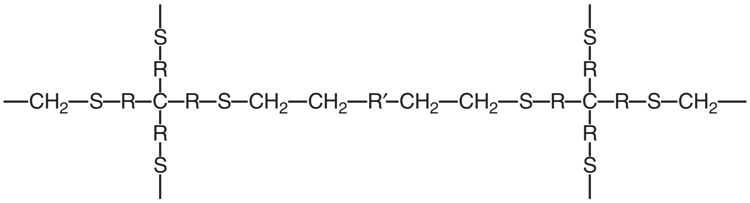
The photoinduced addition of a thiol (RSH) to an olefinic double bond has been used to produce polymer networks by taking multifunctional monomers.[38–45] The thiol-ene polymerization proceeds by a step growth addition mechanism that is propagated by a free radical, chain transfer reaction involving the thiyl radical ($RS^\bullet$). The initial thiyl radicals can be readily generated by UV irradiation of a thiol in the presence of a radical-type photoinitiator. The overall reaction process can be schematically represented as follows:

$$Ar_2C{=}O + RSH \xrightarrow{h\nu} Ar_2\dot{C}{-}OH + RS^\bullet$$

$$RS^\bullet + CH_2{=}CH{-}R' \longrightarrow RS{-}CH_2{-}\dot{C}H{-}R'$$

$$RS{-}CH_2{-}\dot{C}H{-}R' + RSH \longrightarrow RS{-}CH_2{-}CH_2{-}R' + RS^\bullet$$

A polymer chain will be formed only if both the thiol and the olefinic compound contain at least two reactive functions, for example, a diene plus a dithiol. With multifunctional monomers, such as a tetrathiol ($[CRSH]_4$) associated with a diene ($CH_2{=}CH{-}R{-}CH{=}CH_2$), a three-dimensional network is produced, in which the connecting chains are made of an alternating copolymer.



$$-CH_2-S-R-\underset{\substack{|\\R\\|\\S\\|}}{\overset{\substack{|\\S\\|\\R\\|}}{C}}-R-S-CH_2-CH_2-R'-CH_2-CH_2-S-R-\underset{\substack{|\\R\\|\\S\\|}}{\overset{\substack{|\\S\\|\\R\\|}}{C}}-R-S-CH_2-$$

The cross-link density of the polymer network, as well as its properties, depends on the functionality, the length, and the chemical nature of the polyene (R') and thiol (R) prepolymer chains, and it can thus be tailored as desired. Low-modulus polymers suitable for adhesive applications were obtained by using aliphatic prepolymer chains, in particular with polybutadiene-based elastomers that were cross-linked very efficiently by UV irradiation in the presence of a tri- or tetrathiol.[46–49] As only a few cross-links need to be formed between the polymer chains to make the rubber insoluble, low concentrations of thiol (2 wt%) proved to be sufficient to achieve an effective and fast cross-linking. Hardening was found to hardly occur upon UV curing (increase of the Persoz hardness from 40 s to 55 s), which is essential to ensure outstanding adhesion. At the same time, the shear adhesion failure temperature (SAFT) increased from 80 °C to 160 °C because of the formation of the chemical network (Fig. 10.4).

Figure 10.5 shows some typical polymerization profiles recorded by RTIR spectroscopy upon UV exposure of two tetraene-tetrathiol stoichiometric mixtures containing a hydroxyphenylketone photoinitiator. As expected, a more complete polymerization was achieved for the sample containing soft tetraene segments, which leads to a low-modulus polymer well suited for adhesive applications. More than 90% of the thiol groups were found to have reacted within less than 1 s, both for the laminated sample and for the coating in contact with air. It should be noted that the thiol/ene polymerization is less sensitive to O_2 inhibition than typical radical-induced polymerizations (such as acrylates), because the peroxy radicals formed by O_2 scavenging of alkyl radicals are still capable of propagating the chain reaction by hydrogen abstraction from

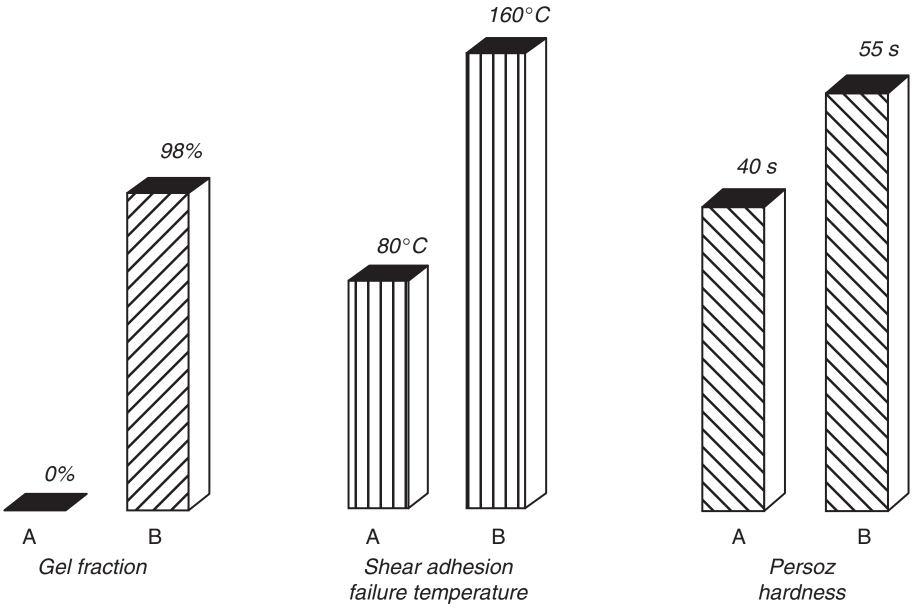


Figure 10.4 Properties of a styrene-butadiene elastomer containing a thiol cross-linker (2 wt%), before (A) and after (B) a 0.2-s UV exposure at 500 mW cm^{-2}.

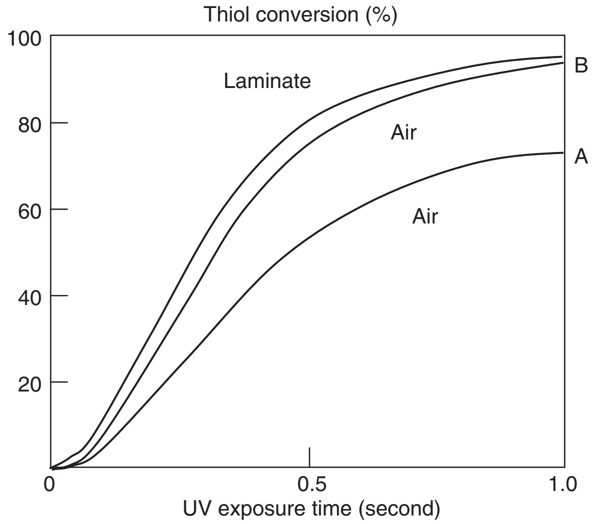
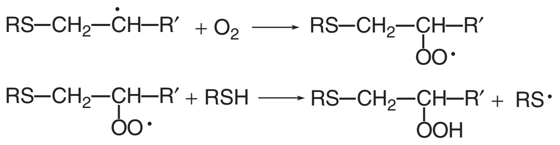


Figure 10.5 Photoinitiated polymerization of a 1/1 molar mixture of a tetrathiol and a tetraene resin containing hard (A) or soft (B) segments (I = 100 mW cm^{-2}). Film thickness: 15 μm.

the thiol and generation of the chain carrier thiyl radical:



$$RS-CH_2-\dot{C}H-R' + O_2 \longrightarrow RS-CH_2-\underset{OO^\bullet}{CH}-R'$$

$$RS-CH_2-\underset{OO^\bullet}{CH}-R' + RSH \longrightarrow RS-CH_2-\underset{OOH}{CH}-R' + RS^\bullet$$

With the development of new types of prepolymers, such as vinyl functionalized silicones,[41] there has been an increased interest in the thiol/ene photopolymerization, in particular for PSAs and sealants applications.[2] The lack of O_2 inhibition is an important advantage here, because siloxane fluids are known to be highly permeable to oxygen. Resistance to moisture ingress and thermal degradation is reported to be superior.[42] Moreover, the use of cyclic alkenes, such as norbornene,[40] in combination with a tetrathiol, yields cross-linked polymers showing a low-volume shrinkage, which makes them particularly attractive for adhesive applications.[2]

10.2.2 Photoinitiated Cationic Polymerization

Light-induced polymerization is one of the most efficient methods to rapidly cure monomers that are inactive toward radical species, such as VEs[50,51] or epoxides.[52–55] The subject has been recently covered extensively by Crivello and Dietliker[56] in an excellent textbook. This technology has not yet achieved the commercial significance of corresponding free-radical processes mainly because of the more limited choice of monomers available and their lower reactivity.

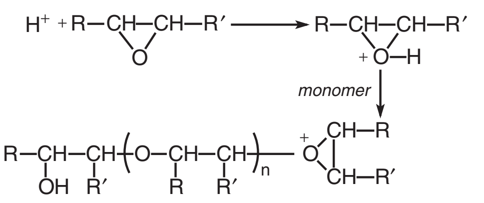
The protonic acid needed to initiate the chain reaction is usually produced by UV irradiation of diaryliodonium or triarylsulfonium salts. The photolysis reaction, which produces both Brönsted acid and free radicals in the presence of a hydrogen donor molecule, can be formally written as follows for the iodonium salt[56]:

$$\left(\Phi-\overset{+}{I}-\Phi\right)\left(PF_6\right)^- \xrightarrow[RH]{h\nu} \Phi I + \Phi^\bullet + R^\bullet + H^+ PF_6^-$$

A distinct characteristic of photoinitiated cationic polymerization is its lack of sensitivity toward atmospheric oxygen that does not scavenge cationic species, as well as its living character, because the propagating polymer cations are not reacting among themselves. In contrast to radical-initiated polymerization, the chain reaction will thus continue to proceed in the dark after the UV exposure, a feature that has been used to assemble nontransparent materials by UV-curable laminating adhesives.[57]

10.2.2.1 UV Curing of Epoxides

In the presence of a photogenerated protonic acid, the ring-opening polymerization of epoxides proceeds efficiently through the chain carrier oxonium ion, to ultimately produce a polyether according to the following reaction scheme:



With difunctional cycloepoxides, the chain reaction develops in three dimensions to form a tightly cross-linked polymer.[58] The rate of polymerization of the widely used aliphatic dicycloepoxide (Cyracure 6105 from Dow Chemicals) is still one order of magnitude lower than that of diacrylate monomers, most probably because of a lower propagation rate constant. In this respect, the remarkable performance of cycloaliphatic epoxy-silicones should be mentioned, as these monomers were shown to polymerize

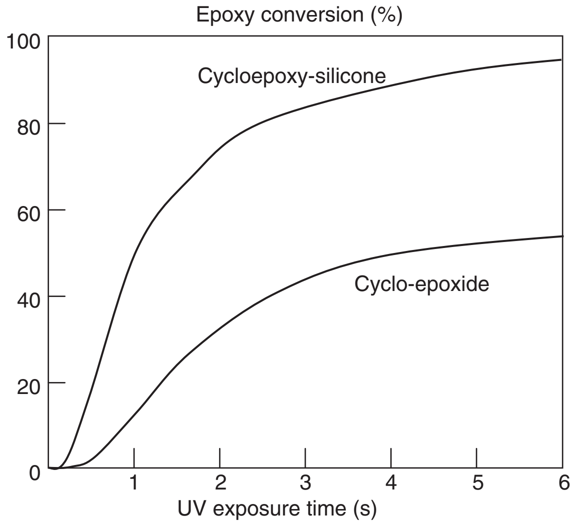


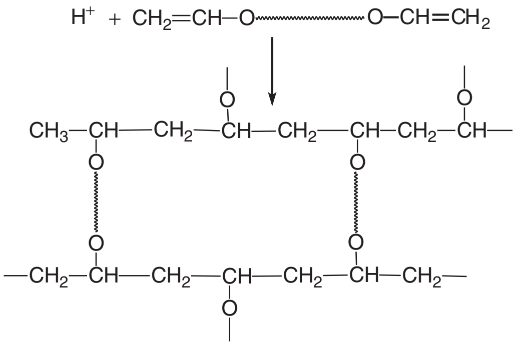
Figure 10.6 Photoinitiated cationic polymerization of an aliphatic dicycloepoxide and a dicycloepoxy silicone. Diaryliodonium salt (1 wt%) photoinitiator (I = 85 mW cm^{-2}).

cationically as fast and as extensively as acrylate monomers, with excellent mechanical properties.[59] One of the additional benefits of epoxy-silicones is their ability to increase the cure rate of conventional diepoxides when incorporated as a blend.[60] Figure 10.6 shows the polymerization profiles recorded by RTIR spectroscopy by following the disappearance of the epoxy ring upon UV exposure of these two monomers in the presence of a diaryliodonium hexafluorophosphate salt. The incomplete polymerization of the cycloaliphatic diepoxide is due to early vitrification and related mobility restrictions, so that the hard UV-cured polymer is ill suited for adhesive applications. The addition of ε-caprolactone triol (Tone Polyol from Dow Chemicals) generates a softer and more completely polymerized polymer by promoting a chain transfer reaction.[61] Higher adhesion was achieved by increasing the polyol content, as well as its molecular weight, up to an optimum value typically reached for an epoxy/hydroxyl ratio of 2.

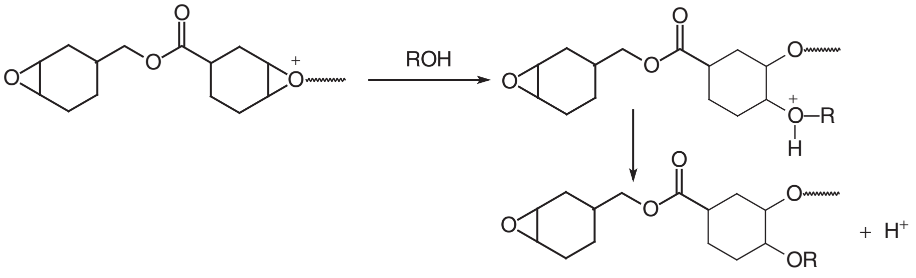
A more flexible UV-cured polymer showing improved adhesion was obtained by using the bis (3,4 epoxy cyclohexyl) adipate (Cyracure UVR-6128 from Dow Chemicals).[62–64] The superior adhesion achieved with such cationically UV-cured epoxides was attributed to the low shrinkage that occurs during the ring opening polymerization: less than 5%, compared with 10% for acrylates. It can be further enhanced if necessary by the addition of a silane adhesion promoter (Silwet A-186), in particular for metallic or silica-containing substrates.[63,64]

10.2.2.2 UV Curing of VEs

VEs are among the most reactive monomers that polymerize cationically, and they are increasingly used in photocurable resins, either neat[65,66] or in association with epoxides,[67,68] acrylates,[69] maleimides,[70] or unsaturated polyesters.[71] VE end-capped polyurethane, polyether, polysiloxane, and polyesters were shown to undergo fast and extensive polymerization when exposed to UV radiation in the presence of an aryliodonium salt, with the formation of tridimensional polymer networks. The photoinitiated cationic polymerization of a divinyl ether can be formally written as follows:



The reaction kinetics has been thoroughly investigated,[51] and the subject has been covered in a comprehensive review article by Lapin.[50]



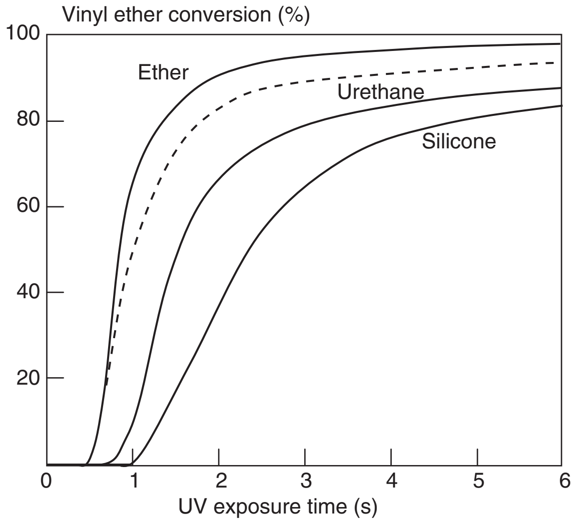


Figure 10.7 Influence of the chemical structure of the functionalized oligomer on the cationic UV curing of a vinyl ether-based resin (I = 20 mW cm^{-2}). (- - - -): Postpolymerization after a 0.7-s UV exposure of the divinyl ether of triethyleneglycol.

Figure 10.7 shows the photopolymerization profiles of VE functionalized urethane and silicone oligomers, in comparison with that of the divinyl ether of triethyleneglycol (DVE-3) often used as reactive diluent. The UV-cured polymers thus obtained have a low elastic modulus and can be designed for adhesive applications by a proper choice of the oligomer chemical structure (aliphatic groups) and of its molecular weight ($M \leq 1000$ g).

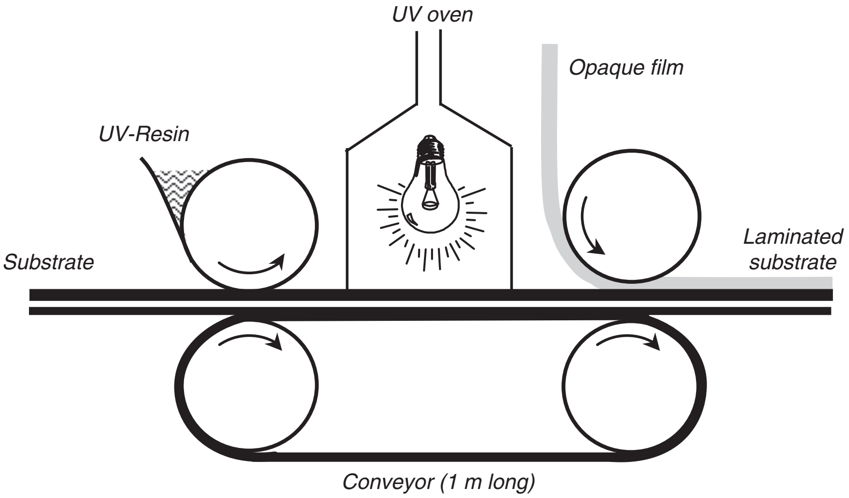
The postpolymerization, which is known to occur just after the UV exposure in cationic photocuring, was easily monitored by RTIR spectroscopy, as shown in Fig. 10.7 for DVE-3 (dashed curve). It can be seen that, after a 0.7 s exposure to UV radiation, the VE continues to polymerize in the dark, the conversion rising from 10% to more than 90% within a few seconds. One can take advantage of such an important dark curing process to assemble nontransparent foils by means of UV-curable adhesives. Figure 10.8 shows a schematic representation of the experimental setup. By running the UV line at a speed of 1 m/s, the second foil will be laminated on top of the irradiated foil only 0.5 s (50 cm) after the UV exposure, so that most of the VE polymerization will occur in the dark. UV-curable epoxy resins were also successfully used as adhesives to laminate opaque films by such an ultrafast dark-cure mechanism.[57,63,64]

VE monomers, such as DVE-3, proved to be very effective reactive diluents in UV-curable epoxy-based resins, not only to lower the formulation viscosity and make it suitable for spray or roller applications but also to achieve a faster and more complete curing, as VE and epoxy monomers were shown to undergo copolymerization by a cation-driven mechanism.[51] Moreover, the addition of VE may impart some flexibility to the UV-cured epoxide, thus improving its adhesion on flexible substrates.

10.2.2.3 UV Curing of Hybrid Systems

The photopolymerization of a mixture of multifunctional monomers or oligomers that polymerize by different mechanisms leads to the build-up of two interpenetrating polymer networks (IPN). An obvious requirement is that the two monomers must be fully compatible, and their polymers as well, to avoid segregation and the formation of heterophasic

Figure 10.8 Experimental setup for the production of nontransparent laminated assemblies by postcuring of a photoinitiated cationic polymerization.



materials. A number of monomer combinations have been successfully used to produce IPNs rapidly at ambient temperature,[72] in particular mixtures of acrylate monomers with epoxides[73] or VEs.[69] Kinetic studies have shown that the two monomers can polymerize either simultaneously or sequentially by a proper choice of the irradiation wavelength.[12]

The major advantages of these UV-curable hybrid systems lie in their superior combination of properties that can be tailor-made for a given application by adjusting the proportions of the two components. The IPN formed will exhibit the main features of the two polymer networks—for instance, the toughness and scratch resistance of UV-cured acrylate polymers and the elastomeric character of the cross-linked polyurethane-VE, with the expected benefit regarding adhesion and impact resistance.

10.2.3 Dual-Cure Systems

When UV-curable resins are used as laminated adhesives to protect three-dimensional objects having complex shapes, it may happen that some remote areas will not be accessible to UV radiation and, therefore, remain uncured. To address the issue of such shadowed areas, dual-cure systems combining UV irradiation and thermal treatment have been developed.[74] They contain two types of reactive functions: a UV-curable functional group (usually an acrylate double bond) and a thermally curable functional group (usually an isocyanate associated with a polyol). The basic principle of this two-step curing process is represented schematically in Chart 10.3 for a hydroxyl functionalized diacrylate prepolymer associated with a diisocyanate.[75] Cross-linking will, thus, occur even in the shadowed areas upon heating, typically at 140 °C for 15 min. As the polyurethane formation by polyaddition occurs slowly at ambient temperature, such dual-cure systems will consist of two-component formulations that, after mixing, have a pot lifetime of less than 1 day.

To achieve the most complete curing of both types of functionality, it is recommended to start with the thermal treatment and perform the UV exposure immediately afterward on the hot sample. Figure 10.9 shows some typical curing profiles obtained by monitoring, by means of infrared spectroscopy, and the disappearance of the isocyanate group (2270 cm^{-1}) upon heating, and of the acrylate double bond (1410 cm^{-1}) upon UV exposure.

It should be noted that the diacrylate prepolymer is usually dissolved in a solvent (−50 wt%), rather than in an acrylate monomer, so as to keep shrinkage to a minimum and ensure good adhesion. The solvent is readily removed in the early stage of the thermal treatment and does not interfere with the curing reactions, which occur actually in a solid but soft material. Here again, it is important for adhesive applications to keep hardening to a minimum, usually by introducing soft segments in the prepolymer chain and by reducing the cross-link density of

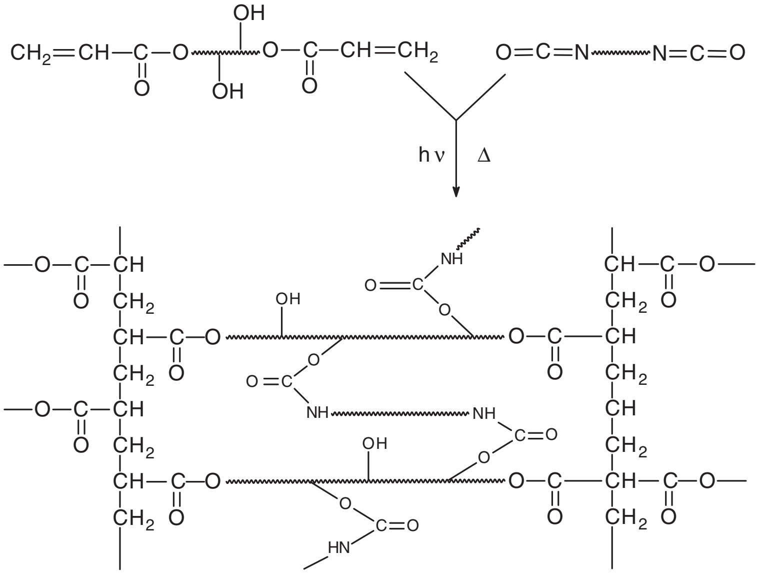


Chart 10.3 Dual-polymer network formed by UV curing of acrylate double bonds and thermal curing of isocyanate and hydroxyl groups.

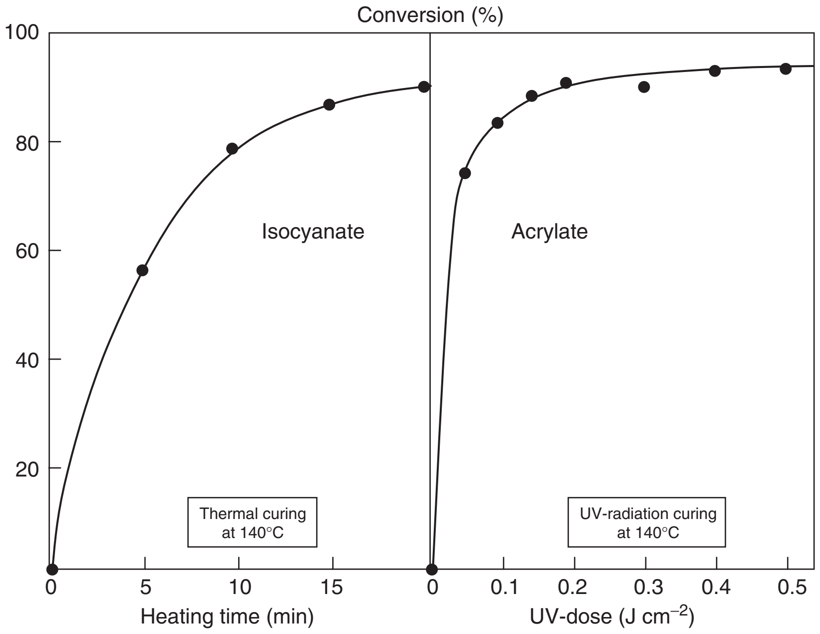


Figure 10.9 Dual curing of an hydroxy-functionalized PUA associated to an isocyanate cross-linker ($I = 500$ mW cm^{-2}).

the polymer network. In the case of heat-sensitive substrates, the polyaddition reaction needs to be performed at ambient temperature, after solvent flash off and UV exposure. Cross-linking will then proceed slowly upon storage of the sample for a few days.[2] This process was shown to be accelerated by moisture curing of the isocyanate that reacts readily with water, and subsequently with the resulting amino group, with formation of a urea bond.[76]

After this survey of the different types of UV-curable resins that can be used as adhesives, and the way they undergo rapid cross-linking upon illumination, we will now review the main applications of such fast-setting adhesives in various industrial sectors.

10.3 Applications of Radiation-Curable Adhesives

Radiation curable adhesives have experienced a steady growth over the past decade in various sectors of applications, because they offer a number of advantages over conventional adhesives, mainly a substantial reduction in processing time for assembly operations, a much reduced emission of volatile organic compounds, a precise control of the light-driven setting process, and low-energy requirements. This environment-friendly technology is now being commonly used in two main classes of adhesives.[2] In the first one, adhesion is achieved by light-induced cross-linking, which will ensure a strong bonding between two components, as with structural adhesives, sealants, composites, and laminating adhesives. In the second class, a tacky polymer is produced by UV curing of a solvent-free resin and will serve as a pressure-sensitive or hot-melt adhesive. In this case, adhesion is achieved by the application of pressure and/or heat, so that the end-user is not required to employ radiation to obtain a strong bonding.

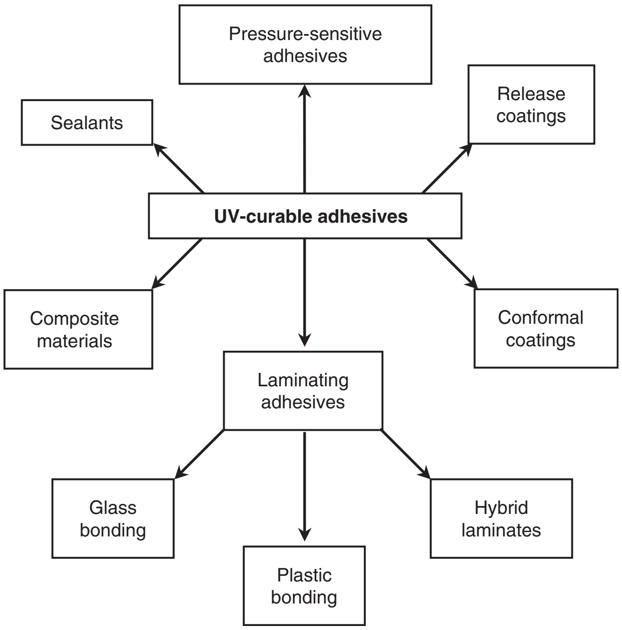


Figure 10.10 Applications of UV-curable adhesives.

The manifold end-uses of radiation curable adhesives have been discussed in several review articles,[3–5,77–80] and in particular by a comprehensive survey of these systems by Woods[2], and more recently by Dowling,[7] who has listed important UV-adhesive applications such as glass bonding, plastic bonding, wire tacking, conformal coatings, potting, and connector sealing in microelectronics. Some typical applications of UV-curable adhesives are summarized in Fig. 10.10. In this last section, we present an overview of three industrial sectors where UV adhesives have found growing applications, namely as structural adhesives, PSAs, and release coatings.

10.3.1 Structural Adhesives

A considerable amount of work has been devoted to the bonding of two elements by means of UV-curable structural adhesives.[81–95] The two parts of the assembly can be identical (homolaminates) or of a different nature (heterolaminates) and consist either of flexible films such as polyesters, poly(vinyl acetate), nylon, aluminum foils and paper, or rigid transparent plates such as poly(methylmethacrylate), polycarbonates, poly(vinyl chloride), and mineral glass. Obviously, one of the two parts must be transparent to ultraviolet radiation to achieve an effective cure of the adhesive. If not, as with photostabilized polycarbonates or polyethylene terephthalates, a photoinitiator absorbing in the near UV and visible range (such as acylphosphine oxides) has to be selected. The light-induced setting process of the adhesive will involve the following three steps:

- The liquid resin is applied to one or both parts to be bonded, so as to ensure a perfect wetting of the clean surface
- The two parts are assembled and positioned precisely, taking care to avoid the formation of air bubbles
- The assembly is exposed to UV radiation, at and during the desired time, to convert the adhesive from the liquid state to the solid state

Some typical applications of UV-curable adhesives and sealants are illustrated in Fig. 10.11.

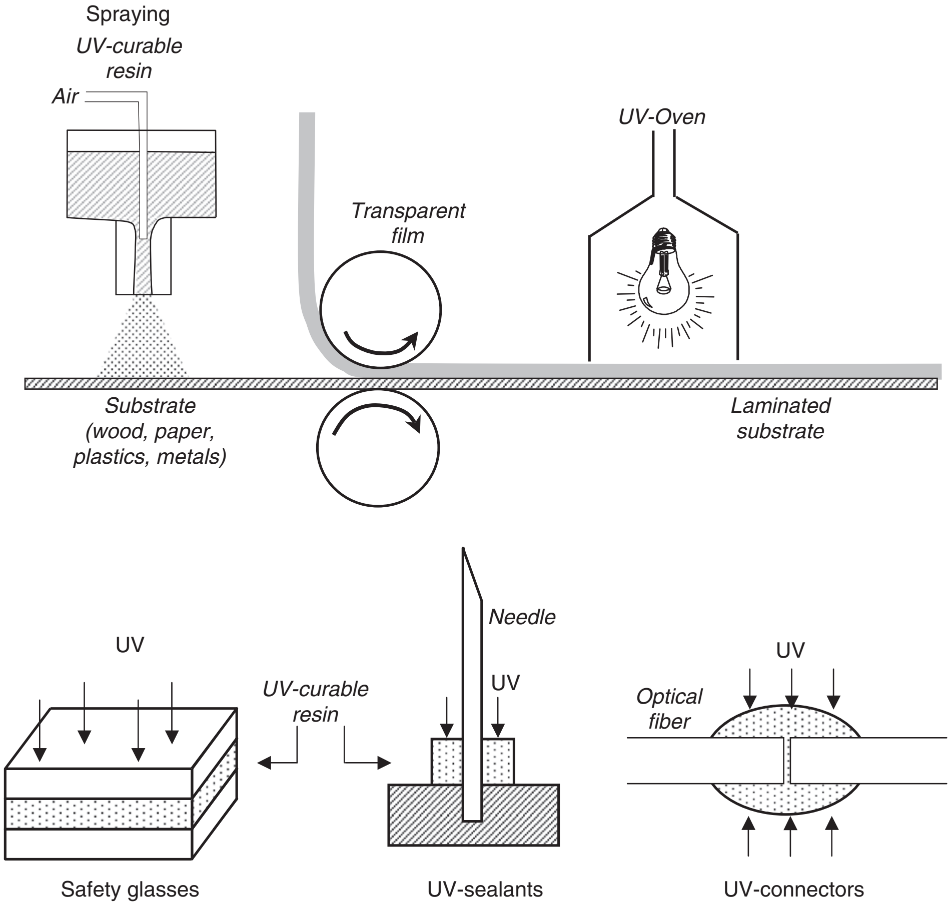


Figure 10.11 Various applications of UV-curable adhesives.

Although the cure extent in thermosetting adhesives is governed by the polymerization kinetics and the difference between the polymerization temperature and the ultimate glass transition temperature (T_g) of the material, other factors, such as the light intensity, the optical absorbance, the sample thickness, and the UV-dose, strongly determine the cure extent of photosetting adhesives.[82] In this respect, it is important to know the relationship existing between these factors and the tensile properties and T_g of the UV-cured polymer that determine the adhesive strength.[83]

Both radical-type and cationic-type UV-curable resins have been used in laminating adhesive applications (acrylates,[13,31,32,84] thiol-ene,[42,85] epoxides,[86,87] and VEs[88]). Below are a few examples where UV adhesives proved particularly successful in achieving fast and resistant bonding of laminates, as well as durable sealing of two components.

- Superfast curing (in less than 0.5 s) of acrylate adhesives for plastics has been achieved by a proper choice of prepolymers, photoinitiators, and photosensitizers and successfully used in blister packaging,[84] as well as for bonding glass to plastics[81]
- Optical fibers can be connected by means of an optically clear UV resin having a refractive index after cure as close to that of glass as possible.[7] The bonding can be easily achieved by firing a laser beam through the fiber and using an appropriate laser-curable resin.[89] UV-cured epoxides containing silica nanoparticles have been successfully used as adhesives for fiber-chip coupling, with low optical loss and low shrinkage.[90] High transparency was achieved by fitting the refractive index of the adhesive to that of the filler ($n = 1.50$)
- For bonding of medical needles, light curable adhesives offer not only the benefit of a rapid processing but also excellent thermal resistance, hermetic seals, and high pull strength on various substrates, including polyethylene.[91] Curing of the shadowed areas was achieved by a combination with cyanoacrylates that undergo a fast anionic polymerization in the presence of a weak base such as water
- The use of UV-curable adhesives is a fastening method that enables quick and easy mounting of optical components in housings, with extreme precision by allowing accurate control of the setting time.[92] This technology is commonly used for the manufacturing of optical disks, where the bonding can be achieved by a cationic UV-curable adhesive.[93] Low-volume shrinkage (1.2%) was achieved with a cyclohexane-type fluoro-epoxy resin undergoing cationic ring opening polymerization. These highly transparent adhesives can be cured to a depth of >5 mm and show high adhesive strength and durability, making them well suited to the fabrication of optical components that require submicron positioning accuracy
- Glass laminates showing high impact resistance, adhesion, and transparency have been obtained by photocuring of an acrylic adhesive consisting either of a liquid resin or a solid thermoplastic polymer at ambient temperature.[37,94] Safety glasses combining chemical inertness, scratch resistance, hardness of mineral glass, and strong impact resistance were obtained with a three-component UV-cured laminate glass/polycarbonate glass. Adhesion on glass was substantially improved by precoating the glass plates with a UV-cured thermoplastic polybutadiene elastomer[95]
- A cohesive bonding of nontransparent materials has been achieved by means of cationic UV-curable resins by taking advantage of the living character of cationic polymerization, the two parts of the assembly being laminated just after the UV irradiation.[57,63,64] With a biscycloepoxide-polyol resin, the peel strength reached values up to 200 g/cm within 30 min after the UV exposure, a polyurethane resin being used if needed to improve tackiness and increase the open time. In the case of polyethylene films, the T-peel strength continued to rise for a few hours upon storage to level up at a value of 500 g/cm.[63,64] Cure speed tackiness, adhesion, and open time can be controlled through the epoxy/polyol ratio, the photoinitiator concentration, and the UV dose.[96] The cohesive energy was improved by changing the molecular weight of the adhesives and the cross-link density
- Another effective way to cure nontransparent samples is by using electron beams (EB) that can initiate both radical and cationic-type polymerization. EB-curable laminating adhesives have been shown to exhibit good performance over a wide temperature range on a variety of

substrate combinations[97] and in particular for flexible food packaging.[98] This novel way of manufacturing food packages offers a number of advantages, namely, instant cure/bond development, reduction or elimination of Volatile Organic Compound (VOC) generation, fewer processing steps, lower overall operation cost, and new design capabilities[99,100]

- To address the issue of the curing of shadowed areas in UV sealants and laminating adhesives, dual-cure systems have been developed.[74] Hardening of the resin containing isocyanates is realized by a thermal treatment (NCO/OH polyaddition) or moisture curing[101] or by a redox reaction in the presence of primers under unaerobic conditions.[102] The potting and encapsulating of electronic components has been recently achieved by a UV-curable epoxy resin, even in shadowed areas, by taking advantage of a self-propagating thermal cure.[103] This allows for rapid, deep, and complete polymerization to occur throughout the entire volume

Recent advances have made radiation-curable laminating adhesives very attractive in terms of economics, automation, quality of adhesive bond, and throughput, while offering distinct advantages with respect to both energy consumption and pollution control.[4]

10.3.2 Pressure-Sensitive Adhesives

The concept of radiation-curable PSAs can be simply described as a rapid photoinitiated cross-linking producing a viscoelastic material in which the properties of tack, peel strength, and shear resistance are predetermined.[4] It is this tackiness that causes the adhesive to stick instantly when pressed against a substrate. Depending on the peel strength, PSA tapes are considered as temporary for values below 350 N/m or permanent for peel strengths above this value. A strapping tape, which is made from a strong glass-fiber reinforced film, uses a high-strength adhesive, whereas carton sealing tape must be quick grabbing to a paperbound and resistant to moisture.[4]

In contrast to UV-laminated adhesives, radiation is applied directly to the photosensitive resin, without having to penetrate through another material, very much like for UV-curable coatings. A characteristic feature of PSAs is that they do not change their physical state during bond formation and that the end-user is not required to employ a curing step to accomplish adhesive bonding. Processing of a typical UV-curable PSA involves the following steps (illustrated in Fig. 10.12)[3]:

1. Application of the liquid adhesive to a substrate
2. UV irradiation to generate a tacky cohesive polymer—protection of the tacky surface by a silicone paper
3. Removal of the protecting film and attachment of the self-adhesive product onto a material by applying pressure

In the production of tape adhesives, step 3 can be skipped by using a polymer film that has been release treated on one side as a substrate.

The photosensitive resin consists either of a liquid functionalized oligomer, usually with acrylate groups or a reactive polymer that will be applied as hot melt.

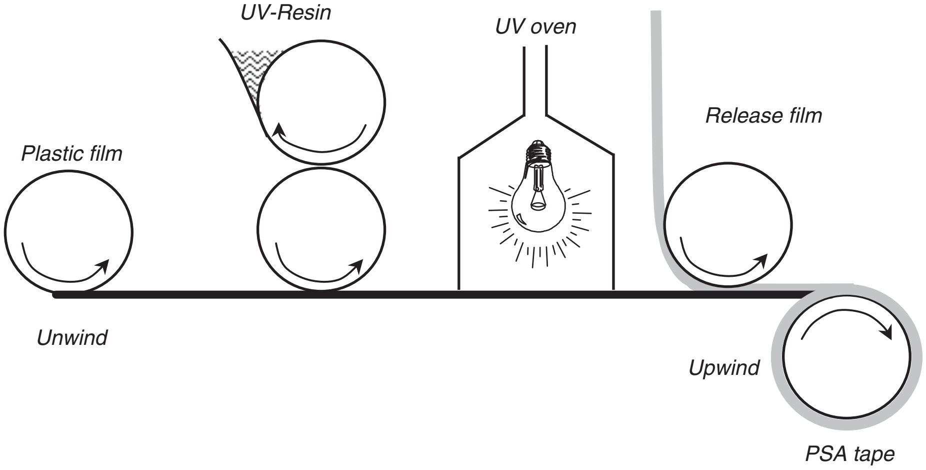


Figure 10.12 Manufacturing of a UV-cured pressure-sensitive adhesive.

There are two main classes of reactive polymers: acrylic hot melts that may contain a tackifying monomer and thermoplastic rubbers that predominantly block copolymers with polybutadiene or polyisoprene chains.[3] A radical-type photoinitiator is always needed to produce, upon UV-exposure, the free radicals that will initiate the polymerization or cross-linking process.

The reasons for using UV-curable PSAs, rather than solvent-based adhesives, remain essentially the same as for the other UV-curable systems and include high cure speed, reduced VOC emission, low energy consumption, and enhanced product performance. The subject has been extensively investigated in recent years, as shown by the abundant literature on this topic.[10,13−17,20,104−126] Today, UV-curable PSAs are mainly utilized in graphic arts, electronics, and packaging to produce self-adhesive foils, tapes and labels.[117]

Below are a few examples of different types of UV-cured PSAs developed in various applications:

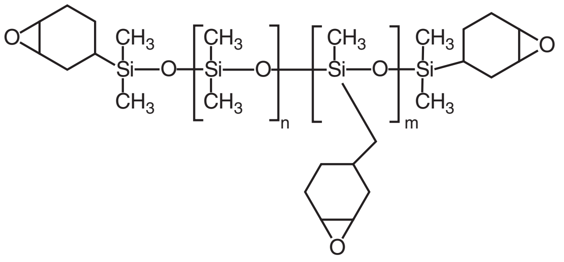
- UV-cured PSAs are often made of low-molecular-weight polymers plasticized with acrylate monomers, so as to obtain a viscous material that will be transformed into a tacky polymer by photocross-linking. The initial resin can also be produced by photopolymerization to form an acrylic syrup of suitable viscosity by UV-dose controlled conversion of the acrylate double bonds.[112] The addition of tackifying agents (hydrocarbon resins) and of monoacrylate reactive diluents to urethane-acrylate oligomers has been shown to be an effective way of obtaining UV-cured PSAs showing excellent peel strength and creep resistance on various substrates (paper, polyethylene, polystyrene, and polycarbonates).[107,108] Depending on the type of applications (labels, adhesives tapes, and protective laminated films), the thickness of the adhesives can be varied between 50 and 500 μm, with peel strength values ranging from 500 to 1200 N/m and shear strength values of more than 10,000 min at room temperature.[108] Because of the required incomplete cross-linking, the gel content of UV-cured PSA is usually less than 60% and can be as low as 30%.[117] Typical applications are viscoelastic backings or transparent acrylic transfer tapes for high-performance bonding tapes. UV-curable PSAs can be applied at room temperature with flexographic and screen-printing units.[111] This technology offers an innovative way to produce new types of labels and other pressure sensitive products. Maleimide functionalized oligomers have recently been used as UV-curable PSAs, in combination with acrylic polymers[123]
- Hot-melt adhesives are dry films that melt and become tacky at elevated temperature. UV-radiation curing is used to make such materials more resistant to chemicals (solvents and hydrocarbons) and to heat, with SAFT values above 150 °C, by creating a covalently bonded polymer network.[112−116] Values up to 180 °C were reached with aromatic urethane acrylate-based tackifying oligomers (CN-3000 from Sartomer), the 180° peel adhesion remaining constant at 800 g/cm after 1 week. As expected, increasing the UV dose from 0.4 to 0.7 J cm^{-2} makes the SAFT and tack values decrease, whereas the adhesion was increased up to 1400 g/cm.[124] Thermoplastic rubbers, consisting of styrenic block copolymers with polyisoprene (SIS) or polybutadiene (SBS) chains, have been successfully used as UV-curable hot-melt adhesives.[14,119,120] Photocross-linking, involving pendent vinyl groups, was greatly accelerated by the addition of an acrylate functionalized oligomer[121] or a trifunctional thiol.[122] Even in the presence of air, the radical-induced chain reaction was shown to proceed within a fraction of a second to yield a low-modulus elastomer having a SAFT value superior to 160 °C and an excellent chemical resistance
- UV-acrylic hot-melts may also consist of low-molecular-weight polymers with chemically built-in photoreactive groups. After being coated onto the substrate at temperatures in the 120−140 °C range, the film is partly cross-linked upon exposure to short wavelength UV radiation (250−270 nm) to impart some cohesion and heat resistance.[114] The ratio of adhesion to cohesion is dependent on the UV dose, which can be precisely controlled by the lamp power output and the web speed. The cross-linking process was followed in real time through the decrease of the photoreactive group (benzophenone) and found to correlate well with the shear strength that increased from an initial SAFT value of 50 °C up to 180 °C at a UV

dose of 1 J cm^{-2}.[125] UV-acrylic hot-melts were shown to outperform the conventional solvent- or water-based acrylic polymers, as well as the thermoplastic rubber hot-melts (SIS/SBS), with respect to heat resistance, shear strength, and peel strength.[111] If necessary, the degree of cross-linking of UV-curable acrylic hot-melts can be increased by the incorporation of defined unsaturations into the saturated polymer chain.[112] A novel UV-curable acrylic hot-melt PSA has been recently developed allowing contactless application, with the benefits of lower coating weights.[126] The ultimate bond strength of conventional permanent UV-curable PSAs can be varied downwards, thus opening up scope for additional applications, especially in the field of removability

10.3.3 Release Coatings

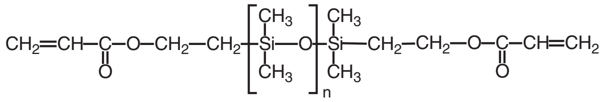
The PSA covered substrates used by the tag and label industry need to be protected during storage by a film that should be easily removed just before use, without loss of shear strength. Such release coatings consist usually of a plastic film or a paper coated with a uniform and thin film of a reactive silicone that is cross-linked via chemical processes promoted by heat or UV radiation.[127,128] Silicones are known to lack adhesion to most substrates because of their low surface energy, a feature that is of advantage in PSA applications for it allows an easy peeling off from the inner tape layer. The reactive group of the polydimethylsiloxane oligomer can be either a cycloaliphatic epoxide[129–131] undergoing cationic polymerization or an acrylate double bond undergoing free radical polymerization.[132,133] Both types of chemistry have been discussed in a comprehensive review article on photopolymerizable silicone monomers, oligomers, and resins.[41]

The introduction of a dimethyl-siloxane group between two cycloaliphatic epoxy groups was found to increase drastically the reactivity of these monomers.[59,134] The cyclo epoxy group can be located at the ends of the polydimethylsiloxane chain and/or on pendent groups.[135]



Such UV-cured polymers can work as release coatings because the low surface energy of the polydimethylsiloxane chains predominates at the coatings interface with a PSA. The higher the work needed to remove a silicone-coated film from an adhesive-coated face stock (label), the tighter the release will be.[127] It can be controlled by the inclusion of polar groups on the silicone backbone, which will affect the bonding between PSA and silicone release coatings. Different controlled release coatings have, thus, been produced by UV curing of mixtures of cycloaliphatic epoxy-silicones and linear epoxy-functionalized silicone fluids.[127] Cationic UV-curable epoxy silicones have been recently developed to achieve very low and stable release, with values as low as 4 cN/cm, for label or mastic release application.[136] The glass transition temperature was shown to strongly influence the release behavior, the best performance being obtained when the T_g of the epoxy silicone resin component is 10–40 °C below its use temperature. It was recently suggested that the UV-cured epoxy-silicone systems control the magnitude of release force in the same manner as their thermally cured equivalents, that is, via the viscoelastic properties of the silicone matrix, rather than through their surface properties.[135]

UV-cured acrylate functionalized silicones have been successfully used as release coatings.[128,132,137] They consist of either acrylate end-capped linear polydimethylsiloxanes or of silicone chains containing pendent acrylate groups.



$$CH_2{=}CH{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}\left[\underset{CH_3}{\overset{CH_3}{Si}}{-}O\right]_n{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}CH_2{-}CH_2{-}O{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH{=}CH_2$$

The versatility of silicone-acrylates with regard to cure speed, coatibility, and release control make them ideally suited for a variety of applications, in particular for coatings having a desired release level.[132] By varying the ratio of unmodified to modified siloxy units, it was shown that the release force and subsequent adhesion are increased with the concentration of acrylate groups.[128] By producing oligomers at both ends of the release spectrum (easy and tight), one can tune the coating performance to the desired application. A kinetic study by RTIR spectroscopy of the UV curing of such functionalized silicones clearly showed that silicone-acrylates

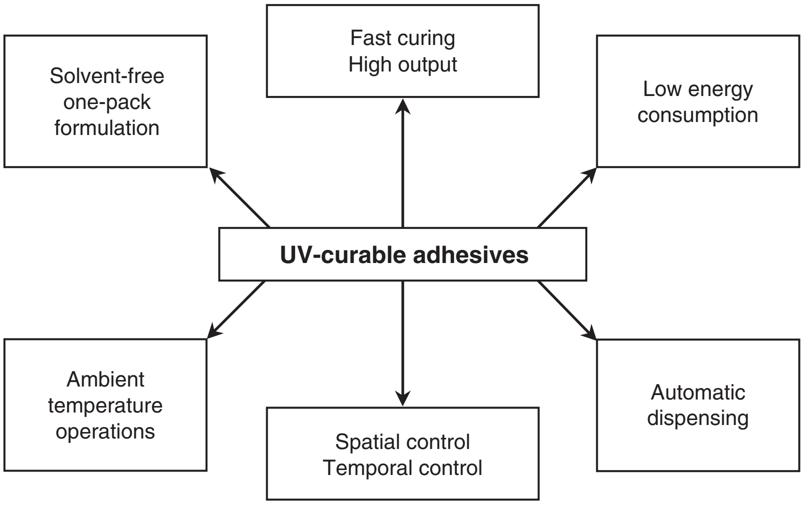


Figure 10.13 Performance of UV-curable adhesives.

polymerize much faster than the epoxy-silicones having the same functional group content and the same silicone backbone. Because of the strong inhibitory effect of atmospheric oxygen on the free radical polymerization of silicone-acrylates,[138] specially in thin films, it is yet necessary to perform the UV curing under inert conditions (N_2 or CO_2 blanketing). Cure line speeds up to 10 m/s have, thus, been reached, with the expected gain in productivity and energy consumption.[132] Oxygen inhibition can be partly overcome by the addition of tertiary amines or trivalent phosphites,[137] thus allowing the UV curing to be performed even in the presence of relatively large amounts of air. Such performances, together with solvent-free formulations and ambient temperature operations allowing work with heat-sensitive substrates, are the main reasons for the increasing use of UV-radiation curable release coatings in the tape and label industry.

10.4 Conclusion

UV-curable adhesives have established themselves as a significant part of the overall market for specialty adhesives, because they offer a number of advantages over traditional adhesives, as illustrated in Fig. 10.13. One can expect this part to increase in the near future, as the ever more stringent regulations aiming to lower air pollution and energy consumption will progressively curtail the use of solvent-based adhesives.

The principal driving force behind the steadily increasing consumption of UV adhesives will be the speed and control of the curing process and the compatibility of radiation products with automated dispensing and assembly equipment.[2] Some progress is still needed to make this technology more competitive by improving the processing and product performance. There is currently a strong research effort aiming toward the development of resins, which can be cured by near UV and visible light, as well as of dual-cure systems to ensure an effective bonding in the shadow regions. It is also important to precisely control the bonding strength of UV-cured adhesives, depending on the considered end-uses, and to improve their toughness. Given the wide range of light-curable materials showing tailor-made properties, one can reasonably assume that there will always be an UV adhesive well suited to any one of the manifold types of bonding applications.

Acknowledgments

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11 Adhesives for Special Adherends

Sina Ebnesajjad

11.1 Introduction

This chapter describes the adhesives for specific adherend types. Tables are occasionally published listing large numbers of adhesive types recommended for specific adherends. Such tables can be misleading in supplying information needed to provide strong durable bonds, because the user may not know that some combinations of adhesives and adherends are superior in durability and resistance to other environments.

11.2 Metals

11.2.1 Aluminum and Alloys

Adhesives recommended include modified epoxies, modified phenolics, epoxy-phenolics, neoprene-phenolics, second-generation acrylics, cyanoacrylates, silicone rubbers, and vinyl plastisols. Sell[1] has ranked a number of adhesives in the order of decreasing durability with aluminum adherends as follows:

- nitrile-phenolics
- high-temperature epoxies
- 121 °C-curing epoxies
- 121 °C-curing rubber-modified epoxies
- vinyl epoxies
- two-part, room-temperature-curing epoxy paste with amine cure
- two-part polyurethanes

Brewis[2] has recently discussed the nature of adhesives used for aluminum. The two major aluminum manufacturers, Aluminum Company of America (ALCOA) and Reynolds Metals, have published compact, useful volumes on all aspects of aluminum bonding, although these volumes are not recent.[3,4] Another excellent detailed discussion of aluminum adhesives, particularly from the viewpoint of durability, is given by Minford of ALCOA.[2]

11.2.2 Beryllium

Adhesives recommended include epoxy-phenolics, nitrile-phenolics, epoxies (RT cure, contact pressure), epoxy-nylon, polyimide (PI), polybenzimidazole (PBI), epoxy-nitrile, and polyurethane. As beryllium retains significant strength at temperatures of up to 538 °C, the high-temperature application area is significant for this somewhat exotic metal. PBIs are relatively stable in air at temperatures of up to 288 °C, and for short periods of time. PIs can be used at somewhat lower temperatures for longer periods. The more conventional adhesives listed above are much more temperature sensitive than PBI and PI, but are considerably stronger at room temperature and have equivalent or even slightly higher strength at 121 °C.[4,5] Bond strengths of >30 MPa in shear and tension can be obtained by adhesive-bonding beryllium, with fracture being due to cohesive failure within the adhesive.[6]

11.2.3 Brass and Bronze

Though the surface preparation methods may be different, adhesives used with copper and copper alloys (see Section 11.2.5) can also be used with brass and bronze.

11.2.4 Cadmium (Plated on Steel)

Adhesives recommended include nitrile-phenolic and anaerobics.

11.2.5 Copper and Copper Alloys

Adhesives recommended include epoxies, polyurethane, silicone, nylon-epoxy, nitrile-phenolic, neoprene-phenolic, acrylic, cyanoacrylate, anaerobics, and partially hydrogenated polybutadiene (for bonding copper to polyethylene).

Only heat-cured epoxies containing dicyandiamide (DICY) or melamine should be used. DICY has been

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shown to be beneficial when used as the sole curing agent with epoxy resins, mixed with other curing agents, or used to pretreat the copper surface before bonding. Even when simply added to coatings (e.g., phenolic-cured epoxies, which cure by a different mechanism), both DICY and a melamine compound increased time to adhesive failure significantly on either bare or alkaline permanganate-treated copper.[7]

11.2.6 Gold

Adhesives recommended include epoxies, epoxy-phenolic, polyvinyl alkyl ether, and anaerobics (need a primer to activate the system).

11.2.7 Lead

Adhesives recommended include epoxies, vinyl alcohol—vinyl acetate copolymer, polyvinyl alkyl ether, polyacrylate (carboxylic), polyurethane (two-part), epoxy-phenolics, silicones, and cyanoacrylates. The high-strength thermoset and alloy adhesives are rarely justified for bonding lead. Even when other properties recommend these adhesives, the designer should check to see whether some low-cost or easier-to-use adhesive is also suitable. An exception is terne (lead-coated steel). This is a much stronger metal than lead, and lap-shear strengths exceeding 2.1 MPa are reported for adhesive joints with terne.[8,9]

11.2.8 Magnesium and Magnesium Alloys

Adhesives recommended include epoxies, epoxy-phenolics, polyurethanes, silicones, cyanoacrylates, polyvinyl acetate, vinyl chloride—vinyl acetate copolymer, vinyl-phenolic, nitrile-phenolic, neoprene-phenolic, and nylon-epoxy. A wide variety of adhesives can be used for bonding magnesium as long as proper corrosion protection is maintained in keeping with joint design and end-use requirements. Owing to magnesium's sensitivity to moisture and the galvanic couple, water-based adhesives would be expected to cause problems. Surface preparation should always be carried out in order to ensure that the adhesive itself does not react with the alloy to create a corrosive condition. Another important observation is that high-modulus adhesives tend to provide lower bond strengths than do lower-modulus adhesives.[10]

11.2.9 Nickel and Nickel Alloys

Nickel is usually used in alloy form. Relatively little work has been carried out on adhesive bonding of nickel-based alloys, because most of these alloys are used at temperatures above the service temperature of organic adhesives or under corrosive conditions. Inorganic adhesives of sufficient ductility and low-enough maturing temperatures have not been developed to compete effectively with brazing and welding for joining high-temperature structures.[11] To date, epoxy adhesives are the most common adhesives used to bond nickel and its alloys. In all likelihood, PBI and PI adhesives can also be used for high-temperature applications. Other adhesives used include epoxy-nylon, polyamides, nitrile-phenolic, vinyl-phenolic, polyisocyanates, melamines, and neoprenes.[12]

11.2.10 Plated Metals

See cadmium (Section 11.2.4) and zinc (Section 11.2.18).

11.2.11 Silver

Adhesives recommended include epoxies, polyvinyl alkyl ether, polyhydroxy ether, and neoprene rubber.

11.2.12 Steel, Mild, Carbon (Iron)

Adhesives recommended include acrylics, epoxies, nitrile-phenolic (high moderate-temperature strength but drops off rapidly at higher temperatures), PBI (high strength over a wide temperature range), PI, and epoxy-phenolic for high-strength applications. For lesser-strength applications, use thermoplastics and rubber-based materials such as chlorinated natural rubber, reclaim rubber, styrene-butadiene rubber (SBR), butadiene-acrylonitrile rubber, neoprene, butyl rubber, polyisobutylene, polyurethane rubber, polysulfide, and silicone rubber.[13]

Bitumen and soluble silicates are also used for some applications.

11.2.13 Stainless Steel

Although surface preparation methods are usually different, the adhesives used for mild steel can generally be used for stainless steel.

11.2.14 Tin

Adhesives recommended include casein glue, epoxies, polyvinyl alkyl ether, polyacrylate (carboxylic), SBR, and polyisobutylene.

11.2.15 Titanium and Titanium Alloys

Adhesives recommended include epoxies, nitrile-epoxy, nitrile-phenolic, PI, and epoxy-phenolic. PI adhesives provide strengths of 11.0−12.4 MPa at 316 °C. These adhesives are not used for skin-to-core bonds, because the environment temperature is not high enough to make them attractive and due to the inherent problems caused by high volatile release during cure. Epoxy-phenolics (novalacs) and nitrile-epoxies are normally tested at 177 °C. Nitrile-phenolics, because of their high peel strengths, are recommended for use in metal-to-metal bonds at the cost of lap-shear strength and at temperatures above 177 °C, provided the application permits a reduction in shear strength. Nitrile-epoxies are recommended for skin-to-core applications, because fewer volatiles are released during cure than are released with epoxy-phenolics. The volatiles released during cure by the latter adhesive and by PIs create internal pressure, which can result in core-node bond and skin-to-core bond failure.[14,15]

The use of titanium adhesive-bonded structures for high-temperature (200−300 °C) applications has been limited because of the rapid degradation of the adhesive at these temperatures. Recently, PI adhesives have been developed with terminal acetylenic groups. These adhesives have been found to retain 45−50% of their original strength after 1000 h of thermal aging at 260 °C. In another approach, the introduction of perfluoro-alkylene groups into aromatic PIs has resulted in a high degree of strength retention after 5000 h at 300 °C. To improve the oxidation resistance at elevated temperatures, many formulations are pigmented with fine alumina powder. The only really high-temperature adhesive not based on PI resin is polyphenylquinoxaline. An adhesive based on this heteroaromatic polymer showed a decrease of only 25% of its original strength after 500 h at 370 °C.[16]

Keith[17] has covered all aspects of titanium adhesive bonding, including adhesive selection, in a 1973 discussion.

11.2.16 Tungsten and Tungsten Alloys

Little information has been found on adhesives recommended for tungsten, although nitrile rubber and epoxies have been used.[12]

11.2.17 Uranium

Epoxies have been used to bond this exotic material.[12]

11.2.18 Zinc and Zinc Alloys

Adhesives recommended include nitrile-epoxies, epoxies, silicones, cyanoacrylates, and rubber-based adhesives.[18]

11.3 Thermoplastics

With these materials, solvent cementing or thermal-welding methods are often preferable alternatives to adhesive bonding. However, where dissimilar materials are being bonded, or where the thermoplastic is relatively inert to solvents, adhesive bonding is recommended.

11.3.1 Acetal Copolymer (Celcon®)

Although thermal welding is ordinarily used for bonding this material to obtain optimum bond strength, adhesives are used under certain conditions. Three types of adhesives are used: solvent, structural, and nonstructural. Hexafluoroacetone sesquihydrate is used for solvent cementing. Structural adhesives are generally thermosets. Many of these adhesives can be used continuously at temperatures up to 177 °C, which is higher than the recommended continuous-use temperature of 104 °C of the copolymer. Structural adhesive types recommended by the manufacturer (Celanese) are epoxy (up to 71 °C), polyester with isocyanate curing agent (up to 121 °C), and cyanoacrylate (up to 82 °C). Structural adhesives for bonding acetal copolymer to itself have yielded shear strengths of 4.1−5.5 MPa. Nonstructural adhesives are usually one-component, room-temperature curing systems based on either thermoplastic resins or elastomeric materials dispersed in solvents. They are normally used in applications that will not have to sustain heavy and/or continuous loading and will not reach temperatures above 82 °C. Neoprene rubber adhesives have been used to provide shear strengths of 2.24 MPa to sanded surfaces and 2.1 MPa to unsanded surfaces. As in structural adhesives, a reduction in strength can be expected under peeling load.[19]

11.3.2 Acetal Homopolymer (Delrin®)

Adhesives used to bond acetal homopolymer to itself and to other materials, such as aluminum, steel, natural rubber, neoprene rubber, and Buna rubber, include polyester with isocyanate curing agent, rubber-based adhesives, phenolics, epoxies, modified epoxies, and vinyls. Solvent cementing cannot be used unless the surfaces are specially roughened because of the high solvent resistance of this material.[20] Other adhesive types sometimes used are resorcinol, vinyl-phenolic, ethylene vinyl acetate, cyanoacrylates, and polyurethane.

11.3.3 Acrylonitrile-Butadiene-Styrene (ABS)

Bodied solvent cements are usually used to bond ABS. Adhesives recommended include epoxies, urethanes, second-generation acrylics, vinyls, nitrile-phenolics, and cyanoacrylates.[21,22]

11.3.4 Cellulosics

These plastics [cellulose acetate, cellulose acetate butyrate (CAB), cellulose nitrate, cellulose propionate, and ethyl cellulose] are ordinarily solvent cemented, but for bonding to nonsolvent-cementable materials, conventional adhesives must be used. Adhesives commonly used are polyurethanes, epoxies, and cyanoacrylates. Cellulosic plastics may contain plasticizers that are not compatible with the adhesive selected. The extent of plasticizer migration should be determined before an adhesive is selected.[21] Recommendations for conventional adhesives concerning specific cellulosic types are as follows:

- *Cellulose acetate*: natural rubber (latex), polyisobutylene rubber, neoprene rubber, polyvinyl acetate, ethylene vinyl acetate, polyacrylate (carboxylic), cyanoacrylate, polyamide (versamid), phenoxy, polyester + isocyanate, nitrile-phenolic, polyurethane, and resorcinol-formaldehyde
- *CAB*: natural rubber (latex), polyisobutylene rubber, nitrile rubber, neoprene rubber, polyvinyl acetate, cyanoacrylate, polyamide (versamid), polyester + isocyanate, nitrile-phenolic, resorcinol-formaldehyde, and modified acrylics
- *Cellulose nitrate*: same as CAB above
- *Ethyl cellulose*: cellulose nitrate in solution (or general-purpose household cement), epoxy, nitrile-phenolic, synthetic rubber, or thermoplastic resin combined with thermosetting resin and resorcinol-formaldehyde

11.3.5 Ethylene-Chlorotrifluoroethylene

See Section 11.3.7.

11.3.6 Fluorinated-Ethylene Propylene (Teflon®)

See Section 11.3.7.

11.3.7 Fluoroplastics

Epoxies and polyurethanes give good bond strengths with properly treated fluoroplastic surfaces.[21]

11.3.8 Ionomer (Surlyn®)

Adhesives recommended are epoxies and polyurethanes.

11.3.9 Nylons (Polyamides)

There are a number of types, based on their chemical structure, but the most important and most widely used is nylon 6,6. The best adhesives for bonding nylon to nylon are solvents. Various commercial adhesives, especially those based on phenol-formaldehyde (phenolics) and epoxy resins, are sometimes used for bonding nylon to nylon, although they are usually considered inferior to the solvent type because they result in a brittle joint. Adhesives recommended include nylon-phenolic, nitrile-phenolic, nitriles, neoprene, modified epoxy, cyanoacrylate, modified phenolic, resorcinol-formaldehyde, and polyurethane. Bonds in the range of 1.7–6.9 MPa, depending on the thickness of the adherends, have been obtained.[21,22]

11.3.10 Perfluoroalkoxy Resins

See Section 11.3.7.

11.3.11 Phenylene Oxide Based Resins (Noryl®)

Although solvent cementing is the usual method of bonding these resins, conventional adhesive bonding can be used. Epoxy and acrylic adhesives are generally recommended because of the versatile product lines and cure-rate schedules. Other adhesives recommended include cyanoacrylates, polysulfide-epoxy, room temperature vulcanizing (RTV) silicones, synthetic rubber, and hot melts. The manufacturer SABIC has recommended specific commercial designations of these types. The cure temperatures of the adhesives selected must not exceed the heat-deflection temperature of the Noryl resin, which ranges from 85 °C to 158 °C, depending on the formulation. Adhesives not tested for compatibility with Noryl resins should be avoided or tested. Such testing should consider operational conditions of temperature and stress.[23]

11.3.12 Polyaryl Ether (Arylon T)

This material is normally joined by solvent cementing.

11.3.13 Polyaryl Sulfone (Astrel 360; 3M Co.)

Hysol EA 9614 (modified epoxy on a nylon carrier) has been used to give good bonds with this plastic in a steel—plastic—steel bond.[24] Curing is at 71 °C for 4 h or 93—121 °C at 0.21 MPa pressure for 1 h. Bonds with strengths up to 14 MPa have been obtained with solvent-cleaned surfaces.

11.3.14 Polycarbonate

Polycarbonate is usually solvent cemented, but it can be bonded to other plastics, glass, aluminum, brass, steel, wood, and other materials using a wide variety of adhesives. Silane primers may be used when joining polycarbonates with adhesives to promote adhesion and ensure a dry surface for bonding.[22] Adhesives recommended include epoxies, urethanes, silicones, cyanoacrylates, and hot melts. Generally, the best results are obtained with solvent-free materials such as epoxies and urethanes. Polycarbonates are very likely to stress crack in the presence of solvents. When cementing polycarbonate parts to metal parts, a nontemperature-curing adhesive should be used to avoid creating strains in the adhesive caused by the differences in the coefficients of thermal expansion. This differential causes adherend cracking and considerably decreases expected bond strengths. Under no condition should curing temperatures exceed 132 °C, the heat-distortion temperature of standard polycarbonate resins.[25]

11.3.15 Polychlorotrifluoroethylene (PCTFE; Aclar)

Epoxy-polyamide and epoxy-polysulfide adhesives have been used successfully for bonding properly treated PCTFE. An epoxy-polyamide adhesive (Epon 828/Versamid 125 60:40 ratio), cured for 16 h at room temperature and followed by 4 h at 74 °C, has given tensile-shear strengths of 19.6—20.8 MPa for various KEL-F resins treated with sodium naphthalene etch solutions and also abraded.[26,27]

11.3.16 Polyester (Thermoplastic Polyester)

Solvent cementing is usually used with these materials. Conventional adhesives recommended include single- and two-component polyurethanes, cyanoacrylates (Loctite 430 Superbonder), epoxies, and silicone rubbers.

11.3.17 Polyetheretherketone

Epoxy adhesives, such as Ciba-Geigy's Araldite AW 134 with HY 994 hardener (cured for 15 min at 120 °C) and Araldite AV 1566 GB (cured for 1 h at 230 °C), give the best results with this new engineering resin, according to the manufacturer (ICI Ltd.). Other adhesives that can be used are cyanoacrylate (Loctite 414 with AC primer), anaerobics (Loctite 638 with N primer), and silicone sealant (Loctite Superflex). The highest lap-shear strength was obtained with Araldite AW 134. This adhesive has balanced properties, good resistance to mechanical shock, thermal resistance to 100 °C, and reasonable stability in the presence of aliphatic and aromatic solvents. Some solvents, particularly chlorinated hydrocarbons, deteriorate the bond.[28]

11.3.18 Polyetherimide (Ultem®)

Adhesives for this new engineering plastic are polyurethane (cure at room temperature to 150 °C), RTV silicones, hot-melts (polyamide types) curing at 205 °C, and epoxies (nonamine type, two-part).[29]

11.3.19 Polyethersulfone

Polyethersulfone may be solvent cemented (see Chapter 8). Conventional adhesives recommended by the manufacturer (ICI Ltd.) are epoxies (CIBA-Geigy's Araldite AV 138 with HV 998 hardener and Araldite AW 134B with HY 994 hardener), Hysol 9340 two-part epoxy paste, and Silcoset 153 RTV silicone sealant supplied by ICI Ltd. with primer OP (also supplied by ICI Ltd.) and Silcoset RTV 2 with Superflex primer, the latter supplied by an English source (Douglas Kane Group, Herts, United Kingdom). The highest lap-shear strength was obtained with the Araldite AW 134B.[28]

Other adhesives recommended by ICI Ltd. are 3M Company's Scotch-Weld 2216 two-part epoxy, Amicon's Uniset A-359 one-part aluminum-filled epoxy, CYTEC's BR-89 one-part epoxy, Bostik's 7026 synthetic rubber and 598-45 two-part adhesive, SABIC's Silgrip SR-573, and Goodyear's Vitel polyester with isocyanate curing agent.[28]

11.3.20 Polyethylene

Acceptable bonds have been obtained between polyethylene surfaces with polar adhesives, such as epoxies (anhydride- and amine-cured and two-component modified epoxies), and solvent cements containing synthetic rubber or phenolic resin. Other adhesives recommended include styrene-unsaturated polyester and solvent-type nitrile-phenolic.

11.3.21 Polymethylmethacrylate (PMMA)

Ordinarily, solvent cementing or thermal welding is used with PMMA. These methods provide stronger joints than adhesive bonding. Adhesives used are cyanoacrylates, second-generation acrylics, and epoxies, each of which provides good adhesion but poor resistance to thermal aging.[21]

11.3.22 Polymethylpentene (TPX)

No information has been found on adhesives for bonding TPX, but that the adhesives used for polyethylene will prove satisfactory for this polyolefin is likely.

11.3.23 Polyphenylene Sulfide (Ryton®)

Adhesives recommended by the manufacturer (Phillips Chemical Company) include anaerobics (Loctite 306), liquid two-part epoxies (Hughson's Chemlok 305), and a two-part paste epoxy (Emerson & Cuming's Eccobond 104). Also recommended are USM's BOSTIK 7087 two-part epoxy and 3M Company's liquid two-part polyurethane EC-3532.[30]

11.3.24 Polypropylene

In general, adhesives recommended are similar to those used for polyethylene. Candidate adhesives include epoxies, polyamides, polysulfide epoxies, nitrile-phenolics, polyurethanes, and hot melts.[22]

11.3.25 Polystyrene

This material is ordinarily bonded by solvent cementing. Polystyrene can be bonded with vinyl acetate/vinyl chloride solution adhesives, acrylics, polyurethanes, unsaturated polyesters, epoxies, urea-formaldehyde, rubber-based adhesives, polyamide (Versamid-base), PMMA, and cyanoacrylates.[21,22,31] Monsanto Plastics and Resins Company has published an excellent bulletin recommending particular cements for both nonporous and porous surfaces. Cements are recommended for the fast-, medium-, and slow-setting ranges.[32]

11.3.26 Polysulfone

Adhesives recommended by the manufacturer, Union Carbide, include the following:[33]

- 3M Company

Scotch-Grip 880 one-part solvent-based chloroprene
Scotch-Weld 1838 two-part epoxy
Scotch-Weld 2214 one-part epoxy
Scotch-Weld 2216 two-part epoxy

- CYTEC

BR-89 one-part epoxy
BR-92 two-part epoxy with either DICY curing agent or curing agent Z

- M&T Chemicals

Uralane 5738 two-part polyurethane
Uralane 8615 two-part polyurethane

The Scotch-Grip 880 elastomeric adhesive is recommended for bonding polysulfone to canvas, and Uralane 8615 is recommended for bonding polysulfone to polyethylene.

11.3.27 Polytetrafluoroethylene (Teflon®)

See Section 11.3.7. Other adhesives used include nitrile-phenolics, polyisobutylene, and silicones, the last two of which are pressure-sensitive adhesives.[31]

11.3.28 Polyvinyl Chloride (PVC)

Solvent cementing is usually used for PVC. Owing to the fact that plasticizer migration from vinyls to the adhesive bond line can cause problems, adhesives selected must be tested for their compatibility with the plasticizer. Nitrile rubber adhesives are particularly good in this respect, although polyurethanes and neoprenes are also useful. 3M Company's Scotch-Grip 2262 adhesive (synthetic resin in solvent) is claimed to be exceptionally resistant to plasticizer migration in vinyls. A number of different plasticizers can be used with PVCs, so an adhesive that works with one plasticizer may not work with another.[21] Even rigid PVC contains up to 5% plasticizer, making bonding with epoxy and other non-rubber type adhesives difficult. Most vinyls are fairly easy to bond with elastomeric adhesives after proper surface preparation. Cyanoacrylates can be used with rigid PVC. The highest bond strengths with semi-rigid or rigid PVC are obtained with two-component, room temperature-curing epoxies. Other adhesives used with rigid PVC include polyurethanes, modified acrylics, silicone elastomers, anaerobics, polyester-polyisocyanates, PMMA, nitrile-phenolics, polyisobutyl rubber, neoprene rubber, epoxy-polyamide, and polyvinyl acetate.

11.3.29 Polyvinyl Fluoride (Tedlar®)

Adhesives recommended include acrylics, polyesters, epoxies, elastomers, and pressure-sensitive adhesives.

11.3.30 Polyvinylidene Fluoride (Kynar®)

See Section 11.3.7.

11.3.31 Styrene-Acrylonitrile (SAN; Lustran®)

Solvent cements are frequently used for SAN. Commercial cements include cyanoacrylate, epoxy, and the following 3M Company elastomeric adhesives:

Scotch-Grip 847 nitrile rubber
Scotch-Grip 1357 neoprene rubber
Scotch-Grip 2262 synthetic rubber

Several other commercial adhesives not specified, with respect to type, can be found in Ref. 34.

11.4 Thermosetting Plastics (Thermosets)

Most thermosetting plastics are not particularly difficult to bond. As a result of these materials not being soluble, solvent cementing cannot be used. In some cases, however, solvent solutions can be used to join thermosets to thermoplastics. In general, adhesive bonding is the only practical way to join a thermoset to a thermoplastic or to another thermoset. Epoxies or modified epoxies are the best adhesives for this purpose.

11.4.1 Diallyl Phthalate

Suggested adhesives include urea-formaldehyde, epoxy-polyamine, neoprene, nitrile-phenolic, styrene-butadiene, phenolic-polyvinyl butyral, polysulfides, furans, polyesters, and polyurethanes.

11.4.2 Epoxies

Suggested adhesives include modified acrylics, epoxies, polyesters, resorcinol-formaldehyde, furane, phenol-formaldehyde, polyvinyl formal-phenolic, polyvinyl butyral, nitrile rubber-phenolic, polyisobutylene rubber, polyurethane rubber, reclaimed rubber, melamine-formaldehyde, epoxy-phenolic, and cyanoacrylates. For maximum adhesion, primers should be used. Nitrile-phenolics give excellent bonds if cured under pressure at temperatures of 149 °C. Lower-strength bonds are obtained with most rubber-based adhesives.

11.4.3 Melamine-Formaldehyde (Melamines)

Adhesives recommended are epoxies, phenolic-polyvinyl butyral, epoxyphenolic, nitrile-phenolic, polyurethane, neoprene, butadiene-nitrile rubber, cyanoacrylates, resorcinol-polyvinyl butyral, furane, and urea-formaldehyde.

11.4.4 Phenol-Formaldehyde (Phenolics)

Adhesives recommended are neoprene and urethane elastomers, epoxies, and modified epoxies, phenolic-polyvinyl butyral, nitrile-phenolic, polyester, cyanoacrylates, resorcinol-formaldehyde, phenolics, polyacrylates, modified acrylics, PVC, and urea-formaldehyde. Phenolic adhesives give good results but require higher cure temperatures and are less water-resistant than resorcinol-based adhesives.

11.4.5 Polyester (Thermosetting Polyester)

These materials may be bonded with neoprene or nitrile-phenolic elastomer, epoxy, epoxy-polyamide, epoxy-phenolic, phenolic, polyester, modified acrylic, cyanoacrylates, phenolic-polyvinyl butyral, polyurethane, butyl rubber, polyisobutylene, and PMMA.

11.4.6 Polyimide

Though rare, published information is available on adhesives for bonding PIs. A recent NASA study[35,36] evaluated six adhesives for this purpose. Those recommended were as follows:

CYTEC's FM-34 polyimide tape

CYTEC's FM-34 B-18 polyimide tape (arsenic-free)

LARC-13, developed at NASA Langley Research Center

NR056X, an adhesive resin of the NR 150 polymer family (PI), developed by DuPont under a NASA contract

11.4.7 Polyurethane

Elastomeric adhesives are prime candidates for polyurethanes, and polyurethane elastomer adhesives are particularly recommended.[22] Other suitable adhesives include epoxies, modified epoxies, polyamide-epoxy, neoprene, and resorcinol-formaldehyde. The latter offers excellent adhesion but is somewhat brittle and can fail at relatively low loads.[21]

11.4.8 Silicone Resins

These are generally bonded with silicone adhesives; either silicone rubber or silicones. Primers should be used before bonding.

11.4.9 Urea-Formaldehyde

Adhesives recommended are epoxies, nitrile-phenolic, phenol-formaldehyde, urea-formaldehyde, resorcinol-formaldehyde, furane, polyester, butadiene-nitrile rubber, neoprene, cyanoacrylates, and phenolic-polyvinyl butyral.

11.5 Reinforced Plastics/Composites

Adhesives that bond well to the base resin can be used to bond plastics reinforced with such materials as glass fibers or synthetic high-strength fibers.

Reinforced thermoplastics can also be solvent cemented to themselves or joined to other thermoplastics using a compatible solvent cement. For reinforced thermosets, in general, the adhesives recommended above for thermosetting plastics apply.

11.6 Plastic Foams

Solvent cements are usually preferable to conventional adhesives for thermoplastic structural foams. Some solvent cements and solvent-containing, pressure-sensitive adhesives will collapse thermoplastic foams. Water-based adhesives based on SBR, polyvinyl acetate, or neoprene, are frequently used. Solvent cementing is not effective on polyethylene foams due to their inertness. Recommendations for adhesives concerning thermoplastic foams are as follows:

- *Phenylene oxide-based resins* (*Noryf*®): epoxy, polyisocyanate, polyvinyl butyral, nitrile rubber, neoprene rubber, polyurethane rubber, polyvinylidene chloride, and acrylic
- Polyethylene-nitrile rubber, polyisobutylene rubber, flexible epoxy, nitrile-phenolic, and water-based (emulsion) adhesives
- *Polystyrene*: for these foams (expanded polystyrene), aromatic solvent adhesives (e.g., toluol) can cause collapse of the foam cell walls. For this reason, using either 100% solids adhesives or water-based adhesives based on SBR or polyvinyl acetate is advisable.[21] Specific adhesives recommended include urea-formaldehyde, epoxy, polyester-isocyanate, polyvinyl acetate, vinyl chloride-vinyl acetate copolymer, and reclaim rubber. Polystyrene foam can be bonded satisfactorily with any of the following general adhesive types:

Water-based (*emulsion*): best for bonding polystyrene foam to porous surfaces

Contact-bond: for optimum initial strength. Both the water- and solvent-based types may need auxiliary heating systems for further drying. Solvent types are recommended for adhering to metal, baked enamel, and painted surfaces

Pressure-sensitive adhesives: these will bond to almost any substrate. Both water- and solvent-based types are used. However, they are not usable in applications requiring long-term resistance to stress or resistance to high heat levels. Those adhesives that are 100% solid are two-part epoxies and polyurethanes. They form an extremely strong heat- and environment-resistant bond

PVC: epoxy, polyester-isocyanate, unsaturated polyester, vinyl chloride-acetate copolymer, polyvinyl acetate, polyvinyl alkyl ether, ethylene-vinyl acetate, nitrile rubber-phenolic, neoprene rubber, polyisobutylene rubber, polyurethane rubber, and polysulfide rubber. See discussion in Section 11.3.28 concerning migration of plasticizers in PVC

- *Polycarbonate*: urethane, epoxy, rubber-based adhesives
- *Thermoplastic polyester*: urethane, epoxy

Recommendations for thermosetting foams are as follows:

- Epoxy (including syntactic foams), heat-cured epoxies (one-part)
- *Phenolic*: epoxy, polyester-isocyanate, polyvinyl acetate, vinyl chloride—acetate copolymer, polyvinyl formal-phenolic, nitrile rubber, nitrile rubber-phenolic, reclaim rubber, neoprene rubber, polyurethane rubber, butyl rubber, melamine-formaldehyde, neoprene-phenolic, and polyvinyl formal-phenolic
- *Polyurethane*: epoxy, polyester, polyacrylate, polyhydroxyether, nitrile rubber, butyl rubber, water-based (emulsion), polyurethane rubber, neoprene, SBR, melamine-formaldehyde, and resorcinol-formaldehyde are specific types. Generally, a flexible adhesive should be used for flexible polyurethane foams. Synthetic elastomer adhesives with fast-tack characteristics are available in spray cans. Solvent-based neoprenes are recommended for resistance to stress, water, and weathering. Solvent-based nitriles are recommended for resistance to heat, solvents, and oil. Water-based adhesives generally dry too slowly for most industrial applications, unless accelerated equipment is used. For immediate stress resistance, contact bonding is preferred. In this method, the adhesive is applied to the foam and to the other substrate by spraying or brushing. Wet bonding can be used where the adhesive is applied to the other surface. This reduces "soak-in" on the highly absorbent and porous foam[34]
- *Silicone*: silicone rubber
- *Urea-formaldehyde*: urea-formaldehyde, resorcinol-formaldehyde

11.7 Rubbers (Elastomers)

Bonding of vulcanized elastomers to themselves and to other materials is generally accomplished using a pressure-sensitive adhesive derived from an elastomer similar to the one being bonded. Adhesives used include the following rubber-based materials: natural, chlorinated, reclaim, butyl, nitrile, butadiene-styrene, polyurethane, polysulfide, and neoprene rubber, as well as acrylics, cyanoacrylates, polyester-isocyanates, resorcinol-formaldehyde, phenolic-resorcinol-formaldehyde, silicone resin, epoxies, polyisocyanates, furanes, nitrile-phenolics, neoprene-phenolic, polyvinyl formal-phenolic, and flexible epoxy-polyamides.[12,21] Neoprene and nitrile rubber adhesives are especially recommended for bonding rubber. Neoprene adhesives are good all-around adhesives for rubber. Nitrile adhesives are particularly recommended for gaskets formulated with nitrile or polysulfide rubber.[34]

11.8 Ceramics and Glass

(This section has been graciously contributed by The Welding Institute, www.twi.co.uk).

Engineering ceramics, such as silicon nitride, silicon carbide, and a large number of oxides, are used in industries ranging from aerospace to automotive and biomedical to electronics. These materials are used because they possess a range of properties that are attractive for particular applications. These include the following:

- Chemical inertness
- High hardness
- High stiffness
- Strength at high temperature

The excellent stability of ceramics under extreme chemical and thermal environments is often the primary reason for their selection. However, the ceramic component must be joined to the rest of the device. There are many joining techniques that can be utilized. These range from mechanical attachment to direct bonding methods such as brazing or adhesive bonding. With all these methods, the correct design criteria for ceramic materials must be followed. These criteria must address issues, such as the following:

- The inherent brittle nature of ceramics
- Their low fracture toughness
- Their low tolerance to high shear and tensile stresses
- Their low coefficient of thermal expansion compared with other materials

The technique selected depends on whether the ceramic is joined to a similar or dissimilar material and on the expected operational conditions at the joint. If the joint temperature is not expected to exceed 150 °C or to only have very short-term excursions to ~200 °C, and the environment is not too chemically aggressive, organic adhesives offer an attractive joining solution.

A range of adhesives, which can be used to bond ceramics, is commercially available, such as epoxy compounds or cyanoacrylates. Each of these has its optimum application method and curing regime to give maximum performance. Optimization may involve the use of a primer or other additive. For example, oxide ceramics are generally porous structures with slightly acidic surfaces. This acidity tends to inhibit the polymerization of cyanoacrylate adhesives, whereas the porosity requires these surface-initiating species to extend across relatively large gaps. Both problems are overcome by the use of small quantities of basic species, such as amines, which activate polymerization of the cyanoacrylate. Other adhesive systems also provide enhanced bonding properties when used in conjunction with surface modifying primers, or when used in conjunction with keying agents, such as silane compounds.

The use of adhesive bonding for ceramics has both pros and cons.

Advantages

- Uniform stress distribution at the joint
- No finishing costs
- Easily automated
- Adhesives seal and join in one operation
- Good fatigue resistance
- Small areas can be bonded accurately

Disadvantages

- Joints can be weak when subjected to peel load
- Limited service temperature, typically <150 °C or <200 °C in special applications
- Poor electrical and thermal conduction, although loading with metal particles improves performance
- Joint integrity is sensitive to cleanliness of the mating surfaces and service environment
- Surface preparation can be critical
- Joints not hermetic

With correct joint design and material selection and consideration of operational conditions, adhesive bonding of ceramics can be used highly successfully. Probably, the most famous application of advanced ceramics uses adhesive bonding. The NASA Space Shuttle employs 24,000 ceramic tiles as a thermal protection system to keep the temperature relatively constant inside the vehicle. The external temperature of the tiles can vary from −80 °C during orbit to 1250 °C during re-entry. These tiles are adhesively bonded through a strain isolation pad to the aluminum skin of the shuttle, which has a design limit of 175 °C. The success of this system not only allows the shuttles to operate, but also permits them to be reused many times.

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12 Adhesives for Electronics

Guy Rabilloud

12.1 Chemical Compounds

Except a few thermoplastic materials that are processed by melting, most adhesives are formed in situ by polymerization or polycondensation of small molecules called “monomers.” Free radical and ionic mechanisms are involved in the polymerization of unsaturated monomers containing carbon−carbon double bonds. Acrylates, cyanoacrylates, or UV-curable compounds are typical examples of such monomers. Rigid and flexible epoxies, epoxy-phenolic, and epoxy-silicone compositions are generally composed of the base resin, a coreactant, and various additives. At moderate temperature, ring opening predominates, whereas condensation reactions occur when the temperature is raised. Silicone resins are formed by polycondensation of two reactive silicon-containing monomers at ambient temperature [room temperature vulcanization (RTV) silicones] or by the addition of silane groups (Si−H) to ethylenic double bonds. Cyanate resins and adhesive compositions containing them polymerize predominantly by cycloaddition. Finally, polyimides are synthesized by reacting, in solution, aromatic dianhydrides with aromatic diamines. The reaction easily proceeds at room temperature to give high-molecular-weight linear polymers called polyamic acids. These polymers are transformed into heterocycles (imidization) by chemical or thermal cyclodehydration.

The chemistry and reaction mechanisms involved in the formation of these macromolecules are not discussed in the present chapter. A number of books, reviews, and review symposia were published, which provide deep insight of the different chemical processes that take place during the formation of the adhesive joint. As far as possible, relevant references are provided in the following sections for readers, scientists, and production engineers, searching extensive information about a particular class of polymer. When necessary, one figure displays the chemical formulae of the organic compounds engaged in adhesive compositions and other figures illustrate either the first “initiation” step when active species are formed or the final polymer structures.

12.1.1 Free Radical and Ionic Polymerization

Aliphatic polymers prepared by the addition polymerization of unsaturated monomers containing −C=C− groups are broadly used in the fabrication of general purpose adhesives. They are, however, of marginal utility in electronics because of their low glass transition temperature (T_g) and poor thermal stability. Poly(methyl methacrylate) (PMMA), for example, has a continuous service temperature limited to 90 °C. Applications for this category of polymers are mainly molding, casting, and coating formulations providing materials with excellent optical clarity. Light emitting diodes (LED) are often protected by a thick layer of PMMA molded in the form of convergent lens. The principle of addition polymerization is sketched in Fig. 12.1.

An initiator, decomposed under the influence of heat or UV irradiation, generates two free radicals **1** containing highly reactive unpaired electrons. Radical **1** reacts with methyl methacrylate **2** to produce the intermediate free radical **3** that constitutes the initial element of chain propagation. Once this reactive species is formed, polymerization occurs extremely rapidly by opening the carbon−carbon double bonds of other monomer molecules to give finally PMMA **4** until termination takes place by radical recombination or disproportionation. Chain polymerization of 2,3-epoxypropyl methacrylate **5** leads to linear aliphatic polymer **6** with pendent epoxy groups. Further reaction with coreactants can be used to increase the T_g. Addition polymerization does not have to occur only via free radicals. For example, the cationic attack of epoxy resins by photosensitive onium salts generates insoluble cross-linked polymers.

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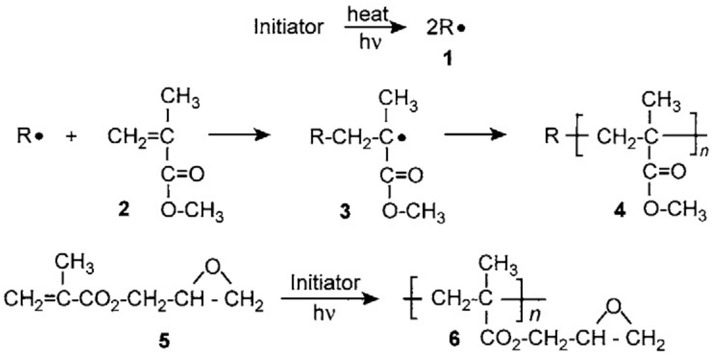

Figure 12.1 Simplified mechanism of free radical chain polymerization. On heating or by UV irradiation, the initiator generates free radicals **1** whose reaction with methyl methacrylate **2** creates the active species **3**. Further reaction with monomer molecules leads to poly(methyl methacrylate) PMMA **4**. Applied to 2,3-epoxypropyl methacrylate **5**, this process gives the linear aliphatic polymer **6** with pendent epoxy groups.

12.1.2 Epoxy Adhesives

Epoxy adhesives typically contain several chemical components, the most important being the epoxy resin constituting the base of the formulation. To the epoxy compound are added a variety of materials including catalysts, coreactants, reactive diluents, solvents, flexibilizing or toughening agents, and fillers. All these additives have a considerable effect on the properties of the adhesive composition before, during, and after the curing process. For instance, fillers impart thixotropy or provide electrical and thermal conductivities, whereas the Young's modulus can be increased by one order of magnitude with multifunctional coreactants. Single or one-part systems are premixed compositions of epoxy resins, hardeners, accelerators, adhesion promoter, and conductive filler. Latent hardeners and catalysts are chemical compounds that react with epoxies only on heating at temperatures higher than 100−120 °C, and such compositions are stable at ambient temperature for at least 6 months. Conversely, frozen one-part adhesives include highly reactive catalysts and must be preserved at low temperature (−40 °C) before use. In two-part systems, the epoxy resin loaded with conductive filler is delivered in one container and the hardener mixed with a solvent or reactive diluent combined with the same or a different filler forms the second component. The chemistry of epoxy resins is now well understood, and pertinent information can be found elsewhere.[1−3] In the particular field of the conductive adhesives used in electronics, relevant references have been recently published.[4]

12.1.2.1 Epoxy Resins

All epoxy resins used in the fabrication of conductive adhesives are commercially available materials that were developed several decades ago to prepare structural adhesives. They can be aromatic, cycloaliphatic or aliphatic, monofunctional or polyfunctional, physically ranging from low-viscosity liquids to high-melting solids. These resins have a common feature: the three-membered oxygen-containing epoxy (oxirane) rings that are incorporated into organic molecules by using either condensation or oxidation reactions. Figure 12.2 shows the synthesis of epoxy resins by the two-step reaction of 1-chloro-2,3-epoxypropane (epichlorhydrin) **7** with 4,4′-(1-methylethylidene)bisphenol (bisphenol-A) **8**. The first stage is the formation of bischlorhydrin **9** that is subsequently dehydrochlorinated with sodium hydroxide to produce the diglycidyl ether of bisphenol-A **10** known as DGEBA. In practice, the reaction is not simple, because the epoxy groups may react with another molecule of phenol to give, as by-products, variable amounts of low-molecular-weight oligomers **11**. According to the quantity of oligomers and their average molecular weight, the mixture of epoxidized material may change from viscous liquids to waxy or even hard solids.

In addition, the conversion of phenols to glycidyl ethers does not follow this ideal pathway, and side reactions or incomplete dehydrochlorination yield compounds containing chlorinated groups such as **12** and **13**. These reactions have a dual effect, because they first reduce the number of epoxy groups, which is generally lower than two, and second, they introduce covalently bonded chlorine atoms that can be hydrolyzed under exposure to high temperature and

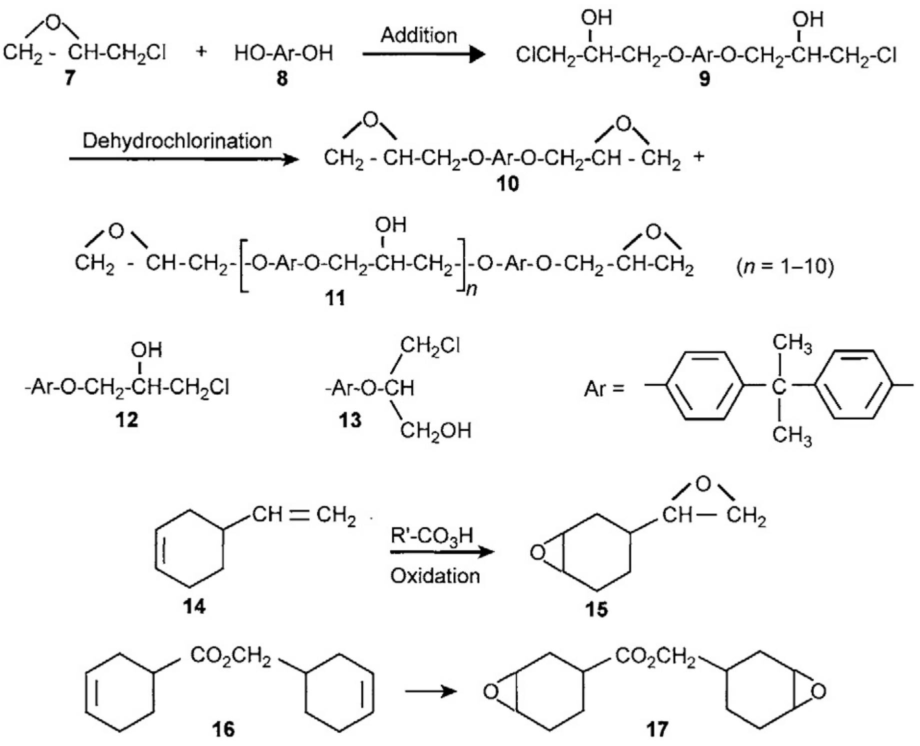

Figure 12.2 Synthesis of epoxy resins by the addition of 1-chloro-2,3-epoxypropane **7** to bisphenol-A **8** providing intermediate compound **9**. Subsequent dehydrochlorination gives a mixture (e.g., Shell Epon® 828) of DGEBA **10**, low-molecular-weight oligomers **11**, and chlorine-containing species **12** and **13**. Cycloaliphatic epoxy resins **15** and **17**, such as Degussa F126®, are prepared by the oxidation of unsaturated compounds **14** and **16** by means of organic peracids.

humidity. Thus, crude epoxy resins contain large amounts of alkali metal (Na^+) and free chlorine (Cl^-) atoms. Manufacturers now offer resins complying as closely as possible with the ionic purity, quality, and reliability requirements of the electronics industry. The high-purity epoxy resins produced for electronic applications are mostly used to make plastic packages and printed circuit boards (PCBs), the adhesive market accounting for only a small part, less than 2%, of the total consumption of these epoxies.

The second important category of epoxies, represented in Fig. 12.2, is known as the cycloaliphatic series because they are prepared by a controlled oxidation of linear and cyclic carbon—carbon double bonds. Organic peracids ($R-CO_3H$), such as peracetic and perbenzoic acids, are used to introduce exocyclic oxygen bridges into the molecules. This is the only class of epoxies that does not contain residual chlorine. A second advantage lies in the lower viscosity of these compounds compared with that of glycidyl ether derivatives, making them very useful for decreasing the viscosity of high-molecular-weight epoxies in packaging formulations. Oxidation of 4-vinylcyclohexene **14** and 3-cyclohexenylmethyl 3-cyclohexenecarboxylate **16** gives 4-vinyl-1-cyclohexene dioxide **15** and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate **17**, respectively.

Figure 12.3 shows the chemical formulae of other epoxy resins commonly used to prepare conductive adhesive compositions. Representative of approximately difunctional compounds are the diglycidyl ether of bisphenol-F (DGEBF) **18** and the diglycidyl ether of 1,3-dihydroxybenzene **19**. Epoxy resins with a functionality higher than two are prepared by the reaction of 1-chloro-2,3-epoxypropane **7** with polyfunctional starting materials.

The reaction with amine derivatives such as 4-hydroxybenzeneamine **20** and 4,4′-methylenebisbenzeneamine **22** is used to produce the tri- and tetrafunctional epoxies N,N,O-tris(2,3-epoxypropyl)-4-hydroxybenzeneamine **21** and *N,N,N′,N′*-tetrakis (2,3-epoxypropyl)-4,4′-methylenebisbenzeneamine **23**, respectively. However, the polyfunctional epoxies that combine the most attractive properties for electronic applications are the resins produced by epoxidation of the phenol novolac **24** and cresol novolac **26**. Novolac resins are obtained by the condensation of a phenol with formaldehyde in the presence of acid catalysts in such conditions that the degree of polycondensation is in the range of 3—5. The epoxy novolacs **25** and **26** are produced by the reaction of epichlorhydrin with the corresponding phenol novolac and *ortho*-cresol novolac resins. Epoxy resins are generally characterized by their dynamic viscosity (η) at 25 °C, expressed in millipascal second (mPa s),

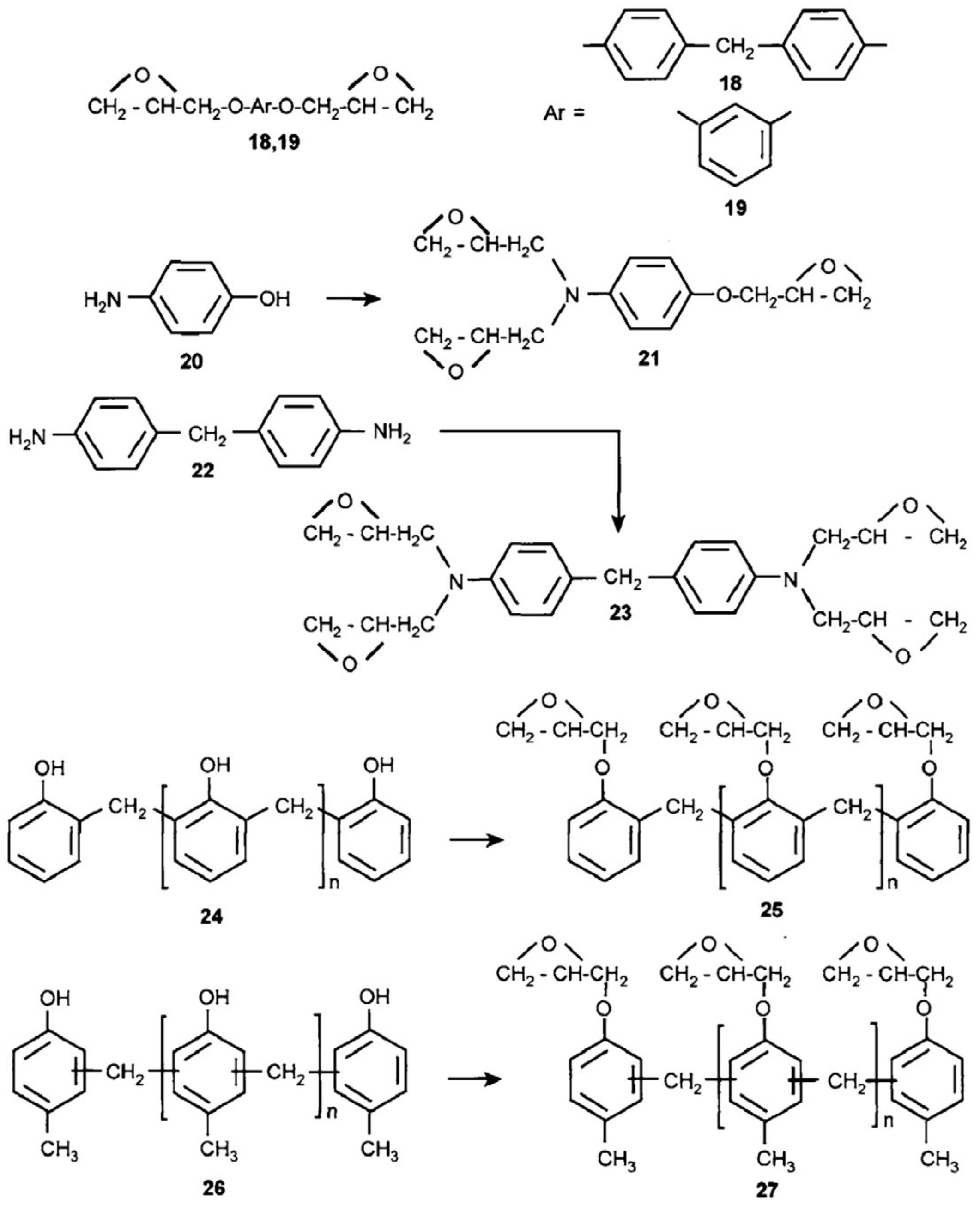

Figure 12.3 Chemical formulae of di- and polyfunctional epoxies commonly used to manufacture electrically conductive adhesives: Dainippon Epiclon 830 **18**, Ciba-Geigy ERE 1359 **19**, Ciba-Geigy MY 0510 **21**, Ciba-Geigy MY 720 **23**, Dow Chemical DEN 438 **25**, and Ciba-Geigy ECN 1280 **27**.

their melting temperature (mp) or dynamic viscosity measured at 50 °C for solid materials, epoxy equivalent weight (EEW), which is the weight of resin corresponding to one epoxy group, number average of epoxy groups (NAE) per molecule, and number average molecular weight M_n.

Today, almost 50% of the semiconductors encapsulated in plastic packages are made for surface-mount assembly that subjects the devices to a considerable thermal shock during the soldering process. Within a few seconds, the internal package temperature rises to 215–260 °C and the moisture absorbed by the plastic encapsulant and the organic adhesive evaporates explosively. This sometimes results in package cracks that start at the interface between the chip and the die pad or in delamination within the die attachment layer. To investigate the relationship between the chemical structure of epoxies and this so-called "popcorn effect," a series of polyfunctional resins has been evaluated.[5] They include new experimental epoxy novolacs whose chemical formulae have been previously displayed.[4]

Because of their excellent adhesive properties on most hard materials and relatively low production cost, poly(glycidyl ethers) have been used for more than 30 years to formulate high-volume consumer-orientated adhesives as well as high-performance structural adhesives. When not loaded with large amounts of inorganic fillers, these resins have dynamic viscosities that are convenient for most applications. However, the addition of metal or oxide fillers dramatically increases the viscosity to a level higher than 10^3 Pa s. To lower the viscosity of the adhesive compositions based on epoxy novolacs or other high-functionality epoxies, low-viscosity materials, also called reactive diluents, are prepared by the condensation of epichlorhydrin with either monophenols or diols such as butanediol or polyetherdiols. Figure 12.4 shows the formulae of phenylglycidyl ether **28** ($\eta = 6$ mPa s) and butanediol diglycidylether **29** ($\eta = 20$ mPa s).

Most of the epoxies used to prepare conductive adhesives are those described in the previous section because they allow the production of systems with high glass transition temperatures and good thermal resistance. However, the cured thermoset is rigid and brittle material that develop significant thermal stresses when applied to large-area substrates. The versatility of the epoxy chemistry permits a substantial reduction of Young's modulus to the detriment of the thermal and mechanical properties. Some flexibility can be imparted to epoxy compositions by using flexible epoxy resins, flexible hardeners, plasticizers or flexibilizers, and elastomeric materials. A brief survey of the chemistry, properties, and applications of flexible epoxy adhesives was published by Edwards,[6] who emphasized that these materials have found limited use in the microelectronic industry. When compared with rigid epoxies, flexibilized systems exhibit degradation in solvent resistance, moisture immunity, and thermal stability. The other drawbacks are low glass transition temperatures and high coefficients of thermal expansion.

Two examples of application are the encapsulation of bubble memory devices and LED, where the flexible material provides the required stress relief. However, the use of flexible epoxy systems is expected to grow with the development of hybrid circuits bonded to large-area ceramic substrates. The three commercial flexible epoxies drawn in Fig. 12.4 were reported by Hermansen and Lau.[7] The aliphatic backbone and a large distance between the epoxy groups explain the flexibility of both the epoxidized poly(oxypropylene)diol **30** (Dow Chemicals DER-732® and DER-736®; www.dow.com) and the diglycidyl ester of the linoleic acid dimer **31** (Shell Epon® 871), whereas the epoxy novolac **32** (Cardolite NC 547®) carries long aliphatic chains acting as an internal plasticizer. The most promising chemistry for the production of high-quality flexible adhesives

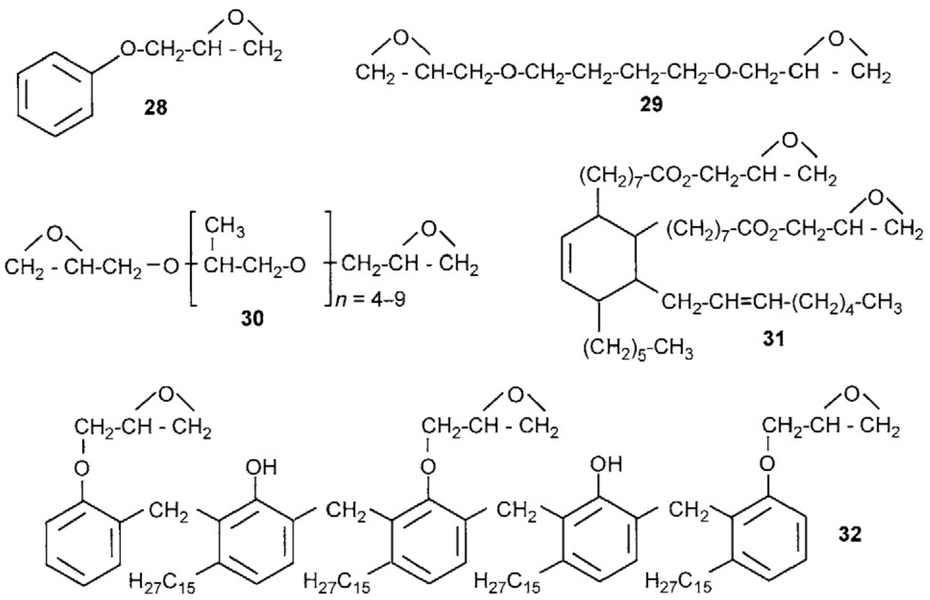

Figure 12.4 Chemical formulae of epoxy reactive diluents such as phenylglycidyl ether **28** and butanediol diglycidylether **29**; and flexible epoxy resins including polyoxypropylene-α,ω-diglycidyl ether **30**, diglycidyl ester of linoleic acid dimer **31**, and epoxy novolac resin of pentadecylphenol **32**.

would be the combination of epoxies and silicones that are thermally stable up to 250 °C. At the moment, these materials are extensively investigated as encapsulants for large-size integrated circuits that are more sensitive than small dice to the thermal stresses generated during the curing process.

12.1.2.2 Reactive and Nonreactive Solvents

The one-part and two-part commercially available conductive adhesives are often claimed as solventless formulations. In fact, many of them contain from 5 to 10% by weight of organic solvents mainly used to lower the viscosity. The hydroxylterminated glycol ethers and esters may possibly react with the epoxy groups during the curing process, whereas nonfunctional glycol derivatives cannot. These organic compounds are commonly introduced into adhesive formulations, in particular 2-butoxyethanol (butylcellosolve), 2-butoxyethyl acetate (butylcellosolve acetate), diethyleneglycol monobutylether (butyl carbitol), diethyleneglycol monoethylether acetate (ethyl carbitol acetate), and γ-butyrolactone.

12.1.2.3 Curing Agents

The reactivity of epoxy groups toward both nucleophilic and electrophilic species is explained by the release of the ring strain inherent to the three-membered oxirane group. Both types of curing agents can take the form of catalysts, such as Lewis acids and tertiary amines, or coreactants, such as primary amines, thiols, carboxylic acids, dicarboxylic acid anhydrides, and phenols. When the curing agents are catalysts, they initiate the homopolymerization of the oxirane rings, so that the properties of the cured adhesive depend primarily on the chemical structure of the epoxy resin. The catalyst activity plays a role in the extent of polymerization that can be achieved under given cure conditions. In contrast, the coreactants, containing mobile hydrogen atoms, offer greater latitude because they become an integral part of the final macromolecular network. The chemical and physical properties of the cross-linked epoxy matrix are equally influenced by the epoxy base and the coreactant. Thus, epoxy adhesives can be produced with virtually any property, ranging from high-glass transition temperature brittle thermosets to low-modulus flexible materials.

As a general guideline, one-part adhesives stable at room temperature utilize latent coreactants or protected catalysts, whereas two-part epoxy compositions contain highly reactive curing agents or catalysts. The frozen one-part adhesives are mainly formulated with catalytic systems. Bauer summarized as follows the curing agents commonly used in electronic applications: dicyandiamide for PCBs and one-part adhesives, aliphatic polyamines for two-part die attach adhesives, anhydrides for glob top encapsulation and die attachment, epoxy novolac resins for transfer molding compounds, and conductive adhesives.[8] Because of the overwhelming number of curing agents developed over the years, the following discussion is limited to the chemical compounds employed to formulate insulating and conductive adhesives. Figure 12.5 shows the chemical formulae of the catalysts and coreactants commonly used to manufacture these adhesives.

Examples of catalysts are shown on the first line, whereas all the other compounds are coreactants including dicyandiamide, ureas, imidazoles, aliphatic polyamines, cycloaliphatic polyamides, and cycloaliphatic dicarboxylic acid anhydrides. As all the corresponding reaction mechanisms have been previously disclosed in detail,[4] the following presentation is limited to the initial reaction steps leading to the active species involved in the polymerization or polycondensation processes. These primary attacks are enlightened in Fig. 12.6, which displays only one epoxy group reacting with catalysts or coreactants.

Polymerization of epoxy groups can be initiated by Lewis or Brönsted acids that lead to a cationic opening and polymerization of the oxirane rings. For example, the chemical complex **33** of boron trifluoride (Fig. 12.5) was used in the past as the catalyst of many one-part adhesive compositions. This acid–base complex is stable at room temperature but rapidly dissociates on heating, generating free boron trifluoride, which induces the polymerization of epoxy groups. In Fig. 12.6, path A, BF_3 is represented as the electrophilic center El^+ that transfers the positive charge to the oxygen atom of the oxirane ring. Subsequent polymerization is initiated by cationic attack of other epoxy groups by the active species **55**. One drawback of this process is the corrosivity of boron trifluoride. Aging tests in humid conditions have demonstrated the destruction of aluminum conductors by this strong acid. The less aggressive trifluoromethanesulfonic acid (CF_3SO_3H), a strong Brönsted acid, is used in the form of an amine salt

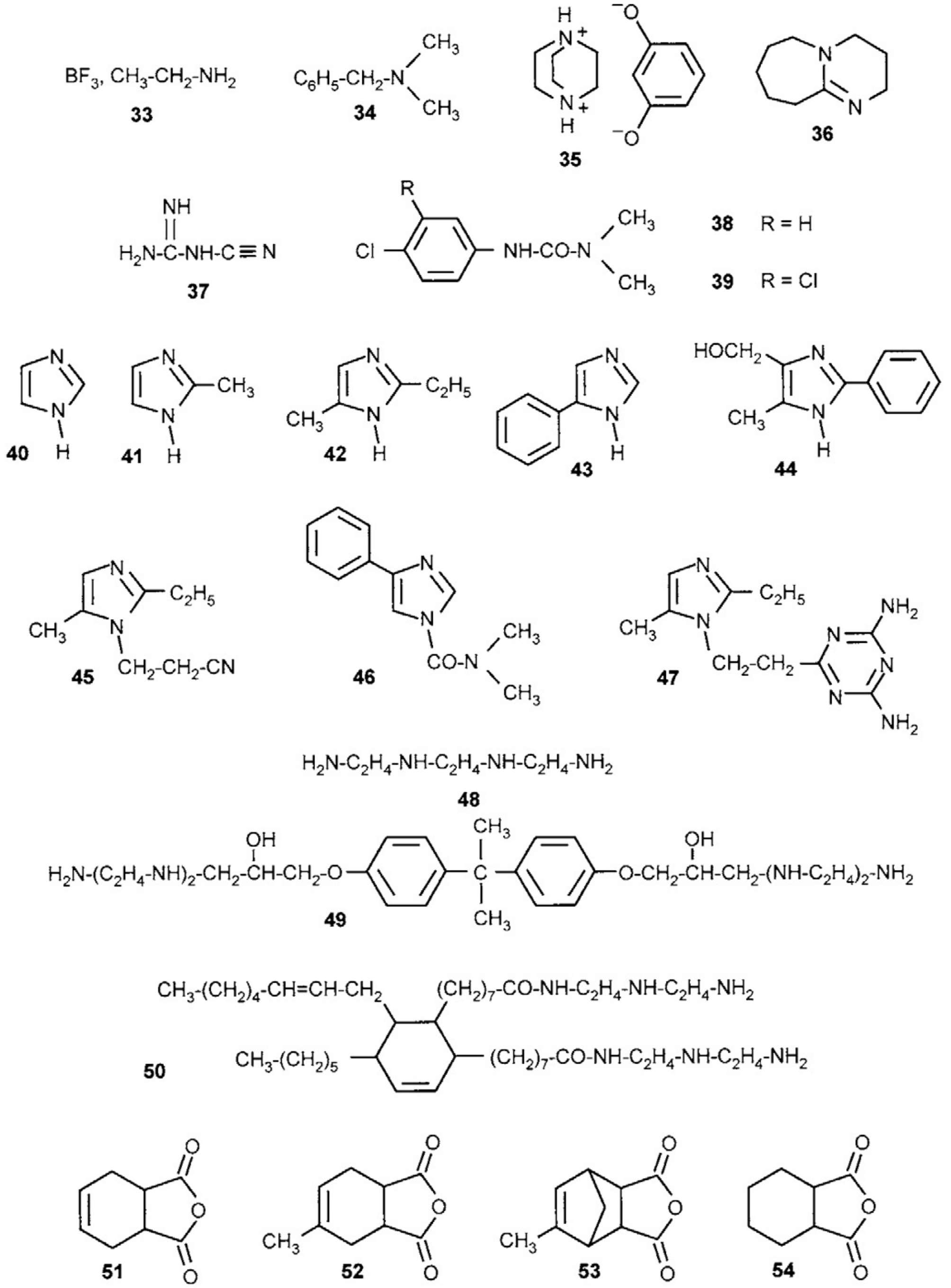

Figure 12.5 Chemical formulae of the catalysts and coreactants used as curing agents of epoxy resins: electrophilic **33** and nucleophilic **34**–**36** catalysts, dicyandiamide **37**, ureas **38** and **39**, imidazoles **40**–**47**, aliphatic amines **48** and **49**, polyamide **50**, and cycloaliphatic anhydrides **51**–**54**.

as a rapid curing agent at relatively low temperatures (5 min at 120 °C).[9]

As represented in Fig. 12.6, path B, catalytic polymerization of epoxies is also initiated by nucleophiles Nu^-, including inorganic and organic bases such as tertiary amines, quaternary ammonium hydroxides, and some heterocyclic compounds. Reaction propagation develops from the initially formed oxygen anion **56**. These catalysts being highly reactive at ambient temperature, they are generally used as curing accelerators combined with less active hardeners. Thus, the reactions of epoxies with

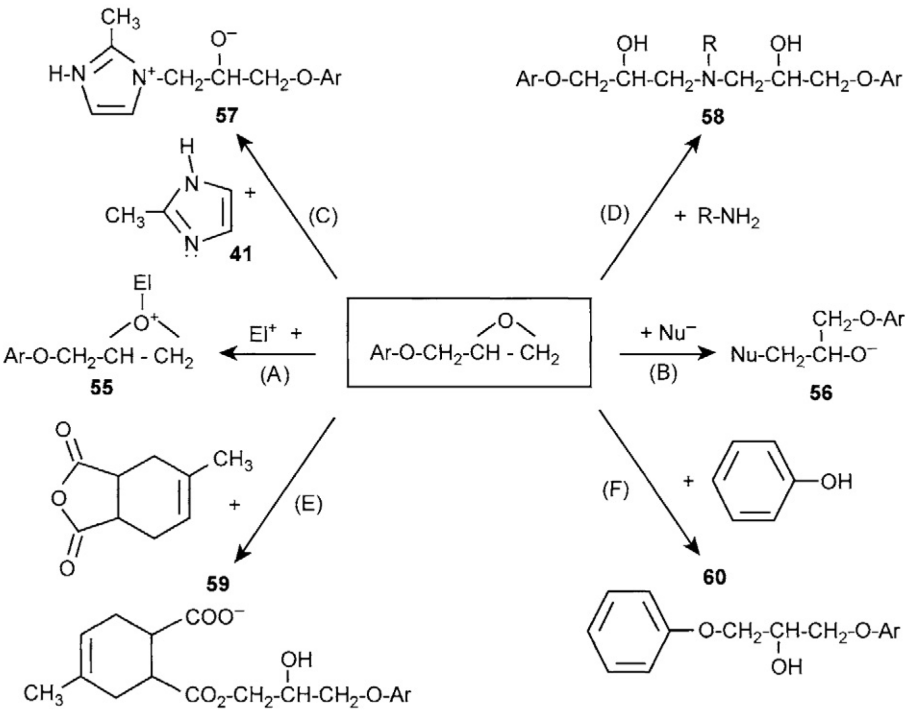

Figure 12.6 First step (initiation) of epoxy ring polymerization using (A) electrophilic, El+, catalysts; (B) nucleophilic, Nu−, catalysts; or coreactants including (C) imidazoles, (D) aliphatic amines, (E) cycloaliphatic anhydrides, and (F) phenols.

phenols, carboxylic acids, and anhydrides are often accelerated by small amounts of benzyldimethylamine **34**, 1,4-diaza-bicyclo[2,2,2]octane (DBO) **35**, represented as its resorcinol salt, and other compounds such as 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) **36**, tris-(dimethyl-aminomethyl)phenol, or tertiary amines prepared by adding secondary amines to epoxy resins. This latter curing agent would allow a pot life of 5 days at room temperature. To impart some latency to the one-part adhesives, the high reactivity of the tertiary amino groups can be masked by using their amine salts with diphenols such as resorcinol, pyrogallol, or hydroquinone.

The chemical formulae of dicyandiamide **37** and of two ureas: 3-(4-chlorophenyl)-1,1-dimethylurea **38** and 3-(3,4-dichlorophenyl)-1,1-dimethylurea **39**, which are accelerators frequently used in combination with **37**, are drawn in Fig. 12.5. The latency of these compounds is largely due to their insolubility in the epoxy resins at 20 °C. On heating to temperatures higher than 120 °C, dicyandiamide becomes soluble and reacts slowly with the epoxy groups, so that the full cure requires temperatures around 170−180 °C. The reaction is accelerated by adding ureas **38** and **39**, benzyldimethylamine **34**, or various imidazoles. The mechanism of addition of dicyandiamide to an epoxy group is complex and depends on the absence or presence of a tertiary base. In the former case, Zahir[10] proposed a reaction sequence with the formation of an adduct leading to cyanamide and different oxazoline derivatives. Adhesive compositions based on dicyandiamide have an extended pot life that can be as long as 1 year at ambient temperature. A disadvantage of dicyandiamide, which has been observed during outgassing tests in hermetic packages, is the continuous formation of ammonia (NH_3).

Despite the adverse effect of ammonia release, the patent literature offers many examples of one-part conductive adhesives formulated with dicyandiamide alone or mixed with 3-(3,4-dichlorophenyl)-1,1-dimethylurea **39** as cross-linking systems. Depending on the epoxy base, the amount of dicyandiamide, and cocatalyst, the pot life is at least 6 months at 25 °C. Typical cure schedules range between 30 min at 170 °C and 90 min at 120 °C, yielding a volume resistivity of 5×10^{-4} Ω cm, and adhesive strengths in the range 5.9−19.6 MPa at 20 °C. Some patents report that 2-phenyl-4-methyl-5-(hydroxymethyl)-imidazole **44** can also be used to increase the reactivity of dicyandiamide. The combination of dicyandiamide and imidazole **44** produces either a heat-resistant adhesive with a mixture of the tetra-epoxy **23** and 4-vinyl-1-cyclohexene dioxide **15** or a fast cure formulation based on bisphenol-F epoxy resins. These adhesives are solventless one-part compositions that can be cured for 1 min at 180 °C, giving device-shear strengths of 19.8 and 6.7 MPa at 25 and 350 °C, respectively.

Imidazoles are strong organic bases and unusually good nucleophiles, these properties being explained by the resonance interactions, which increase the basicity of the 3-nitrogen atom. Imidazole chemistry is so versatile that most modern epoxy adhesives used in electronics contain an imidazole either as the unique curing agent or as an accelerator. Figure 12.5 shows the formulae of the imidazoles that have been cited in recent patents reporting the fabrication of adhesive compositions. Imidazole **40** was early utilized in one-part adhesive formulations, because it presents some latency because of its insolubility at ambient temperature in epoxy resins.

The mechanism of homopolymerization of epoxy resins initiated by imidazoles is now well established. A first nucleophilic attack by the unsubstituted nitrogen atom of the imidazole ring forms zwitterion **57** (Fig. 12.6, path C), which rearranges to an adduct by internal proton transfer. This is followed by a nucleophilic reaction of the newly formed unsubstituted nitrogen, opening a second epoxy group to give the 2:1 adduct that promotes the anionic polymerization of the epoxy. Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) have shown that two types of etherification reactions occur with the imidazoles unsubstituted at the 1-nitrogen atom.[11] When an epoxy resin (DGEBA) is cured with variable amounts of 2-ethyl-4-methylimidazole **42**, the N—H stretching vibration disappears within the first 10 min of cure. The decrease in epoxy concentration as a function of time indicates that this step corresponds to the formation of both the 1:1 and 2:1 adducts. The generation of the adducts is characterized by a slow initial rate of epoxy conversion followed by a sudden increase corresponding to the initiation of the polyetherification reaction by the oxygen anion.

Compounds such as 2-methylimidazole **41**, 2-undecylimidazole, and 2-ethyl-4-methylimidazole **42** are highly reactive materials. It has been stated that soluble imidazoles are too reactive to permit their use in one-part adhesive systems stable at ambient temperature.[12] Among the other compounds, the less reactive 4-phenylimidazole **43** would be a convenient curing agent at elevated temperature, although the reaction still occurs over a few days of storage at 25 °C. 4-Methyl-2-phenylimidazole is cited in different patents allowing a 3-day pot life at room temperature for silver-filled epoxy resins based on bisphenol-A, bisphenol-F, and phenol novolac hardener. Imidazole **44** mixed with bisphenol-F epoxy resin, an epoxidized phenol novolac, and silver flakes, provides a conductive adhesive that can be cured in 20 s at 300 °C. Die-shear strengths of 15.7 N at 25 °C and 7.1 N at 280 °C have been claimed for compositions comprising imidazole curing agents, liquid cycloaliphatic epoxies, and diglycidyl ether resins.

A method known to slow down the degree of polymerization of epoxies at low temperatures while maintaining a satisfactory reaction rate at elevated temperature is the use of "protected" curing agents. In the case of imidazoles, this goal is achieved by masking the N—H proton. Because of the reversibility of the protection by the cyanoethyl group, 2-ethyl-4-methyl-1-(2-cyanoethyl)imidazole **45** is used in several two-part compositions. One package comprises bisphenol-F epoxy resin and silver flakes, whereas the second package includes imidazole **45,** γ-butyrolactone, and silver flakes. After curing for 15—30 min at either 120 or 150 °C, a shear strength of 9.8 MPa and a volume resistivity of 2.22×10^{-3} Ω cm are achieved. 1-(*N,N*-dimethylcarbamoyl)-4-phenylimidazole **46** is an imidazoleurea exhibiting the stability of the substituted ureas at room temperature. On heating to 175—185 °C, it reacts with the residual hydroxyl functions of the epoxy resins to generate the freed imidazole available as a catalyst. Used in combination with resorcinol diglycidyl ether **19**, an epoxy novolac, and 1,4-butanediol diglycidyl ether **29**, it provides an adhesive curable at 175 °C, exhibiting a volume resistivity of 10^{-4} Ω cm and a T_g in the range 83—93 °C. One-part conductive adhesive with a pot life of 10 days at 25 °C has been prepared by using 2,4-diamino-6-[2-(2-ethyl-4-methyl-1-imidazolyl)ethyl]-1,3,5-triazine **47**.

Amine curing agents include aliphatic amines, polyamide amines of fatty acid dimers and trimers, and aromatic amines. In electronics, epoxy-amine compositions are used to make die attach and surface-mounting adhesives as well as encapsulants for discrete devices. According to Lyons and Dahringer, the first commercial conductive epoxy adhesive, marketed in the early 1960s, was a two-part system using triethylenetetramine **48** as the curing agent.[13] High reactivity, short pot life, moderate T_g, and very good adhesion at ambient temperature characterize the epoxy-amine systems. Aliphatic polyamines such as diethylenetriamine and triethylenetetramine **48** contain five and six active NH bonds that may react by the addition to the oxirane ring (see Fig. 12.6, path D). This means that full cure is achieved with only 12−14 wt% of curing agent. An adhesive composition, prepared with DGEBA resin, phenylglycidyl ether, diethylenetriamine, and 75−90% silver powder, and cured at 80 °C, provides a lap-shear strength of 13.8 MPa and a volume resistivity of $5 \times 10^{-4}\ \Omega$ cm.

The ideal structure of polyamide **50** represents the product obtained by reacting diethylenetriamine with linoleic acid dimer. It can be seen that this compound contains two primary and four secondary amine functions and two amide groups. The commercially available polyamides are in fact mixtures of oligomers that are characterized by their hydrogen equivalent weight. When used in combination with the epoxidized fatty acid dimers such as **31** (Fig. 12.4), the mixing ratio can be varied to achieve the desired balance between flexibility, adhesion, and chemical resistance. A typical formulation curable at room temperature is prepared as follows: a liquid DGEBA resin is mixed with a flexible epoxy resin based on dimer acid (11%), polyamide (89%), 2,4-bis [(dimethylamino)methyl]phenol catalyst, titanium dioxide, Cab-O-Sil thixotropic agent, and carbon black. The gel time is 45 min at 20 °C, but 24 h are required to achieve maximum strength.

Free carboxylic acids are not very popular for electronic applications, but their anhydrides are widely used because of the long pot life that can be achieved. Epoxy resins cured with anhydrides have excellent dielectric properties, high temperature stability, and glass transition temperatures as high as 270−300 °C. The formulae of commercial anhydrides are shown in Fig. 12.5 including tetrahydrophthalic **51**, methyltetrahydrophthalic **52**, methyl-endomethylenetetrahydrophthalic **53**, and hexahydrophthalic **54** anhydrides. The uncatalyzed reaction of carboxylic acid anhydrides with epoxies is initiated by traces of hydroxyl groups (alcohols or water) leading to the formation of an *ortho*-acid-ester or a dicarboxylic acid. The free carboxylic acid group then adds to the oxirane ring to produce a hydroxy-ester **59** (Fig. 12.6, path E) that can react with another anhydride ring, and so on. The reaction is sluggish even at 150−200 °C and the homopolymerization of the epoxy competes with the esterification reaction. The base-catalyzed addition of the anhydrides to the epoxies exhibits a greater selectivity toward polyester formation, even though conflicting mechanisms have been published so far.[14] A typical second-generation two-part epoxy adhesive comprises a liquid DGEBA epoxy loaded with silver flakes for the resin-based component and a coreactant system formed of hexahydrophthalic anhydride **54**, benzyldimethylamine, and silver flakes.[13] The catalyzed epoxy-anhydride system has a pot life of 16−24 h and is cured at 150−180 °C for 2 h.

12.1.3 Epoxy-Phenolic Resins

In the electronic industry, phenols are widely used as coreactants of epoxy novolac resins to encapsulate the integrated circuits. As shown in Fig. 12.6, path F, the uncatalyzed reaction of phenolic compounds with an epoxy proceeds through the nucleophilic addition of the phenolic hydroxyl group to the oxirane ring leading to the hydroxy-ether **60**. The subsequent reaction is the etherification of a second epoxy group by the aliphatic hydroxyl function that generates another hydroxy-ether, and so on. Using model compounds, Schechter and Wynstra[15] indicate that the reaction rate is very slow at temperatures up to 100 °C, whereas at 200 °C, the epoxy disappears at a faster rate than the phenolic hydroxyl functions. In practical applications, the reaction of phenols with epoxies is catalyzed by organic bases or triphenylphosphine [P(C6H5)3] or both.

Three main classes of polyphenols are used to prepare high-performance adhesives and molding materials: phenol novolacs, resols, and poly(*para*-hydroxy-styrene). A few chemical formulae of these polyphenols are shown in Fig. 12.7. The phenol novolac **61**, *ortho*-cresol novolac **62**, and *para*-xylene-modified phenol novolac **63** are prepared by the reaction of phenol and substituted phenols with carbonyl-containing compounds (aldehydes and ketones) in the presence of acid catalysts. The *ortho*−*ortho*-resol of *para*-cresol **64** is an example of a resol that is stable at ambient temperature, produced by reacting formaldehyde with *p*-cresol using carboxylate salts as catalysts. In addition to phenolic hydroxyl groups, resols have highly reactive terminal hydroxymethylene ($-CH_2-OH$) functions. Poly(*para*-hydroxy-styrene) **65** was introduced by Toshiba Chemical Corp. (www.toshiba.com) to prepare flexible adhesives.

Novolac resins are broadly used in electronics because their functionality higher than two increases the cross-linking density and yields cured resins exhibiting enhanced chemical and physical properties. Mixtures of epoxy resins and phenol novolacs **61** are excellent structural adhesives in the aerospace industry. However, the phenolic hydroxyl groups are

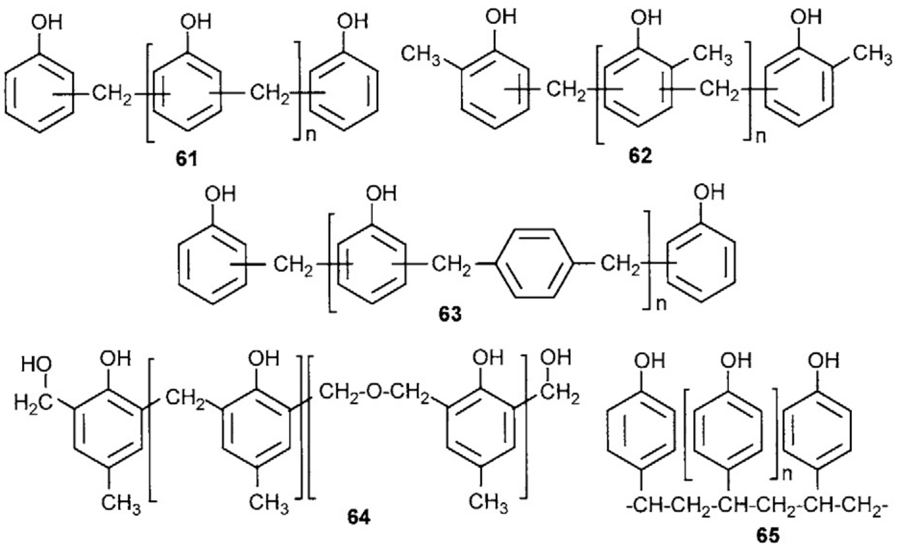

Figure 12.7 Chemical formulae of phenolic resins used to prepare epoxy-phenolic adhesives based on Gunei Kagaku phenol novolac **61**, Dow Chemical OCN *ortho*-cresol novolac **62**, Mitsui Toatsu *para*-xylene-modified phenol novolac **63**, phenolic *ortho*–*ortho*-resol of *para*-cresol **64**, and poly (*para*-hydroxystyrene) **65**.

not very reactive at moderate temperatures and most systems include catalysts or accelerators. Classical adhesive compositions are prepared by mixing a solid epoxy resin, typically an epoxidized phenol novolac resin (60 parts), a phenol novolac resin (40 parts), and a solvent such as 2-butoxyethanol or butylcellosolve acetate, an imidazole catalyst, and silver flakes.

Various curing schedules are reported in the patent literature, the best volume resistivity ($5.7 \times 10^{-5}\ \Omega$ cm) being achieved after curing for 24 h at 120 °C and 5 h at 180 °C. It has been claimed that a die attach adhesive composed of an epoxy-phenol novolac system and a catalyst of the $Ph_4P^+\ BPh_4^-$ complex type provides die-shear strengths of 43 and 9 N at 20 and 350 °C, respectively, after curing for 30 s at 250 °C. Thermally conductive adhesives are also prepared by loading epoxy-phenolic compositions with crystalline silica powder.

Because of their inherently high reactivity, resols generally provide epoxy adhesive compositions with a limited shelf life at ambient temperature. In the coating industry, epoxy-resols combine good heat and moisture resistance along with improved flexibility. A typical adhesive paste contains a phenolic resol (molecular weight, 750 g mol^{-1}), an epoxy resin, phenyl glycidyl ether, and silver flakes.[16] After curing at 170 °C for 20 min, the adhesive affords a die-shear strength of 4 MPa and a volume resistivity of $5 \times 10^{-5}\ \Omega$ cm. Poly(*para*-hydroxystyrene) **65**, commercialized by KYOCERA Chemical Corp. (www.kyocera-chemi.jp/english/index.html) under the trade mark Maruzen® resins, has been employed to prepare either conventional or fast cure conductive adhesives. To enhance the reactivity of the phenolic hydroxyl groups, boron trifluoride–ethylamine complex **33** is used as a catalyst in most formulations and norbornene resins are added to improve the resistance to hydrolysis. Semiconductor devices are bonded to lead frames by using a two-step cure schedule. The assemblies are first heated at 130–170 °C for 20–30 s and then at 300 °C for 30 s. According to the chemical composition, the die-shear strength is in the range 49–62 N at 25 °C and 4.9–7.9 N at 350 °C, whereas the volume resistivity is of the order of $2.1 \times 10^{-4}\ \Omega$ cm.

12.1.4 Epoxy-Silicone Compositions

Multifunctional epoxy resins provide brittle materials, whereas silicones have a high degree of flexibility. The glass transition temperature, Young's modulus, and coefficient of linear thermal expansion (CTE) of epoxy resins are high enough to generate significant mechanical stresses. In contrast, some stress relief is expected for silicone resins, in particular the polydimethylsiloxane series, because of their low modulus and low glass transition temperature. However, silicones exhibit poor adhesive properties and large coefficients of thermal expansion. The incorporation of silicone rubber particles into brittle thermoset networks is commonly used to increase the impact resistance and reduce the crack propagation within the matrix of composite materials. Another approach consists in producing elastomeric particles by a phase segregation during the polymerization process to produce a block copolymer with alternate epoxy hard segments and polysiloxane soft

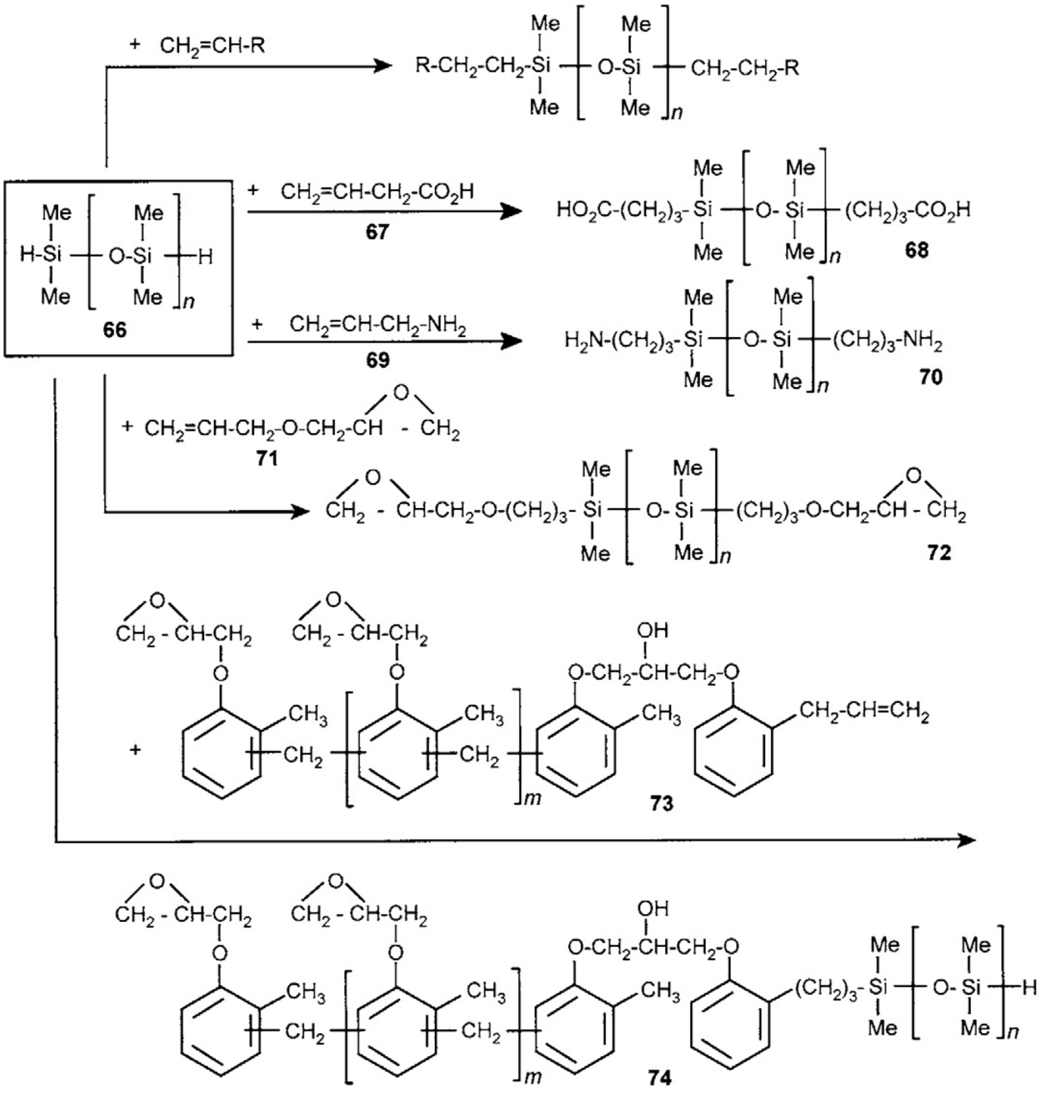

Figure 12.8 Examples of polydimethylsiloxane resins terminated by either oxirane rings **72** or chemical groups containing labile hydrogen atoms, such as carboxylic acid **68** and aliphatic amine **70.** These compounds are synthesized by hydrosilylation of carbon—carbon double bonds using hydrogen-terminated polydimethylsiloxanes **66** as starting reactant. This reaction is also employed to produce epoxy-silicone **74** from allyl-terminated epoxy resin **73**.

segments. This implies a judicious control over the polymerization conditions to achieve phase separation. Figure 12.8 displays some of the chemical reactions that have been studied to produce polydimethylsiloxanes terminated with either reactive groups or oxirane rings, most of these siloxane telechelic oligomers being based on the commercially available α,ω-dihydropolydimethylsiloxane **66**.

All the difunctional compounds are prepared by the hydrosilylation reaction, which is a selective addition of the Si—H terminal groups to carbon—carbon double bonds in the presence of noble metal catalysts such as chloroplatinic acid. This general reaction is shown at the first line of Fig. 12.8. The addition of hydrogen-terminated silane **66** to protected 2-propenoic acid **67**, 2-propenylamine **69**, and allyl glycidyl ether **71** leads to α,ω-bis(3-carboxypropyl) polydimethylsiloxane **68**, α,ω-bis(3-aminopropyl) polydimethylsiloxane **70**, and α,ω-bis[(2,3-epoxypropyloxy)propyl]polydimethylsiloxane **72**, respectively. It has been shown that tris(triphenylphosphine) rhodium chloride and polymer-bound Wilkinson's catalysts are able to promote selectively the hydrosilylation reaction of allyl glycidyl ether **71** without any side reaction with the oxirane ring.[17] The other approach illustrated in Fig. 12.8 is the "sea—island" concept developed to reduce the stress of epoxidized *ortho*-cresol novolacs for the encapsulation of electronic devices.[18] Islands of silicone rubber particles are dispersed in a sea of uncured epoxy matrix. In the first reaction step, 2-(2-propenyl)phenol is allowed to react with an epoxy *ortho*-cresol novolac to prepare the partially functionalized compound **73** containing both oxirane rings and unsaturated allyl substituents. Hydrosilylation of this "macromonomer" is then performed with a series of hydrogen-terminated polydimethylsiloxanes **66** with average molecular weights of $4 \times 10^2 - 6.2 \times 10^4$ g mol^{-1}. Polydimethylsiloxane carrying either lateral hydrogen atoms on the main chain or both terminal and lateral hydrogen atoms can be used as well. Because of the incompatibility between the epoxy novolac and the silicone phases, the epoxy-silicone compound **74** is an epoxy resin containing about 10 wt% of homogeneously dispersed silicone rubber particles.

12.1.5 Silicone Resins

Silicon-containing organic polymers are used to formulate adhesive compositions with low elastic modulus and high elongation at break. The main chain of polydimethylsiloxane is made of silicon−oxygen bonds with methyl groups stemming from the silicon atoms. According to their molecular weight, these polymers are either liquids, greases, rubbers, or hard solids with a glass transition temperature of −123 °C. They have reasonably good thermal resistance but poor adhesive properties. Commercial silicones are available either as one-part or two-part systems that can be cured at room temperature (RTV-resins) or on heating to 160−180 °C depending on the monomer structures. Figure 12.9 illustrates one of the different RTV-silicone cure process using methoxysilyl-terminated polydimethylsiloxane **75** and methyltrimethoxysilane **76**.

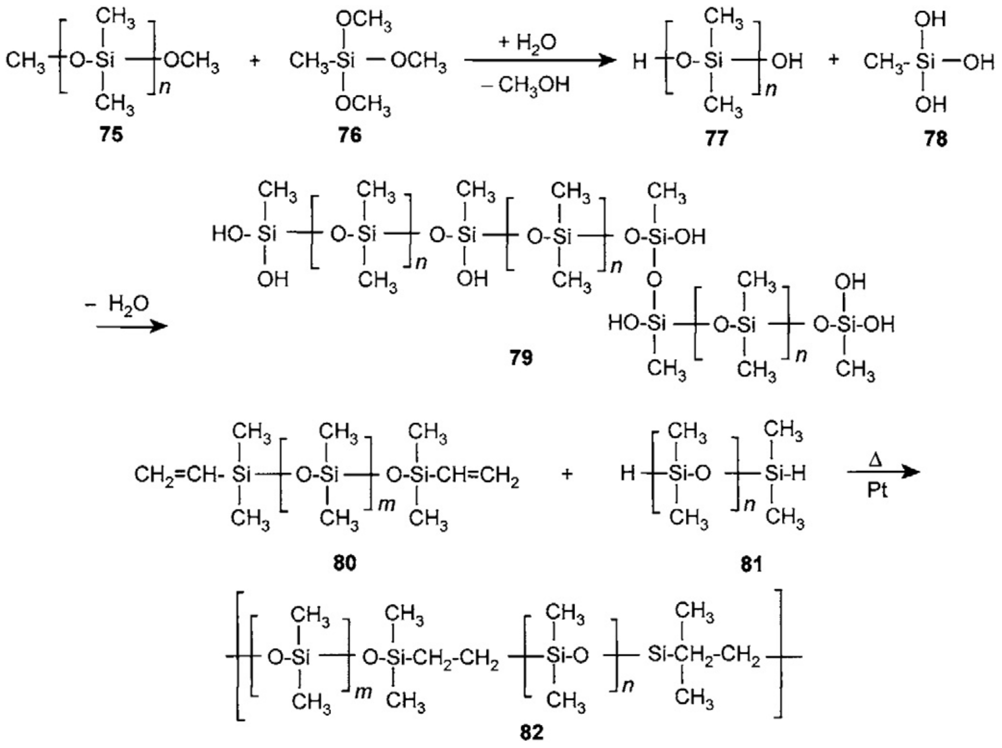

Figure 12.9 Formation of linear and cross-linked polydimethylsiloxane networks. Room temperature vulcanization (RTV) is performed by reacting methoxysilyl-terminated polymer **75** and methyltrimethoxysilane **76**. Hydrolysis produces transient silanols **77** and **78** whose dehydration yields silicone precursor **79**. Two-part systems are based on the platinum-catalyzed addition reaction between vinyl-terminated polysiloxane **80** and polydimethylsiloxane carrying either only terminal **81** or multiple silane (Si−H) pendent groups. Silicone main chains of the resulting polymer **82** are linked through silicon−carbon bonds.

These siloxanes are easily hydrolyzed by ambient humidity and water bound to the substrates to generate transient silanols **77** and **78**. Subsequent dehydration initially provides a precursor **79** of cross-linked polydimethylsiloxane network, which is formed by further condensation of the silanol groups. With many variants, this process constitutes the base of the RTV silicones that are mainly used as protection shields in the glob top encapsulation process. Low-stress conductive adhesives have been prepared by the condensation reaction of ethylphenylsilanediol, 1,4-phenylenebis(dimethylsilanol), and trimethylsilyl-terminated polydiethylsiloxane. When loaded with carbon particles and cured at 180 °C, this composition exhibits a volume resistivity of 1.2×10^{-3} Ω cm and a thermal conductivity of $2.1 \text{ W m}^{-1} \text{ K}^{-1}$.

Hydrosilylation in the presence of platinum catalysts is used to prepare heat-curable silicone adhesives and encapsulants. Polydimethylsiloxanes carrying terminal and eventually side vinyl groups **80** are blended with polymers containing silane (Si−H) linkages **81** and chloroplatinic acid. On heating, addition of Si−H to vinyl unsaturations provides interchain connections by the formation of silicon−carbon bonds leading to polymer **82**. Infrared spectroscopy (IR) and microdielectrometry show that complete curing is achieved after 30 min at 175 °C.[19] This technique has been used to prepare thermally conductive adhesives by mixing vinyldimethylsiloxy-terminated poly(methylphenylsiloxane), α,ω-(dihydrosilyl)-polydimethylsiloxane, chloroplatinic acid, 2-(3,4-epoxycyclohexyl)ethyltri-methoxysilane, tetrabutoxytitane, and alumina powder. Electrically conductive adhesives utilizable from −to 180 °C in bonding sensitive electronic components to substrates were also prepared by addition of hydrogen siloxanes to vinyl-terminated siloxanes in the presence of hydrosilylation catalysts.

12.1.6 Cyanate Ester Resins

Cyanate esters are organic compounds containing −OCN groups. Figure 12.10 shows the thermal cyclotrimerization of cyanic acid phenyl ester **83** yielding 2,4,6-triphenoxy-1,3,5-triazine **84**. The commercial cyanate esters **85**−**89** have glass transition temperatures in the range of 190−350 °C.[20] Biscyanates **85** and **86** are crystalline materials melting at 79 and 106 °C, respectively, whereas compound **87** is a liquid with a dynamic viscosity of 100 mPa s, and products **88** and **89** are semisolid waxes.

The trimerization reaction of the polyfunctional cyanates is catalyzed by zinc or manganese octoate, copper carboxylates, and acetylacetonate metal chelates with a synergistic effect when the catalyst is mixed with 4-nonylphenol.[21] The final cure or post-cure temperature depends on the glass transition temperature of the tridimensional network. This means that the semisolid biscyanate **88** is cured at 180−195 °C (T_g 192 °C), whereas the biscyanate **85** is cured at 250−300 °C (T_g 290 °C). However, the maximum cure temperature can be reduced to 120 °C in the former example by adding 6−10% of 4-nonylphenol. When compared with epoxies, cyanate esters have higher glass transition temperatures, better thermal stability, and improved dielectric properties. Cyanate esters have been primarily developed as a substitute for epoxies in the fabrication of multilayer PCBs. They have been more recently incorporated in the formulation of adhesives to attach silicon dice in hermetic and nonhermetic packages.[22] High-modulus materials are intended to be used for die attachment in hermetic packages with temperature exposures up to 370 °C.

Two silver-filled adhesives, Johnson Matthey JM® 7000 and JM® 7800, have respective elastic modulus of 10 and 5.8 GPa, T_g of 250 and 210 °C, thermal conductivity of 1.1 and $1.6 \text{ W m}^{-1} \text{ K}^{-1}$, and volume resistivity of 2×10^{-3} and 5×10^{-5} V cm. According to the manufacturer, the thermal stresses, determined by measuring the radius of curvature of silicon chips, are far from the level of stress where the risk of cracking and delamination increases considerably. In 1994, Johnson Matthey proposed a low-stress cyanate adhesive (JM® 2500) exhibiting a modulus of elasticity of only 0.4 GPa. The low-stress properties of this material were demonstrated by the large radius of curvature (1 m) of a $15 \times 15 \text{ mm}^2$ die bonded to a 0.15-mm-thick lead frame. This value remained constant after 1000 thermal cycles from −65 to 150 °C.

12.1.7 Polyimides

In electronics, polyimides are now extensively used in the form of self-standing films for flexible circuitry, deposited films for interlayer dielectrics, passivation and buffer coatings, molding thermoplastic powders for PCBs, and adhesive pastes or tapes. The basic polyimide chemistry has been adapted to fulfill the specific requirements of these

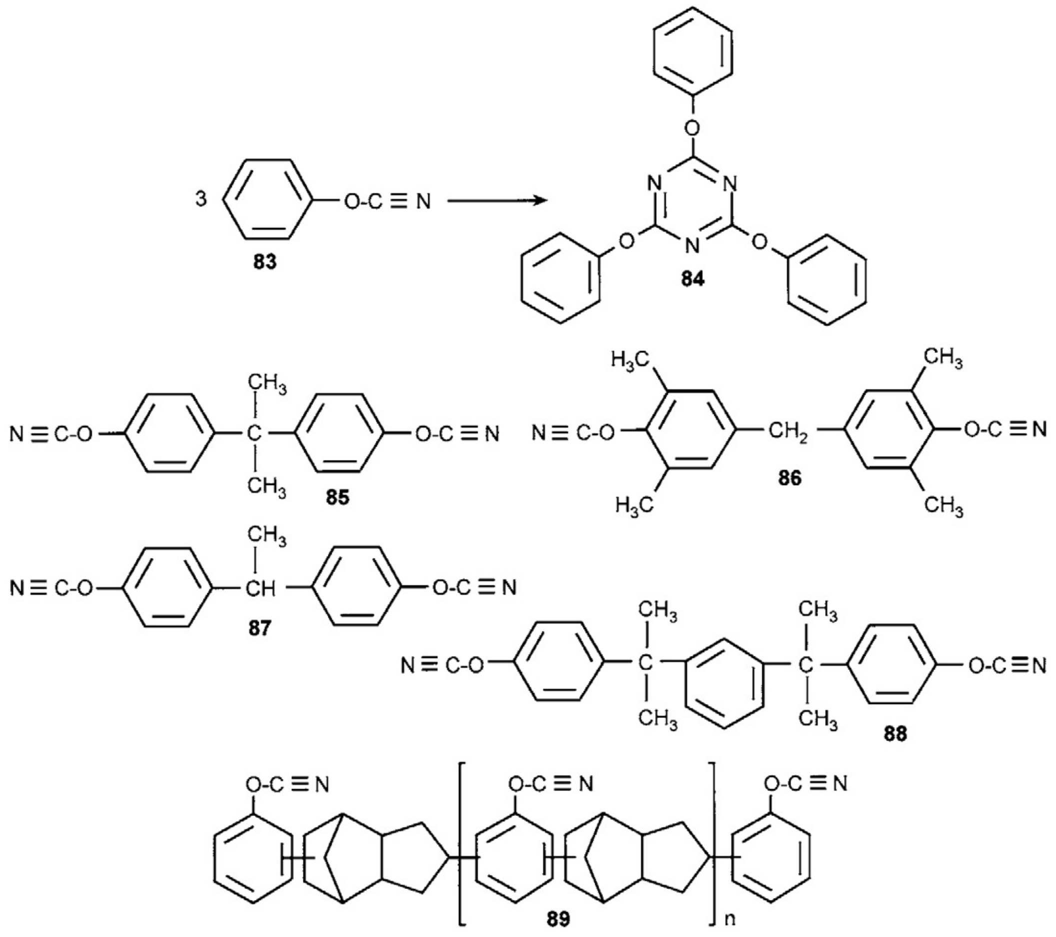

Figure 12.10 Thermal cyclotrimerization of cyanic acid phenyl ester **83** yielding 2,4,6-triphenoxy-1,3,5-triazine **84** and chemical formulae of commercial cyanate esters **85**–**89** used as base resins to produce heat-resistant adhesives and molding materials.

applications. A series of books provides complete information not only on the chemistry of polyimides but also on their utilization in electronics.[4,23,24] The following figures summarize the chemical formulae of the most important categories of polyimide precursors or precyclized polymers that are commonly used in electronics.

12.1.7.1 Polyimide Precursors

In electronics, thin polyimide films are formed on the surface of silicon wafers by depositing a solution of polyamic acid, which is then subjected to a thermal treatment to perform the cyclodehydration reaction yielding ultimately the heterocyclic polymer. Figure 12.11 illustrates this general technique patented by DuPont de Nemours in the early 1960s. Here, 1,2,4,5-benzenetetracarboxylic acid dianhydride (pyromellitic acid dianhydride, PMDA) **90** is opposed to 4,4′-oxybisbenzeneamine (4,4′-oxydianiline, ODA) **91** to produce the intermediate high-molecular-weight linear PMDA–ODA polyamic acid **92**. Solutions of this polymer in *N*-methylpyrrolidone (NMP) are marketed by DuPont as Pyralin® PI 2540 and PI 2545. Once deposited on the substrate, polymer **92** is imidized by a multistage heating ending at 300–400 °C to produce films of PMDA–ODA polyimide **93**.

12.1.7.2 Self-Standing Polyimide Films

Self-standing polyimide films with thicknesses ranging between 25 and 150 μm are commercially available either as nonoriented amorphous materials primarily used as adhesives or oriented films with

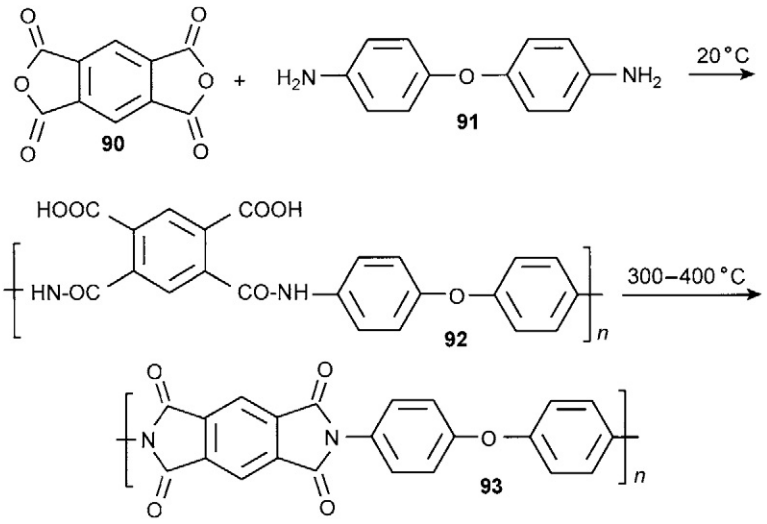

Figure 12.11 Reaction of 1,2,4,5-benzenetetracarboxylic acid dianhydride (PMDA) **90** with 4,4′-oxybisbenzeneamine (ODA) **91** yielding high-molecular-weight polyamic acid **92**, which is then subjected to thermal cyclodehydration to give the PMDA–ODA polyimide **93**.

high mechanical properties. They are manufactured by using two main processes that differ by the reaction temperature. The first technique consists in coating a viscous solution of polyamic acid on the surface of a conveyor belt and then converting it into polyimide. Imidization is accomplished either by heating the film to temperatures in excess of 300 °C or chemically with a mixture of acetic anhydride and triethylamine. This latter process is followed by a heating stage to remove all volatile materials and to complete the formation of imide rings. In the second method, developed by Ube Industries, the reaction is performed in 4-chlorophenol at 160 °C to produce a viscous solution of 95% imidized polymer, which is subsequently deposited on a substrate heated to 100 °C, and then cured at 300 °C.

Figure 12.12 shows the repeating units of commercial polyimide films whose trade marks, commonly accepted acronyms, and mechanical properties including tensile modulus E, tensile strength σ, and elongation at break ε are the following: Kapton® and Apical® **93** (PMDA–ODA), $E = 2.97$ GPa, $\sigma = 173$ MPa, $\varepsilon = 70\%$; Upilex R® **94** (BPDA–ODA), $E = 2.62$ GPa, $\sigma = 172$ MPa, $\varepsilon = 130\%$; Upilex S® **95** (BPDA–PPDA), $E = 6.20$ GPa, $\sigma = 275$ MPa, $\varepsilon = 30\%$; Novax® **96** + **93** (PMDA–2,2′-dimethyl ODA + PMDA–ODA), $E = 6.86$ GPa, $\sigma = 324$ MPa, $\varepsilon = 40\%$; Regulus® **97** (BTDA–3,3′-BP–ODA), $E = 3.04$ GPa, $\sigma = 118$ MPa, $\varepsilon = 110\%$. Glass transition temperatures increase from 285 °C (Upilex R) to 350 °C (Novax), 385 °C (Kapton), and 500 °C (Upilex S). For drawn films, the rigid structure of Upilex S explains the high T_g, a low CTE (8×10^{-6} K^{-1}), a water uptake of 1.2%, and a hygroscopic linear expansion coefficient of 1×10^{-5}% RH^{-1}, where RH is the relative humidity. The other films exhibit a twofold increase for the thermal expansion coefficient and water uptake. All of them have good dielectric properties with permittivity of 3.0–3.5, dissipation factor of 0.001–0.003, dielectric strength of 2.0–2.8 MV cm^{-1}, and volume resistivity of 10^{15}–10^{16} Ω cm.

12.1.7.3 Polyimide Adhesives

Compared with epoxy adhesives, polyimides share a very small part of the global market, limited to military, aerospace, and geothermal applications requiring long-term stability at elevated temperatures. Owing to their aromatic heterocyclic structure, virtually all polyimides are stable at 300 °C. When loaded with inorganic particles such as alumina, silica, silicon nitride, or aluminum, the thermal stability is still better. By contrast, some metals used in the composition of conductive adhesives, in particular silver and nickel, dramatically decrease the thermal resistance. This means that the adhesive strength of most polyimides is excellent at 200 °C,

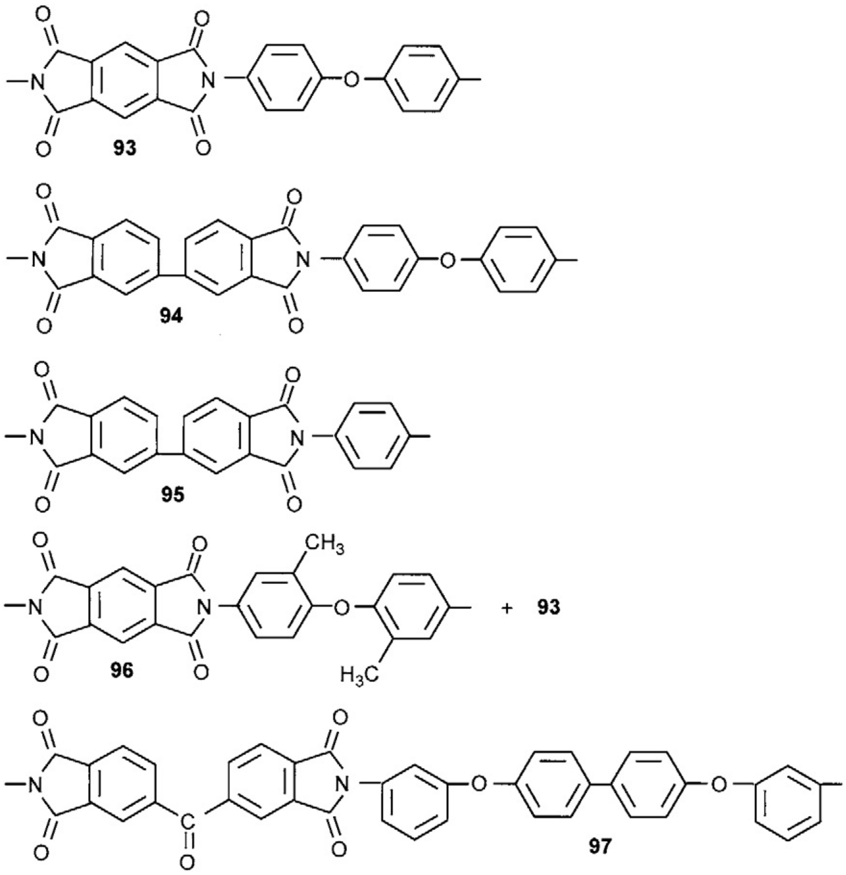

Figure 12.12 Repeating units of commercial polyimide films: Kapton® and Apical® **93**, Upilex R® **94**, Upilex S® **95**, Novax® **96** + **93**, and Regulus® **97**.

good at 250 °C, but limited to short-term uses at 300 °C. Information retrieval indicates that, for the past three decades, only three series of conductive adhesives have been developed and manufactured. The open market has been covered by the polyimide precursor **99** as shown in Fig. 12.13.

A marginal production is based on the acetylene-terminated oligoimides, and a proprietary composition has been used at National Semiconductors.[25] In this latter example, the die attach material is prepared from a PMDA–ODA polyamic acid solution in NMP (DuPont PI 2561) mixed with γ-aminopropyltriethoxysilane and loaded with silver flakes. The adhesive composition is used to bond semiconductor dice in ceramic packages with a first cure at 125 and 180 °C for 2 h each with a final imidization occurring under vacuum when the ceramic lid is sealed with a glass frit at 400–450 °C.

For die attachment, polyimide adhesives have reached a peak and now the market is progressively slowing down. However, for other applications, there is a trend in the direction of thermoplastic polyimide films that can be used as interlayer adhesives. Flexible circuits and MCMs seem to be the main target for these materials. In the polyimide chemistry, high plasticity is obtained by introducing either molecular symmetry disruption or flexible links, in particular ether bridges. In 1974, General Electric

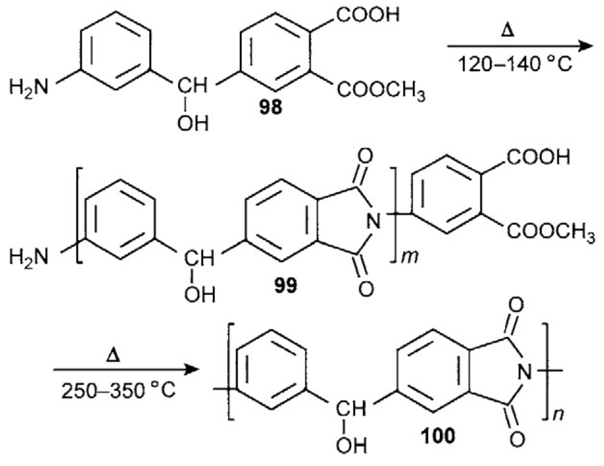

Figure 12.13 Polycondensation of self-condensable monomer **98** providing low-molecular-weight oligomer **99**, which, on heating at high temperature, gives high-molecular-weight polyimide **100**.

(GE; www.ge.com) patented both the synthesis of a new dianhydride with two ether-linking units and its use to produce poly(ether-imides). The production process, chemical, mechanical, and electrical properties of Ultem® 1000 (www.sabic-ip.com) have been recently reviewed.[26] Research at Occidental Chemical (www.oxychem.com) has focused on the synthesis of 4,4′-oxybis(1,2-benzenedicarboxylic acid) dianhydride (OPDA, **103**) and on the polyimides prepared from this compound and various aromatic diamines.[27] For the past 15 years new poly (ether-imides) have been proposed as thermoplastic materials to produce adhesives, self-standing films, and interlayer dielectrics. Chemical formulae of typical ether-linked aromatic diamines are illustrated in Fig. 12.14.

The initial goal has been the production of melt-processable polyimides without taking into account the enhanced solubility provided by two oxygen atoms and other flexible bonds. In electronics, poly (ether-imides) are extensively studied as interlayer dielectrics for MCMs in which electrical conductors are grown by electroless plating. Another important application is the fabrication of adhesive layers for flexible circuits and TAB laminates. The patent literature has been previously reviewed,[23,24] so only a brief information is given hereafter. A thermoplastic polypyromellitimide has been synthesized by reacting PMDA **90** with 3,3′-[1,3-phenylenebis-(oxy)]bisbenze-neamine **105** alone or combined with ODA **91** or 1,3-benzenediamine. The homopolymer, with inherent viscosity 0.66 dL g^{-1}, has crystalline

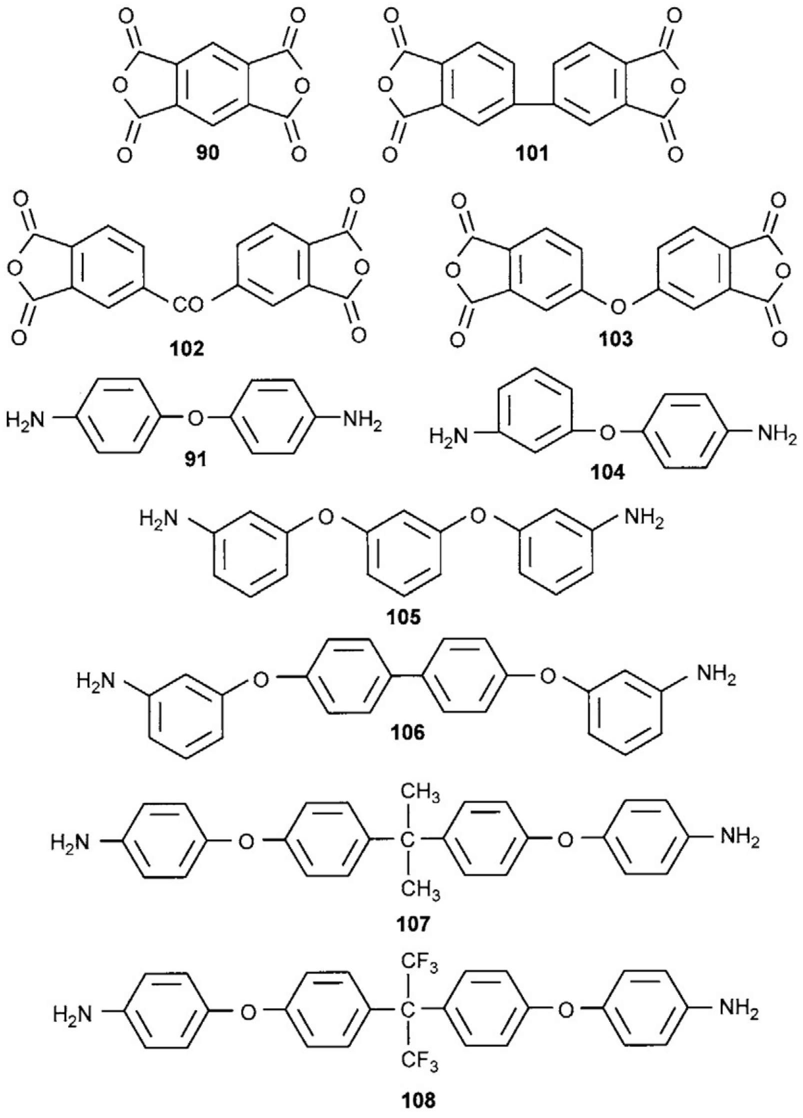

Figure 12.14 Chemical formulae of the dianhydrides and diamines used to synthesize thermoplastic adhesive films of the poly(ether-imide) series.

melting temperature 307 °C and glass transition temperature 218 °C, similar to that of Ultem® 1000. 3,3′-[[1,1′-biphenyl]-4,4′-diylbis(oxy)]bisbenzeneamine **106** was used to develop a series of polyimides commercialized by Mitsui Toatsu under the trade marks Aurum® for molding resins and Regulus for self-standing films. The polyamic acid prepared from dianhydride OPDA **103** and diamine **105,** mixed with aluminum powder, has been proposed as an adhesive for sealing ceramic packages. Polymerization of diamine **105** and 4,4′-[(1-methylethylidene) bis(4,1-phenyleneoxy)]bisbenzeneamine **107** with BTDA **102** and OPDA **103** gives polyimide films for bonding Upilex® S tapes (www.ube.com) to copper foils, whereas the combination of BPDA **101** and diamine **105** provides an adhesive for bonding Upilex to Upilex with peel strength of 2.94 kN m^{-1}.

12.2 Electrical and Thermal Conductivities

12.2.1 Inorganic Fillers

Conductive adhesives are prepared by loading organic resins with small particles of inorganic fillers that are generally metals, metal oxides, and metal nitrides. Silver is the metal of choice for the manufacture of electrically conductive adhesives. The fabrication and characterization of silver flakes have been previously reported.[4] It is worth noting that the manufacturers of conductive adhesives try to exceed the percolation threshold with minimum amount of silver flakes. This can be achieved by incorporating flakes with broad particle size distributions (3−10 μm). Nevertheless, stable electrical conductivity requires approximately 30% by volume (70−80 wt %) of silver particles. Gold is reserved for military and aerospace applications requiring long-term reliability in severe thermal and aggressive environments. Spherical nickel particles, which are commercially available with tightly controlled diameters up to 50 μm, are mainly used in the fabrication of low-cost anisotropic adhesive films. Copper-filled adhesives do not retain stable electrical conductivity after exposure to elevated temperatures because surface copper oxide is easily formed. Tin and solders have also been proposed to prepare low-cost conductive adhesives. Removable adhesive layers have been experimented by using powdered solders with a solidification temperature and a eutectic melting point higher than the polymer curing temperature but lower than the onset of polymer thermal degradation.

Metal oxides and ceramic precursors are commonly used to enhance the thermal conductivity and decrease the thermal expansion coefficient (CTE) of the organic binder. Fused silicon dioxide and crystalline quartz are mainly employed in the production of plastic encapsulant packages exhibiting CTE values of 2.5×10^{-5} K^{-1}. Most commercial adhesive pastes include a small amount (0.5−2.5 wt %) of fused or colloidal silica as thixotropic agent. Aluminum oxide powders are the predominant materials in the manufacture of low-cost thermally conductive adhesives with a thermal conductivity of approximately 1.5 W m^{-1} K^{-1} at the maximum loading level of 75 wt%. Crystalline boron nitride is an expensive material with a thermal conductivity of 1300 W m^{-1} K^{-1}, but the particles commonly used to produce the adhesive compositions are of pyrolytic quality (30 W m^{-1} K^{-1}). Sintered ceramic sheets of aluminum nitride have a thermal conductivity in the range of 170−220 W m^{-1} K^{-1} and various grades of powdered material are commercialized. The highest thermal conductivity (2000 W m^{-1} K^{-1}) is that of diamond, which was expected to provide the material of choice for high-end applications. It will be seen later that diamond-filled adhesives are not better than pastes loaded with boron or aluminum nitrides.

12.2.2 Electrical Conductivity

ASTM (American Society for Testing Material) designation D257 draws the test methods and procedures to determine the direct current resistance or conductance of insulating materials. The volume resistance R_v between two electrodes in contact with a specimen is directly proportional to the thickness h (cm) and inversely proportional to the area A (cm^2) of the sample according to the equation $R_v = \rho_v (h/A)$, where ρ_v is the volume resistivity expressed in ohm cm (Ω cm). Figure 12.15 shows the methods used to determine the volume resistivity of conductive adhesive films or pastes deposited on the surface of substrates carrying metallic electrodes.

A current of intensity I is applied between two electrodes and the electrical resistance R of the adhesive strip, measured with an ohm-meter, provides the volume resistivity by the relation $\rho_v = Rhw/l$.

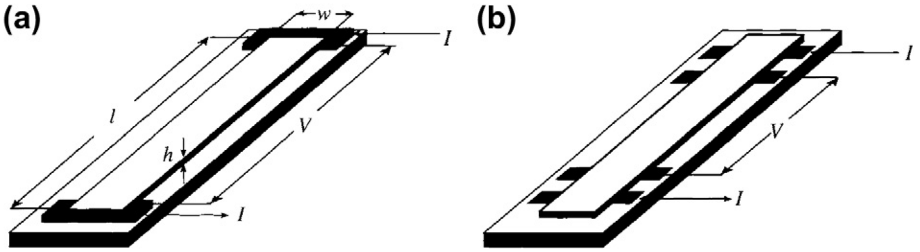

Figure 12.15 Methods used to determine the volume resistivity of conductive adhesive strips with thickness *h*, width *w*, and length *l*, printed on (a) two-point and (b) four-point probes.

Table 12.1 lists the volume resistivity values measured for some metals, eutectic solders, electrically conductive adhesives, oxide-filled resins, and unfilled polymers.

Although all metals have a good electrical conductivity and might be used to make conductive adhesives, most of them readily form an insulating oxide layer by air oxidation in normal ambient conditions. Moreover, in the case of copper, nickel, and silver, the metal oxides are chemically reactive and may catalyze the decomposition of the organic matrix when the adhesive is subjected to isothermal aging or temperature cycling. Silver-filled adhesives are prepared by dispersing silver particles in an insulating polymer matrix to form a metallic network within the organic binder. Electrons can circulate between the two surface boundaries only across the points of contact between adjacent particles, and the current flow through the conductive adhesive layer is generally described by the percolation theory. As regards electrical conduction, the percolation model predicts a critical volume fraction φ_c of the conducting material randomly distributed within the insulating medium, below which the overall conductivity is zero. In other words, for volume loadings φ_f smaller than the percolation threshold, that is for $\varphi_f < \varphi_c$, the probability that a conductive path will cross the thickness of the sample is zero, because the formation of such conductive channels requires uninterrupted contacts between the particles of metallic filler. The critical concentration corresponds to a transition from isolated aggregates of particles to an "infinite" cluster spanning the whole lattice. A continuous electrical path can be produced through either a random network of conductive particles or a segregated system, the former being the most common morphology encountered with metal-filled epoxy or polyimide adhesives. Figure 12.16 illustrates the geometry of the random and segregated structures and the change of the volume resistivity as a function of the percentage by volume of filler.

The conditions necessary for the segregation to appear in a given filler-matrix combination were

Table 12.1 Volume Resistivity, ρ_v, of Metals, Electrically Conductive Adhesives, and Insulating Materials

Materials	ρ_v (Ω cm)	Materials	ρ_v (V cm)
Silver	1.6×10^{-6}	Silver-filled inks	1.0×10^{-4}
Copper	1.7×10^{-6}	Silver-filled polyimides	5.0×10^{-4}
Gold	2.4×10^{-6}	Silver-filled epoxies	1.0×10^{-3}
Aluminum	2.8×10^{-6}	Graphite	1.3×10^{-3}
Molybdenum	5.4×10^{-6}	Low-end silver epoxies	1.0×10^{-2}
Tungsten	5.5×10^{-6}	Graphite-filled coatings	$10–10^{2}$
Nickel	7.8×10^{-6}	Polyamide	10^{13}
Palladium	1.1×10^{-5}	Oxide-filled epoxies	$10^{14}–10^{15}$
Platinum	1.1×10^{-5}	Unfilled epoxies	$10^{14}–10^{15}$
Tin–lead solder	1.5×10^{-5}	Dielectric polymers	$10^{16}–10^{17}$
Au–Si eutectic	2.5×10^{-5}	Poly(tetrafluoroethylene)	10^{18}

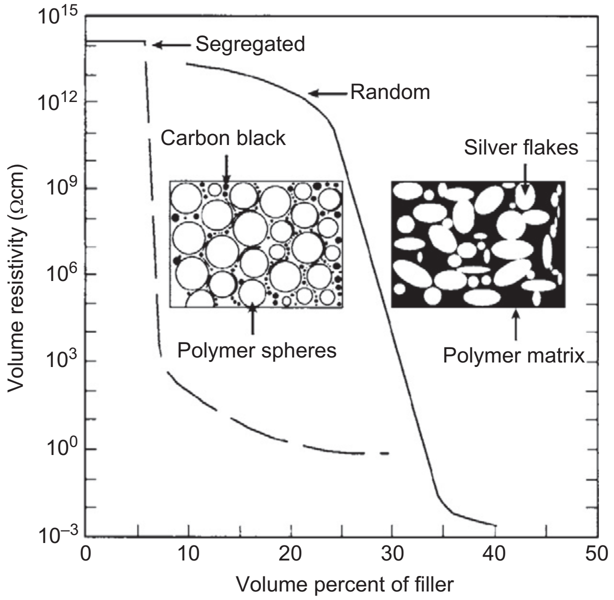

Figure 12.16 Variation of volume resistivity as a function of volume percent of filler for random and segregated conductive adhesive compositions. The exploded designs reflect the arrangements of the conductive particles in the two networks.

reviewed by Kusy,[28] who underlined the importance of the respective radii of the two materials. When spherical particles of polymer (rubber or thermoplastic resin) of radius R_p are mixed with smaller spheres of a conductive filler of diameter R_f, the higher the ratio R_p/R_f the lower the critical volume fraction of filler. This can be explained by the restricted volume that the conductive particles can occupy and by the fact that a partial coverage of the surface of the polymer spheres by a thin layer of conducting material is sufficient to build a conductive path. The particle size ratio R_p/R_f plays a significant role in the case of the segregated model because of the theoretical hyperbolic function $R_p/R_f = f(\varphi_f)$ indicating that the conductivity can be achieved at a normalized filler content of about 0.05 when the ratio R_p/R_f is in the range of 40−80. In contrast, the electrical continuity of the random packing is governed by the probability of forming a continuous network, which is related to the statistical average number of contacts between contiguous particles. This means that the same conductivity level requires 25−40 vol% of randomly distributed conductive particles in most die attach adhesives. The conductivity threshold depends on at least seven factors: the particle size distribution, particle shape, metal penetration, thickness of the oxide layer, electrostatic attraction, viscosity of the organic resin, and polymer bead shear.[29]

Except for some anisotropic adhesive films, the resins used to prepare most silver-epoxy adhesives are low- or medium-viscosity fluids that act as interstitial binding materials preserving the integrity of the closely packed random conductive lattice. An adequate resin viscosity and a clean filler surface are prerequisite to produce homogeneous and highly conductive adhesive pastes. The former condition can be managed to avoid metal sedimentation by adjusting the initial viscosity and eventually adding thixotropic agents. On the other hand, the native oxide layer that forms on the surface of most metals contributes to the reduction of electrical conductivity, and this requires that the electrons be able to jump this insulating gap between the particles. Also, the good wetting properties of epoxy resins and polyimide solutions should provide a 5−10-nm-thick insulating coating of organic material that impedes actual contact between the conductive particles. It has been suggested that metal particles and fibers mainly conduct by electron hopping although physical contact between contiguous particles is also possible in highly loaded adhesives.[30]

Whatever the mode of conduction, the electron mobility augments when the ratio of the surface area to the volume of filler particles is increased. In this regard, the critical volume fraction of filler for electrical continuity decreases when elongated flakes, needlelike, or metallic fibers are used, instead of spherical or cubic particles. However, as the current flow only occurs over the very small area of each point of contact, the volume resistivity of the adhesive composition is higher than that of the metal filler. The following data are typical: silver, $\rho_f = 1.6 \times 10^{-6}\ \Omega$ cm; epoxy resin, $\rho_p = 5 \times 10^{14}\ \Omega$ cm; conductive epoxy loaded with 75 wt% silver flakes, $\rho_a = 1 \times 10^{-3} - 5 \times 10^{-4}\ \Omega$ cm. The curves plotted in Fig. 12.16 show that the composite materials change from insulators to conductors over a narrower range of filler concentration for the segregated systems than for the randomly dispersed materials. This sharp decrease in resistivity reflects the formation of a conductive network that has been treated as a percolation process.

The relationship between the statistical probability P_c of forming a conductive lattice, the critical number of contacts N_c between contiguous particles, and the coordination number Z, which is the maximum number of possible contacts allowed by an ideal crystallographic arrangement, is $N_c = P_c Z$.[31] It has been pointed out that N_c remains virtually constant ($N_c = 1.5$) whatever the geometry of the conductive particles, even for a random dispersion of spheres in the matrix. Obviously, the average number of contacts N per particle is related to the volume fraction of filler by a general function $N = f\ (\varphi_f)$, which depends on Z, P_c, and the maximum packing fraction φ_m. At the critical loading for the formation of a conductive lattice, Bigg shows that Jantzen's model

$$\phi_c = \frac{1}{1 + \frac{Z}{N}\left[\frac{1-\phi_m}{\phi_m}\right]} \tag{12.1}$$

leads to a critical volume fraction $\phi_c = 0.305$ representing the percolation threshold at which the drop in resistivity starts, when the values of the different parameters are $N_c = 1.5$, $Z = 6$, and $\varphi_m = 0.637$.[30] As a general guideline, it can be expected that the value of φ_c is in the range of 0.35–0.38 when the formation of the conductive network is completed and the lowest resistivity is achieved. The different approaches considering the electrical conductivity under qualitative and quantitative aspects have been previously discussed.[4] A percolation threshold at about 25 vol% silver is a typical value for the commercial silver-filled epoxy adhesives, which exhibit a volume resistivity lower than 10^{-3} Ω cm at a silver content of 25–30 vol%.

12.2.3 Thermal Conductivity

For a flat slab specimen of thickness h (m), the thermal conductivity λ (W m^{-1} K^{-1}) is the heat flux per unit of temperature gradient in the direction perpendicular to an isothermal surface and is a material constant defined by the one-dimensional Fourier equation $\lambda = Qh/A(T_1 - T_2)$ where Q is the time rate of the heat flow (W), A the area (m^2) on a selected isothermal surface, and T_1 and T_2 the temperatures of the hot and cold surfaces, respectively, and h the sample thickness (m). Several steady-state or transient methods are available to measure the thermal conductivity of organic and inorganic materials.[4] The guarded-hotplate (ASTM F433), heat-flow (ASTM C518), and Colora thermoconductometer methods are accurate for thick plastic samples with thermal conductivity of 0.1–10 W m^{-1} K^{-1}. In electronics, steady-state techniques suffer from inaccuracies, primarily due to the small thickness of the adhesive layer and to the thermal resistance in the two interfacial regions. Contact and noncontact transient systems have been developed to measure the time–temperature dependence of the heat flow through the adhesive film. Flash radiometry, transient hot wire, and heat-generating test chips are well adapted to measure the bulk thermal conductivity and thermal resistance of thin adhesive layers. The thermal conductivities λ of various metals, oxides, ceramics, and filled polymers are listed in Table 12.2.

The data of this table show that unfilled polymers and plastics have rather low λ values and are very good thermal barriers or insulators. Furthermore, the thermal conductivity of most polymers falls in the tight range indicated for unfilled epoxy resins, about 0.2 W m^{-1} K^{-1}, which is more than three orders of magnitude less than that of silver. Currently, the heat dissipation of advanced CMOS (Complementary Metal-Oxide-Semiconductor or Complementary Metal-Oxide-Silicon) silicon chips approaches 10–30 W cm^{-2} and exceeds 100 W cm^{-2} for the power devices used to control heavy electrical machines. This means that dissipation of heat is a major concern, because semiconductors have a maximum operating temperature. In the case of plastic-encapsulated dice bonded with organic adhesives, the polymers used in intimate contact with the electronic devices require a high thermal conductivity to transfer the heat generated at the junction to the surrounding atmosphere. Polymers filled with metal powders or flakes give adhesives that conduct both electricity and heat with a 10-fold improvement in heat dissipation capabilities. However, the thermal conductivity of silver-filled epoxies and polyimides is still at least one order of magnitude below the values of solder alloys. This means that the thermal resistance $R^{\Theta}{}_{JA}$ from the die surface to the ambient of a silver-filled adhesive is 1–2 °CW^{-1} higher than that of a solder.[32] This is not a major concern in the case of plastic packages, because they already exhibit values of $R^{\Theta}{}_{JA}$ between 30 and 100 °C W^{-1}.

Some applications, however, require adhesives that conduct heat but not electricity to bond power devices to heat sinks, metal substrates, or ceramic plates. The thermal transfer efficiency obviously depends not only on the thermal conductivity of the adhesive but also on the thickness of the bond line, and on the homogeneity of the adhesive layer, which must be free of voids and other defects. The addition

Table 12.2 Thermal Conductivity λ of Metals, Oxides, Ceramics, Conductive Adhesives, and Unfilled Polymers

Materials	λ (W m^{-1} K^{-1})	Materials	λ (W m^{-1} K^{-1})
Diamond	2000	Steel	43–70
Boron nitride	1200	Eutectic solders	34–51
Silver	420–430	Sapphire	35
Copper	380–400	Boron carbide–Al_2O_3	30
Gold	318	Boron nitride pyrolytic	29
Au–Si eutectic	294	Aluminum oxide 94%	28
Beryllium oxide	294	Si_3N_4-Al_2O_3	25
Aluminum	200–237	80% Ag/epoxies	2.5–5.0
Aluminum nitride	170–220	50% Al/epoxies	3
Silicon	149	Silicon dioxide	1.67
Si–SiC	130	75% Al_2O_3/epoxies	1.4–1.7
Silicon carbide	90–120	50% Al_2O_3/epoxies	0.5–0.7
Nickel	91	25% Al_2O_3/epoxies	0.3–0.5
Boron carbide	80	Unfilled epoxies	0.1–0.3
Silver-glass	79	Low-density foams	0.02–0.05
Palladium	72	Air	0.0255

of fillers to polymeric materials increases the thermal conductivity by at least one order of magnitude and, as shown in Table 12.2, the conductivity increases when the volume fraction of filler is increased. No organic material yet exists that combines the high thermal conductivity and the low electrical conduction of diamond, beryllia, and aluminum nitride. The inherent thermal conductivity of the filler is an important parameter, but the particle shape is often more significant in the sense that high aspect ratio particles increase the λ value more effectively than small cubic or spherical particles. For most applications requiring only thermal conductivity, the filler selected should be a good electrical insulator to avoid any ohmic contact. The commonly used fillers that meet these requirements are aluminum oxide or alumina (Al_2O_3), silicon oxide or silica (SiO_2), mica, and beryllium oxide or beryllia (BeO). As an example, the thermal conductivity of an Epon 828 (www.hexion.com) epoxy resin-diethylenetriamine formulation is improved three- to fourfold by adding silica, aluminum, or beryllium oxide fillers, but it is still far below the thermal conductivity of the filler alone.

Many equations have been proposed for the transport properties of two-phase systems and in-depth details of the existing models are discussed elsewhere.[4] Noticing that virtually all the early theories neglected the effects of the particle shape, their packing density, and the possible formation of anisotropic clusters, Lewis and Nielsen modified the Halpin–Tsai equation for the elastic modulus of composite materials by incorporating the maximum volume fraction of filler φ_m while still maintaining a continuous matrix phase.[33,34] Transposed to thermal conductivity Lewis and Nielsen's equation becomes

$$\frac{\lambda_a}{\lambda_p} = \frac{1 + \mathrm{Ab}\phi_f}{1 + \Psi \mathrm{b}\phi_f};\ \mathrm{A} = k_E - 1;\ \mathrm{B} = \frac{\frac{\lambda_f}{\lambda_p} - 1}{\frac{\lambda_f}{\lambda_p} + A};\ \Psi = 1 + \frac{1 - \phi_m}{\phi_m^2}\phi_f \tag{12.2}$$

where λ_a, λ_p, λ_f are, respectively, the thermal conductivities of the adhesive, polymer matrix, and inorganic filler, *A* a function of the generalized Einstein coefficient k_E and depends primarily on the geometry of the dispersed particles and *B* a factor that takes into account the relative conductivity of the two

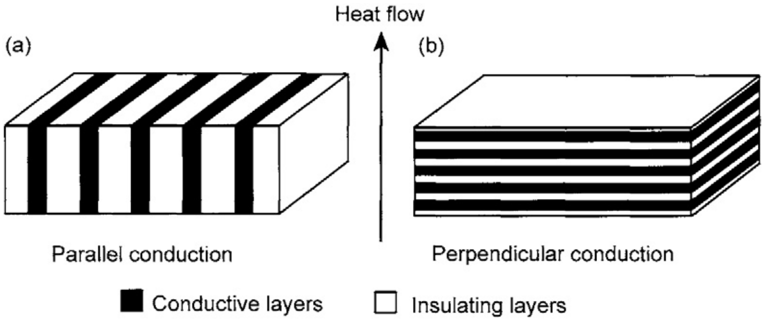

Figure 12.17 A schematic representation of the concept of parallel and perpendicular arrangements as ideal planes of alternate conductive and insulating layers either parallel or perpendicular to the heat flow.

components. The factor Ψ is related to the maximum filler content possible φ_m, and φ_f is the volume fraction of the filler particles in the adhesive. The authors calculated the typical values for the shape factor A and showed that for spherical or cubic particles the volume fraction of filler determines the thermal conductivity of the composite whereas for flakes, rods, or fibers, increasing the aspect ratio of the filler increases the thermal conductivity values of the filled polymer. Nielsen outlines that Eqn (12.2) includes virtually all laws of mixture from the ordinary "rule of mixture" often referred to as the parallel conduction model described by the equation $\lambda_a = \lambda_f\varphi_f + \lambda_p\varphi_p$ to the inverse rule of mixture also known as the perpendicular plate model given by the relation $1/\lambda_a = \varphi_f/\lambda_f + \varphi_f/\lambda_f$. Figure 12.17 sketches the concept of the parallel and perpendicular arrangements as ideal planes of alternating conductive and insulating layers either parallel or perpendicular to the heat flow. These equations represent the upper and lower bounds of the thermal conductivity, respectively.

Being inexpensive and providing an excellent shear strength, alumina is broadly used to formulate thermally conductive adhesives. The best solventless epoxy adhesives contain about 70% of aluminum oxide and give thermal conductivities in the range of 1.4–1.7 W m^{-1} K^{-1}. These values are 8–10 times more than for the unfilled epoxy resins but are still much lower than for pure metals or solders. Nevertheless, Bolger and Morano[35] point out that the heat flow is adequate for bonding most electronic components. For example, an adhesive with a thermal conductivity of 1.6 W m^{-1} K^{-1} and a bond thickness of 75 mm would be able to transfer about 20 W cm^{-2} with a ΔT of 10 °C above the heat sink temperature. In the same conditions, an unfilled epoxy resin, with a heat conductivity of 0.17 Wm^{-1} K^{-1}, would cause a ΔT of almost 100 °C. For at least two decades, alumina and crystalline silica have been used to boost the thermal conductivity of epoxy resins. When highly conductive fillers such as boron nitride, aluminum nitride, and diamond powders become commercially available, these materials have been incorporated in adhesive compositions. The expected target was the attainment of λ_a values of at least 10 W m^{-1} K^{-1}, if not better. Such high values have been claimed for diamond-filled adhesives[36] but they remain currently questionable with regard to the experimental results summarized in the graph of Fig. 12.18.

Curves of Fig. 12.18 compare the data published for (a) boron nitride,[37,38] (b) aluminum, (c) diamond,[37,39,40] (d) aluminum nitride,[37–42] and (e) crystalline silica. It can be seen that, at 45 vol%, the maximum thermal conductivity achieved with diamond powder is 1.5 Wm^{-1} K^{-1}, whereas crystalline boron nitride at 35 vol% affords 2.0 W m^{-1} K^{-1}. The thermal conductivity of silver-filled adhesives was studied by using silicon test chips attached to copper and molybdenum substrates.[43] The authors outline the importance of the shape factor A, related to the aspect ratio of the particles, to achieve the highest level of thermal conductivity. Another study reports the variation of the effective thermal resistance, between a test chip and the chip carrier, in relation to the volume fraction of silver and the thickness of the bond layer.[44] The ultimate value of bulk thermal conductivity is 2 W m^{-1} K^{-1} at 25 vol% silver. However, the effective thermal conductivity, calculated from the thermal resistance measurements, is only one fifth of the bulk value when the silicon chip is bonded to a copper substrate.

Another work provides numerical examples using epoxy and silicone resins with thermal conductivity

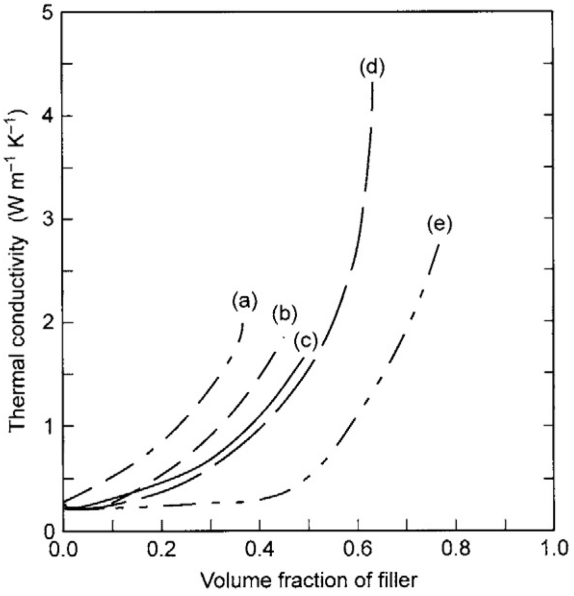

Figure 12.18 Comparison of the thermal conductivity data published in the literature: (a) adhesives filled with boron nitride,[37,38] (b) aluminum, (c) diamond,[37,39,40] (d) aluminum nitride,[37–42] and (e) crystalline silica.

0.15–0.2 W m^{-1} K^{-1}.[45] The addition of 0.25 volume fraction of silver to these resins results in an increase of the bulk thermal conductivity up to 2.46 and 1.86 W m^{-1} K^{-1} for the epoxy and silicone adhesives, respectively. In contrast, the normalized thermal resistance declines from 1.00 to 0.52 cm^2 KW^{-1} for the epoxy but increases from 1.00 to 1.01 cm^2 KW^{-1} for the silicone. These calculated data are confirmed by a measurement of the thermal resistance of silver-filled epoxy adhesives showing that the initial thermal resistance of the unfilled resin is lower than that of many of the silver filled materials. There seems to be an optimum volume fraction of approximately 0.15 corresponding to a minimum thermal resistance lower than 1 cm^2 KW^{-1}. Somewhat better values were obtained with two commercial adhesives with thermal conductivities of 3.4 and 1.6 Wm^{-1} K^{-1}, resulting in thermal resistances of 0.75 and 0.95 cm^2 KW^{-1}.

The conclusion that can be drawn from these experiments is that the use of highly priced fillers such as diamond powder does not improve the thermal conductivity better than less expensive materials such as aluminum nitride, boron nitride, boron carbide, or silicon carbide. Within certain limits, the higher the λ value of the filler particles, the higher the thermal conductivity of the adhesives with respect to the λ_f/λ_p ratio that exhibits a favorable optimized value at about 100. This means that fillers with a thermal conductivity in the range of 20–50 W m^{-1} K^{-1} are particularly suitable for the preparation of good thermally conductive adhesives. The results of experiments performed by loading an epoxy resin with silver flakes, aluminum spheres, diamond powder, and alumina particles help to clarify the actual thermal conductivity achievable with adhesive films.[46] The thermal conductivity measurements in decreasing order are 3.8, 2.6, 2.4, and 0.8 W m^{-1} K^{-1} for silver, aluminum, diamond, and alumina, respectively. From these data, the author suggests that the extrapolated λ value of the neat diamond powder is not 2000 but only 300 W m^{-1} K^{-1} because of the impurities included in the synthetic diamond. Maximum electrical and thermal conductivities are achieved by using silver flakes with a relatively high aspect ratio. With silver-filled epoxies and polyimides, an electrical conductivity of 1–5 × 10^{-4} Ω cm can be reliably obtained. For electrically insulating adhesives, boron nitride and aluminum nitride particles provide a thermal conductivity of 2.5 W m^{-1} K^{-1} at a loading level of 55 vol%.

12.3 Material Properties

The first specification for the selection and use of organic adhesives in hybrid microcircuits was reported in 1983.[47] Application of this qualification method to commercially available gold-filled epoxies was described 3 years later.[48] MIL-A-87172 of MIL-STD-883C, method 5011-2 released in 1989, establishes the evaluation and qualification requirements for the polymeric adhesives used in military hybrid circuits. The last version of MIL-STD-883D published in 1991 is currently used as a guide for the die attach materials utilized for nonmilitary applications of hermetic packages as well.[49] This specification does not include any test methods for the devices encapsulated in plastic packages which, according to the final use, rely on JESD-22 and JESD-26 test standards of the Joint Electronic Devices Engineering Council (www.jedec.com). The former specifies the procedures for plastic packaged devices intended for car and transportation markets, whereas the latter reports the sequences of tests applicable to high-reliability plastic encapsulated devices for commercial applications in severe environments. In the following sections, some important qualification standards are discussed, even if some criteria, such as the 15,000g acceleration test, are not used to qualify general-purpose adhesives.

12.3.1 Properties of Uncured Adhesives

12.3.1.1 Materials

Being composite materials, prepared by loading an organic matrix with very large amounts of inorganic fillers, typically from 70 to 80% by weight, the appearance and uniformity of the adhesive pastes may change during storage. In particular, the components of two-part adhesives pastes have to be of uniform consistency, and free of foreign materials, and any filler must remain homogeneously dispersed and suspended during the required pot life when inspected at 30 times magnification. The electrically conductive fillers are gold, silver, or alloys of silver or gold, or other precious metals. The specification excludes metals such as copper, nickel, tin, and solder alloys. The implementation of these tests to actual adhesives has been illustrated by using the two proprietary compositions sketched in Fig. 12.19.[4]

The epoxy adhesive is a two-part system whose first container comprises equal weights of bisphenol-F diglycidyl ether **18** and epoxydized novolac resin **25** and 144 parts per hundred resin (phr) of silver flakes with average particle diameter 5 μm. The composition is then homogenized for a few hours in a three-roll mill. The second container is prepared by mixing 100 parts of *N*-(2-cyanoethyl)-2-ethyl-4-methylimidazole **45**, 108 parts of γ-butyrolactone **109**, and 739 parts of silver flakes (average particle diameter ≤2 μm). The two containers are degassed in partial vacuum if the adhesive is dispensed with an automatic mixing-metering device. The two compositions are designed to provide a convenient 40:60 mixing ratio leading to the adhesive composition referenced IP 670 in the following discussion. A series of electrically and thermally conductive polyimide adhesives are prepared by using a solution containing 60% by weight of polyimide oligomer **99** (IP 605 with $m = 9$, corresponding to a number average molecular weight of 2.56 kg mol^{-1}) in NMP **110.** When cured at 300 °C, the degree of polycondensation increases to about 100 and the molecular weight rises to 25 kg mol^{-1}. According to the application, the base resins are loaded with aluminum, silver, gold, aluminum nitride, or diamond, and the pastes are processed in a three-roll mill for 10 h. The composition and physical properties of these polyimide adhesives are listed in Table 12.3.

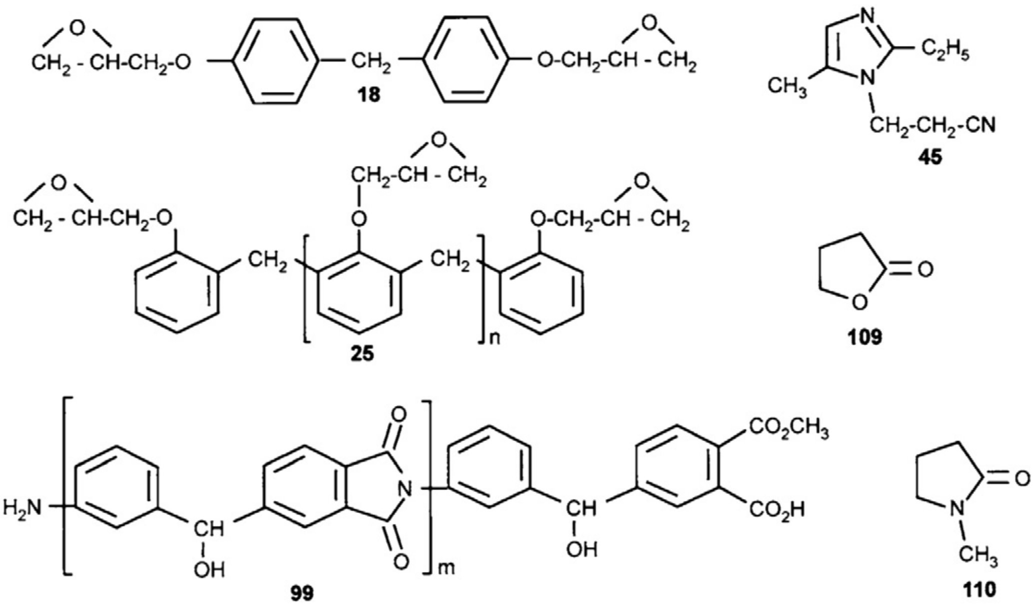

Figure 12.19 Chemical formulae of the organic compounds used to prepare a two-part silver-filled epoxy adhesive and a series of polyimide adhesives loaded with aluminum, silver, gold, diamond, or aluminum nitride.

Table 12.3 Composition and Properties of Electrically and Thermally Conductive Adhesive Pastes Based on Polyimide Oligomer 99 (IP 605)

Trade Marks[a]	**IP 675**	**IP 680**	**IP 685**	**IP 690**	**IP 695**
Filler	Al	Ag	Au	A1N	Diamond
Polyimide IP 605	100	100	100	100	100
Solvent (phr)	106	100	100	133	133
Fillers[b] (phr)	80	400	547	400	400
Solid content[c]	63.5	77.5	86.5	79.1	79.1
Density (g cm^{-3})	1.34	2.65	3.6	2.0	2.5
Viscosity (Pa s)	6	25	60	80	100
Filler after cure[d]	46	81	83	80	80

[a] Trade marks of IFP-Cemota polyimides.
[b] This item comprises the main filler and, if any, silicon dioxide thixotropic agent.
[c] Percent by weight of polyimide and filler in the adhesive composition.
[d] Percent by weight of fillers after curing the adhesives for 30 min each at 150 and 275 °C.

12.3.1.2 Viscosity and Rheology

The viscosity of adhesive pastes, which is specified in the supplier's document, is determined using any acceptable method. For example, it can be measured with a cone-and-plate viscosimeter at a constant temperature and a given shear rate. The thixotropy of the paste is not taken into account in the qualification standard. Viscosimetric measurements are used to control the raw materials, the changes due to incorporation of metal or inorganic fillers, and the effect of thixotropic agents. The final goal for manufacturers of conductive adhesives is to supply materials with constant batch-to-batch quality. The rheological behavior of silver-filled adhesives has been analyzed in terms of frictional forces between the flake surfaces.[50] This means that the larger the flakes, the higher the frictional forces, and the higher the viscosity. Experimental data show that the viscosity increases from 1 to 7 Pa s when the tap density of silver flakes decreases from 4.3 to 3.1 g cm^{-3}. Also, the electrical conductivity increases by a factor of 4—5 for an increase of the apparent density of 25—30%. Another study suggests that both the flake size and the specific surface area have a combined effect on the viscosity.[51] Thus, a viscosity of 26 Pa s can be achieved with a median flake size of 7 μm and a surface area of 1.3 $m^2\ g^{-1}$ or with a flake size of 12 μm and surface area of 0.9 $m^2\ g^{-1}$.

Adhesive pastes are non-newtonian fluids whose viscosity depends upon temperature, time, and shear rate. They are applied to the substrates by means of either stamping (pin transfer), screen printing, or dispensing. The performance of the last technique depends on a key factor: the paste rheology. There exists at least six semiempirical models to describe the rheological response of non-newtonian fluids.[4] For shear-thinning fluids (thixotropic materials), it has been reported[52] that the relationship between viscosity and shear rate is best described by Carreau's model, which can be written as $\eta = \eta_0\,[1 + (\lambda\gamma)^{0.5}]^{(n-1)/2}$ where η_0 is the zero shear viscosity, γ a characteristic time constant, and n a dimensionless power law index.

The incorporation of fillers into organic resins results in increased viscosity with the maximum loading of filler being restricted by the permissible working viscosity, which in turn depends on the dispensing equipment and method.[53] The decrease in viscosity of conductive adhesives with increased shear rate is a time-dependent property, known as shear thinning or thixotropy. Some fillers, in particular silica particles, exert an effect that enhances the thixotropy already provided by many silver flake varieties. The metal and inorganic particles dispersed in the organic resin affect the rheological properties by their nature, size, and shape, thus allowing the desired thixotropy to be engineered.

Thixotropy is generally determined using the thixotropic loop test, where the shear rate is continuously ramped from zero to a maximum value, depending on the measuring device and on the rheological properties of the adhesive as well and then ramped back to zero. The competition between

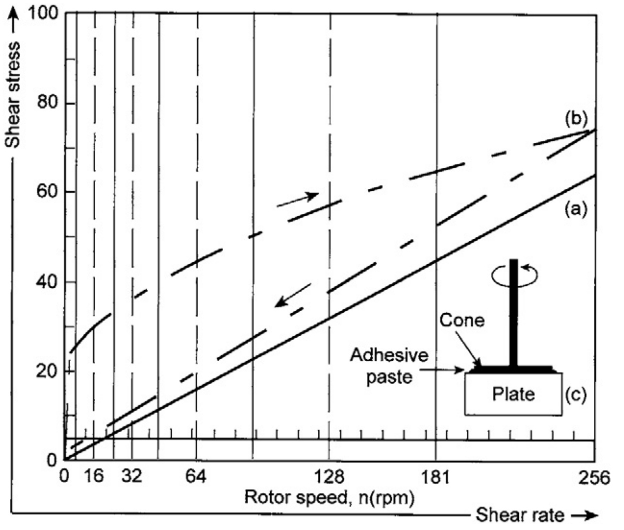

Figure 12.20 Rheological behavior of (a) newtonian solution of oligoimide 99 (IP 605) in NMP and (b) thixotropic adhesive paste IP 680 prepared by loading this solution with silver flakes. Insert (c) represents the cone and plate viscosimeter principle.

the kinetics of structural breakdown, due to the increasing shear rate, and the kinetics of reaggregation is such that the shear stresses are higher in the increasing than in the decreasing ramp. The region in between the two ramps is the thixotropic loop. It provides valuable information on the rheological behavior of the materials that need some time at rest to recover their original viscosity. This is illustrated by comparing in Fig. 12.20 the newtonian behavior of the polyimide oligomer **99** in solution in NMP (straight line (a)) to the thixotropic loop exhibited by its silver-loaded version IP 680 (curve (b)).

The rheological curves of thixotropic fluids, such as IP 680 in Fig. 12.20, show that there is a yield stress τ_0 to overcome before shear can take place. This phenomenon is taken into account in Casson's model represented by the equation $\tau^{0.5} = (\tau_0)^{0.5} + [\eta_0(\mathrm{d}y/\mathrm{d}t)]^{0.5}$, where the yield stress τ_0 is usually determined by extrapolating to zero shear the curve representing the variation of the shear stress at different shear rates. For the sake of convenience, conductive adhesive pastes are often characterized by a thixotropy index, which is the ratio of the viscosities measured at low shear rate, typically at a rotation speed of 0.5 rpm, and at high shear rate, for example, 5, 10, or 30 rpm.

A feature related to viscosity is the resin bleed effect that has been observed with several die attach materials. The event occurs when low-molecular-weight epoxy resins, reactive diluents, or low-viscosity curing agents migrate away from the adhesive layer to the surface around the chip. A definite degradation in the bond strength has been observed when the gold balls are wedged through the bleed area, compared with bonds made on pure metal surfaces.[54] In the resin bleed test, the silver-filled adhesive paste is applied on the surface of the lead frames or ceramic substrates as a drop, 2 mm in diameter, and the length of the resin bleed is measured after leaving the paste at rest for a few hours. Particularly susceptible to resin bleed-out are ceramic chip carriers, and the severity of the phenomenon was investigated with epoxy and polyimide adhesives coated onto different ceramic substrates.[55] The most serious phase separation was observed with epoxy adhesives deposited on a ceramic with a porous surface that appeared to contribute substantially to the resin spreading. Resin bleed-out can be eliminated by combining high temperature (200−250 °C) and high vacuum to clean the substrates.

Other distinctive elements connected to thixotropy are tailing and cobwebbing. The processability of silver pastes depends to a large extent on their thixotropy, because high viscosity at low shear rates improves the sagging property, whereas low viscosity at high shear rates helps to limit the defects due to tailing or cobwebbing. The formation of a cobweb not only gives irregular drops of silver paste but very often includes air bubbles under the tail after sagging. In the case of multineedle dispensers (16−25 hole nozzles), cobwebbing may cause adjacent drops of silver paste to be connected by the tail formed during the operation. Tailing and cobwebbing tests can be performed with a simple setup. A pin, 2.8 mm in diameter, is plunged into the paste to a depth of 5 mm. Then, the pin is pulled up at a constant speed and the height where the cobweb is cut is measured and drawn versus the pull-up speed. In a recent study, an oscillating rheometer was used to measure the tangent of the phase angle (tan δ) between the sinusoidal stress applied to uncured adhesives and the resulting sinusoidal strain.[56] In these experiments stringiness was estimated by separating the plates of the rheometer and measuring the distance between the plates where the string broke.

These two aspects, bleeding and tailing, have also been considered for using adhesives in surface-mount technology. Various nonconductive adhesives are currently used to hold the components during the assembly and wave soldering operations required for bonding surface-mounted devices to PCBs. For this application, the bleeding and stringing effects have to be carefully controlled, because they are prominent factors for producing dots of adhesive with consistent size and shape.[57] Stringing is the result of a combination of factors including the viscosity of the adhesive, its wetting properties, and the relevant machine parameters, that is, the nozzle diameter, the distance between the nozzle and the board, the dispensing pressure, and the dispensing time. Stringing can be circumvented when the diameter of the dispensed dot of adhesive is twice the internal diameter of the nozzle with a further parameter being the ratio of the internal diameter of the nozzle to the distance between the nozzle and the board. The wet adhesion of the glue with the PCB terminations must be better than its adhesion to the nozzle to avoid the formation of the string as the nozzle lifts. Additionally, the larger the glue dot diameter, the higher the surface tension of the dot and the sooner the adhesive dot will pull off the nozzle. This can be achieved by using nozzles with a smaller internal diameter and by increasing the dispensing pressure, time, and temperature. By changing the nozzle distance, it is possible to dispense, all other parameters being constant, dots of the same volume but with different diameters and shapes.

12.3.1.3 Pot Life

One-part epoxy adhesives generally need to be kept frozen and allowed to come to room temperature before use. In this case, the pot life is the time where the adhesive is workable at the ambient. With two-part systems, the epoxy resin and hardeners are mixed just before use and the pot life is taken from that time. Any change in parameters such as viscosity, skin-over, or loss of bond strength may be used to determine the pot life. The qualification requirement is 1 h minimum and the change in viscosity as a function of storage time at a given temperature is often used to predict the period of time during which the adhesive may be safely used.

12.3.1.4 Shelf Life

According to their chemical composition, conductive adhesive formulations have to be preserved either at low temperature, typically −40 °C for one-part epoxies, or at room temperature. For example, IP 680 polyimide or two-part epoxies can be kept at 20 °C for at least 6 months, whereas one-part epoxies have a shelf life of 2 months at −10 °C and 6 months at −40 °C. The minimum shelf life requirement is 6 months at the temperature indicated by the supplier. Material inspection includes the measurement of the pot life, corrosivity, volume resistivity at 25 °C, and lap-shear strength at 25 °C. Typically, pot life, bond strength, and volume resistivity have been used by adhesive manufacturers to determine the shelf life of the formulated materials. However, other methods such as DSC can predict the remaining shelf life by a quantitative measurement of the heat of reaction.[58]

12.3.1.5 Infrared Spectroscopy

Infrared spectroscopy (IR) provides rapid access to the changes induced by chemical reactions within the organic matrix. The absorption bands characteristic of the epoxy groups and curing agents are altered in position or intensity if they react during storage. Any shift, disappearance, or introduction of absorption bands throughout the specified wavelength range (2.5−15 μm) means that the whole batch will be rejected, but minor changes in peak intensity are allowed.

12.3.1.6 Corrosivity

It has been shown that some latent hardeners of the epoxy resins may corrode the aluminum wires or bonding pads. This corrosivity has been demonstrated for the complex of boron trifluoride and monoethylamine. In the specification NSA 77-25A, small dots of adhesive are applied to the aluminized side of a Mylar® polyester film (www.dupont.com) and are allowed to stand in the room ambient without cure. After 48 h, the dots are removed from the film by washing with acetone and the requirement is that there are no changes in the light transmission of the film.

12.3.2 Properties of Cured Adhesives

All the other test requirements deal with the performance and reliability of the adhesive joint, starting with the cure schedule that very often conditions the quality of the attachment. The bond strength requirements have been established to ensure that the assembly can be subjected to the subsequent manufacturing steps such as wire bonding, molding of plastic packages, or sealing of hermetic packages. Volume resistivity has to be determined for type I adhesives (electrically conductive), whereas thermal conductivity is the most adequate measure of the particle-to-particle contacts. Finally, a series of environment tests have been issued to check the resistance of the bonded devices used in the aerospace industry. However, these tests are also employed to evaluate the behavior of all die-bonding materials currently in development.

12.3.2.1 Adhesive Cure

The adhesive cure temperature of MIL-STD-883 is limited to a maximum of 165 °C for a maximum of 4 h. This specification constitutes the requirements for the adhesives used in space applications, and the upper limit is set at 165 °C to minimize the degradation of the wire bonds. The polyimide adhesives requiring temperatures as high as 275−350 °C are therefore excluded from this specification. The cure schedule, reported by the supplier, has to be identical for all tests. DSC can be used to observe the exothermic cure reaction of thermosetting resins. Figure 12.21, curve (a), shows a typical DSC profile in the scanning mode. The area under the curve represents the total heat of polymerization, ΔH_T. A partially cured adhesive will exhibit a less intense signal (curve (b)) with a residual heat of reaction, DH_R. The degree of cure D_c is determined by the relationship $D_\mathrm{c} = (\Delta H_\mathrm{T} - \Delta H_\mathrm{R})/\ \Delta H_\mathrm{T}$.

12.3.2.2 Thermal Stability

A convenient way of assessing and comparing the thermal stability of the conductive adhesives is to measure the total weight loss as a function of time and temperature. The recommended temperature is 150 °C, because this is the maximum that hybrid circuits generally encounter in either screen testing or actual operation. A plot of the isothermal weight loss as a function of time up to 1000 h gives a good picture of the thermal stability and the amount of volatile materials that can be expected to outgas. It has been demonstrated that solventless epoxies pass this test with a weight loss of approximately 0.5%.[59]

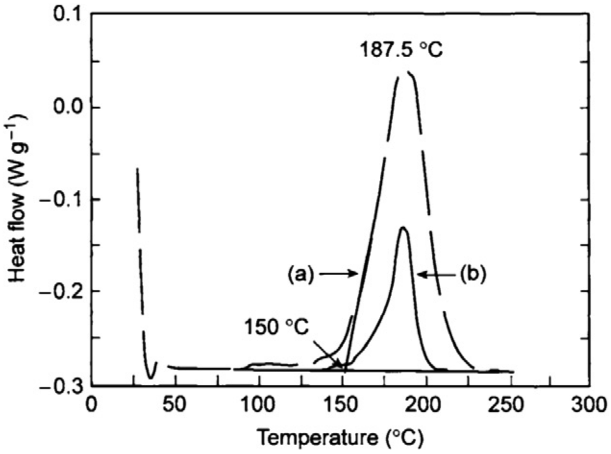

Figure 12.21 Differential scanning calorimetry profile of a silver-filled epoxy adhesive using a temperature ramp of 10 °C min^{-1}. The area under the first scan (a) provides the total heat of polymerization ΔH_T, whereas the area under the second scan (b) gives the value of the residual heat of reaction ΔH_R of a partially cured material.

Polyimide adhesives are generally subjected to isothermal gravimetric analyses at much higher temperatures. Figure 12.22 compares the behavior of IP 670 silver-epoxy, IP 680 silver-polyimide, and IP 685 gold-polyimide when they are heated in air at 250, 300, and 350 °C.

The first observation is that gold-filled polyimide IP 685 is more stable than the silver-filled version IP

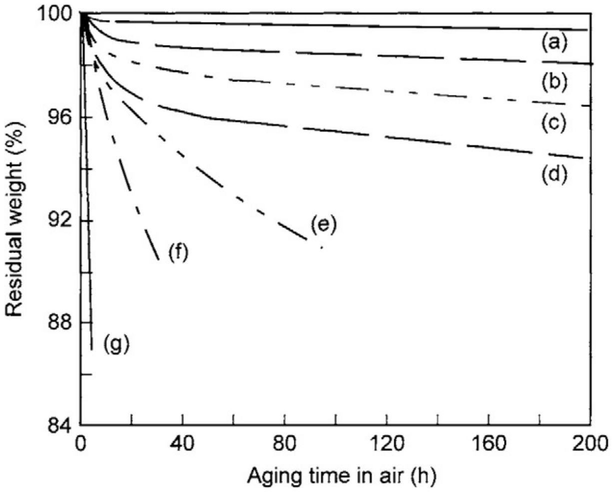

Figure 12.22 Isothermal aging of conductive adhesives in air: gold-filled polyimide IP 685 at (a) 250 °C, (b) 300 °C, and (c) 350 °C; silver-filled polyimide IP 680 at (d) 250, (e) 300, and (g) 350 °C; silver-filled epoxy IP 670 at (e) 250 °C and (f) 300 °C.

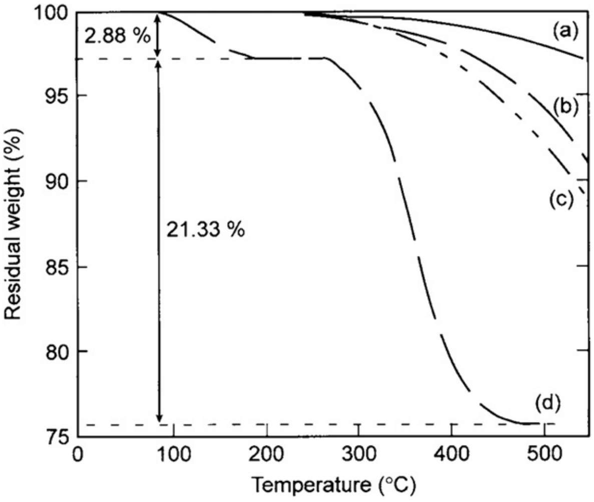

Figure 12.23 Dynamic thermogravimetric analysis of conductive adhesives: (a) Al-filled IP 675 in air and Au-filled IP 685 in argon, (b) Ag-filled IP 680 in argon, (c) IP 680 and IP 685 in air, and (d) Ag-filled IP 670 epoxy adhesive in air.

680 at any temperature. After 200 h at 250 °C, the weight loss of IP 685 is negligible, whereas the residual weights are 98 and 96% at 300 and 350 °C, respectively. During the same period, the weight loss of IP 680 is 6% at 250 °C, 9% after 100 h at 300 °C, and 14% in less than 1 h at 350 °C. For the silver-filled epoxy adhesive IP 670, the residual weights are 91% after 90 h at 250 °C and 89% after 38 h at 300 °C.

Because of the long duration of this test, the thermal stability is determined by thermogravimetric analysis (TGA) in accordance with ASTM D3850 using 10 mg samples tested from 25 to 350 °C at a heating rate of 10 °C min^{-1}. The specification requires that the weight loss must not exceed 0.3% at 250 °C and 1% at 300 °C. The TGA curves provide a quick picture of the onset of thermal decomposition of organic materials. It indicates the temperature at which volatile compounds are released, but it does not provide the same information as the isothermal weight loss of the previous test. A complete thermal assessment should therefore employ both tests and also DSC. Figure 12.23 shows the results obtained with aluminum-filled (IP 675), gold-filled (IP 685), and silver-filled (IP 680) polyimide adhesives, compared with silver-filled epoxy IP 670. The same trends have been observed by other research groups at the Sandia National Laboratories,[60] Ablestik Laboratories,[61] Epoxy Technology,[62] and Amicon Corporation.[63,64]

12.3.2.3 Filler Content

The filler content is determined using TGA by heating the sample from the ambient temperature to 600 °C in air. The temperature is maintained at 600 °C until a constant weight is achieved. Figure 12.23 shows the TGA profile of uncured IP 670 silver-filled epoxy adhesive heated from 25 to 500 °C. The initial weight loss (2.9%) between 100 and 250 °C gives information on the amount of volatile materials evolved during the curing stage. The onset of rapid thermal decomposition is approximately 270 °C and the residual weight left at 500 °C (75%) corresponds to the amount of silver loaded into the epoxy adhesive composition.

12.3.2.4 Outgassing

A major concern in using organic adhesives to assemble semiconductor dice and hybrid microcircuits is the effect that the outgassed products have on the electrical performance of the devices and circuits. The main concern is water, although other constituents, released in smaller amounts, may be even more damaging than water. TGA curves of Fig. 12.23 do not provide clear information on the outgassed products. The damage initiated by moisture on the chip devices and microcircuits is due to a combination of factors. They include the sensitivity of devices and circuits, the nature and integrity of the device passivation, the amount of moisture, the time and temperature of exposure, gases other than water, and ionic contaminants on the surface. In view of the number of parameters and the difficulty in controlling them, the industry and government agencies have settled on specifying the amount of moisture that is allowable in a hermetically sealed circuit package. The moisture requirement for Class B circuits has been set at 5000 ppmv (part per million in volume equivalent to 0.5% v/v) maximum and for Class S circuits at 3000 ppmv. Although hybrid circuits can meet these requirements, it is still not a guarantee that the circuit will be reliable. Other constituents that may evolve, such as ammonia, amines, ketones, alcohols, chlorinated hydrocarbons, hydrogen chloride, and boron trifluoride, must be reported, if detected, but quantitative requirements for these gases have not been established.

Moisture in itself, if pure, is probably not harmful but, in a packaged microcircuit, it is unlikely that water would remain pure, because there are other constituents from the epoxy resin that could contaminate the circuit, including chlorides, metal ions, and amines. Moisture then acts as a medium dissolving and transferring these ions and contaminants to other portions of the circuit. The specific effects may be electrochemical corrosion of the aluminum metallization causing electrical shorts, deterioration of the wire bonds with increases in resistance or bond lifts, device leakage current, and metal migration. To avoid these failure mechanisms, other tests have been specified in MSFC-SPEC-592 including weight loss at elevated temperature, corrosivity, total ionic impurities, and concentrations of the Cl^-, Na^+, and K^+ ions. In recent years, the manufacturers of adhesives have made significant improvements in reducing the amounts and types of outgassing products and ionic species in their formulations. Both epoxy resins and hardeners have been purified through distillation or extraction with solvents to remove chloride and other ionic contaminants. The manufacturers of hybrid circuits have also reduced outgassing by optimizing the vacuum bake schedule used prior to hermetically sealing the circuits. Vacuum baking at 150 °C for 16−96 h has been found effective in removing most of the moisture and other volatile materials from the adhesive and the package as well. The analysis of the materials outgassed per Method 1018 of MIL-STD-883, following a 168-h bake at 125 °C, shall be made by the users.

12.3.2.5 Ionic Content

Epoxies of the first generation used in electronic assemblies as adhesives and molding compounds were commercial grades containing large amounts of sodium and chloride ions that are byproducts of the synthesis of diglycidyl ethers. It has been outlined that ionic contaminants not only adversely affect device performance, but are also the most frequent cause of component failure, through either direct shorting or corrosion effects.[65] The epoxies that are produced today for semiconductor and hybrid applications are purified to reduce the ionic content or are synthesized by procedures that avoid the generation of sodium chloride. The quantitative analysis of the individual ions in the adhesive may be performed by atomic absorption spectrophotometry or ion chromatography. Analysis is conducted using a powdered sample of cured adhesive that is extracted in deionized water for 24 h either at 100 °C with full reflux or in a Teflon-lined Parr bomb heated at 121 °C. The aqueous extracts are then analyzed with a Dionex ion chromatograph using a column for anions and a column for cations. In another method, the sample is burnt in the flame of a Wickbold oxyhydrogen blowpipe at a temperature of 2000 °C, the combustion gas flow being flushed through the chromatographic medium. The mineralization is made according to ASTM D-2785 standard. Anions such as Cl^- and NO_3^- are analyzed with a Vidac-Anions column, whereas cations (Na^+, K^+, NH_4^+) are separated with a Mitsubishi SCK01 column.

Typical values for Cl^-, F^-, Na^+, and K^+ are less than 10 ppm for purified silver-filled epoxies and 1−5 ppm for polyimides. In addition, the following data have to be reported: the total ionic content as the specific electrical conductance, which must be ≤ 4.5 mS m^{-1}; the hydrogen content, which must be in the range of $4.0 \leq \text{pH} \leq 9.0$, and the presence of NH_4^+ cations if their level is more than 5 ppm. The determination of the total ionic content may be obtained by measuring the electrical resistivity of a water extract of the adhesive because ions are readily soluble in water. The test involves 3 g of ground sample that is heated for 20 h in 100 mL of boiling deionized water of known resistivity and measuring the decrease in resistivity. The total ion content is then calculated according to Method 7071 of FED-STD-406 and reported as NaCl in ppm.

12.3.2.6 Bond Strength

A major requirement for devices attached with an organic material is an adhesive strength sufficient to last the life of the circuits and to withstand the environmental, thermal, and mechanical exposures during processing and testing. Generally, shear strength is not a problem with epoxies because values over 20 MPa are easily attainable. However, to obtain reliable results, the properties of the materials and the process parameters must be carefully controlled. In particular, the surfaces to be bonded are thoroughly cleaned with both polar and nonpolar solvents to remove all organic and inorganic residues. Because of its general use in the semiconductor industry to remove traces of organic materials, plasma cleaning is now widely accepted to produce clean surfaces before die attachment. In the case of gold-plated

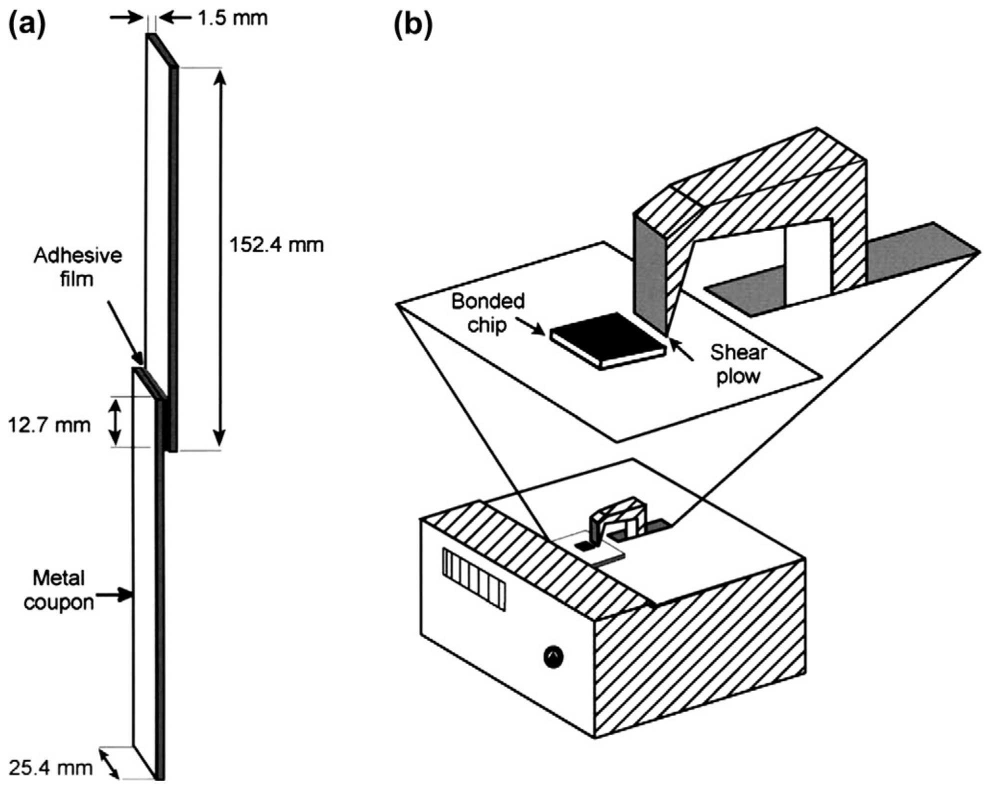

Figure 12.24 (a) Single lap-shear configuration recommended in ASTM D1002 specification. (b) Principle of the die-shear tester.

surfaces, the adhesive strength is improved either by abrading the gold layer or by using a primer or a coupling agent. The qualification of an adhesive for a given application requires a series of tests to determine the process parameters, the resistance to organic solvents, and the behavior of the assembly during thermal aging and environmental stressing. The procedures and conditions for the bond-shear strength are given in MSFC-SPEC-592 for dice, substrates, and capacitors bonded with organic adhesives. It specifies measurements at room temperature, at 150 °C, after solvent immersion, after temperature cycling, and after aging for 1000 h at 150 °C. For the last three conditions, a 70–80% retention of the initial bond strength is required.

In electronics, the adhesive strength of bonded parts is determined primarily by applying an in-plane shear stress using both lap-shear and die-shear tests. The lap-shear trial is performed by the vendor using standard aluminum tensile specimens in accordance with ASTM D1002. Figure 12.24(a) shows the single lap-shear configuration recommended by this specification. Requirements for the lap-shear strength are values $\geq$6.9 MPa at 25 °C, $\geq$3.5 MPa at 150 °C, and $\geq$80% of the initial strength after 1000 h at 150 °C. The device-shear tests are conducted by the user in accordance with MIL-STD-883, Method 2019, and performed with the die-shear tester illustrated in Fig. 12.24(b). Requirements for the device-shear strength are at least 6.9 MPa at 25 °C for dice and substrates and 10.3 MPa for capacitors. These values may decrease to 3.5 and 5.2 MPa, respectively, at 150 °C. A 70% retention of the initial device-shear strength is required after solvent immersion and after temperature cycling and 80% after 1000 h aging at 150 °C.

Specimens for lap-shear strength are prepared by applying the adhesive paste or tape between two aluminum coupons (2024-T3 alloy) whose dimensions are given in Fig. 12.24(a). The assembly is cured in an air-circulating oven according to the appropriate thermal schedule. The lap-shear strength is measured with a tensile machine at a pull rate of 1–2 mm min^{-1} and expressed in MPa on an average of five specimens at least. Most commercially available silver-filled adhesives exhibit a lap-shear strength in the range 6–20 MPa at ambient temperature, dropping to 5–10 MPa at 150 °C for materials with a glass transition

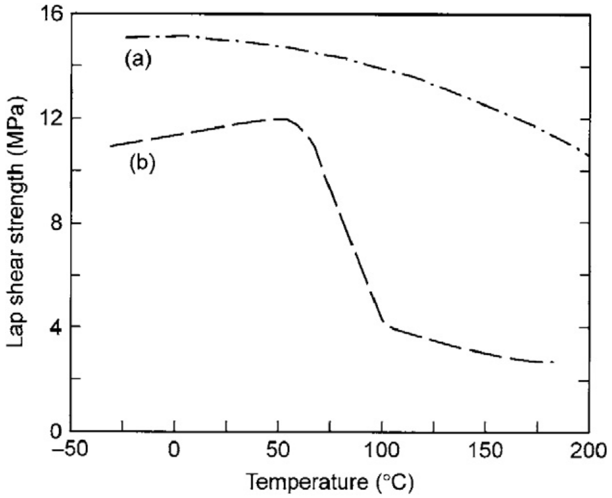

Figure 12.25 Variation of the lap-shear strength as a function of temperature for conductive adhesives: (a) IP 680 silver-filled polyimide cured at 300 °C and (b) IP 670 silver-filled epoxy cured at 120 °C.

temperature higher than 180 °C. Typical lap-shear strength data for IP 670 silver-filled epoxy and IP 680 silver-filled polyimide adhesives are plotted in Fig. 12.25, which shows that the adhesive strength considerably drops when the temperature approaches the T_g of the epoxy resin at 110−120 °C.

Representative values obtained for the lap-shear strength of polyimide adhesives are 8.5 MPa (IP 680-Ag), 7.9 MPa (IP 685-Au), 8.5 MPa (IP 690-A1N), 8.9 MPa (IP 695-diamond), and 16.1 MPa (IP 675-Al), all adhesives being cured at 275 °C. It has been reported that the lap-shear strength is a function of the adhesive thickness.[66] A maximum value is attained when the thickness is in the range of 35−75 μm and then it significantly decreases beyond 200 μm. In addition, the lap-shear strength is reduced by 5−10% when the die size increases from 25 to 100 mm^2. The adhesive strengths, measured with different substrates commonly encountered in the semiconductor industry, indicate that bare silicon chips with rough surface give better values than metallized devices.

Lap-shear test conditions are not really convenient in electronics involving small dice and two substrates with different CTE. The stresses generated during the cure cycle by this CTE mismatch account for possible crack formation and delamination, which in turn may degrade the adhesive strength. The die-shear strength method consists in the measurement of the force required to shear the die from the chip carrier. Although any die size can be used, a standard technique is to bond 1.27 × 1.27 mm^2 nonfunctional silicon dice to silver-plated lead frames.

The dice and lead frames are first cleaned in stirred freon and dried at 100 °C for 15 min. Drops of adhesive paste are dispensed onto the lead frames (20 positions) with an automated pneumatic syringe. The dice are then placed on top of the adhesive drops with a pick-and-place machine, and the assemblies are cured either in a forced-air oven or on a heating block. The die-shear strength of each individual die is measured with a die-shear tester working as shown in Fig. 12.24. The die-shear strength is calculated by averaging the results obtained from the 20 individual dice tested and expressed either as a force (N) or as a stress (MPa) if the bonded area is introduced into the calculation. The average values determined with polyimide adhesives are 22 MPa (IP 680-Ag), 16.3 MPa (IP 685-Au), 22 MPa (IP 690-A1N), and 15 MPa (IP 695-diamond). For IP 680, the initial value of 22 MPa regularly decreases to 20.7 MPa at 250 °C and then dramatically drops to 8 MPa in the region of the glass transition temperature (230 °C).

The effect of isothermal aging at 200 and 300 °C on the die-shear strength of commercial polyimide adhesives has been studied with small dice (1.12 × 1.12 mm^2) bonded to silver-plated copper lead frames, using the usual cure cycle of 30 min each at 150 and 275 °C.[67] The results indicate that the die-shear strength variation in the temperature range 20−250 °C for the two adhesives exceeds the requirements of MIL-STD 883B. Using the same cure cycle with IP 680-Ag to bond 1.27 × 1.27 mm^2 dice to silver-plated copper lead frames, it has been shown that the die-shear strength, measured at ambient temperature, remains virtually constant after 100 h of aging in air at 200 °C, whereas the adhesive loses 50% of the initial shear strength after 20 h at 300 °C.[4] The adhesive strength of one-part and two-part silver-filled epoxies has been measured by using semiconductor devices and chip capacitors, ranging in size from 0.508 × 0.508 to 2.286 × 2.286 mm^2, and bonded to gold-plated alumina substrates.[68] The general trend is that the die-shear strength drops to about 92% of the initial value after 150−200 h at 150 °C and then decreases at a lower rate for 2000 h of aging in air. The two adhesives pass the strength requirements for long-term uses at 150 °C with a safety margin of 2−3. A study performed with four epoxies and one polyimide shows that the die-shear strength decreases during long-term aging in air at

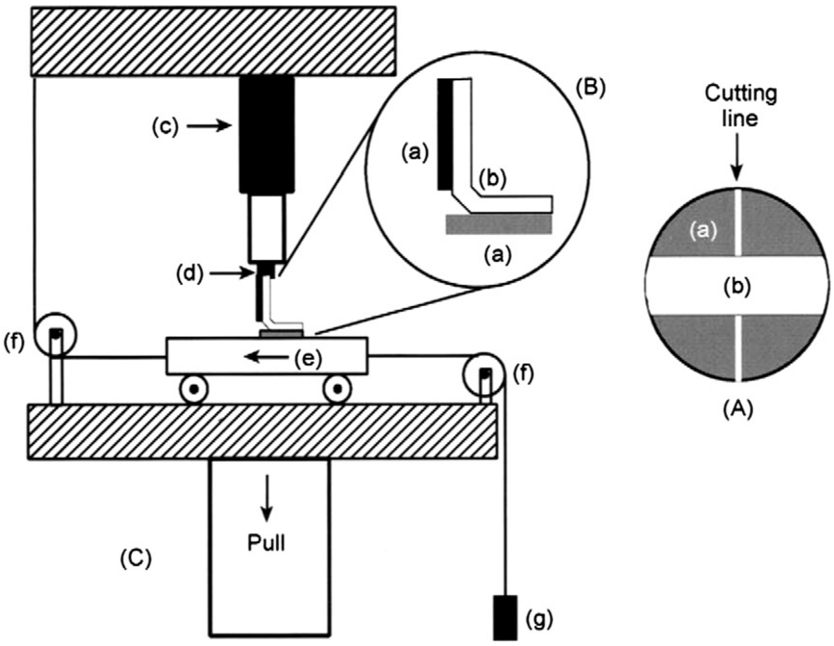

Figure 12.26 Measurement of adhesion by the peel test method using thin film specimens coated on silicon wafers and cured at 350–400 °C. (A) A 1-cm wide strip is cut in the polyimide film. (B) The wafer (a) is cut and broken perpendicularly to the film (b). (C) One end of the specimen is fixed with a clip (d) into the upper jig (c) of an Instron testing machine. The other part lies on a mobile carrier (e) designed to maintain a 90° peeling by means of pulleys (f) and counterweight (g).

200 °C with, however, the lowest strength degradation for adhesives with low glass transition temperature.[69] The authors suggest that this behavior is related to the smaller residual stresses generated in low-T_g adhesive layers that keep 63–80% of their initial mean shear stress after 504 h at 200 °C. For the epoxy with a glass transition temperature of 250 °C, only 24% of the initial value remains after the same aging test, whereas the polyimide with a T_g of 200 °C works better with a retention of 62%.

As stated earlier, adhesion is a major concern in electronic applications involving thin polyimide films either coated on hard substrates or laminated with metal ribbons. In these cases, neither lap-shear nor die-shear techniques allow the determination of the adhesion strength; this can be done by using either the 90° peel test or the island blister test whose principles are sketched in Figs 12.26 and 12.27. The 90° peel test provides reliable data for the measurement of "practical adhesion," especially useful for comparing the effect of surface treatments on the interfacial adhesion. The standard peel test procedure has been modified to determine the adhesive strength of thin polyimide films coated onto 10-cm silicon wafers. The equipment illustrated in Fig. 12.26 maintains a 90° peel effort during the test conducted at room temperature with a constant rate of crosshead displacement of 2 mm min^{-1}.

A more sophisticated peel tester has been implemented to evaluate the adhesion of polyimide films at elevated temperature and in high-humidity environment.[70] The peel strength values, measured in "dry" atmosphere, rapidly degrade when the devices are exposed to humidity, temperature–humidity, or thermal cycle tests. As stated above, peel tests provide practical adhesion values that include polymer and substrate mechanical properties, stored stresses, plastic deformation, and other parameters. It has been demonstrated that an analysis of the peel test mechanics allows extraction of the "fundamental adhesion" from the experimental data.[71] A method to calculate the interfacial fracture energy of a polymer bonded to a rigid substrate by using peel tests has also been presented.[72]

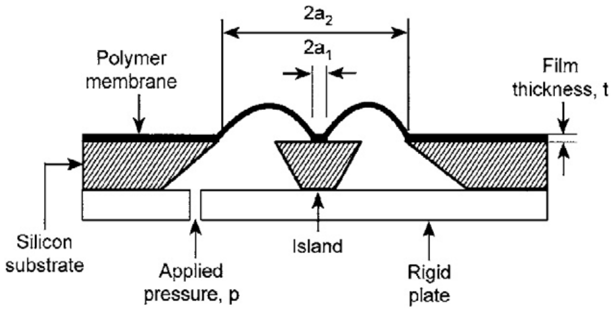

Figure 12.27 In the island blister test, the values of the diameters of the coating adhering part $2a_1$ and suspended membrane $2a_2$ are measured as a function of the pressure p necessary to peel the polymer.

Microfabricated structures based on suspended membranes have been developed to determine in situ the values of adhesive strength, film modulus, and residual stress.[73,74] Figure 12.27 shows that the island blister test consists of a suspended membrane of polymer with an island of substrate attached to the center. Pressure is applied through holes patterned into the supporting plate and the pressure p at which the film begins to peel is observed with an optical microscope as a function of the radius of film still adhering to the island. Film thickness, residual stress, radius of suspended film a_2, and radius of adhered polymer a_1 are introduced in constitutive equations to calculate the debonding energy.

The blister test applied to metal/polyimide and polyimide/silicon interfaces has provided self-consistent values for the adhesion energy G_a calculated from five different equations.[75] G_a can be reliably determined from the pressure data alone, without using the blister geometry. The effect of cure temperature on the adhesion energy of PMDA–ODA polyimide **93** coated over silicon wafers illustrates the need for high temperature curing. G_a increases from 1.37 to 25 J m^{-2} for final cure temperature of 300 and 450 °C, respectively. By contrast rigid BPDA–PPDA polyimide **95** exhibits poor adhesion ($G_a = 0.1–0.3$ J m^{-2}) weakly dependent on the final cure temperature except on silicon-modified surfaces.[76] Experimental data also show that adhesion energies of PMDA–ODA are only 0.03, 0.52, and 13.8 J m^{-2} for Au, Cu, and Al, respectively. Further studies have shown that most of the energy expended is responsible for interfacial fracture, allowing the determination of a fracture energy that represents the true adhesion strength.[77]

12.3.2.7 Coefficient of Linear Thermal Expansion

Silicon dice, lead frames, and ceramic or metal substrates have different coefficients of linear thermal expansion that can cause significant normal and shear stresses after the adhesive layer has been cured, as well as throughout the life of the device during power cycling. The coefficient of thermal expansion must be determined from −65 to 150 °C or to the glass transition temperature and above the T_g. The specification requires the determination of the CTE in accordance with ASTM D3386. This is done to incorporate the use of thermomechanical analyzers. The requirements are a CTE $\leq 6.5 \times 10^{-5}$ K^{-1} from −65 °C to the glass transition temperature and a value $\leq 3.0 \times 10^{-4}$ K^{-1} above the T_g. The coefficients of linear thermal expansion of the materials commonly used in the manufacture of electronic components are listed in Table 12.4.

CTE are determined by thermomechanical analysis using a dilatation–penetration probe for adhesive pastes and an extension probe for self-standing films. The output of the thermal analyzer equipped with a dilatation probe is a curve plotting the variation of adhesive thickness as a function of the temperature.

For thin films, thermomechanical analysis is performed by measuring the length variation of specimens (15 × 5 mm^2) under load (0.02 N) applied to the free end of the film. Extension is recorded when the temperature is increased at a rate of 10 °C min^{-1}. These techniques are illustrated in Fig. 12.28, which shows (curve a) the dilatation of IP 680 silver-filled polyimide adhesive cured at 275 °C. The first linear region with a slope of 4.5×10^{-5} K^{-1} (left Y axis) is associated with the glassy state and is followed at 230 °C by a second linear region of higher slope of 1.2×10^{-4} K^{-1}. This change in slope is a second-order thermodynamic transition of the material from the glassy to the rubbery state, which is one definition of the glass transition temperature. An example of film elongation (right Y axis) is also shown in the figure (curve a) for a high T_g self-standing polyimide film exhibiting a thermal expansion coefficient of 6.9 $\times 10^{-5}$ K^{-1} (Fig. 12.29).

12.3.2.8. Thermal Conductivity

When a high level of thermal transfer must be assured, soft solders and eutectic alloys present the best choice. Adhesives filled with metals and certain oxides generally have sufficient thermal conductivity to transfer the heat generated by metal oxide semiconductors and other low-power devices. Thermal conductivity is measured by ASTM C117 or C518 at 121 °C. The requirements are ≥ 1.5 W m^{-1} K^{-1} for electrically conductive adhesives and ≥ 0.17 W m^{-1} K^{-1} for insulating adhesives.

12.3.2.9 Volume Resistivity

The electrical conductivity of metal-filled adhesives is discussed in detail in Section 12.3.2, which provides the theoretical models and the necessary conditions to build a continuous electrical path. In summary, it is a function of the number of physical contacts between contiguous particles, so that the

Table 12.4 Coefficient of Thermal Expansion α at 25 °C of the Metals, Oxides, Ceramics, and Polymers Commonly Used in the Fabrication of Microcircuits and Electronic Components

Materials	α (K^{-1})	Materials	α (K^{-1})
Silicon dioxide	4.2×10^{-7}	Beryllium oxide	7.5×10^{-6}
Silicon nitride	1.8×10^{-6}	Iron	1.2×10^{-5}
Silicon	3.0×10^{-6}	Gold	1.4×10^{-5}
Silicon carbide	3.8×10^{-6}	Silver glass adhesives	1.5×10^{-5}
Aluminum nitride	4.1×10^{-6}	Copper alloy	1.7×10^{-5}
Alloy-42	4.2×10^{-6}	Silver	2.0×10^{-5}
Tungsten	4.5×10^{-6}	Aluminum	2.1×10^{-5}
Si/SiC	4.9×10^{-6}	Low CTE polyimides	10^{-6}–100^{-5}
Molybdenum	5.1×10^{-6}	Silver-filled epoxies	$3–5 \times 10^{-5}$
Boron carbide/Al_2O_3	5.3×10^{-6}	Al-filled epoxies	$4–6 \times 10^{-5}$
Silicon nitride/Al_2O_3	5.5×10^{-6}	Polyimides	$4–6 \times 10^{-5}$
Kovar alloy	5.5×10^{-6}	Unfilled epoxies	$6–8 \times 10^{-5}$
Aluminum oxide	6.0×10^{-6}	Poly(imide-siloxanes)	$6–12 \times 10^{-5}$
Boron nitride	7.3×10^{-6}	Silicone rubbers	$1–2 \times 10^{-4}$

higher the filler content the higher the conductivity. However, the maximum volume fraction of metal particles that can be dispersed in an organic resin depends on the flow properties required by the dispensing equipment. Thus, to maximize electrical conductivity, the size and shape of the filler particles must be selected to provide the highest filler content allowed by the processing characteristics. The volume resistivity of the best silver-filled epoxies is of the order of 10^{-3}–10^{-5} Ω cm, about two orders of magnitude lower than pure silver metal but convenient for most applications. Licari and Enlow[59] reported the results of tests conducted with five commercial adhesives. They showed that the electrical conductivity of the silver-filled epoxies is relatively stable, decreasing slightly at elevated temperatures and increasing after aging for 1000 h at 150 °C. Although these characteristics are excellent, many examples have been reported that indicate the formation of a resistive path during accelerated environmental testing. This increase of volume resistivity can be explained by the formation of an oxide layer at the interfaces as well as voiding, cracking, and delamination within the adhesive joint. The specification uses a four-point probe measurement of an adhesive strip (0.254 cm wide and at least 5.08 cm long) on a glass slide. The tests are performed at 25, 60, and 150 °C and at 25 °C after 1000 h at 150 °C in nitrogen. The volume resistivity measurements for

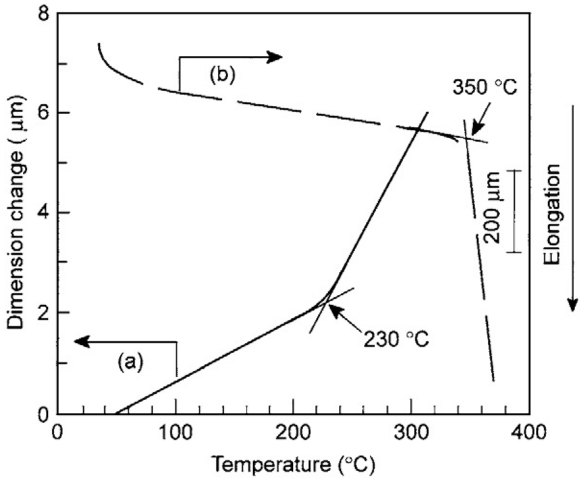

Figure 12.28 Determination of thermal expansion coefficients and glass transition temperatures by thermomechanical analysis of conductive adhesives: (a) IP 680 silver-filled polyimide analyzed with a dilatation probe (T_g = 230 °C) and (b) self-standing polyimide film studied with an extension probe (T_g = 350 °C).

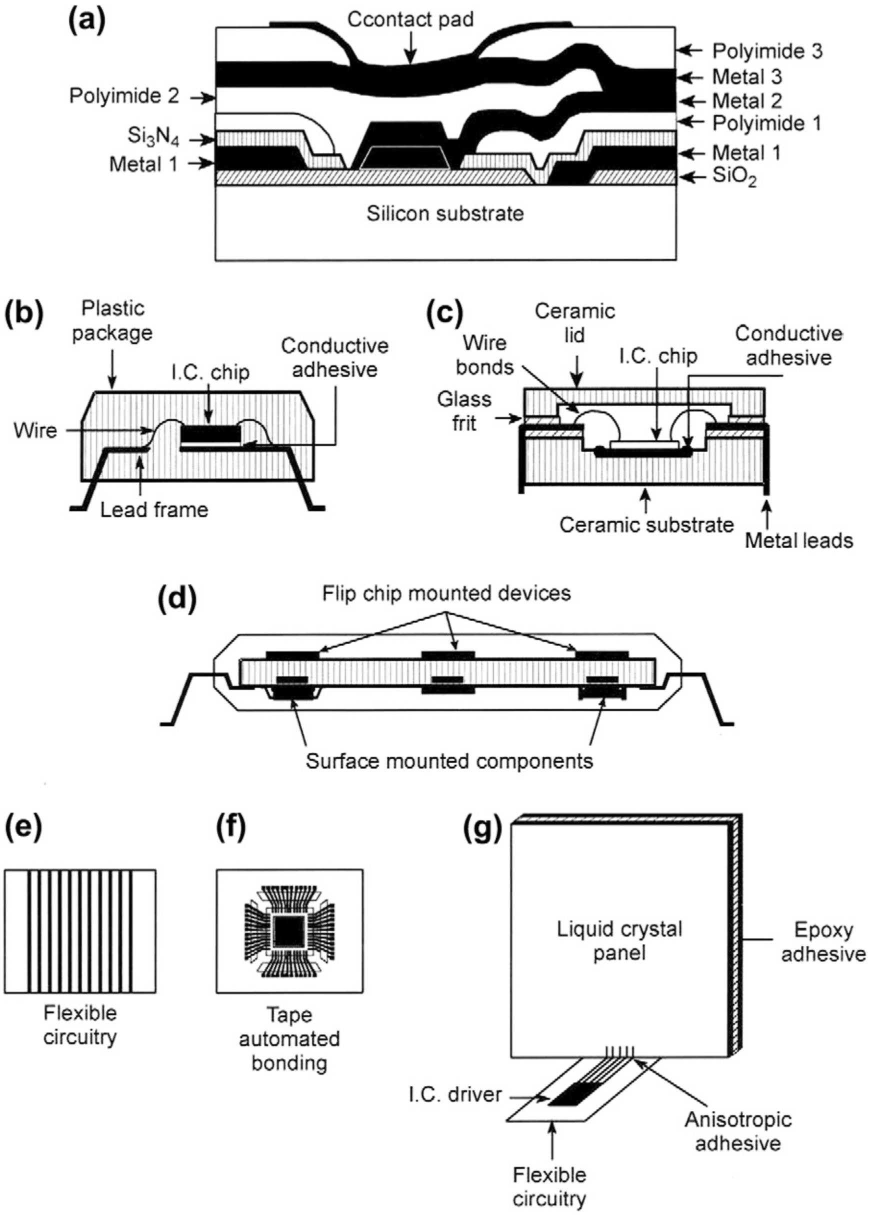

Figure 12.29 Main applications of adhesives in electronic and semiconductor industries: (a) polyimide interlayer of dielectric films in the fabrication of integrated circuits, (b) die attachment in plastic packages, (c) die attachment in ceramic packages, (d) multichip module with flip chip and surface-mounted devices, (e) flexible circuitry, (f) tape-automated bonding and (g) liquid crystal display panels.

electrically insulating adhesives must be performed at 25 and 125 °C. The requirements are 5.0×10^{-4} Ω cm for silver-filled adhesives and 1.5×10^{-3} Ω cm for gold-filled materials, whereas it would be $\geq 10^{12}$ and $\geq 10^{8}$ Ω cm at 25 and 125 °C, respectively, for the electrically insulating adhesives.

12.3.2.10 Dielectric Properties

The measurement of the dielectric constant and dissipation factor for electrically insulating adhesives is performed in accordance with ASTM D150 at 1 kHz and 1 MHz at 25 °C. The requirement for the permittivity is $\varepsilon' \leq 6$ and the dissipation factor must be ≤ 0.03 at 1 kHz and ≤ 0.05 at 1 MHz.

12.3.2.11 Electrical Stability

The stability of the electrical parameters after aging at high temperature under power is of prime importance in the selection of die attach adhesives. The test requires a current density of 139.5 A cm^{-2} applied to five gold-plated Kovar tabs, each tab being adhesively bonded to thin film gold conductors and series bonded with gold wires. The biased test specimens are heated at 150 °C in nitrogen for 1000 h, and the electrical resistance of the bonds is measured at 25 °C at 200-h intervals. The specification requirement states that the resistance of the five tabs does not increase by more than 5%.

12.3.2.12 Sequential Environmental Testing

To complete the selection trials applied to the conductive adhesives, MIL-STD-883 has issued a series of sequential environmental tests mainly aimed at devices used in the aerospace industry. The three tests are humidity-induced stress tests at elevated temperatures with and without bias, temperature-induced stress tests with and without bias, and a mechanical shock comprising acceleration 3000g, 0.3 ms and constant acceleration 15,000g (MIL-STD-883, Method 2001). The most severe tests are those involving both humidity and temperature, because they simulate the harshest conditions that a plastic package would be subjected to. An excellent overview of the two former test procedures was published by Khan,[78] who outlined that the tests listed under the environmental category are not all related to the environment. The moisture—temperature testing procedures include the following:

Moisture resistance: 10 cycles from 25 to 65 °C under 90—100% RH with an applied voltage, 3 h at 65 °C, cool at 25 °C, and repeat the cycle.

Cycled temperature—humidity—bias life: the test devices are subjected to a temperature cycle between 30 and 65 °C, with a RH of 90—98% and the operating voltage turned on and off at 5-min intervals. The specification requires a minimum of 63 cycles (total of 1008 h).

Steady temperature—humidity—bias life (85 °C/85% RH): the test specimens are stored for 1000 h or more at 85 ± 2 °C and a relative humidity of 85 ± 5% with, depending on the device, a voltage applied either constantly or intermittently.

Unbiased autoclave: in the steam cooker test, the packaged devices are stored at 121 °C under a saturated steam pressure of 0.103 MPa in a sealed autoclave. Depending on the intended application, the test conditions vary from 24 to 48 or 96 h of storage. The electrical measurements are performed at ambient temperature after the devices have been stored at room temperature for 48 h.

Biased autoclave: the test procedures are similar to the unbiased, except that a bias is applied through hermetic electrical connections.

Highly accelerated stress testing: unlike the pressure cooker tests, this test uses unsaturated steam, varying from 50 to 100%, at temperatures of 105—150 °C, the experimental data being extrapolated to any temperature—humidity conditions by using theoretical models based on the usual Arrhenius equation.

The temperature stressing refers to burn-in, steady-state life, endurance life, high-temperature storage, and temperature cycling. In the burn-in test, the devices are biased at the maximum-rated operating voltage and a minimum temperature of 125 °C for 160 h (Class B) or 240 h (Class S). The duration of the test decreases with increasing temperature and is, for instance, 12 h at 250 °C. In the steady-state life test, the temperature and duration as well as the conditions of applying the voltage comprise six categories from A to F. The failure data are recorded in any of the 10 time—temperature couples varying from 1000 h at 125 °C to 30 h at 190 °C or more. In the high-temperature storage test, the plastic packaged devices are stored at 150 °C for 1000 h without bias. Finally, in the temperature cycling test for military applications, the lower-limit temperature is either −55 or −65 °C, whereas the upper limit can be 85, 125, 150, 175, 200, or 300 °C. For commercial applications in the automotive industry, the temperature limits are −40 and 125 °C. The number of cycles is 10 for screening and 1000 for qualification.

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13 Adhesives for Aerospace Structures

John Bishopp

Both toward the end of and immediately following the Second World War, wooden structures in military, passenger, and freighter aircraft were slowly replaced by metals; more recently, composites have begun to replace the metallic structures. This has meant that individual components and structures have been required to carry higher loads because of more demanding aircraft performances, and this, in its turn, demanded significantly improved adhesive systems.

13.1 Early Structural Adhesive Bonding in Metallic Aircraft Structures

The first of this new generation of structural adhesives, developed in the United Kingdom by Norman de Bruyne and George Newell of Aero Research Limited, Duxford, Cambridge, was Redux® (*Research at Duxford*), which was based on a formulated P/F resin and was the first synthetic adhesive for bonding structural components constructed from composite and metallic materials.

13.1.1 Redux and the Redux Process

It was the search for a suitable adhesive to bond Gordon Aerolite®, a structural composite developed in 1936 and comprising a phenolic resin matrix reinforced with flax fibers, which led to the development of Redux and the Redux Process.

Gordon Aerolite was the result of work on phenolic molding materials for the manufacture of variable pitch propellers for de Havilland. The use of continuous flax fibers enabled de Bruyne to produce unidirectional prepregs instead of producing reinforced moldings.

These prepregs were laid up in sheets—either in the 0° direction or cross-plied at 0°/90°—and cured to give a structural composite having, at an S.G. of 1.36, nearly half the density of the Duralumin then in use. It exhibited an ultimate tensile strength of nearly 500 MPa and a Young's modulus of nearly 50,000 MPa.

This novel concept of using synthetic structural composites was immediately taken up by the Air Ministry, who placed an initial order for a prototype 30-ft wing spar for the Bristol Blenheim fighter-bomber, the design being based on the metacarpal bone of the vulture (Fig. 13.1).

With the outbreak of the war, work was immediately commenced on producing a prototype Supermarine Spitfire cockpit and fuselage out of Gordon Aerolite[1] (Fig. 13.2). In the event, although a replacement for aluminum was not required for the Spitfire, some 30 Miles Magister tailplanes were produced out of Gordon Aerolite.

From the start, de Bruyne and Newell realized that use of the available adhesives (or glues) would not be suitable for joining nonporous substrates such as Gordon Aerolite. As Gordon Aerolite was based on phenolic resole chemistry, it was toward these systems that de Bruyne turned for his adhesive. Several years of noncontinuous research led to the discovery, on February 24, 1942, of an adhesive

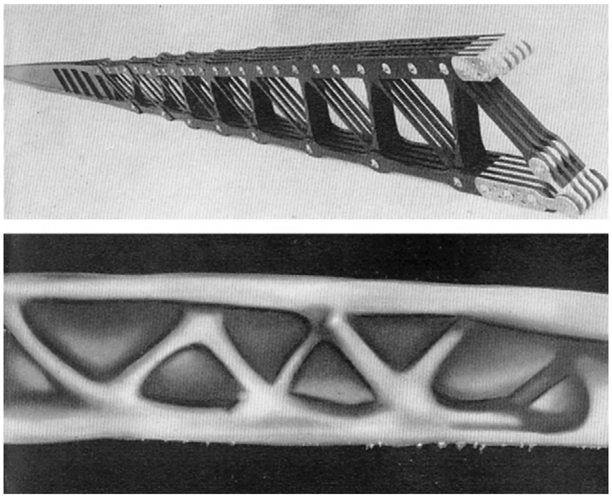

Figure 13.1 Gordon Aerolite Blenheim spar modeled on the wing of the vulture.

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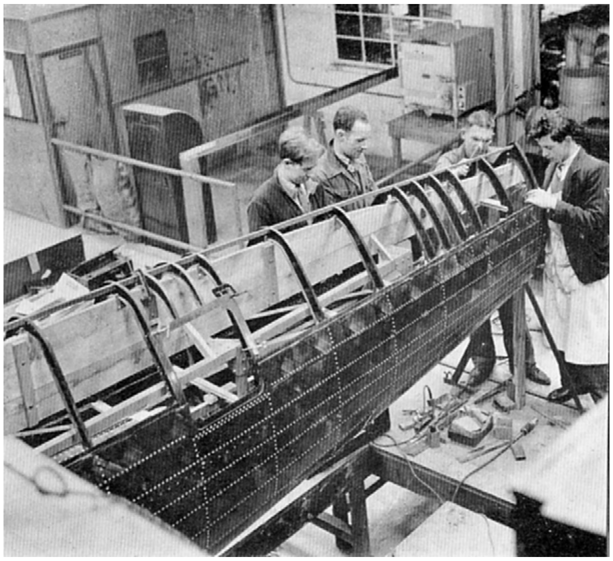


Figure 13.2 The Gordon Aerolite Spitfire prototype.

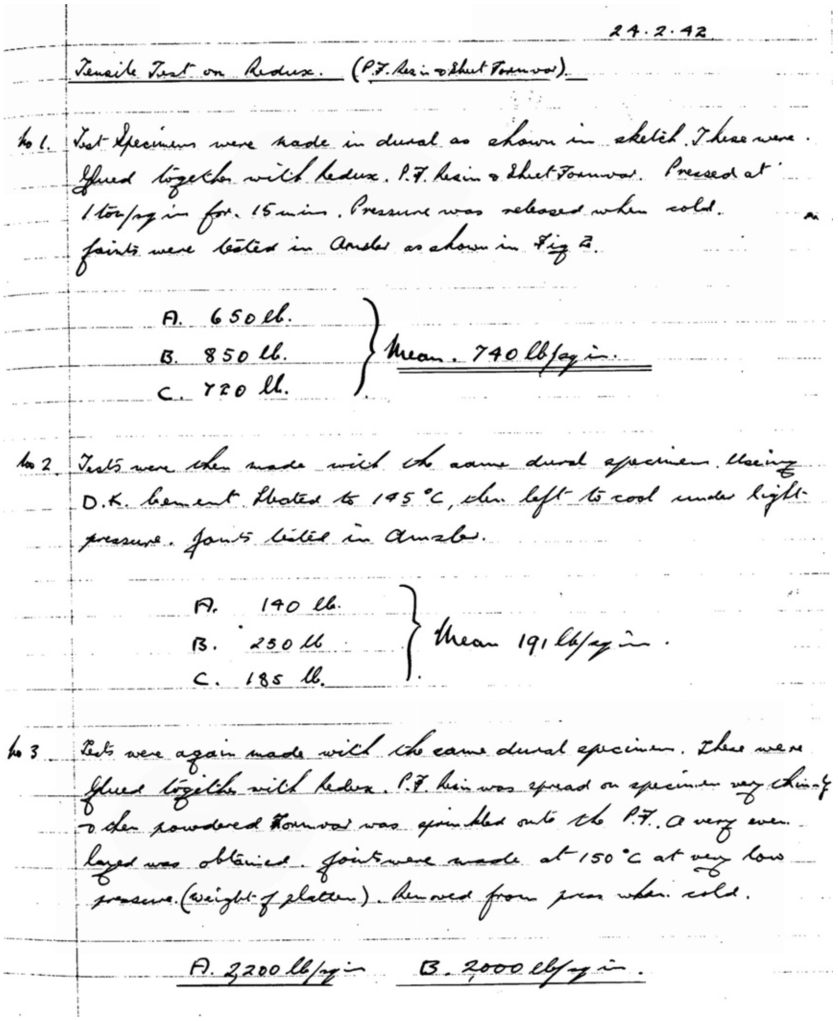
system that could not only successfully bond Gordon Aerolite but also, for the first time, gave a shear strength on aluminum substrates of more than 2000 lb/in^2 (>13.8 MPa) (Fig. 13.3).

The liquid component of the adhesive (Liquid E) was a phenolic resole having a controlled phenol to formaldehyde ratio of 1:1.57 and a relatively high alkaline content. It was painted onto the substrate to be bonded and was then covered with polyvinyl acetal, a high-molecular-weight polymer in powder form. Figure 13.4 shows the chemical structure of the adhesive, and Fig. 13.5 illustrates the typical application process for Redux liquid and powder, which is still valid today.

It is no small example of the trust that the aircraft manufacturers had in adhesive bonding that bonded structural components using Redux were in operational aircraft within 2 years of the product's development.

Oddly, the first use of Redux was not in a metal aircraft or to bond Gordon Aerolite components but

Figure 13.3 George Newell's notebook—the discovery of Redux (Exp. No. 4.3).



24.2.42

Tensile Test on Redux. (P.F. Resin & Shot Formvar).

No 1. Test Specimens were made in dural as shown in sketch. These were glued together with Redux. P.F. Resin & Shot Formvar. Pressed at 1 ton/sq in for. 15 mins. Pressure was released when cold. Joints were tested in Amsler as shown in Fig 2.

A. 650 lb.
B. 850 lb.
C. 720 lb.
} Mean. 740 lb/sq in.

No 2. Tests were then made with the same dural specimen. Using D.K. Cement Heated to 145 °C, then left to cool under light pressure. Joints tested in Amsler.

A. 140 lb.
B. 250 lb
C. 185 lb.
} Mean 191 lb/sq in.

No 3. Tests were again made with the same dural specimen. These were glued together with Redux. P.F. Resin was spread on specimen very thinly & then powdered Formvar was sprinkled onto the P.F. A very even layer was obtained. Joints were made at 150 °C at very low pressure. (weight of platten). Removed from press when cold.

A. 2200 lb/sq in B. 2000 lb/sq in.

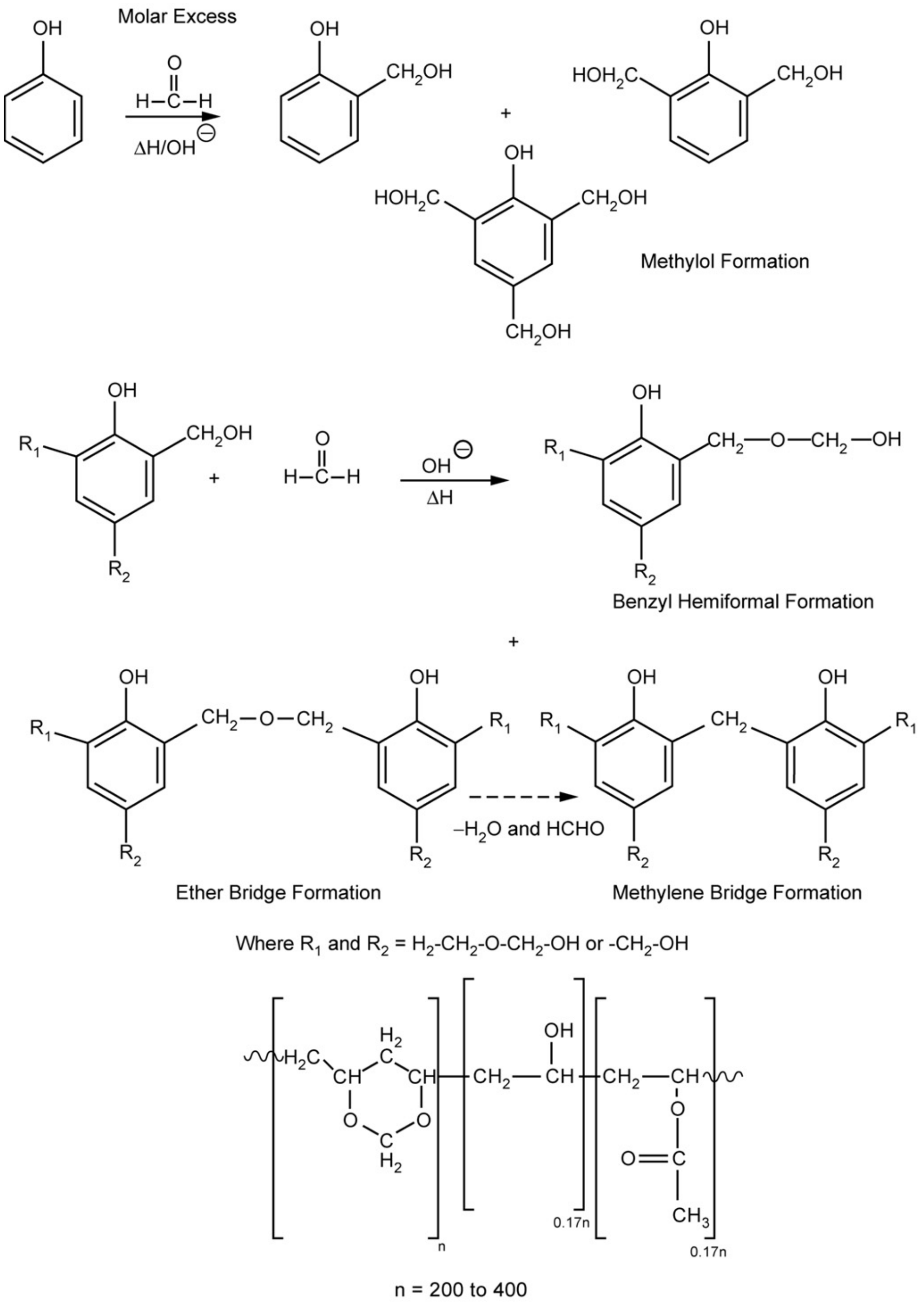


Figure 13.4 Chemical structure of a typical phenolic resole and of polyvinyl formal resin.

in the essentially all-wood, long-range versions of the Mosquito: the de Havilland DH103 Hornet and Sea Hornet; the latter was the version intended for naval carrier use.[2–4]

The design of both aircraft was such that the wings were expected to have to carry very high tensile stresses in flight. Furthermore, in the naval version, the wings were folded when stowing the aircraft below decks, putting even greater stresses on the “hinge” and the wing roots. To ensure that the wing was strong enough to withstand these loads without increasing the overall weight of the aircraft, aluminum (duralumin) stiffeners were Redux bonded to the wooden components in the wing ribs, spar booms, and stringers as shown in Fig. 13.6.

It is interesting to note that British Tego film had also been evaluated for bonding aluminum-skinned

Figure 13.5 Application of Redux liquid and powder adhesive to an airframe component.

sandwiches, but this approach had never progressed beyond the initial laboratory trials.

Stiffeners were also bonded into the fuselage to strengthen areas where internal attachments were to be made, and this culminated in the first structural metal-to-metal bonding when integrally bonded metal reinforcements were built up on the rear bulkhead at the points where the arrestor hook and the tail wheel were located.

From these beginnings have come the commercial ranges of structural adhesives based, particularly, on phenolic, epoxy, polyimide (PI), and now cyanate ester chemistries that have been tailor-made for the various applications within the aircraft industry and, in the last few years, for space applications. These adhesives impart, as required, a combination of toughness, thermal resistance, and durability to the bonded joint.

13.2 The Acceptance of Structural Bonding by the Postwar Aerospace Industry

It is clear from the foregoing that the aircraft industry embraced the concept of adhesive bonding from the very start in 1903; the step from gluing furniture to gluing wooden structures in airplanes obviously was not seen as a major one.

However, following the end of the Second World War, structural bonding in the burgeoning aerospace industry was no longer simply an extension of techniques used for centuries in the furniture industry. To all intents and purposes, with the advent of the all metal constructions, for example, the de Havilland DH104 Dove (Fig. 13.7) (the first all-metal passenger aircraft; initial flight in 1945), the day of the wooden commercial and military aircraft had begun to come to an end.

The industry, therefore, needed to reassess its commitment to adhesive bonding. The extension of this acceptance to bond structures, which used permeable substrates, to the concept of bonding nonpermeable metal components is, at first sight, not so readily understandable. There are probably three major reasons why it happened.

First, the immediate postwar industry was emerging from a major conflict, which had driven the acceptance of innovation at a greater pace than in peacetime. Second, the strong support of de Havilland was clear for all to see, and third, there were, in Europe, two passionate advocates for this approach. One was Bob Schliekelmann who was head of the Production Research Department at Fokker (then called N.V. Koninklijke Nederlandse Vliegtuigenfabriek Fokker) who, from the very first, used Redux bonding in Fokker's airplanes. This commenced in the late 1940s with the Fokker F-27 Friendship (Fig. 13.8) and continued to the present day with the F-28, F-50, F-70, and F-100.

The other was, not unnaturally, Norman de Bruyne, who was effectively the "father" of modern day structural adhesives and structural adhesive bonding. de Bruyne had 11 compelling reasons why structural adhesive bonding was the better option to bolting and/or riveting and, hence, why it would be beneficial for the post-1945 aircraft industries.[5] These concepts were disseminated to aircraft designers and engineers at series of "Summer Schools" that were run by de Bruyne in the early 1950s. The reasoning is as valid today as it was in 1950.

13.2.1 Why Bond?

de Bruyne's 11 reasons can be summarized as follows:

> *Reduction in weight*: As for timbered structures, the weight of the final metallic or composite structure can be significantly reduced by, for

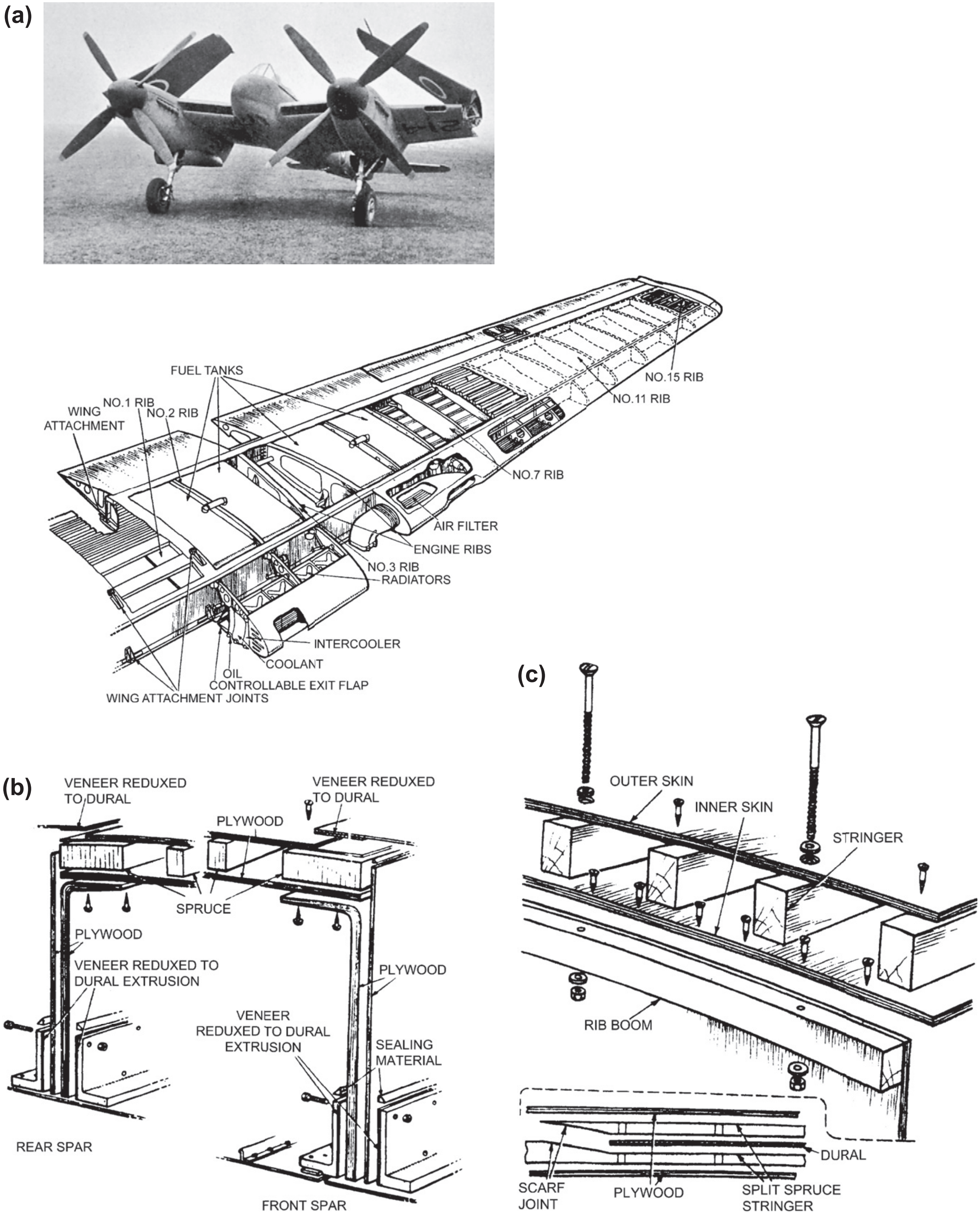


Figure 13.6 (a) Redux bonding in the DH103 Sea Hornet—structure of the wing. (b) Redux bonding in the DH103 Sea Hornet—reinforced spars. (c) Redux bonding in the DH103 Sea Hornet—reinforced stringer.

Figure 13.7 de Havilland DH104 Dove.

Figure 13.8 Fokker F-27 Friendship.

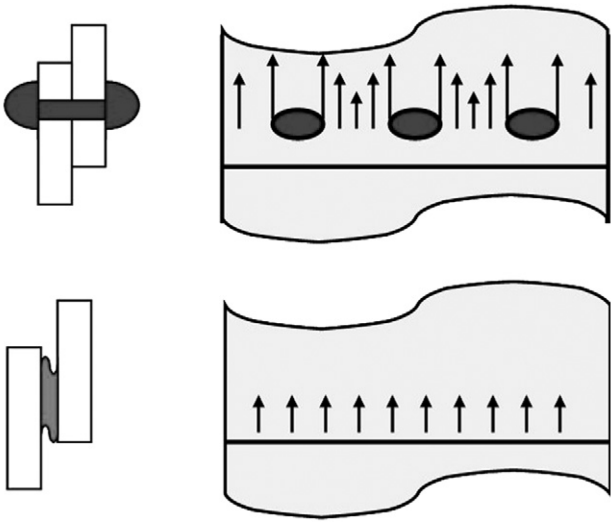


Figure 13.9 Stress concentrations in riveted and bonded joints.

example, using essentially "hollow," preformed stringers that are bonded into place or honeycomb sandwich structures (see below) instead of solid constructions. Further weight reductions can be achieved by the use of thinner gauge metal; reinforcements can then be bonded into place only in areas of high load or stress.

Increase in fatigue life and improved sonic damping: Rivet and bolt holes act as stress concentrators that can readily lead to failure—for example, the Comet disaster where catastrophic fatigue crack growth occurred following unacceptably high stresses around the rivets in the window construction.

As Fig. 13.9 shows, a bonded joint gives no such areas of high stress concentration; a uniform stress distribution across the bonded joint is achieved. The glueline also absorbs some of the acoustic energy associated with the structure that leads to reduced high frequency noise propagation.

In Fig. 13.10, the fatigue curves for both riveted and Redux-bonded joints—plotting cyclic load against a number of cycles to failure—are shown. It is clear that all the bonded specimens failed outside the bonded area. Furthermore, it can be seen that the bonded joint can support about 6–7 times the fatigue load for any given "cycles to failure" value or, to look at it in another way, at any given cyclic load, the bonded joint can be seen to withstand many orders of magnitude of more cycles.

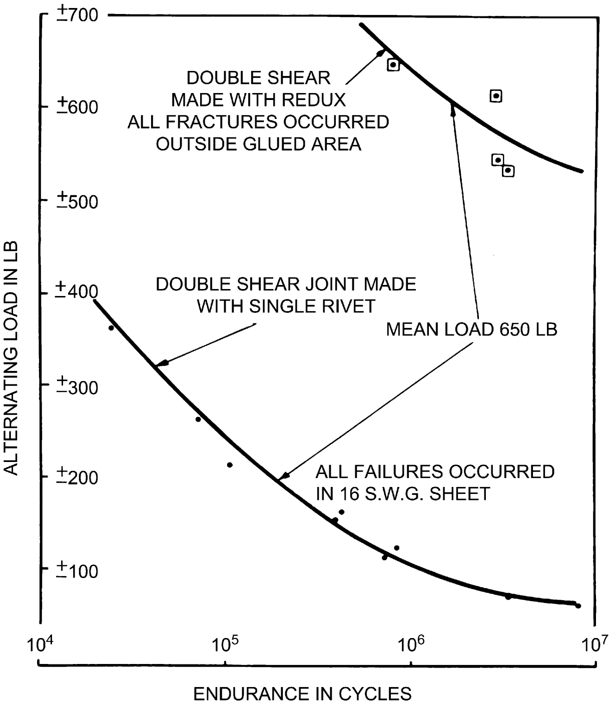


Figure 13.10 Fatigue curves for riveted and bonded joints.

Simplification in design: In general, the designs associated with bonded structures are simpler than those using rivets. For example, only simple design criteria were used to produce the Redux bonded wing sections of the Fokker F-27 Friendship and the RJ 80 (Figs 13.11 and 13.12, respectively).

Smooth external finish: When attachments are riveted to external skins, the closing of the rivet tends to pull in the skin and cause local distortion, which can lead to some disruption in the aerodynamic properties of the surface. If the same area is bonded, distortion is reduced to an acceptable level, and as can be seen in Fig. 13.13, bonding also improves the overall stiffness of the final structure when compared with a riveted component of the same pitch between points of joining.

The ability to join thin substrates: If thin pieces of, for example, aluminum are joined using rivets, the final component is susceptible to a tearing failure through the substrate that emanates at the rivet and its associated hole in the substrate. Any tensile load across the riveted joint (as seen in Fig. 13.9) is maximized at the point where the rivet enters the skin. Thus, when the substrate is thin, this can readily lead to crack and/or tear initiation and failure of the structure. Using bonding technology within these components eliminates these bearing stresses and minimizes the chance of premature failure.

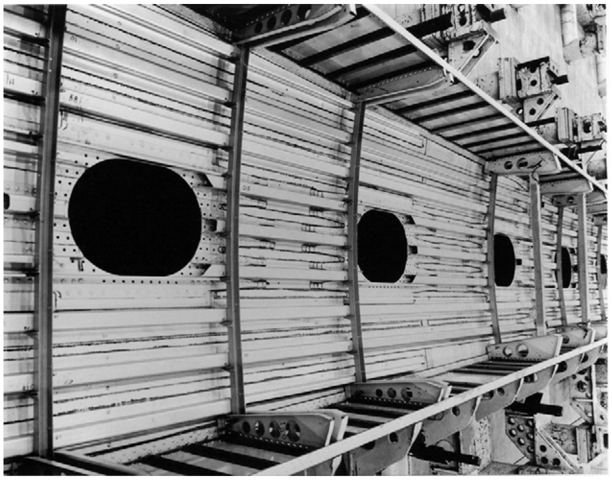


Figure 13.11 Redux-bonded wing assembly in the Fokker F-27.

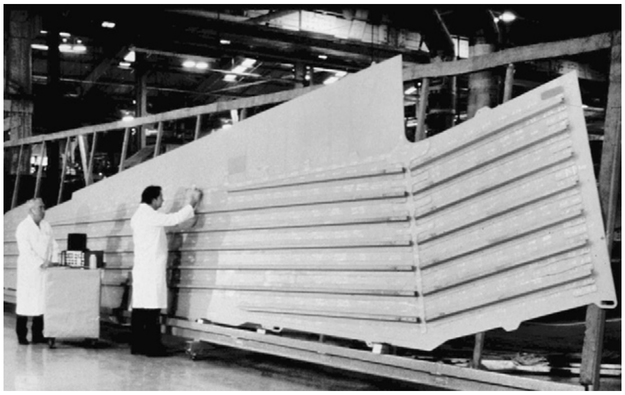


Figure 13.12 Redux-bonded wing assembly in the BAE SYSTEM's RJ 80 (formerly the BAe 146).

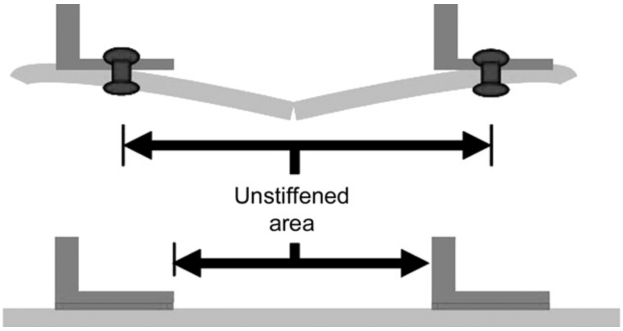


Figure 13.13 A schematic representation of the effect of riveting and bonding on the aluminum skin.

Reduction in production costs and time: When adhesive bonding is used, as opposed to producing a riveted structure, an entire component can be assembled and bonded in one operation. Furthermore, the jigging required is often simpler, which means that assembly is quicker. The thinner gauge metal that can be used reduces costs. As soon as the bonded component reaches a certain size, irrespective of all the other benefits, bonding becomes progressively cheaper than automatic riveting. This latter point can readily be seen from de Bruyne's calculations carried out in the early 1950s (Fig. 13.14). He evaluated the labor and monetary commitments and showed that, at stringer lengths of more than about 8 m, bonding was more economic both in terms of time and overall costs.

Crack growth arrest: A crack growing in an external skin is neither stopped nor is its rate of growth retarded in a riveted structure; the crack simply grows round the rivet or through the rivet hole. Any crack meeting, for example, a bonded stringer such as those represented schematically above, is turned back on itself and cannot progress.

As an example, Fig. 13.15 shows the slow rate of crack growth in two samples of Glare® (q.v.)—a bonded laminate—compared with the catastrophic

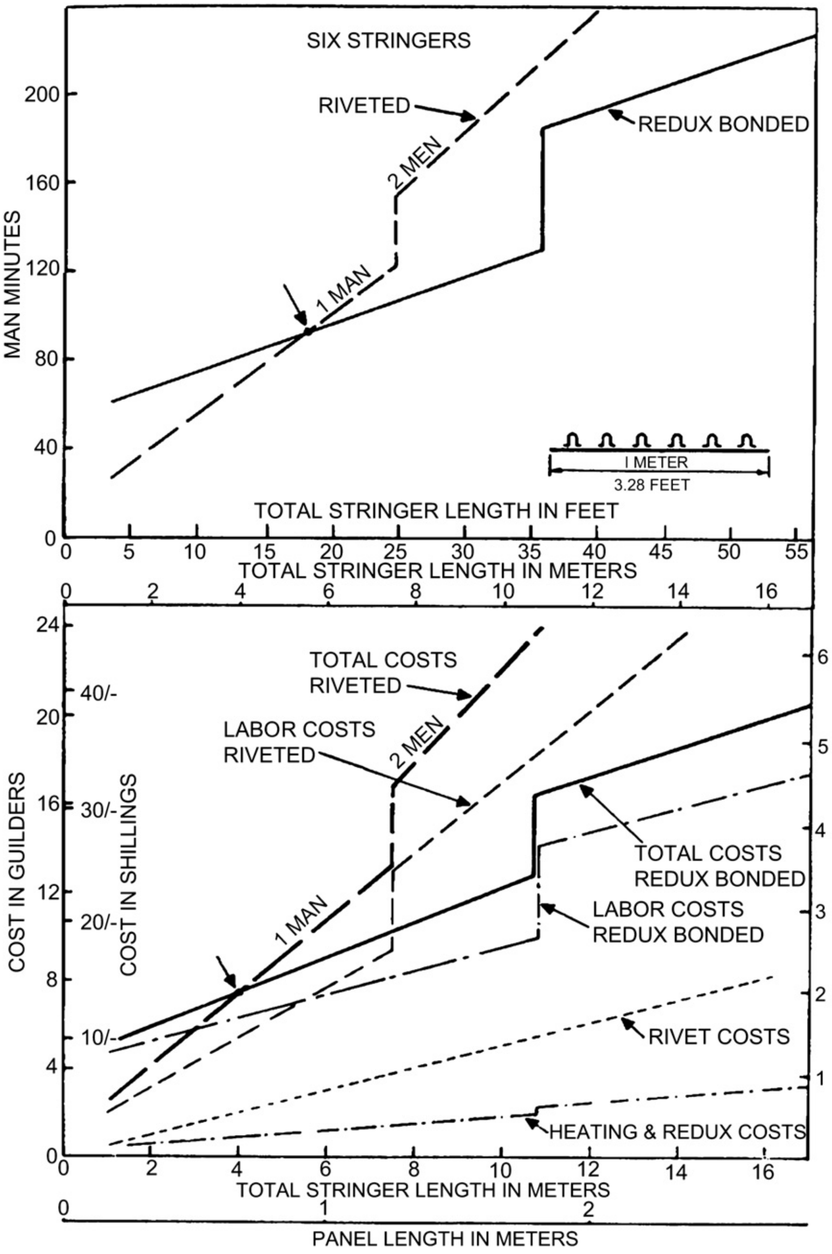


Figure 13.14 Economics of bonding versus riveting (early 1950s).

crack growth associated with aluminum alloy sheet. For an explanation of the Glare designations, see Section 13.3.1.6.

Joint sealing: As can be judged from Fig. 13.13, the integral bonding of components in the main aircraft frame, particularly in the fuel tanks, makes internal pressurization a much simpler process.

Increased strength: The strength of a riveted structure is essentially that of the bearing strength of the rivet on the skin to which it is fixed. One simple experiment showed that a riveted structure having an area of about 7000 mm^2 failed at a shear load of about 3.5 kN. The same structure, when adhesively bonded, failed at a load in the region of 55 kN.

New types of structure utilized: As far as the aerospace industry is concerned, one of the most important, novel structures since the early 1950s has been the honeycomb sandwich panel (Fig. 13.16). It could be argued that the wood-skinned balsa sandwich panels used in the Mosquito or the metal skinned version used by Chance Vought (Metalite®—q.v.) could have been joined by some other method than adhesive

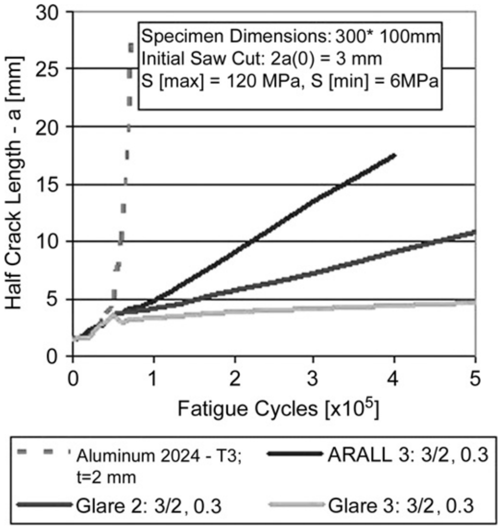


Figure 13.15 Crack growth in fiber-metal laminates compared with aluminum alloy (courtesy of Fibre Metal Laminates, Delft).

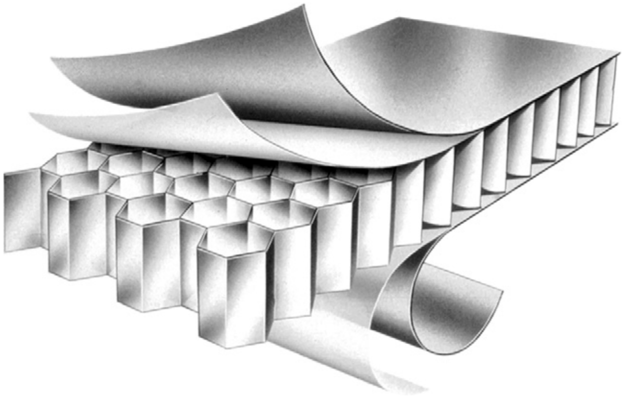


Figure 13.16 Schematic representation of a bonded honeycomb sandwich.

bonding. However, it is nearly impossible to argue such a case for the structures using aluminum, aramid, glass, or carbon honeycomb. It is the filleting effect of the adhesive (q.v.) that enables the skins to be securely fixed to the honeycomb core.

The ability to join dissimilar materials: de Bruyne originally had in mind the use of adhesives to join combinations of metal, wood, and Gordon Aerolite. However, it is just as valid today when considering the structural bonding of the range of fiber-reinforced composites that are now used in the aerospace industry: particularly glass, carbon, and aramid fiber-reinforced epoxy, phenolic, cyanate ester, and PI matrices.

Having spent a significant amount of effort in both optimizing the chemistry and the structure of the matrix and prepreg and the orientation of the prepreg in the final laminate to produce optimum properties, the last thing that many designers want to do is to drill holes through it, so that other components can be attached. What is needed, therefore, is a range of adhesives that will join components without affecting their overall properties.

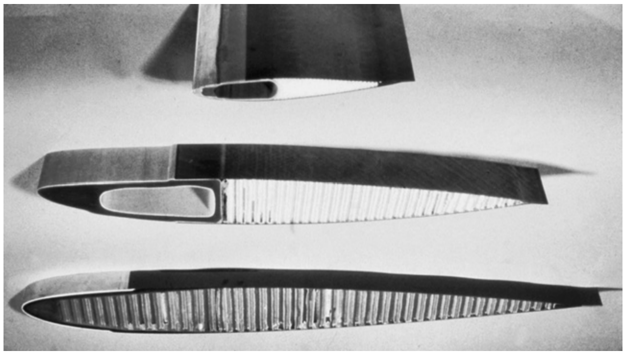


Figure 13.17 Bonded Westland helicopter rotor blade sections.

Fig. 13.17 shows helicopter rotor blade sections where adhesive bonding is used to produce components from carbon and glass composites, aluminum and Nomex® honeycombs, and simple "plastic" foams.

13.3 The Adhesive Joint

Any adhesive joint comprises two substrates, which may or may not be of the same material, which are joined by means of an adhesive.

13.3.1 Substrates

Although aircraft structures comprise thousands of components produced from a myriad of basic materials, the most common substrates for structural adhesive bonding are wood, aluminum, titanium, stainless steel, and the composite materials such as bonded sandwich structures, fiber-reinforced plastic (FRP) laminates, and fiber–metal laminates (FML) in which the metal is usually aluminum.

13.3.1.1 Wood

In postwar applications, wood is nearly always used as bonded plywood.

13.3.1.2 Aluminum

The aluminum alloys most frequently encountered are the 2000, 7000, and, occasionally, the 6000 ranges with 2024 and 7075 grades being the most common aluminum–lithium alloys such as 8090C are also used in special applications.

13.3.1.3 Titanium

Occasionally, aerospace applications utilize commercially pure titanium, but the most commonly encountered substrate is an alloy of titanium that is designated Ti 6A14V, which contains 6% aluminum and 4% vanadium.

13.3.1.4 Stainless Steel

Stainless steels are alloys of iron with a low carbon content (usually $<<2\%$) and a minimum of 10.5% chromium. Dependent on the grade, stainless steels can also contain nickel, manganese, molybdenum, titanium, copper, and nitrogen. These other alloying elements are used to enhance properties such as formability, strength, and cryogenic toughness. The main requirement for stainless steels is that they should be corrosion resistant for a specified application or environment.

Typical stainless steels specified for aerospace use (many are covered by the BS 500 specifications) contain $\leq 0.15\%$ carbon, 11–20% chromium, $\leq 2.0\%$ manganese, 4–10% nickel, and 0–2% molybdenum. Other trace elements, including titanium and niobium, can also be present as stabilizers.

A few structural applications, particularly in missile construction, utilize the so-called carbon steels (mild steels); these are of high carbon and low chromium content. These will be covered under the relevant application section.

13.3.1.5 Fiber-Reinforced Plastics

FRPs are usually constructed of unidirectional or woven fibers imbedded in a specifically formulated resin matrix. The fibers are usually of glass and/or carbon although some specific applications call for aromatic polyamide (e.g., Kevlar®), quartz, or even boron fibers.

The resin matrix is usually a formulated thermoset system (i.e., a reactive matrix, which on the application of heat and pressure, chemically reacts to form an infusible reinforced laminate). The thermosetting matrices are most often based on epoxy chemistries although there are plenty of examples of phenolic, bismaleimide (BMI), and PI matrices (e.g., the HexPly® range from Hexcel Composites) and a few where the resin is based on cyanate esters. Thermoplastic matrices are also encountered (i.e., matrices that can change from a solidus to a liquidus form by the application of heat and pressure and then revert to the solid state on cooling), which are usually, but not exclusively, based on polysulfone, polyethersulfone, or polyether ether ketone chemistries.

In all cases, the substrates are prepared by the careful orientation of the individual prepreg layers (to obtain the properties required) which, after being cured under pressure at temperatures between 120 and 175 °C, form the composite laminates that become the adherends in the structure.

13.3.1.6 Fiber–Metal Laminate

FML materials are the most recent substrates to be used in aircraft construction. The first products, initially designated Arall® (aramid fiber-reinforced aluminum laminates), Glare® (glass fiber-reinforced aluminum laminates), and Care® (carbon fiber-reinforced aluminum laminates), were invented by Prof. Boud Vogelesang of the Aerospace Faculty of the Technical University of Delft. Development to full commercial product status took place from 1978 to 1989 for Arall and to 2001 for Glare®.

The laminates consist of alternate layers of aluminum (0.2–0.5 mm thick), which has been anodized and then primed with Cytec-Fiberite's BR-127 corrosion-inhibiting primer, bonded together with fiber-rich, epoxy-based "adhesive-prepregs" (about 0.125 mm thick). The reinforcing fiber is usually unidirectional in nature, although woven fabric is occasionally used. Generally two or three sheets of adhesive separate each sheet of aluminum; this can be in the 0° direction or laid up in a cross-plied orientation.

In all cases, a fatigue-resistant metal laminate is produced, which not only resembles aluminum but can also be worked, machined, and bonded in a similar manner.

A typical Glare® structure (glass fiber reinforcement) is given in Fig. 13.18 and Glare® product designations are given in Table 13.1; the designations for Arall® are very similar.

The product designation, for example, Glare® 3-4/3-0.4, indicates, therefore, that the laminate is produced from 0.4-mm-thick 2024-T3 aluminum alloy and comprises four layers of aluminum and

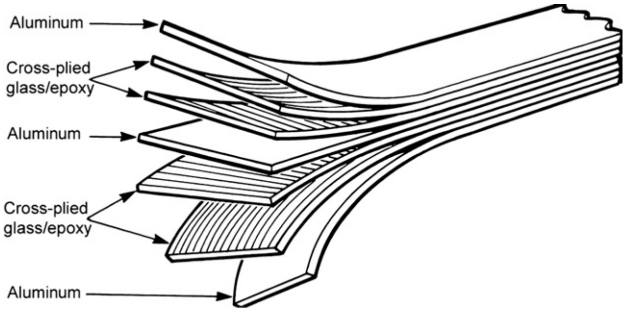


Figure 13.18 Schematic representation of a typical Glare (FML) structure.

three fiber layers, each fiber layer being two sheets of adhesive prepreg orientated in the 0°/90° direction.

13.3.1.7 Sandwich Panels

Bonded sandwich structures are vital in aircraft design as they enable significant weight reduction without the loss of stiffness and strength. A sandwich panel comprises metallic or synthetic surface skins integrally bonded to a central core. In some instances, this core is balsa wood or, because of objections to using "natural" products in structural components,[6] a foamed "plastic." Typical examples of the latter are foams of polyvinyl chloride, phenolic, and polyurethane (PUR).

It was the former, however, that, initially, proved to be of great interest to the aircraft industry. The essence of an idea of de Bruyne was worked on by Chance Vought in the United States. They used Redux 775 liquid and powder adhesive to bond thin aluminum skins to "end-grain" balsa wood sheets to produce sandwich panels. These panels were called Metalite (Fig. 13.19).

This was first used in skinning the fuselage and wings of the relatively unsuccessful F-6 Pirate and the F-7 Cutlass. It is reported that Metalite was used extensively in skinning the Chance Vought F-4-Corsair,[3] but no corroboration can be found for this statement. However, Metalite did come into its own when the skins of the wings and tail planes of the Regulus guided missile (Fig. 13.20) were constructed from it, leading to significant weight reduction while retaining the required stiffness.

However, the majority of sandwich panels now utilize a honeycomb core rather than either balsa wood or plastic foam; the adhesive can be based on either thermosetting or thermoplastic chemistries. The three basic components used in honeycomb sandwich construction are discussed later.

13.3.1.7.1 Honeycomb Core

In 1938, de Bruyne was contemplating the use of a metallic "reinforcement" of the Miles Magister tailplane, which was to be constructed of either Gordon Aerolite or plywood. This reinforcement was to be a "honeycomb of hexagons" and would be inserted between the upper and lower skins of the tailplane. Like the Blenheim spar mentioned earlier, the idea for honeycomb had its roots in the natural world. This time, it was the lightweight cellular structure seen in the human skull (Fig. 13.21). This concept is shown in his laboratory notebook (Fig. 13.22). A potential method of manufacture was also patented in 1938.[7]

In 1938, when de Bruyne patented honeycomb, there were no suitable adhesives to join the outer skins to the inner core, so he dropped the idea. Eventually, it was Hexcel, in the United States, that started honeycomb production in 1946 supplying glass honeycomb sandwich panels for the construction of the wings of the B-36 in 1949. In Europe, it was not until the early 1950s, with the introduction of Redux 775 Film, that de Bruyne's original concept came to fruition with the production of the so-called "corrugated" honeycomb that was sold as Aeroweb®. Here, thin foils (up to about 0.1 mm thick) were corrugated to give a sheet of half-hexagons (Fig. 13.23). An adhesive, initially an epoxy-based Araldite® formulation, was applied to the flat surface of the half-hexagon. Layers of corrugated foils were stacked on top of each other until the required thickness was achieved. Glass rods were inserted into the hexagonal apertures and the whole assembly was clamped together, to apply pressure to the gluelines, and then heated in an oven to cure the adhesive.

The resultant honeycomb had a perfect hexagonal structure that has never been improved on even by modern advances in manufacturing technology.

As can be seen in Fig. 13.24, the flat areas of foil that are coated with adhesive are called the "nodes" of the resultant honeycomb cell, and hence, the adhesives used are often referred to as node-bonding adhesives.

Although it was of very high quality, manufacture of the corrugated honeycomb was both time consuming and labor intensive. The major advance, to improve

Table 13.1 Glare® Product Designations

Grade	Subgrade	Metal sheet thickness in mm, alloy	Prepreg orientation in each fiber layer
Glare 1		0.3–0.4, 7475-T761	0/0
Glare 2	2A	0.2–0.5, 2024-T3	0/0
	2B	0.2–0.5, 2024-T3	90/90
Glare 3		0.2–0.5, 2024-T3	0/90
Glare 4	4A	0.2–0.5, 2024-T3	0/90/0
	4B	0.2–0.5, 2024-T3	90/0/90
Glare 5		0.2–0.5, 2024-T3	0/90/90/0
Glare 6	6A	0.2–0.5, 2024-T3	+45/−45
	6B	0.2–0.5, 2024-T3	−45/+45

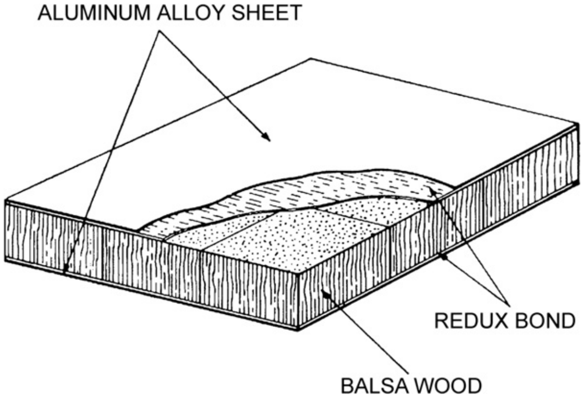


Figure 13.19 Schematic representation of Metalite-bonded sandwich structure.

Figure 13.20 Chance Vought Regulus-guided missile (image courtesy of: Lockheed Martin missiles and fire control).

the situation, was the production of "expanded" honeycomb (Fig. 13.25). In this case, stripes of adhesive (usually a formulated phenolic resole or epoxy) are printed across the aluminum foil. The next step is the accurate cutting of the roll of printed foil into sheets, which are then stacked, so that the stripes of adhesive are offset by exactly half a cell's width from one sheet to the next. The laid-up block is put into a heated press (usually at about 150–160 °C) to cure the adhesive. "Hobes" are then cut from the block, dimensions dependent on the requirements, and these are then expanded to give the resultant honeycomb slice. In some instances, (see later) the whole block, rather than the smaller hobes, is expanded.

Either process lends itself to the use of a significant variety of aluminum foils. For example, the

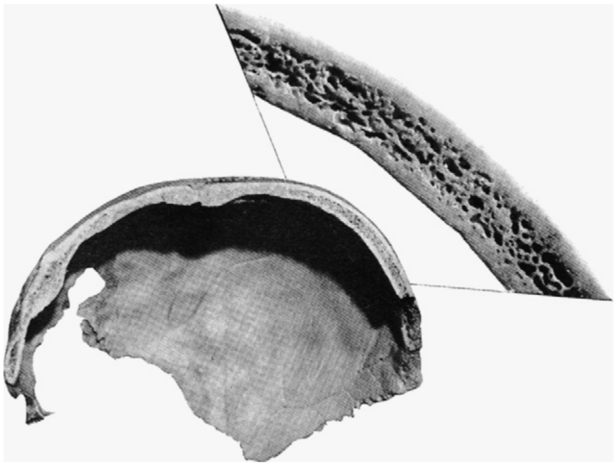


Figure 13.21 Structure of a human skull cellular bone between two solid outer surfaces.

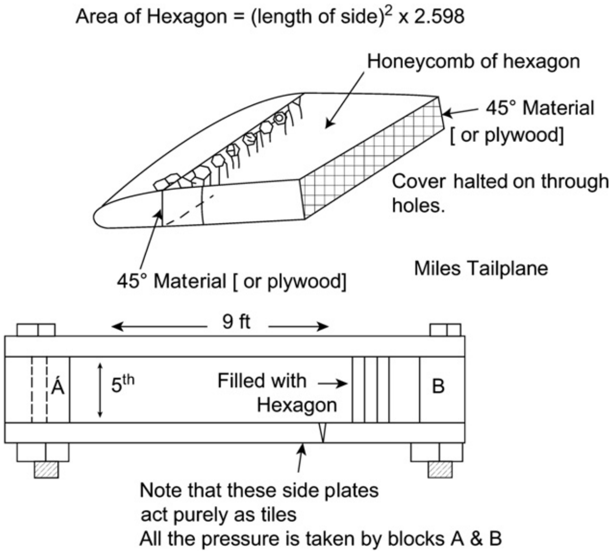


Figure 13.22 From de Bruyne's notebook for August 1938—the use of honeycomb "Reinforcement."

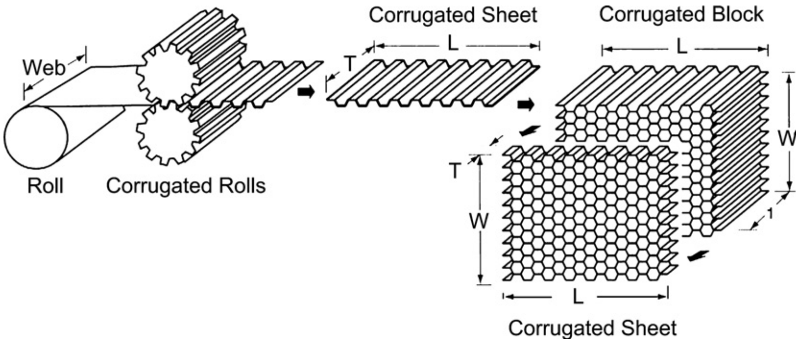


Figure 13.23 A schematic diagram showing the manufacture of corrugated honeycomb.

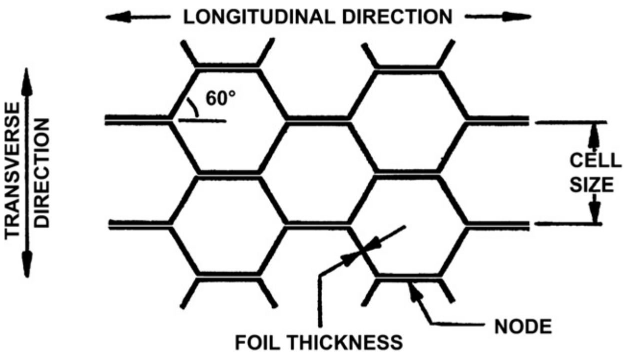


Figure 13.24 Schematic diagram showing the lay up of corrugated honeycomb.

HexWeb® (originally Aeroweb®) range of honeycombs uses 3003, 5052, and 5056 alloys—the aerospace grades having a corrosion-resistant treatment (e.g., HexWeb CR-PAA/CRIII 5052). The expanded process is also particularly suited to a variety of nonmetallic foil materials.

For these nonmetallic honeycomb cores, the manufacturing procedure, as given earlier, is augmented with one or two further steps. Once the basic block or hobe has been expanded into the conventional honeycomb configuration, it has to be pinned as it has as yet no integral strength. Then, for materials such as Nomex, the structure is heat set by taking its temperature above its glass transition point. The final step is to convert the so-called "green honeycomb" structure into a product having the required density and mechanical performance properties. To achieve this, aramid and paper cores are generally dipped, often several times, in suitable baths containing simple or formulated phenolic resole or PI systems. Once dried, the phenolic coating can be fully cured to give the final honeycomb structure its required density and its well-known engineering properties. Typical products are Nomex® (e.g., HexWeb HRH-10), Kevlar® (e.g., HexWeb HRH-49), the

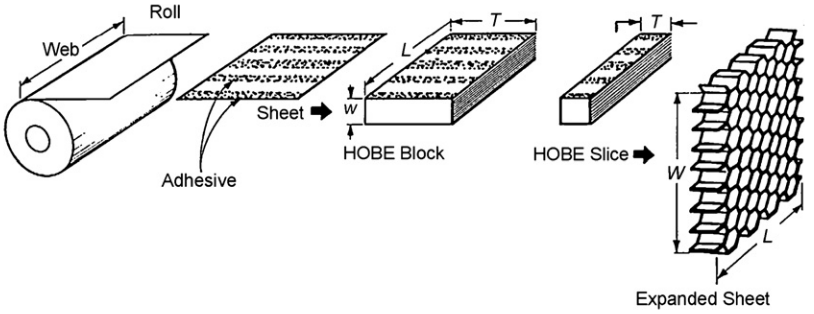


Figure 13.25 Schematic diagram showing the manufacture of expanded honeycomb.

hybrid Korex®, and cellulosic paper (e.g., HexWeb HRH-86).

A similar procedure is carried out for fabric-based honeycombs. Here, the pinned honeycomb structure is immersed in an impregnating solution, which is then dried and cured. Typical chemistries used are peroxide-cured polyesters for glass fabrics, and phenolic resole formulations or PI systems for glass and carbon. Typical products are glass (e.g., HexWeb HRH-327) and carbon (e.g., HexWeb HFT-G).

For substantially, but not exclusively, aluminum core, the conventional hexagonal configuration can be varied with a range of other shapes:

"OX Core," where the core has been overexpanded in the "W" direction

"Flex Core," which enables exceptional formability of the core to take place with tight radii of curvature being possible

"Double Flex Core," which has a large cell size and possesses high compression properties

"Reinforced Hexagonal Core," which provides a honeycomb of higher density for use at, for example, attachment points

Figure 13.26 shows these configurations, in comparison with the conventional hexagonal core.

If the adhesive used to form the integrally bonded sandwich panel is of such a chemistry that volatile matter is evolved during cure, then the potential pressure built up inside the individual honeycomb cells can be alleviated by using perforated honeycomb core; this is particularly relevant to aluminum honeycombs. During processing, prior to applying the node bond adhesive stripes, the aluminum foil is passed over a perforating roll, which punches small holes in the foil.

Finally, honeycombs made from titanium are also available (e.g., from Darchem Engineering). These are manufactured by a corrugation technique, the nodes being laser spot-welded rather than adhesively bonded.

13.3.1.7.2 Skins

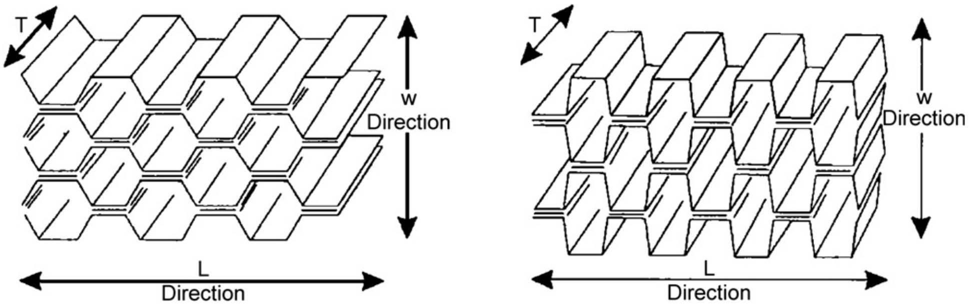
The potential skinning material for honeycomb sandwich panels can cover all the other substrates mentioned earlier—in flat sheet form—and can be augmented with decorative laminates based on melamine−formaldehyde, P/F laminates, or any other suitable plastic. The latter are to be seen in aircraft interiors.

13.3.1.7.3 Adhesive

The adhesive can be of any chemistry and/or format; the latter includes liquid, paste, or film adhesives. It must rigidly attach the skins to the core and, generally, should be of high modulus when cured. It is accepted that brittle adhesives, that is, adhesives showing relatively low peel strength, should not be used in very light sandwich structures that are likely to be submitted to a significant degree of abuse in use.

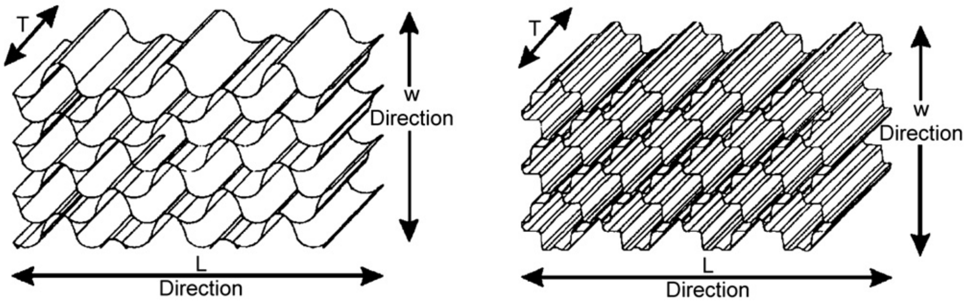
It is of paramount importance that the adhesive should be capable of forming the so-called "fillets" during cure. This means that during its cure cycle, the adhesive will melt and flow away from the skin, lying at the center of the honeycomb, first to the cell edges and then down the sides of the cell. This leaves a conical "fillet" of adhesive on the cell walls and only a very thin coating on the skin. The adhesive between the edge of the cell and the skin should form a butt joint between the two materials.

It is common with many structural adhesives that the size of the fillet on the bottom of the panel is



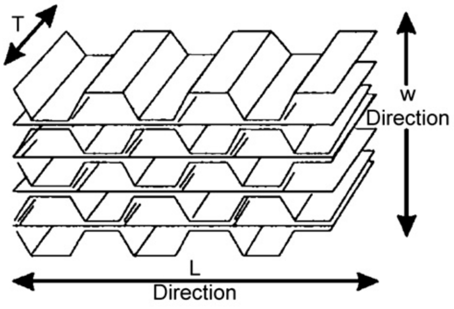
Hexagonal Core

OX Core



Flex Core

Double Flex Core



Reinforced Hexagonal Core

Figure 13.26 Honeycomb core configurations.

larger than that at the top. This is attributed to preferential flow from the top fillet to the bottom one.

Figure 13.27 illustrates the filleting phenomenon; the size of the fillet has been deliberately exaggerated.

The combination of core (aluminum, aramid, paper, carbon, glass, or balsa), skins (aluminum, steel, titanium, FRP, melamine, or wood), and adhesive (film or paste, epoxy, phenolic, PUR, PI, cyanate ester, acrylic, or thermoplastic) gives a sandwich panel that is an integrally bonded, load-bearing structure.

Using bonded sandwich beams, of different core thicknesses (*t* and 3*t*), in place of all metal components (a bonded metal beam of overall thickness *t*), it is possible to increase the stiffness and strength, with minimum weight penalty. This can be seen in Table 13.2.

If, however, weight saving is the important criterion, rather than an increase in strength or stiffness, then Table 13.3 shows what is possible by indicating the beam thickness required to maintain a deflection of 1 mm under a load of 500 kg over a span of 1 m.

13.3.2 Substrate Surface Pretreatment

To form a strong, integrally bonded, load-bearing structure, the surface of the adherend should be pretreated before application of the adhesive; this is vital if good environmental or thermal durability is required. Such a procedure ensures that the surface

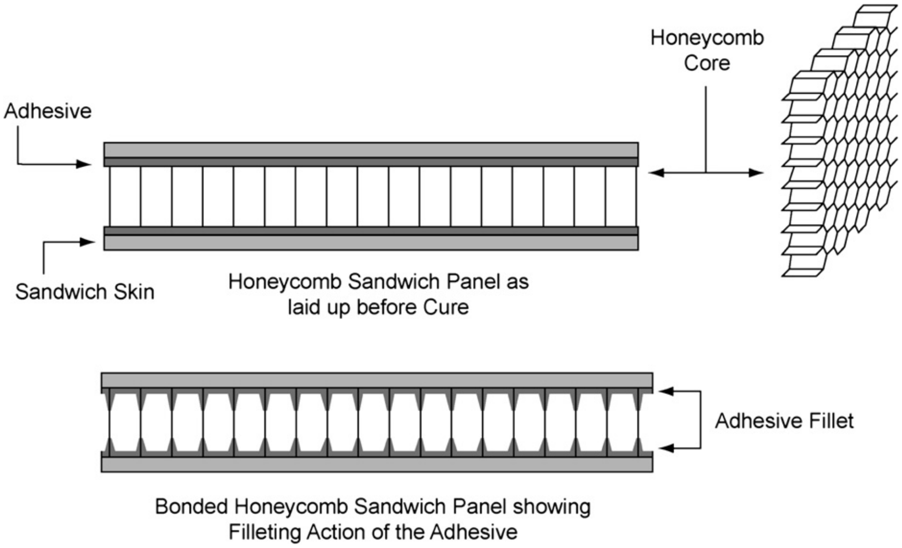


Figure 13.27 Schematic representation of the adhesive filleting action in a bonded honeycomb sandwich panel.

is in as clean a condition as possible, removing weak boundary layers that could adversely affect the performance of the resultant joint.

13.3.3 Primers and Priming

In aerospace applications, once metallic adherends have been pretreated, it can be several weeks before they are bonded. In view of the fact that most of the oxide or “fresh metal” surfaces are stable for considerably less than 24 h, these surfaces have to be protected during the time that the component is stored prior to bonding. This is invariably achieved by priming the dried adherend immediately after pretreatment; such techniques rarely, if ever, apply to fiber-reinforced composite components.

The perceived drawback with primers, however, is that both the surface protection and, particularly, the corrosion inhibiting systems, can be very sensitive to coating thickness. It is possible almost to halve the peel performance of some adhesives when going from primer coating thicknesses in the region of 2−5 μm to thicknesses above 8−10 μm.

Currently, the structural adhesive market essentially relies on two classes of primer: surface

Table 13.2 Comparison of Weight, Stiffness, and Strength for Bonded Beams

Bonded beam thickness	Honeycomb thickness	Relative		
		Stiffness	Strength	Weight
T	0	1.0	1.0	1.0
2*t*	*T*	7.0	3.5	1.03
4*t*	3*t*	39.0	9.25	1.06

Table 13.3 Bonded Sandwich Panels—Potential Weight Savings Over Metal Plate

Beam material	Beam thickness (mm)	Beam areal weight (kg/m^2)
Steel plate	12.5	98
Aluminum alloy plate	18.3	49
Aluminum honeycomb sandwich panel	33.0	9

protection primers and corrosion inhibition primers. There is a further class of materials that are said to act as surface pretreatment agents in their own right as well as offering surface protection and, it is claimed, bond enhancing primers: these are the organosilanes. By far, the greatest numbers of commercial products are now corrosion-inhibiting primers.

13.3.3.1 Surface Protection Primers

These are usually solvent-based systems of low solids content (ca. 10%). Their chemistries should match those of the structural adhesives to be used in the bonding application. To this end, in a commercial range of adhesives, each primer offered is often a simple solution of its equivalent adhesive, where any insoluble fillers and so on have been removed.

This means, therefore, that the chemistries associated with the primers could be as varied as the adhesives used with them. In aerospace applications, however, the predominant surface protection primer chemistries, for structural bonding, are those based on epoxy; phenolic-, PI-, and PUR-based primers are also encountered.

These primers are applied to the abraded or chemically pretreated substrate by brush, roller, or spray-gun. The wet coating is dried, usually in an extracted, air-circulating oven at about 60−80 °C, to remove the solvent(s).

There is, however, no hard and fast rule about the next step in the process. In some applications, the primed substrates are then stored in a clean, dry area until needed for component assembly and bonding. However, other applications call for the primer to be cured, by oven-stoving, at the requisite temperature. These components would then be similarly stored until required.

In the first case, the primer co-cures with the adhesive, and in the second, the adhesives wet and bond to the already cured primer coating. Irrespective of which route is followed, the primer protects the integrity of the pretreated surface prior to bonding, ensuring that as high a quality bond as possible is formed.

It should, however, be remembered that surface protection primers essentially donate nothing to the bonded joint apart from the protection of the pretreatment applied to the substrate and acting as an adequate "key" between adhesive and adherend. Enhancement of the mechanical performance of the adhesive being used is rarely seen. Indeed, in a few cases, a reduction in bonding strength occurs.

13.3.3.2 Corrosion Inhibiting Primers

These not only do the same job as the surface protection primers but also impart a degree of corrosion resistance into the bonded joint, protecting it against the attack of moisture and electrolytic corrosion. As for the surface protection systems, the primer can be dried or dried and cured following application.

Until recently, the classic example of this type of primer has been Cytec-Fiberite's BR-127. This comprises an epoxy−phenolic system dissolved in a blend of solvents. Corrosion inhibition is achieved through the addition of a significant loading of strontium chromate to the resin solution; this is present as a fairly unstable suspension.

The mechanism of corrosion inhibition, with these heavy metal chromates, hinges on the fact that they can passivate aluminum.[8−10] When such a corrosion-inhibited bonded joint is attacked, a mixture of hydrated aluminum oxide and chromic oxide (Cr_2O_3) is formed (cf. the Alocrom process). This not only seals the "oxide" film, repairing the damage caused by the ingress of the electrolyte, but the presence of the stable chromic oxide also reduces the rate of dissolution of the aluminum oxide. The longevity of such a protection is due to the low solubility ($\sim$1.2 g/L at 15 °C) of the chromate in water,[11] which means that the chromate remains "active" for a considerable period of time.

The possibility of using other inorganic compounds such as the oxides, hydroxides, phosphates, and borates of calcium, magnesium, and zinc, to replace the potentially carcinogenic chromates, has recently been investigated by many companies including Hexcel Composites and 3Ms.

Another approach has been the evaluation of suitable "ion-exchanged silicas." In the presence of electrolytes, such materials give protection by releasing passivating ions that can interact not only with the matrix but also with the electrolytic species themselves and the substrate. Such type of inhibitor is characterized by the fact that it is completely insoluble in water and only works on demand, that is, only when invading electrolytic species are present. Fletcher[10] has given a schematic mechanism for this method of corrosion inhibition, which is summarized in Fig. 13.28.

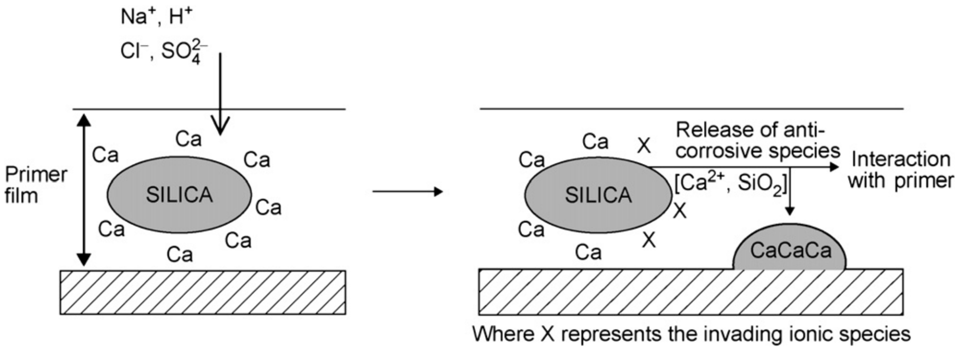


Figure 13.28 Schematic representation of the corrosion inhibition reaction mechanism for ion-exchanged silicas.

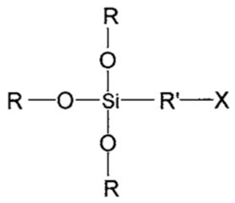
Research is now strongly centered on producing primers with low volatile organic contents (VOCs) by using water as the primary solvent or dispersion medium or actual water-based primers in which the organic solvent content is zero. Furthermore, as indicated earlier, the move to chromate-free systems is also underway.

This has culminated in the 2003 qualification by Boeing, to BMS 5-42, of a water-based (low rather than zero VOC) phenolic primer from SIA Adhesives Inc. (Aqualock® 2000); polyacrylate and amorphous silica are used as toughener and corrosion inhibitor, respectively.

13.3.3.3 Organosilanes

Researchers in industry, governmental institutes, and academy have been evaluating the efficacy of organosilanes. Edwin Plueddemann, who is seen as the "father" of this class of compounds, has advocated their use[12] as methods of surface pretreatment as well as adhesive primers and adhesion promoters in structural bonding applications.

The generic chemistry associated with most of the silanes used in these applications can be represented as:



$$R{-}O{-}Si(OR)_2{-}R'{-}X$$

Where R represents a simple alkyl group, which is generally methyl or ethyl, R′ is an alkyl chain, which is often propyl, and X is the end group, which can be H but is more usually a functional group such as amino, epoxy, mercapto, ureido, isocyanato, vinyl, or methacryloxy.

Although some of the silanes encountered can be very complex, the two most commonly employed (Fig. 13.29) are γ-aminopropyl triethoxy silane (e.g., Silquest® A-1100) and γ-glycidoxypropyl trimethoxy silane (e.g., Silquest A-187).

The theory behind their use is that the alkoxysilane groups will hydrolyze to form silanol groups, which can then react with the metal oxide/hydroxide surface. Further hydrolyzation will form an organic−inorganic hybrid at the metal surface that can lead to either a continuous or a randomly discontinuous film, as shown in Fig. 13.30. This is very much akin to one

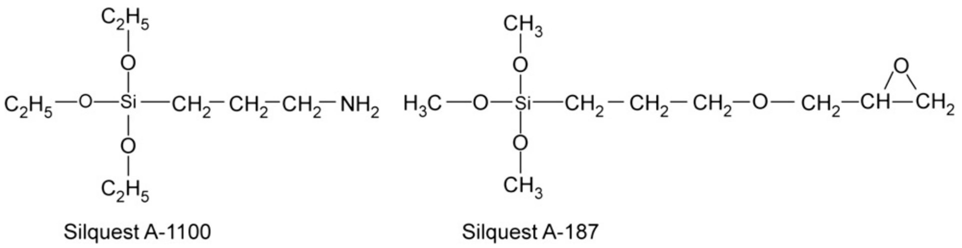


Figure 13.29 Typical monofunctional silanes.

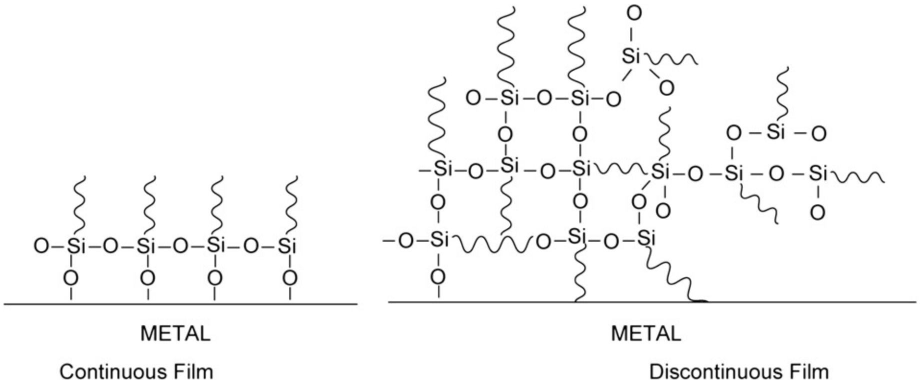


Figure 13.30 Films of monofunctional silanes on metal oxide/hydroxide surfaces.

particular aspect of the sol–gel pretreatment approach.

The key to the use of silanes, whether as sole pretreatment systems or adhesion promoting primers, is how they are prepared for application. Researchers have found the following parameters to be critical:

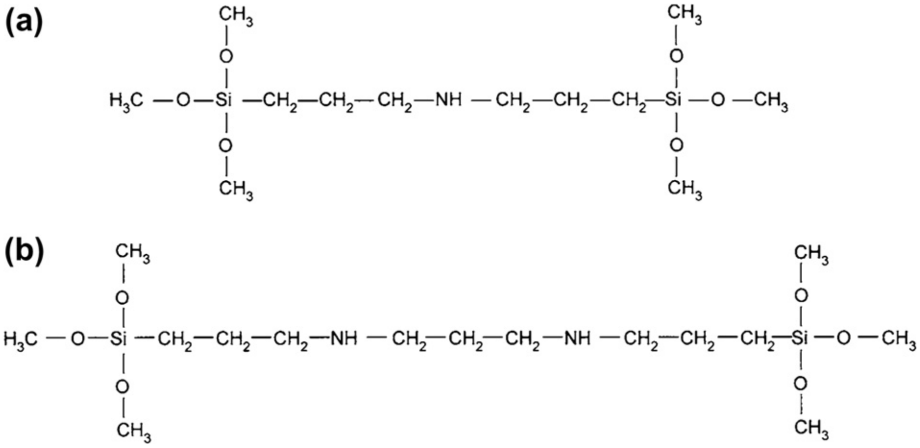
- Carrying medium (water or alcohol) silane concentration, solution pH, and temperature
- Current indications are that low concentrations of silanes in water at a pH of about 5 yield optimum performance

However, although their structures have, over the years, multiplied in number and complexity and although a considerable amount of work has been carried out in this field, the use of silanes as an accepted pretreatment or primer, prior to structural bonding in the aerospace industry, is still relatively limited; 3Ms do, though, market two silane bonding primers: EC 2333 and EC 3903. Certainly, they are used as formulating ingredients in epoxy-based primers, paste adhesives, and film adhesives. However, many formulators admit, that they are not included for any particular scientific reason, simply because "they don't appear to detract from the properties and might enhance them!"

More complex bis-silanes are now being considered not only as potential replacements for conventional metal pretreatment but also as chromate replacements in the formulation of corrosion-inhibiting primers for metals in many varied application areas.[13] van Ooij et al. advocate, among others, the use of both mono- and diamino based bis-silanes[13] (Fig. 13.31).

These bis-silanes can readily form continuous networks on the metal surface (Fig. 13.32), potentially giving excellent protection. Their post-hydrolysis film thickness has been measured in the region of 400–500 nm.

In several instances, van Ooij et al. have found that mixtures of mono and bis-silanes give the best corrosion protection.



$$H_3C-O-Si(OCH_3)_2-CH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-Si(OCH_3)_2-O-CH_3$$

$$H_3C-O-Si(OCH_3)_2-CH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-Si(OCH_3)_2-O-CH_3$$

Figure 13.31 (a) Bis-(trimethoxysilylpropyl) amine. (b) Bis-(trimethoxysilylpropyl) ethylenediamine.

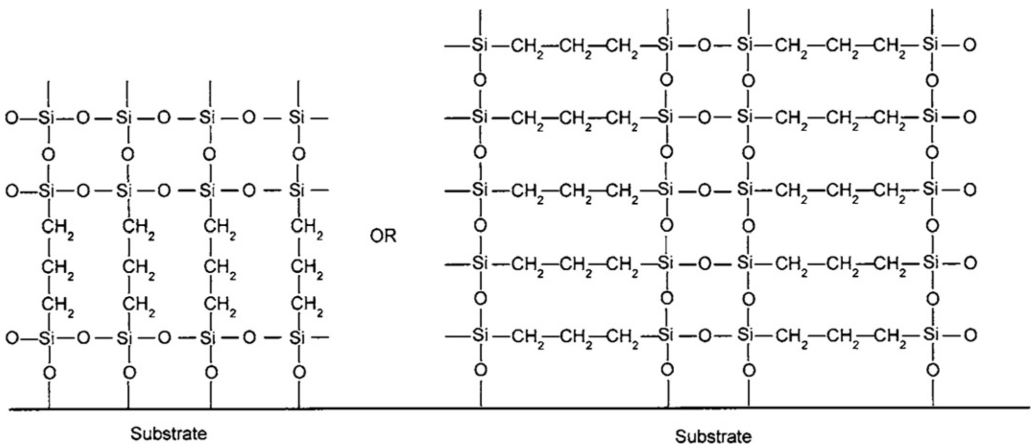


Figure 13.32 Continuous network formations of "bis-Silanes" on metal surfaces.

As with their mono functional counterparts, these materials are not yet in common use.

13.3.4 Adhesives

The heart of any bond is, of course, the adhesive. Most bonding in the aerospace industry relies on the so-called structural adhesives, that is, adhesives based upon monomer compositions, which polymerize, or cure, to give high modulus, high-strength bonds between relatively rigid adherends, such as those discussed earlier, so that a load-bearing structure is produced.

To achieve this state, many of these adhesives are reactive, that is, multicomponent systems that, after application to the adherend, change their physical format from liquidus to infusible solid by chemical reaction. These polymerization and cross-linking reactions, often thermally induced, are achieved using one or more of the following reaction mechanisms:

- Condensation
- Addition
- Rearrangement
- Polymerization through the double bond

13.3.4.1 Adhesive Ranges for Aerospace Applications

There are no "universal adhesives" for the diverse applications seen in the aerospace business. Adhesives not only have to operate in space applications from about −100 to +120 °C, in civil and military aircraft under "hot/wet" climatic conditions, where relative humidities can approach 100% at temperatures up to 60−80 °C, and close to aero engine assemblies where temperatures can reach in excess of 220 °C but also have to resist the numerous fluids that are present in most modern aircraft: deicing fluid (alcohols and phosphate esters), fuels, bilge fluid, oils and lubricants, water, and water-based electrolytes.

To meet these varied requirements, a "family" of adhesives generally has to be offered to the end-user. These adhesives will vary in the actual role they have to play, their format, the chemistry used, and the cure temperature employed to achieve the required property levels. The end-users, drawing on advice from the relevant adhesives producers, may, and probably will, use several adhesives from this range to meet their design requirements.

13.3.4.1.1 "Role" of Adhesives

Generally, any structural adhesive range will include the primary adhesive itself plus two different types of supporting products that have structural adhesive properties in their own right; the chemistries and formulations of these supporting products are often strongly related to that of the primary adhesive which they accompany.

The first of these supporting adhesives, the surface protection primers and/or the corrosion inhibiting primers, have been dealt with in Section 13.3.3.

The second range of products contains the foaming and syntactic adhesives. These are the materials which can be used to splice sheets of honeycomb together, to join honeycomb to metallic channelling,

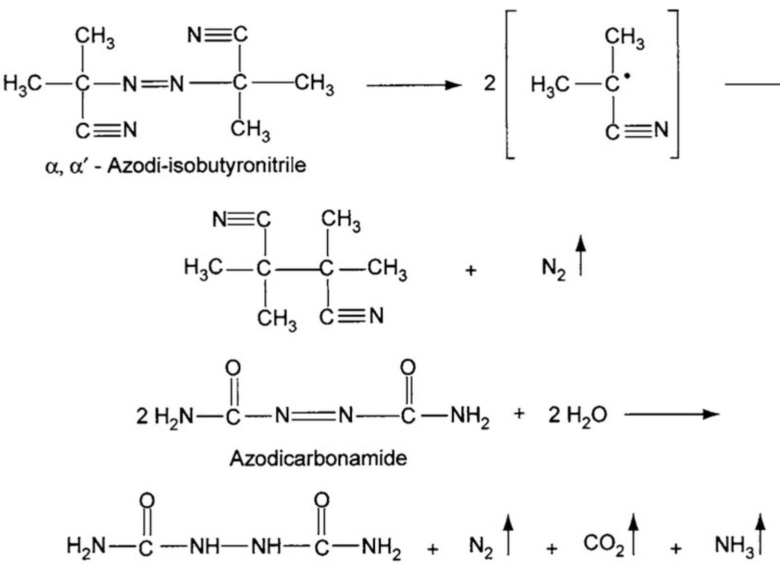


Figure 13.33 A schematic representation of the reaction for two typical blowing agents.

or simply to seal the edges round honeycomb sandwich structures. These adhesives are (1) formulations that, during the thermal cure cycle, generate controlled gaseous products (usually, but not exclusively, nitrogen) to yield an infusible structural lightweight foam or (2) lightweight pastes.

The lightweight syntactic paste adhesives are conventional, usually two-part, adhesive formulations, which contain a considerable loading of a lightweight filler to reduce the cured Sg to well below 1; Sgs of 0.55–0.75 are typical. The lightweight fillers are invariably the so-called "microballoons." These are thin-walled, generally, ceramic hollow spheres; in the case of glass microballoons, the original solid glass density of 2.48 is reduced to a value in the region of 0.3.

In the case of the foaming adhesives, the formulation very often mirrors that of the primary adhesive being used. Invariably, antislump (thixotropic) fillers have been added as well as calculated quantities of suitable foaming (or blowing) agents which break down as shown in Fig. 13.33.

The choice of the blowing agent will depend on the cure temperature being used; the curative will also often have an unexpected influence. Thus, α, α′ – Azodi-isobutyronitrile (AZDN), although its theoretical breakdown temperature is much higher, can be used in epoxy-based foaming adhesives that are designed to cure at 120 °C. The key to achieve this is the hardener. Curatives such as dicyandiamide have been found to act as powerful initiators/accelerators for the thermal decomposition reaction. For the same reasons, the azodicarbonamide, which breaks down at >200 °C, can be used under 175 °C curing conditions.

13.3.4.1.2 Formats of Adhesives

Essentially, all structural adhesives are offered in one of the three formats:

- *Solvent-based liquids*: These are usually single-component systems, which are dissolved and/or dispersed in a liquid medium that can be aqueous

Although many nonstructural adhesives can be solvent or water based, in aerospace applications, this format is usually the preserve of the surface protection and corrosion inhibiting primers. However, as indicated, there are exceptions and these are often those adhesives that are based on phenolic resoles (e.g., Redux 775 Liquid) or on PIs (e.g., PMR$^{®}$-2).

- *Pastes*: These can be single-component or two-component systems that contain no solvent and whose physical state can vary from very low viscosity liquids, for example, adhesives that can be injected into the glueline, to relatively high viscosity, pasty materials that are often thixotropic. Primary adhesives, lightweight syntactic, and foaming paste adhesives fall into this category

In the case of the two-component systems, one component is usually a formulated resin system and the

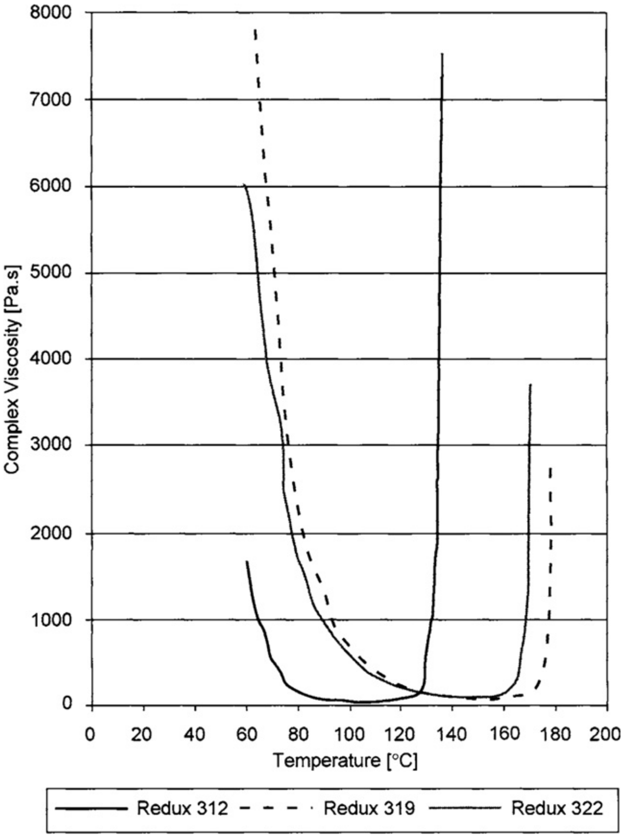


Figure 13.34 Dynamic viscosity traces for three film adhesives.

other a formulated hardener. The two-component systems are often supplied in twin cartridges, which pump out the two parts of the adhesive through an efficient mixing head. Thus, the adhesive can be easily mixed and applied to the substrate in one operation.

- *Film adhesives*: Film adhesives are supplied as foils and can be cut to the shape and size of the area to be bonded. The matrices, therefore, are solid at room temperature but, critically, will liquefy but do not cross-link on moderate heating. Thus, on heating from ambient to cure temperature, they will first melt, and then flow and displace the air in the bond and, in so doing, wet the substrates to be bonded, and finally cure to an infusible solid. This can be readily seen by examining the dynamic viscosity traces for three typical film adhesives: Redux 312, Redux 319, and Redux 322 (Fig. 13.34)

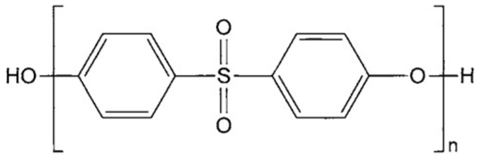
It can be clearly seen that all three systems yield low-viscosity resinous matrices at temperatures well below their cure temperature (120, 175, and 175 °C, respectively) and that there is an adequate window for flow of the adhesive to displace any trapped air and hence ensure that an intimate wetting of the substrate occurs prior to gelation taking place. The latter is indicated by the asymptotic rise in matrix viscosity.

Furthermore, because of their ability to be easily cut, these adhesives can be supplied in any desired width from more than 1 m down to about 5 mm. Their very format means that contact between operator and adhesive can be kept to a minimum. This ensures that the adhesive can be easily maintained in a contamination-free condition and, more importantly, virtually eliminates any chances of skin irritation as far as the operator is concerned.

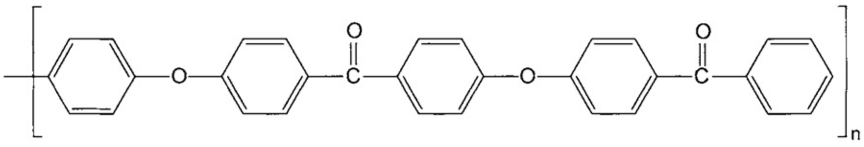
Primary adhesives and foaming film adhesives fall into this category.

13.3.4.1.3 Chemistries of Adhesives

There are many formulations, based on a large variety of backbone chemistries, which can be used as adhesives. As indicated earlier, apart from a few thermoplastic adhesives such as polyethersulfone



and polyetheretherketone (Victrex® PEEK)

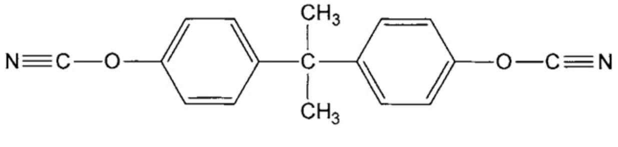


which are used in specialist applications, most aerospace adhesives utilize "reactive" chemistries. These can be summarized as follows:

- *Acrylic*: anaerobics, conventional acrylics, cyanoacrylates, the so-called "second generation," toughened acrylics, and adhesives having UV-activateable or UV-curing capabilities

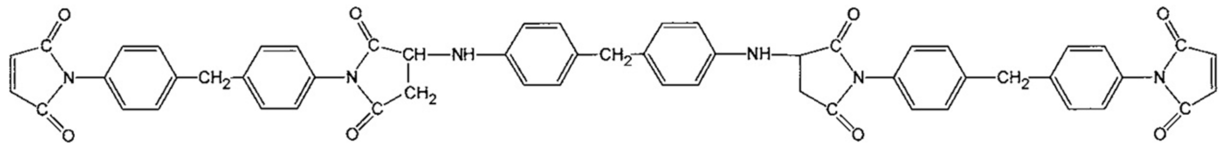
- Amino-formaldehyde
- Ceramic
- Epoxy
- Cyanate ester
- Phenolic: novolacs and resoles
- PI: BMIs and PIs (e.g., PMR-2)
- PUR
- Silicone

Of these, apart from the amino-formaldehyde systems used on wooden structures, the aerospace industry currently concentrates on epoxies, phenolics, and PIs for the majority of its structural bonding applications; it is the epoxies that are the real "workhorse" for the industry. Acrylic and PUR chemistries are used in but very few applications of a structural nature. The relatively novel chemistry based on cyanate esters, for example, Arocy B 10 (dicyanate ester of bisphenol A)



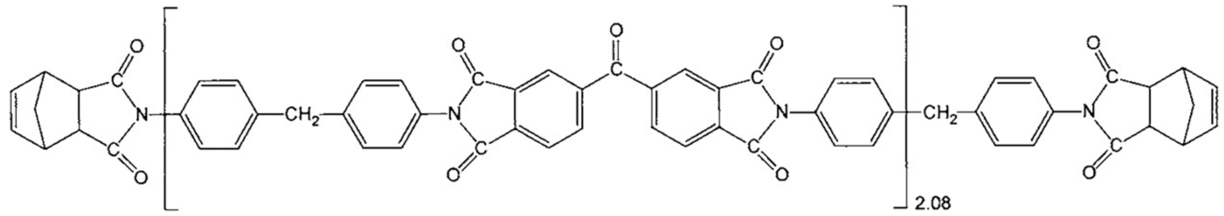
is, though, now gaining a foothold, especially for space applications, because of its proven low moisture uptake in service.

Of the PI resins available, it is the specific family based on maleic anhydride that is most commonly encountered; these are the BMI-based adhesives:



It is of interest to note that before the advent of the BMI, and the PIs in general, high service temperatures were achieved using combinations of solid bisphenol A-based epoxies with conventional phenolic resoles, the interaction between phenolic and epoxy often being promoted by the incorporation of dicyandiamide. The first "toughener" for high temperature matrices, namely finely divided aluminum powder, was also incorporated into these formulations.[1]

Thermosetting PIs are encountered for specialist, usually space, applications. These are the adhesive and composite PMR systems that are based on nadic anhydride and benzophenone tetracarboxylic dianhydride.



13.3.4.1.4 Adhesive Cure Temperatures

With such a plethora of chemistries available, the adhesives formulator can generally tailor an adhesive to meet any required cure temperature—usually in the range of ambient (i.e., about 22 °C) to as high as 230 °C. Cure times can range from several seconds, particularly with PUR-based systems and to a certain

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[1] A discussion of heat-stable adhesives is provided in Chapter 9 (by Guy Rabilloud) of this book.

extent with acrylic systems, to several hours, as is the case with BMI and PI adhesives. In this latter instance, cure, or more usually postcure, temperatures as high as 300 °C often have to be used to ensure that the final rearrangement reactions go to completion.

13.3.4.1.5 Formulations of Adhesives

Similarly, by careful formulation using this significant range of resins and the large number of curative chemistries and compatible polymeric modifiers that are available, novel adhesives can also be tailored to meet the physico-chemical and mechanical requirements of any individual bonding application. The following demands can readily be encompassed: adhesive format (liquid, paste, or film and, in the latter case whether it is supported or unsupported), shelf life, gap-filling properties, volatility, and out-gassing characteristics during cure, shrinkage, service temperature (from sub-zero to about 200–220 °C), strength requirements, environmental resistance, and toughness.

Possible adhesive formulations, therefore, are legion, so it is not possible to give examples to cover all potential adhesive ranges. However, as the workhorse of the industry is the epoxy adhesive, it is valid to give the breakdown of a generic formulation.

Thus a typical, epoxy-based structural film adhesive would comprise the following:

- *Liquid epoxy resin*(*s*): the backbone of the adhesive giving the basic properties required
- *Solid epoxy resin*(*s*): primarily as a film former but also to modify the end properties of the adhesive
- *Polymeric modifier*(*s*): primarily as a toughener and in many cases to improve the thermal resistance of the adhesive; it can also aid in film forming
- *Hardener*: usually solid and of low solubility to give a degree of latency to the adhesive and hence improve the shelf life
- *Co-hardener/accelerator*: to adjust, if necessary, the cure temperature to that which is specified
- *Formulation additive*(*s*): this/these could include such components as flame retardants for low fire, smoke, and toxicity products; coupling agents; and/or surfactants to improve the wetting and bonding with the substrate, fillers—thixotropic or otherwise—to control Sg, viscosity, flow and slump, and blowing agents for foaming applications
- *Pigments/dyestuffs*: essential for the manufacturer to aid in mixing and for the operator to identify that adhesive has actually been applied to the substrate
- *Support carrier*: to impart better handleability and to give good control of the final glueline thickness. Support carriers come in many formats and chemistries. The most commonly encountered are made from glass, polyamide (usually nylon 6 or nylon 6,6), or polyethylene terephthalate. Their format can range from random mats to highly structured woven or knitted fabrics. Typical examples of the latter are shown in Fig. 13.35

13.3.4.1.6 Typical Commercial Range of Structural Adhesives

The tables and text below show the makeup of a typical range of commercially available structural adhesives (Redux from Hexcel Composites[14]) and their supporting primers, syntactic pastes, and foaming adhesives. The whole range is considerably larger—to meet the demands of other industries such as road and marine transport, electrical, and electronics, and so on—but here only the key products for the aerospace market are shown. Table 13.4 shows the chemistries employed, and Table 13.5 gives the different formats in which this range is supplied.

Tables 13.6 and 13.7 indicate the different cure cycles that need to be applied to obtain optimum properties for each of the adhesives shown above.

It can be seen that several of the range have the ability to be cured under two or more completely different regimens that give them the so-called “dual cure” capability. This is particularly important with room-temperature-curing paste adhesives where the extended cure at ambient cannot always be contemplated by the end-user. Dual cure capability with foaming adhesives is also important as this allows the bonding shop to use only one foaming adhesive with a large range of structural adhesives.

Curing pressures range from minimal contact pressure (about 70 kPa) to about 350 kPa for the

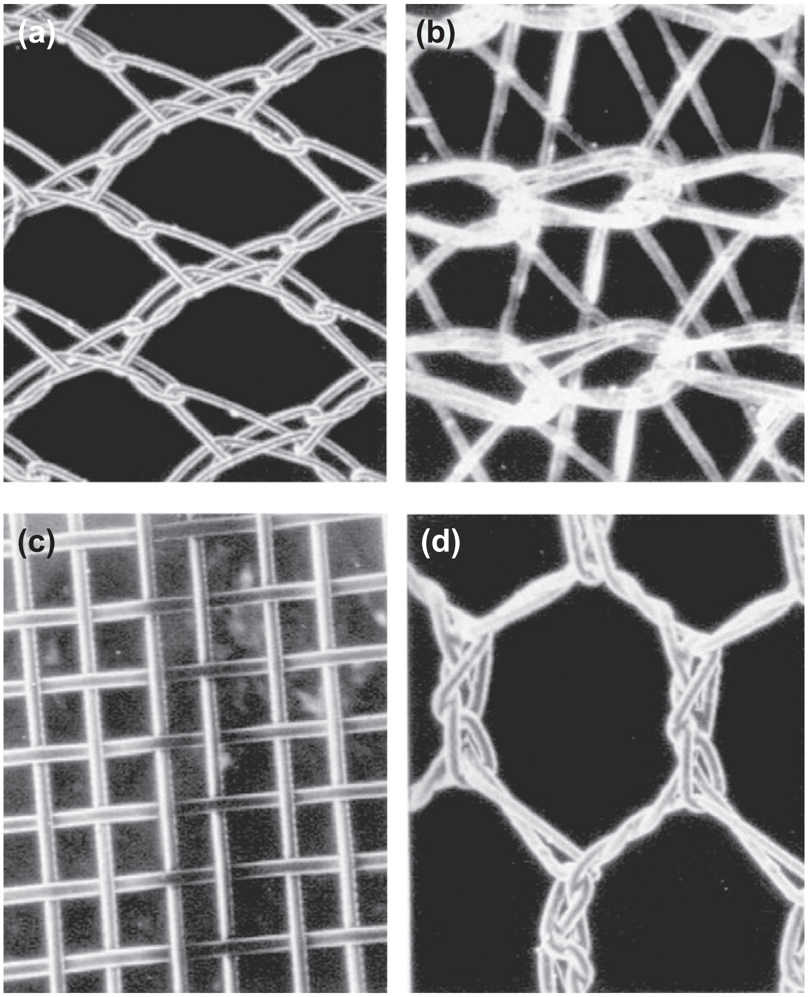


Figure 13.35 Typical woven and knitted carrier structures: (c) conventional weaving; (a), (b), and (d) various knitting styles.

Table 13.4 Chemistries Employed in the Redux Range of Structural Adhesives

	Chemistry			
Role	**Phenolic**	**Epoxy**	**Cyanate ester**	**Bismaleimide**
Primer	Redux 101	Redux 112, Redux 119, Redux 122		Redux HP 655P
Foam		Redux 206, Redux 212, Redux 219, Redux 260, Redux 840		
Lightweight syntactic		Redux 830		
Primary adhesive	Redux 775	Redux 312, Redux 319, Redux 322, Redux 330, Redux 340SP, Redux 810, Redux 850	Redux A54	Redux AP 655

Table 13.5 Adhesive Formats Employed in the Redux Range of Structural Adhesives

Format	Chemistry			
	Phenolic	**Epoxy**	**Cyanate ester**	**Bismaleimide**
Solution	Redux 101	Redux 112, Redux 119, Redux 122		Redux HP 655P
One-part paste		Redux 840		
Two-part paste		Redux 810, Redux 830, Redux 850		
Film	Redux 775	Redux 206, Redux 212, Redux 219, Redux 260, Redux 312, Redux 319, Redux 322, Redux 330, Redux 340SP	Redux A54	Redux HP 655

Table 13.6 Typical Cure Cycles for the Redux Range of Primers and Structural Film and Paste Adhesives

Chemistry	Products	Cure cycles	Service temperature (°C)
Phenolic	Redux 101	15 min at 45 °C (to dry) + 30 min at 150 °C or co-cure with the adhesive	
	Redux 775	30 min at 150 °C	75
Epoxy	Redux 810	5 days at ambient, 1 h at 70 °C, <30 min at 100 °C or <10 min at 120 °C	100
	Redux 850	16 h at ambient + 1 h postcure at 120 °C, 16 h at 60 °C or 1 h at 120 °C	100
	Redux 112	20 min at 70 °C (to dry) + 30 min at 120 °C or co-cure with the adhesive	
	Redux 312	30 min at 120 °C	100
	Redux 119 and Redux 122	30 min at 70 °C (to dry) + 60 min at 175 °C or co-cure with the adhesive	
	Redux 330, Redux 319, Redux 322 and Redux 340SP	60 min at 175 °C	135/150/175/175, respectively
Cyanate ester	Redux A54	120 min at 175 °C	160
Bismaleimide	Redux HP 655P	30 min at 70 °C (to dry) + co-cure with the adhesive	
	Redux HP 655	4 h at 190 °C + 16 h free-standing postcure at 230 °C	230

Table 13.7 Typical Cure Cycles for the Redux Range of Syntactic and Foaming Adhesives

Chemistry	Products	Cure cycles	Foaming ratio/(cured Sg)
Epoxy	Redux 830	5 days at ambient or 5 h at 50 °C	(0.66–0.68)
	Redux 840	30–60 min at 120 °C, 30 min at 150 °C, or 20–60 min at 175 °C generally co-curing with the adhesive	1:1.5–1:2.1 dependent on cure cycle
	Redux 206	30–60 min at 120 °C co-curing with the adhesive	1:3–1:4
	Redux 212	30–60 min at 120 °C co-curing with the adhesive	1:1.5–1:2
	Redux 260	60 min at 120 °C or 60 min at 175 °C co-curing with the adhesive	1:2.4
	Redux 219	60 min at 175 °C co-curing with the adhesive	1:1.9–1:2.0

epoxies and the cyanate esters, about 415 kPa (at 130 °C) for the BMI, and about 700 kPa for the phenolic adhesives to counterbalance the condensation products evolved during cure.

For the structural paste and film adhesives (Table 13.6), some indication as to the maximum service temperatures obtainable, under these cure cycles, is given. In the case of the syntactics and foams (Table 13.7), the cured Sg or expansion ratio is given.

A detailed examination of several products within this range not only reaffirms why a range, rather than a "universal" adhesive, is needed but also reinforces the versatility of structural adhesives and their "tailoring" to specific end applications.

> *Redux 312*: A cure temperature of 120 °C gives the ability to bond more delicate components while, at the same time, being more energy efficient. The service temperature of 100 °C is sufficient for most civil aircraft applications, and its performance in honeycomb structures is excellent (Fig. 13.36). It is, therefore, a good general purpose adhesive for structural bonding in many airframe applications.
>
> *Redux 319* and *Redux 322*: A cure temperature of 175 °C ensures a good elevated temperature performance for these two adhesives. They are complementary with excellent toughness, as evidenced by good peel strength, being seen with Redux 319. Optimum high temperature performance is shown by Redux 322, which has a service temperature of 175 °C with thermal excursion up to about 200 °C being possible.

Applications in military aircraft and in areas closer to engine structures are, therefore, possible with these two systems, the choice being whether toughness or

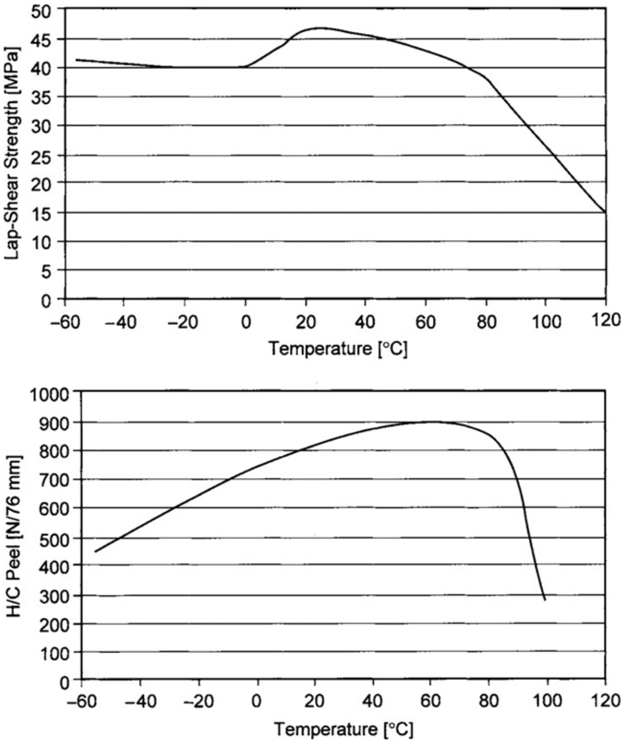


Figure 13.36 Lap-shear and honeycomb peel performance of Redux 312.

very high temperature performance is required by the design. The comparative shear performances can be seen in Fig. 13.37. Figure 13.38 shows the peel properties.

Redux HP655: This adhesive utilizes BMI chemistry and, therefore, a more demanding cure cycle is required to extend the structural adhesive's service temperature to well above 200 °C. Apart from the use of PIs based on benzophenone tetracarboxylic dianhydride, nadic anhydride and diamino diphenyl methane, for example, PMR-2 (see above), the formulated BMI adhesives offer the best resistance to extreme thermal oxidative conditions.

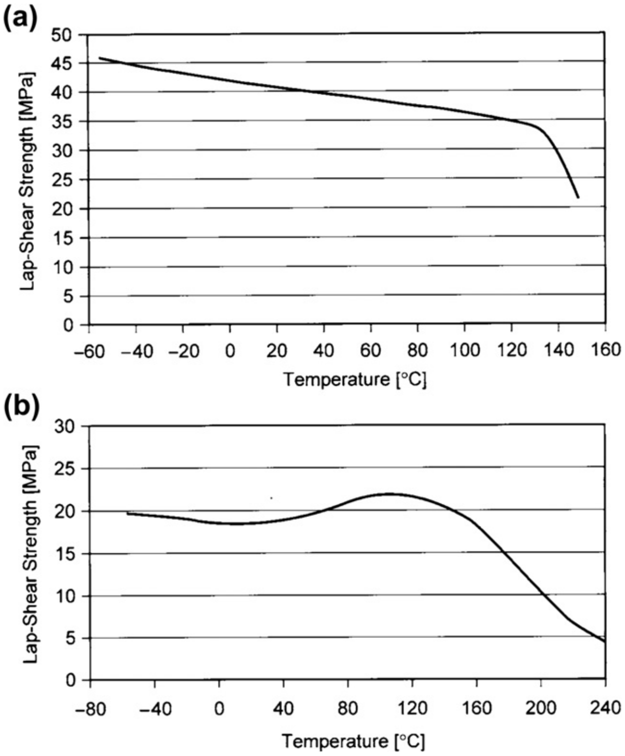


Figure 13.37 Lap-shear performance of (a) Redux 319 and (b) Redux 322.

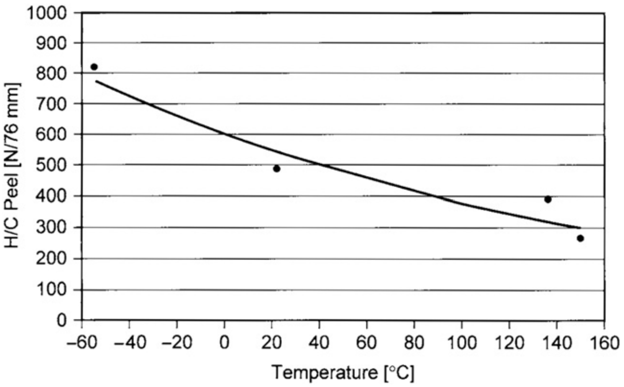


Figure 13.38 Honeycomb peel performance of Redux 319.

Redux 810: Redux 810 is a good example of two-component, high strength, high peel, general-purpose paste adhesives used in structural applications, particularly in the aerospace industry. It is capable of bonding a variety of metallic and nonmetallic substrates utilizing cure cycles, which can range from days at room temperature to minutes at elevated temperatures up to 120 °C. The system rheology is carefully controlled to ensure easy mixing and, on application, a thixotropic (nonslump) behavior. These rheological properties are also important in allowing the adhesive to be supplied in cartridges enabling the adhesive to be metered, mixed by a static mixer in the dispensing head, and dispensed directly into the glueline.

Excellent mechanical properties are augmented by a corrosion-inhibiting performance, and the incorporation of solid glass beads having a specific particle size distribution builds in an automatic glueline thickness control.

Redux 850: This two-component, essentially hot-curing, paste adhesive is a good example of the formulator co-operating with the end-user.

One of the research teams within the Airbus consortium (TANGO—Technology Acquisition of Near-term Goals and Objectives) was examining the possibility of producing the wing sections for the Airbus A.380 airliner out of carbon fiber composite. Of the various means of joining such a structure, adhesive bonding was clearly a significant possibility. With the design engineers from Airbus working very closely with the adhesives chemists from Hexcel Composites, a novel composite-bonding and shimming paste adhesive was tailor-made for the application giving the desired rheological and handling characteristics, pot life, cure cycles, and performance at elevated temperatures on both metallic and composite adherends.

Finally, to gauge the complexity of gaining acceptance for any new structural adhesive by the aerospace market, all the data that have to be generated to meet relevant specifications in both

Europe and the United States are shown for Redux 319 and Redux 319A (supported version).

The data sets are split into standard metal-to-metal tests, honeycomb sandwich tests, effect of multiple cures, fatigue and creep, thermal-oxidative testing, and, finally, immersion testing. Where necessary, an explanation of the tests being used is given with each individual table (Tables 13.8—13.13). Until recently, few physico-chemical tests were carried out for qualification purposes. Thus, for Redux 319, the only tests performed were Flow (53.7%) and Volatile Content (0.99%).

Lap shear: Conventional single overlap specimens.

Blister detection: Large area metal-to-metal bonding to ascertain adhesive flow characteristics during bonding. Conventional lap-shear specimens are machined from the bonded sheet and are tested. The specimens are examined for evidence of air entrapment ("blistering").

Floating roller and BS 5577 peel: Fig. 13.39 shows a typical peeling rig for the floating roller peel test. The differences between this test and the BS 5577 specification are the peeling angle, which is about 70° for the floating roller or Bell peel test and 90° for the BS 5577 test, and the aluminum alloy used; BS 5577 uses a much softer alloy.

T-peel: No jig is used for this test. Both adherends are of same thickness and the peeling angle is 180°.

Honeycomb peel: A conventional thin-skinned honeycomb sandwich panel is tested in peel using the so-called climbing drum peel rig (Fig. 13.40). Applying a measurable torque to the drum forces it to "climb" the specimen and, hence, peel off the bonded skin; enough specimens are tested for one to be able to assess the adhesive bond to both top and bottom skins in the sandwich.

Beam shear: Here, the bond line in a thick-skinned honeycomb sandwich panel is subjected to shear stresses utilizing three- or four-point loading (Fig. 13.41).

Honeycomb flatwise tensile: 50 × 50-mm specimens are cut from similar sandwich panels as are prepared for the beam shear test. These are

Table 13.8 Specification Data for Redux 319: Physical Properties and Standard Metal-to-Metal Properties

	Test temperature (°C)	Redux 319 (175 °C cure)		Redux 319A (175 °C cure)	
		Mean	**Range**	**Mean**	**Range**
Physical properties					
Flow (%)				53.700	
Volatiles (%)				0.99	
Standard metal-to-metal properties					
Lap shear (MPa)	22	40.5	37.2—47.0	35.7	29.2—39.3
	135	32.8		19.2	17.8—22.9
	150	20.7	17.2—25.0	16.4	13.4—23.6
Blister detection (MPa)	−55			31.3	
	22			28.8	
	135			22.1	
Floating roller peel (N/25 mm)	22	178	133—223	178	
BS 5577 peel (N/25 mm)	22	75		157	
MMM-A-132 T-peel (N/25 mm)	22	80		61	

Table 13.9 Specification Data for Redux 319: Standard Honeycomb Sandwich Properties

		Redux 319 (175 °C cure)		Redux 319A (175 °C cure)	
	Test temperature (°C)	**Mean**	**Range**	**Mean**	**Range**
Honeycomb peel (N/76 mm)	−55			820	666–974
	22	594	320–790	487	
	135	546		390	320–460
	150			264	
Beam shear (kN)	−55			10.7	
	22			10.5	
	135			8.8	
Honeycomb flatwise tensile (MPa)	−55	10.7		10.0	
	22	8.2	4.9–11.8	9.0	8.1–10.2
	135	6.5		3.6	4.3–2.9
	150	5.5	3.3–9.0	2.9	

Table 13.10 Specification Data for Redux 319: Effect of Multiple Cures on Metal-to-Metal and Honeycomb Sandwich Panels

		175 °C cure (mean)	
	Test temperature (°C)	**Redux 319**	**Redux 319A**
Lap shear (MPa)			
Control	22	44.0	37.3
	135		22.9
	150	25.0	
Second cure	22	46.0	36.7
	135		19.4
	150	22.5	
Third cure	22	45.5	40.9
	135		21.6
	150	24.2	
Fourth cure	22		36.7
	135		17.1

(*Continued*)

Table 13.10 Specification Data for Redux 319: Effect of Multiple Cures on Metal-to-Metal and Honeycomb Sandwich Panels (*Continued*)

		175 °C cure (mean)	
	Test temperature (°C)	**Redux 319**	**Redux 319A**
Fifth cure	22		34.7
	135		16.4
DTD 5577 peel (N/25 mm)			
Control	22	242	
Second cure	22	240	
Third cure	22	234	
Honeycomb peel (N/76 mm)			
Control	22		481
	135		460
Second cure	22		378
	135		396
Third cure	22		392
	135		371
Fourth cure	22		182
	135		331
Fifth cure	22		369
	135		416
Flatwise tensile (MPa)			
Control	22		8.8
	135		2.9
Second cure	22		7.7
	135		3.2
Third cure	22		7.1
	135		3.5
Fourth cure	22		8.0
	135		3.4
Fifth cure	22		7.5
	150		3.9

then bonded to rigid blocks, generally using a paste adhesive having a cure temperature at ambient or, at least, lower than that used to cure the adhesive under test. The whole is then loaded in such a manner as to subject the bond between honeycomb and skin to tensile stresses (Fig. 13.42).

Fatigue and creep tests: Conventional single overlap lap-shear and beam-shear specimens are used.

Heat aging: Conventional single overlap lap-shear, honeycomb climbing drum peel, and beam-shear specimens are exposed to the requisite temperature in an air-circulating oven.

Immersion testing: Conventional single overlap lap-shear and honeycomb climbing drum peel specimens are immersed in the requisite liquid or vapor for the requisite time.

Table 13.11 Specification Data for Redux 319: Fatigue and Creep

	Test temperature (°C)	**Redux 319A (175 °C cure)**
		Mean
Fatigue		
Lap shear at 50 Hz ($s_{\max} = 5.2$, $s_{\min} = 0.5$ MPa)		$<10^6$ cycles
Creep		
Lap shear: 8 days at 22 °C under 11 MPa (mm)	22	0.013
Lap shear: 8 days at 22 °C under 5.5 MPa (mm)	135	0.090
Beam shear: 8 days at 22 °C under 4.4 kN (mm)	22	0.14
Beam shear: 8 days at 135 °C under 3.5 kN (mm)	135	1.14

Table 13.12 Specification Data for Redux 319: Thermal-Oxidative Aging

	Test temperature (°C)	**Redux 319 (175 °C cure)**		**Redux 319A (175 °C cure)**
		Mean	**Range**	**Mean**
Lap shear (*MPa*)				
42 days at 135 °C	135	31.8		23.7
90 days at 150 °C	22			28.0
183 days at 150 °C				25.6
42 days at 150 °C	150	20.8	15.1–25.7	
90 days at 150 °C				18.5
183 days at 150 °C				15.8
Honeycomb peel (*N/76 mm*)				
8 days at 150 °C	22			246
21 days at 150 °C				264
42 days at 150 °C				192
Beam shear (*kN*)				
8 days at 135 °C	135			8.9

13.3.4.2 Adhesives Manufacture

13.3.4.2.1 Primers

Simple stainless steel, glass-lined, or even mild steel vessels, fitted with a suitable stirrer, are more than adequate for the production of solvent-based primers. These vessels will often be fitted with internal or external heating elements and water-cooled condensers, so that, for example, polymeric ingredients can be more readily dissolved at temperatures close to the reflux temperature of the solvent or solvent blend. This procedure is also valid for solvent-based structural adhesives.

If water-based primers are being manufactured, then the situation is slightly more involved. The use of water means that only glass-lined or stainless steel vessels can be used for the final stage of mixing. In many instances, solid raw materials will not be

Table 13.13 Specification Data for Redux 319: Immersion Resistances to Fluids

	Test temperature (°C)	Redux 319 (175 °C cure)		Redux 319A (175 °C cure)	
		Mean	**Range**	**Mean**	**Range**
Lap shear (*MPa*)					
JP4 *at 22 °C*					
7 days				33.1	
30 days		41.4			
90 days	22	39.0			
365 days		38.3			
30 days		16.2			
90 days	150	17.6		35.0	
365 days		14.8		11.0	
Kerosene fuel at 22 °C					
30 days		36.6			
42 days		43.3			
90 days	22	39.7			
365 days		38.3		34.0	
30 days		16.9			
90 days	150	13.1			
365 days		13.4		13.0	
Silcodyne "H" at 22 °C					
30 days		37.2			
42 days		41.6	39.9–43.4		
90 days	22	38.6			
365 days		39.7		34.0	
30 days		16.2			
90 days	150	17.9			
365 days		14.5		12.0	
Hydraulic oil at 22 °C					
7 days				35.7	
30 days		37.9			
42 days	22	42.0			
90 days		26.9			
365 days		36.9		35.0	
30 days		18.6			
90 days	150	17.6			

(*Continued*)

Table 13.13 Specification Data for Redux 319: Immersion Resistances to Fluids (*Continued*)

		Redux 319 (175 °C cure)		Redux 319A (175 °C cure)	
	Test temperature (°C)	Mean	Range	Mean	Range
365 days		17.9		13.0	
Standard test fluids at 22 °C					
7 days				36.5	
30 days		42.5	39.0–46.1		
90 days	22	38.6			
365 days		40.0			
30 days		24.4	20.3–28.5		
90 days	150	18.3			
365 days		14.1			
Deicing fluids at 22 °C					
7 days		36.2			
30 days		39.3			
42 days	22	41.5	38.7–44.3		
90 days		39.0			
365 days		39.7		36.0	
30 days		14.1			
90 days	150	14.8			
365 days		15.2		13.0	
Synthetic ester-based lubricant at 22 °C					
30 days		37.9			
42 days		41.3	39–43.7		
90 days	22	39.3			
365 days		40.0		35.0	
30 days		16.9			
90 days	150	16.6			
365 days		15.9		12.0	
Skydrol 500A at 22 °C					
30 days		34.8			
42 days		38.4	35.9–42.2		
90 days	22	39.7			
365 days		38.6		39.0	
30 days		18.6			
90 days	150	14.8			
365 days				13.0	

(*Continued*)

Table 13.13 Specification Data for Redux 319: Immersion Resistances to Fluids (*Continued*)

	Test temperature (°C)	Redux 319 (175 °C cure)		Redux 319A (175 °C cure)	
		Mean	Range	Mean	Range
Skydrol 500A at 70 °C					
30 days				29.0	
90 days	22			33.8	
365 days				28.3	
30 days				16.2	
90 days	150			15.5	
365 days				11.7	
Water/Methanol at 22 °C					
30 days		33.8		35.2	
42 days	22	40.6	38.2–43.1		
90 days		16.6		35.2	
365 days		10.3		33.8	
30 days		12.4		12.1	
90 days	150	5.9		10.3	
365 days		0.0		5.9	
Distilled water at 22 °C					
30 days		34.1		34.1	
42 days	22	39.5	37.2–41.5		
90 days		32.1		34.8	
365 days		32.4		31.0	
30 days		14.8		12.4	
90 days	150	9.0		10.3	
365 days		3.4		7.6	
Tap water at 22 °C					
30 days	22	36.6		34.2	
90 days		27.6		32.4	
365 days		31.0		32.8	
30 days	150	19.7		9.7	
90 days		13.4		10.3	
365 days		3.4		7.6	
Salt spray at 35 °C					
30 days		33.4		32.8	31.8–33.8
90 days	22	30.7		33.8	
365 days		0.0		33.8	

(*Continued*)

Table 13.13 Specification Data for Redux 319: Immersion Resistances to Fluids (*Continued*)

	Test temperature (°C)	**Redux 319 (175 °C cure)**		**Redux 319A (175 °C cure)**	
		Mean	**Range**	**Mean**	**Range**
30 days		12.8		12.7	
90 days	150	9.7		11.0	
365 days		0.0		2.1	
100% relative humidity at 49 °C					
30 days		32.5	29.3—35.8	31.6	30.1—33.1
90 days	22	30.0		30.3	
365 days		32.8		31.7	
30 days		14.6	12.8—16.4	11.7	
90 days	150	4.8		6.2	
365 days		1.0		4.8	
98% relative humidity at 70 °C					
30 days		29.7		26.5	
42 days					
90 days	22	21.4		27.6	
365 days		9.3		18.6	
30 days	150	8.3		3.8	
90 days		2.8		2.4	
365 days		1.4		2.8	
Honeycomb peel (N/76 mm)					
100% relative humidity at 49 °C					
8 days	22			420	
21 days				480	
42 days				252	

supplied as a water-based solution or dispersion and, hence, the first stage of any manufacturing process requires suitable solution/dispersions to be made. This is often achieved using a conventional bead mill (Fig. 13.43), where bead size, bead volume, temperature, pump rate, solids content, pH, and so on, all have to be optimized.

This is best carried out using statistical experimental design techniques,[15,16] optimizing the process conditions against the critical parameter of resultant particle size distribution. Once the variables to be studied have been identified, an experimental design can be created. This is usually a standard quadratic model, which can fit nonlinear data. The experimental designs produced allow several variables to be studied at once, which enables a wide area of experimental space to be mapped. This enables interactions to be identified and areas of optimum performance to be found.

The resultant matrix of experiments comprises a series of trials with each chosen variable set at high, low, or intermediate values; replication of some trials is used to assess error; other parameters are held at a constant value.

Data analysis then fits a polynomial equation to the collected data. The magnitudes of the coefficient estimates in the equation indicate the importance of the variables. This equation can be simply viewed as

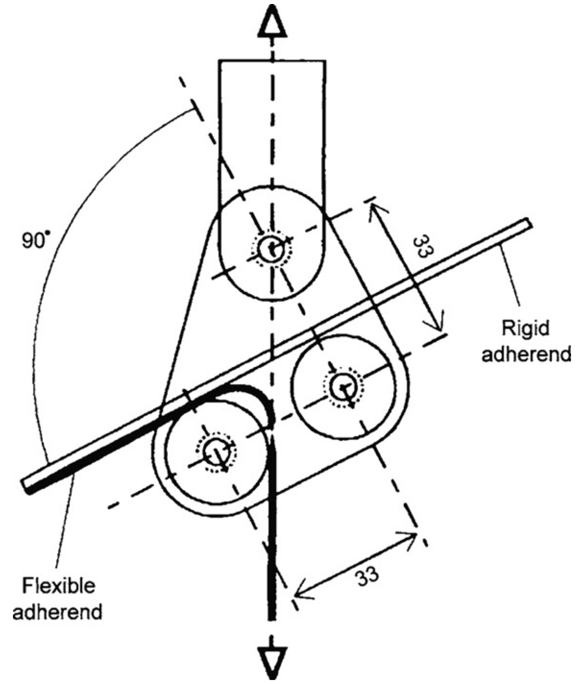


Figure 13.39 Schematic representation of the floating roller peel test.

a multidimensional French curve to illustrate the relationship between variables and responses. Those coefficient estimates with statistical significance are highlighted and are used to select the axes for contour plots.

Bishopp et al.[17] show a contour plot, or response curve, for the variation in bead size and pump rate against the $D_{0.9}$ value for the particle size ($D_{0.9}$ is the particle size, in μm, below which 90% of the particles fall); constants are bead volume at 75% and mill speed at 4000 rpm.

Contour plots allow the relationship between significant variables and responses to be visualized. These plots resemble topographical maps in that contour lines are drawn on a two dimensional plane to represent the surface of a response variable. This allows a highly visual, easily interpreted "picture" to be used to understand the process or system being studied. Thus, in the example given in Ref. 17, it is very clear that the lowest particle size is achieved using intermediate bead dimensions and that it is essentially independent of pump rate.

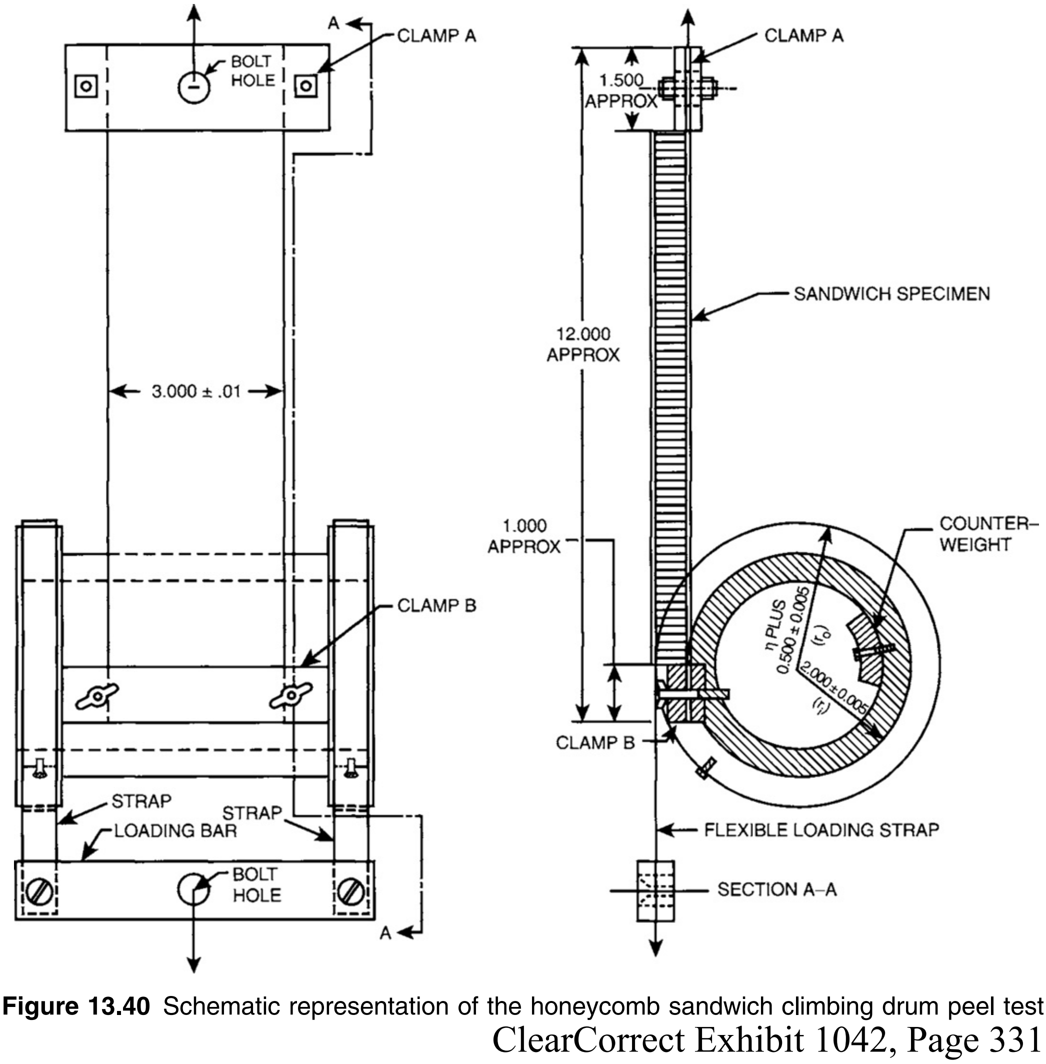
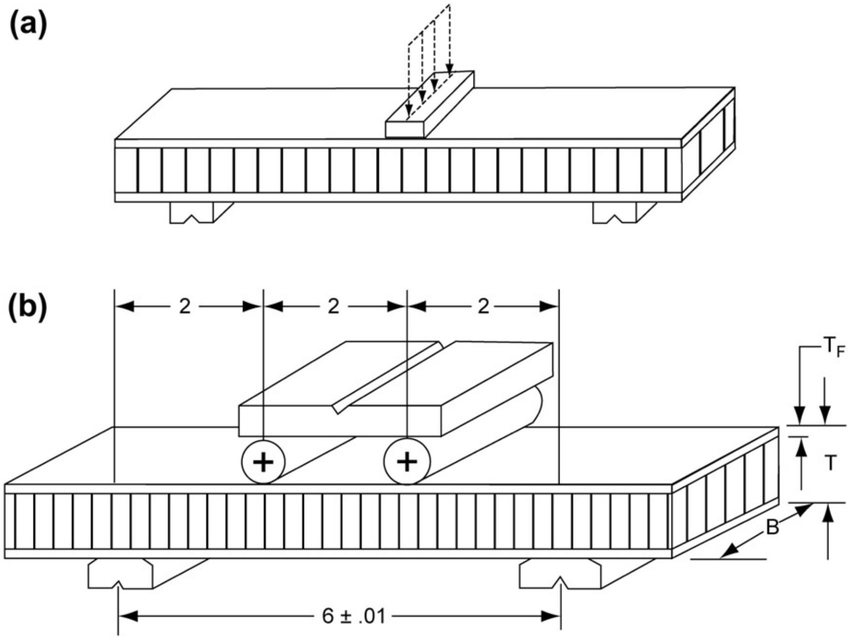


Figure 13.40 Schematic representation of the honeycomb sandwich climbing drum peel test.

Figure 13.41 Schematic representation of the beam shear test. (a) Three-point and (b) four-point loading.



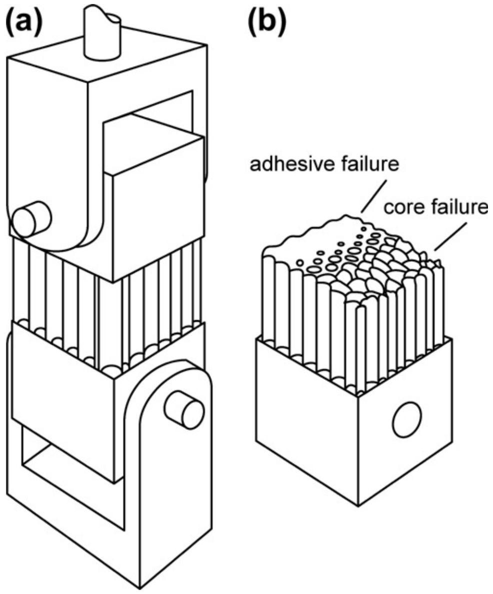


Figure 13.42 Schematic representation of the flatwise tensile test. (a) Test jig and (b) ruptured specimen.

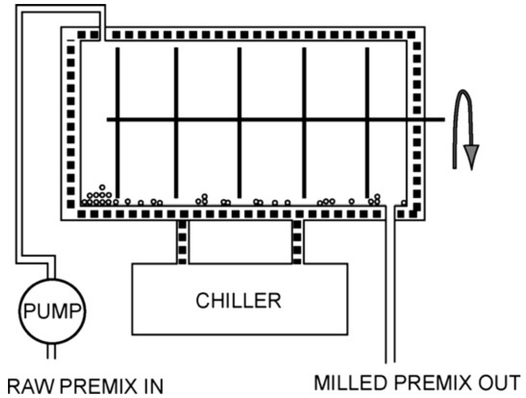


Figure 13.43 Schematic representation of a typical bead mill.

13.3.4.2.2 Paste Adhesives

Although the general method of manufacture of paste adhesives is fairly straightforward, the viscosity and chemistry of the matrix will determine the actual procedures to be followed.

Generally, both one- and two-component paste adhesives can be made in the simple mixing vessels outlined above without the need for condensers and usually without the need for heating.

Corrosive ingredients will require stainless steel or glass-lined vessels, but the remainder can use simple mild steel mixing chambers.

Low-viscosity pastes can usually be manufactured using simple stirrers to disperse and/or dissolve the raw materials. However, as the viscosity increases so does the need to use high-shear stirrers such as toothed-bladed stirrers, planetary mixers, and/or Z-blade mixers.

Insoluble powders, which can include blowing agents for foaming adhesives, curatives, fillers, and so on, can be predispersed in any liquid polymer or resin present, thoroughly wetted out using a conventional two-roll paint mill and then added as an intimate dispersion to the main mix.

Other techniques such as mixing under vacuum or under a nitrogen blanket might be necessary should incorporated air prove a problem or, as is the case with isocyanate resins and some aliphatic amines where the raw materials are reactive with moisture in the air.

13.3.4.2.3 Film Adhesives

In essence, there are two methods of manufacturing film adhesives: from solution or from a melt. In the first case, the film has to be cast and the solvent has to be removed in a continuous operation. In the second case, as there is no solvent to be removed, the matrix has to be melted and then cast into film; this is the so-called "hot melt" film technique.

The initial stage, in either case, is to produce the fully formulated matrix; the solvent-based system can use similar equipment as is used to manufacture primers and the hot-melt route would use the same sort of plant as is used for the high-viscosity pastes except that the capability of heating and then cooling the matrix during the mixing cycle will be required.

Film casting also gives rise to, essentially, two different procedures. When preparing films from solvent-based matrices, the actual equipment used can be dependent on the final areal film weight. Low areal weights, for example, 50−100 g/m^2, can utilize conventional reverse roll coating of a continuous film onto a backing "paper." This would pass straight into an air-circulating oven whose various zones would be set to drive off the residual solvent without leading to skinning or blistering of the final film. For areal weights more than 100 g/m^2, lower weight films can be laminated together through nip rollers or a suitable metering device; for example, a doctor knife-over-table or knife-over-roll technique can produce film at the correct weight, which can then be dried as before.

When 100% solid matrices are employed, manufacture of the film is simplified because no solvents have to be removed, but, nevertheless, highly specialized equipment has to be used. Figure 13.44 shows a schematic representation for a "batch" process in which the mixed formulation is metered, at a suitable elevated temperature, under a doctor knife to produce the final film.

Using the hot-melt approach, it is possible to mix and cast the adhesive film as a continuous operation. Here, the individual raw materials are fed into a conventional screw extruder, are mixed under controlled temperature conditions, and are then pumped out into a reverse-roll coating machine that can produce film adhesives from as low as 50 g/m^2 up to about 1800 g/mm^2. The schematic representation of such a process is shown in Fig. 13.45.

Mention has already been made of Redux 775, the first structural adhesive film. Its manufacturing process has not changed since 1954. A film of phenolic resole is cast under a doctor knife, a considerable excess of the Polyvinyl Fluoride (PVF) powder is curtain coated onto the phenolic film, and the excess is then

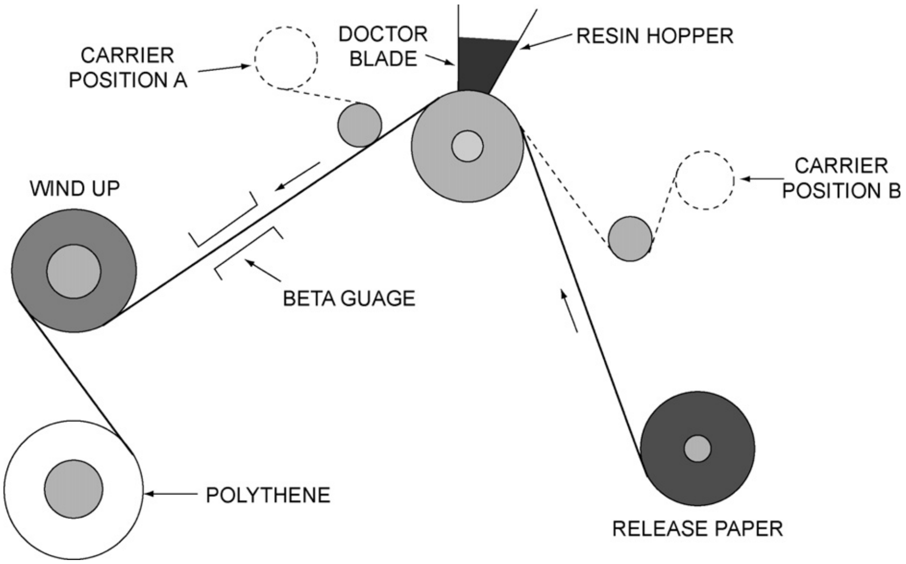


Figure 13.44 Schematic representation of a knife-over-roll "hot melt" film casting procedure.

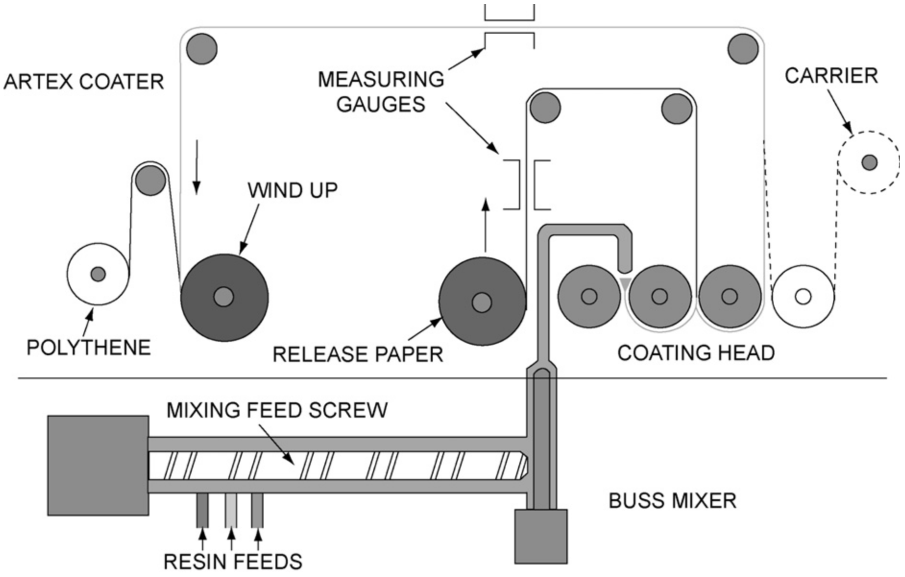


Figure 13.45 Schematic representation of the continuous manufacture of a "hot melt" adhesive film.

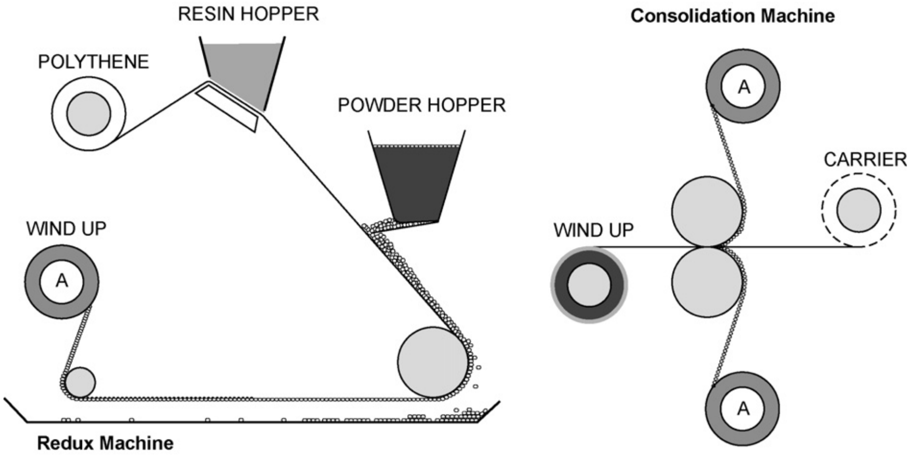


Figure 13.46 Schematic representation of the Redux 775 manufacturing process.

removed. Two of these "half-webs" are then laminated together to produce the final film adhesive. This is shown schematically in Fig. 13.46, and Fig. 13.47 shows the slightly modified original 1954 film-making equipment.

13.3.4.3 Methods of Application of Adhesive

13.3.4.3.1 Primers

For small areas, these can be brushed on and slightly larger areas can be covered using a conventional roller-coater. For the large areas generally associated with the aerospace industry, spray coating is recommended.

Spray coating generally uses either a high-volume/low-pressure or a low-volume/high-pressure technique often using robotic applicators.

The primed surfaces are then allowed to dry. This can be accomplished by forced drying (at elevated temperatures in an air-circulating oven) or, traditionally, overnight at ambient temperature. Depending on the primer and the application, the primed surfaces can be stored in the dried state until required or they can be oven-cured prior to later use.

13.3.4.3.2 Paste Adhesives

A variety of methods can be used to apply these adhesives. The actual method chosen will often

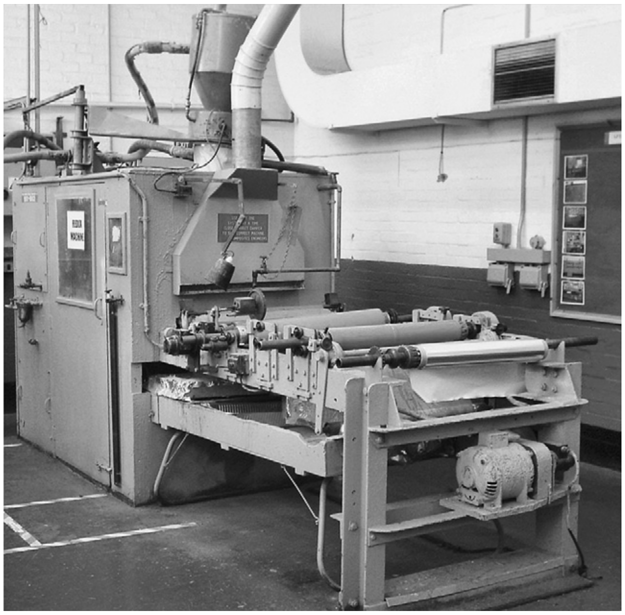


Figure 13.47 The original Redux film machine.

depend on the component to be bonded—its size and the complexity of its shape—and the viscosity of the adhesive.

As many, but not all, of these systems are two-component, they first have to be mixed together. The oldest method is simply to weigh out the components and then mix by hand; where syntactic adhesives, which contain delicate glass microballoons, are concerned, hand mixing is often the safest and ideal method. Other possibilities encompass simple mechanical mixing using a bladed stirrer or pumping the two components, either by hand using a cartridge gun or using some hydraulic method (a typical setup is given in Fig. 13.48), through a mixing head, which contains either static or dynamic mixing tubes, to an applicator.

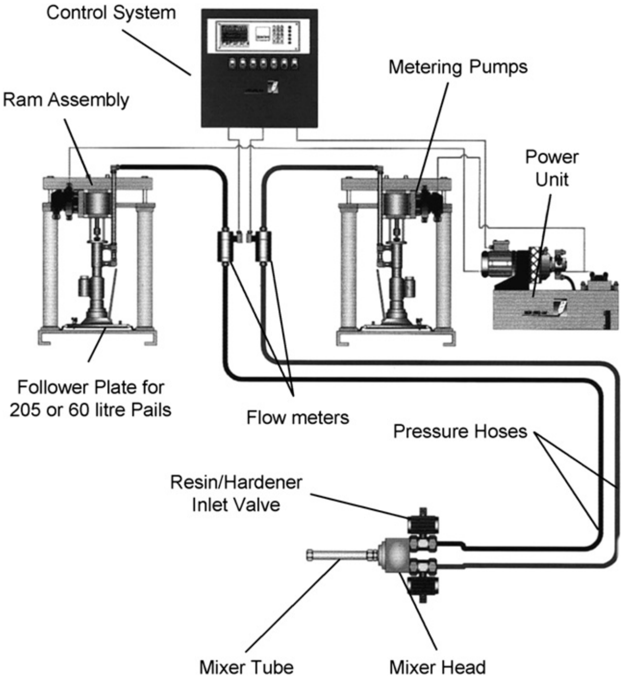


Figure 13.48 Schematic representation of a typical paste adhesive mixing and delivery unit (courtesy of: 2KM (UK) Limited).

Independent of final adhesive viscosity, hand application by spatula, palette knife, or trowel is often the favored method. However, once mixed, low-viscosity adhesives are frequently pumped to an applicator gun, which is often robotically controlled. High-viscosity paste adhesives can make use of hand-held cartridge dispensers that not only mix the adhesive, as indicated earlier, but also can apply a bead or stripe of adhesive to the substrate, dependent on the design of the applicator head.

For the high-viscosity adhesives, reverse roll applicators can be used. Here, the adhesive is pumped into the nip of the applicator rollers and the adherend to be coated is passed between a pressure roller and the metering roller. This allows an accurate coating of adhesive to be applied to the substrate.

Other methods, particularly for large areas, can make use of comb and coating bar devices.

13.3.4.3.3 Film Adhesives

Film adhesives offer the simplest method of adhesive application to the substrate to be bonded. This is particularly so when the tack of the film is highly controlled: enough tack to ensure the film stays where it is put but not so high as to prevent repositioning.

For the simplest structures, for example stringers, the adhesive film can be cut into tapes of the correct width by the supplier and can then be laid down onto the stringer by hand or by a tape laying machine.

Tape laying machines can be used for larger bond areas or the film can be precut or die-stamped to the correct geometry and then put into position by hand or by robot.

When using adhesives such as foaming films, the easiest method of application is often by hand; cutting the film to size and dropping it into place.

13.3.4.4 Curing of Adhesives

There are, essentially, only three methods of curing structural adhesive joints: press, autoclave, and oven.

Figure 13.49 Typical press bonding shop.

To some extent, the method used will be dependent on the adhesive but, more often than not, it is dependent on the complexity of the structure and the overall policy of the company producing the bonded component.

Simple, flat components are best cured in a press; Fig. 13.49 shows a typical press shop. Generally, the lay up is faster, and the total time to produce the cured component is less than by either of the other methods. However, this is, of course, limited by the size of the component over a certain size and the press might be too small and other methods have to be contemplated.

More complex components, which can be accommodated in a simple, flat tool, for example, the EH101 rotor blade, can also be press cured.

Large, complex shapes, where high bonding pressures (>100 kPa) are required, have to be either clamped up (Fig. 13.50) or jigged up on an appropriate tool, utilizing vacuum-bag techniques (Fig. 13.51), and this assembly is then cured in an autoclave. A typical autoclave bonding shop is shown in Fig. 13.52.

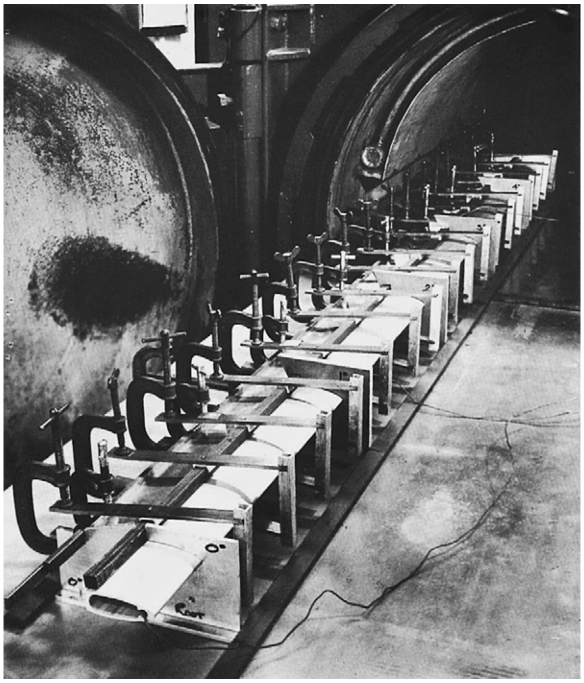


Figure 13.50 Dornier helicopter rotor blade clamped before autoclave curing.

A good example of oven-curing is during the first stage of the process to bond the propellant to the motor lining in rocket motor production. Here, pressure bags, rather than vacuum bags, are used to apply >>100 kPa bonding pressures to the surface of the adhesive film (Fig. 13.53), which can then be cured in a simple air-circulating oven.

Figure 13.51 Rolls Royce engine nacelle component—Vac-Bag assembly before autoclave curing.

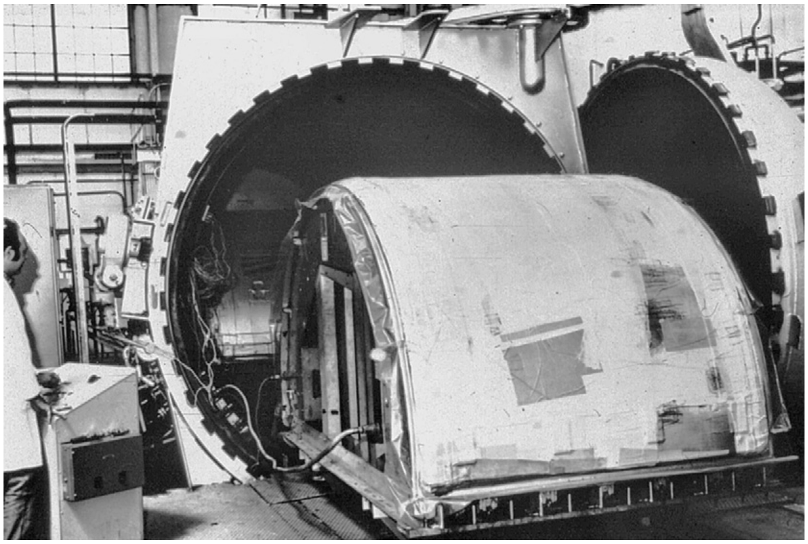


Figure 13.52 Autoclave bonding shop; railway system to take the tools to the autoclave (courtesy of BAE SYSTEMS, Broughton).

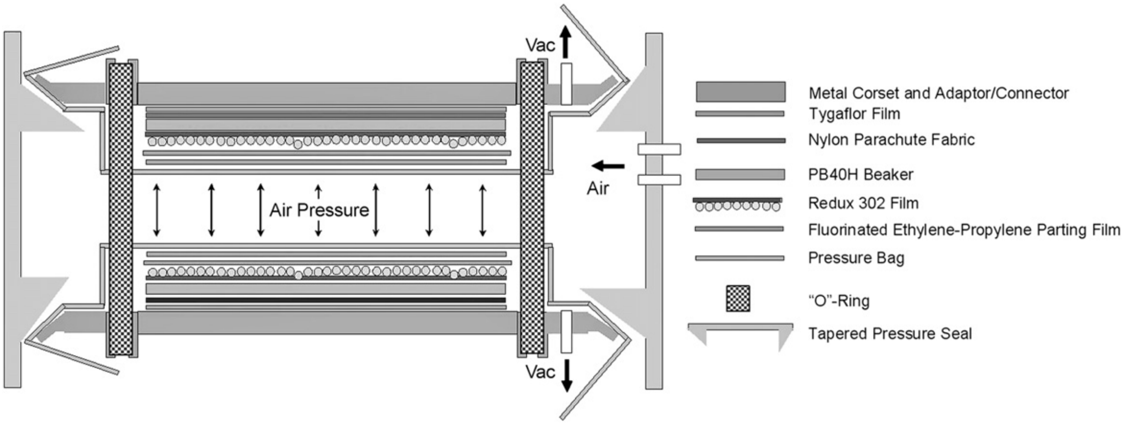


Figure 13.53 Schematic representation of a pressurized oven curing rig used in rocket motor applications.

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14 Adhesives for Medical and Dental Applications

Sina Ebnesajjad

This chapter focuses on adhesives used in direct physiological contact during dental and medical procedures. Involvement in both areas has been extensive outside the United States for decades. Adhesive use in medical devices, patches, and plasters has been on-going in the United States for a longer period. Regarding medical devices, adhesion concerns the joining of materials such as plastics, elastomers, textiles, metals, and ceramics, which are examined in alternative chapters of the present volume and are covered in various references.[1−7] This chapter is devoted to describing applications where adhesives are in direct contact with tissues and other live organs.

14.1 Introduction

The use of adhesives in medicine and dentistry is often critical and functional and with little exposure to patients. Infant immunization, flu shots, restorative dental fillings, blood transfusions, heart bypass surgery, urological surgery, anesthetic administration, intravenous drug delivery, and numerous other medical procedures would not be possible today if not for the existence of advanced adhesives. Modern adhesives assemble thousands of medical devices on highly automated assembly lines about the globe, or they are used in direct physiological interactive modes.[8]

The annual real volume growth, coupled with the market for adhesives used in the assembly of disposable medical devices, results in the disposable medical device segment being one of the most active in the specialty chemical industry. Some estimates even forecast growth as high as 24% annually for the next 5 years. However, most participants peg annual real volume growth at about 13−15%, which, by most standards in the adhesives industry, is remarkable in these times of challenged growth. Perhaps even more exciting are estimates that only about one-half of the applications that could be served by adhesives are using adhesives in assembly, enabling for significant growth in the industry. By all measures, growth potential is very attractive, and this market segment generates much interest among adhesive suppliers.[8]

14.1.1 Medical Applications

The use of adhesives in medical applications has been restricted, for some time, to the manufacture of self-adhesive bandages (plasters, self-adhesive strips of fabric, etc.).[9] The first pressure-sensitive adhesives used for this were based on natural rubber, concocted decades ago. This first usage was later partly superseded by synthetic rubbers (e.g., polyisoprene, polyisobutylene). In the mid-twentieth century, pressure-sensitive adhesives based on polyacrylic acid esters gained predominance in general use and in the composition of bandage materials.

Today, adhesives are used[9] in vast areas of medicine, replacing traditional methods with “friendlier” processes. Often, stitches can be avoided by applying special cyanoacrylate (CA) adhesives to quickly close skin wounds. An advantage of this method is that the entire wound can be covered, thereby largely suppressing secondary bleeding[1] and the risk of infection. Cyanoacrylic acid butyl ester is normally preferred over the methyl and ethyl esters, because it cures at a slower pace and the polymerization produces less heat. Cyanoacrylic also causes less tissue irritation. By and large, this adhesive is only used for small wounds and is occasionally used in vascular surgery.

Consider the transdermal patches where the drug delivery mechanism is through the skin and to the bloodstream: adhesives enable a more efficient method of drug delivery, rather than prescribing a high-ingestion dosage (first pass metabolism or detoxification, which means drug’s removal out of the body through the liver). Transdermal patch technology is highly effective because the adhesive

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[1] In layman’s terms “secondary bleeding” refers to post surgical bleeding of a wound which is well into healing.

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that sticks the patch to the skin—made of products of chemistry like acrylic, acrylic–rubber hybrid, polyisobutylene, and styrenic rubber solution—actually controls the rate at which the drug enters the body. This mechanism ensures that the drug dosage is continuously and evenly administered throughout the day, without the spikes and falls associated with medicines administered orally.[9]

The applications of these patches are numerous. Commonplace applications include smoke cessation, hormone replacement, and cardiovascular aids such as nitroglycerin delivery. New transdermal patches hit the market every day, with more items that enable pain cessation becoming a reality. Other innovative products, such as foot care and cosmetic patches, and nasal dilator strips, have entered the market in recent years. Their existence is possible because of the unique functional properties of the pressure-sensitive adhesives integral to the product.[9]

One of the newest bioadhesives on the market enables drugs to be delivered through the mouth, nasal passages, and other mucous membranes, rather than only being administered through skin. The newest bioadhesives adhere extremely well to the soft, wet mucous membranes of the body because these adhesives are made from starch–polyacrylic acid blends, which completely erode and disappear upon use. Drug makers are able to put their medicine into tablet, film, or powder form, and the patient is able to attach the product directly to a mucous membrane, providing a means for controlled delivery of drugs to specific areas of the body or systemically (throughout the body).[9]

Fibrin, which is made from fibrinogen, a soluble protein recovered from blood, is a key sealing agent in heart surgery. It has a hemostatic effect, meaning (antihemorrhagic agent): a substance that promotes hemostasis or the halting of blood flow. Fibrin is much gentler on the body tissues when compared with CAs. The disadvantage of fibrin is that before use, it must undergo a special treatment to prevent microbial infection.

The use of methacrylate-based adhesives has been a great success in orthopedics, for the purpose of anchoring hip socket implants to the bone. There are currently no other types of adhesive used for this application. The adhesive products are comprised of (a) a powder component (a mixture of polymethyl methacrylate and a polymerization initiator) and (b) a liquid component [whose main components are methyl methacrylate (MMA) and a polymerization accelerator]. Despite the considerable stress that these adhesives exert on bone and tissue because of intense heat development, hip and knee implants anchored using this adhesive are, in 90% of cases, functional for 15 years.[9]

Poly methyl methacrylate has also been used in verterbroplasty procedures. Verterbroplasty is an image-guided therapy procedure to relieve pain from oteoparotic or neoplastic vertebral body fractures. It involves the percutaneous injection of polymethyl methacrylate into the vertebral body and had been found to improve pain relief and patient function significantly.[10]

In dentistry, restorative fillings based on UV curing acrylates have largely replaced traditional filling materials such as amalgams. The products have a long pot life or *open time* (the period during which they can be used after mixing), and they bond in just a minute or so when exposed to UV light.

There are numerous orthodontic appliances or devices that are used to correct dental conditions in minor and adult patients. Most of these appliances involve the use of adhesives. The advent of adhesive dentistry and direct bonding of orthodontic brackets is a dramatic event that has changed the course of clinical orthodontics. Product development and technological advances have occurred quite rapidly. This rapidity has, at times, complicated the decision-making process for practitioners.[11]

14.2 Adhesives for Skin Closure

This section reviews the use of adhesives as an alternative to stitches. The key advantage of supplanting stitches with an adhesive is that the adhesive overlays the entire wound as a continuum. The global coverage prevents secondary bleeding and reduces the risk of infection by creating a temporary barrier while healing takes place. Other advantages of gluing the skin are that the method is quick, saves surgery time, is inexpensive, does not require stitch removal, and is waterproof. The disadvantage of gluing is that doing so can be messy if applied incorrectly.

One of the adhesive options is copolymeric hydrogels,[12] composed of aminated star polyethylene glycol and dextran aldehyde (PEG:dextran). These materials exhibit physico-chemical properties that can be modified to achieve organ- and tissue-specific adhesion performance. The investigators reported that resistance to failure under specific loading conditions, as well as tissue response at the adhesive material–tissue interface, can be modulated through regulation of the number and density of adhesive aldehyde groups.

There are two common adhesive choices: cyanoacrylic and methyl metacrylic. Cyanoacrylic acid butyl ester is usually preferred over the methyl and ethyl esters because of its slower cure (polymerization) rate. Consequently, the polymerization produces less heat; it also causes less tissue irritation. CA glue is commonly used for approximation of skin after various surgical procedures,[13] and it is occasionally used to embolize blood vessels[14,15] and to occlude fistulas.[16]

There is no need to apply a dressing to cover the wound after gluing the skin. Apart from eyes and mucous membranes, adhesive may be used to close various clean wounds of the skin, including to cover wounds of the face if there is no contraindication. However, glue application has a few disadvantages: some glue applications are messy, may not hold oozing wound edges, and may stick to the instruments and gloves. Meticulous attention to different techniques in various situations may avoid most of these disadvantages. Gluing is common in surgery, but it is not formally taught.

The Food and Drug Administration (FDA) approved CA adhesives being considered comparable with 5-0 sutures, but they are not recommended to be used alone in high-tension areas.

14.2.1 Cyanoacrylic Adhesives

These so-called "wonder" adhesives are thermosetting materials and were first introduced commercially by Eastman Chemicals. They form strong thermosetting bonds between many materials without heat or an added catalyst. They are particularly useful in bonding metal to nonmetal. Lap-shear strengths of 13.7 MPa have been reported. However, the resistance capability of these adhesives to moisture is still somewhat low.[17] These materials set very quickly when squeezed out to thin film between many types of adherends.

A CA adhesive is a relatively rapid curing adhesive, also from the acrylic family tree, but it has a completely different cure system. CA monomer (Fig. 14.1) is made from a complex chemical process. The monomer produces a very reactive polymerization. The reaction or polymerization process is stabilized, and the monomer is kept in the liquid state by the addition of a small amount of an acid stabilizer material.[18]

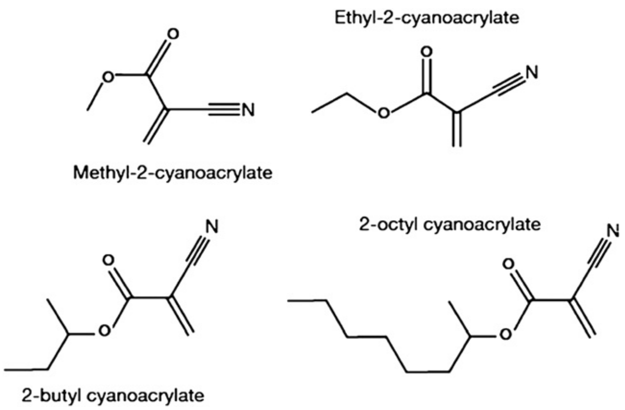
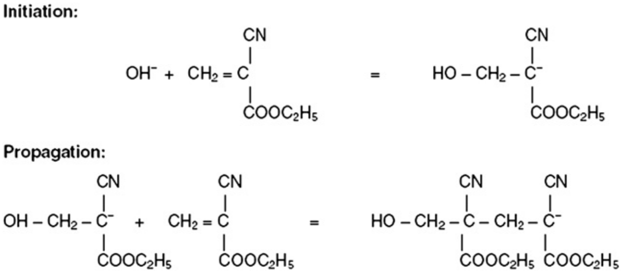


Figure 14.1 Structures of some cyanoacrylate monomers.

When a drop of CA adhesive is put on the surface of a part, the acid stabilizer molecules react with the water molecules present on the surface of the part from the relative humidity in the air. The reaction of the water and acid causes the acid stabilizer to be neutralized. The CA molecules then react with each other and form polymer chains without cross-linking.[18]

CA adhesives undergo anionic polymerization in the presence of a weak base, such as *water*, and are stabilized through the addition of a weak acid. The stabilizer is usually in the form of a weak acidic gas such as SO_2, NO, or BF_3. An essential function of the stabilizer is to prevent polymerization in the container, which is usually made of polyethylene. When the adhesive contacts a slightly alkaline surface, trace amounts of adsorbed water or hydroxide ions (OH^-) that are present on the substrate's surface neutralize the acidic stabilizer in the adhesive, resulting in the rapid polymerization shown in Fig. 14.2.

The amount of stabilizer molecules in CA is miniscule—measured in parts per million—and very few moisture molecules are required to cause rapid polymerization. Canoacrylates begin to form polymer chains immediately on contact with the water



$$OH^- + CH_2{=}\overset{CN}{\underset{COOC_2H_5}{C}} = HO-CH_2-\overset{CN}{\underset{COOC_2H_5}{C^-}}$$

$$OH-CH_2-\overset{CN}{\underset{COOC_2H_5}{C^-}} + CH_2{=}\overset{CN}{\underset{COOC_2H_5}{C}} = HO-CH_2-\overset{CN}{\underset{COOC_2H_5}{C}}-CH_2-\overset{CN}{\underset{COOC_2H_5}{C^-}}$$

Figure 14.2 Polymerization reaction of cyanoacrylate adhesives.[19]

vapor on the surface of the part. If parts are moved during initial contact, the polymerization process and polymer chains are stopped. The process must start again at a new catalyzed site.[18]

CAs are very rapid in curing, and they provide high bond strengths on plastic and rubber materials. These adhesives are versatile, which renders them highly useful in all industries. Some of the larger application areas are in electronics for printed circuit board wires and components and in medical technology for disposable plastic medical devices. Other applications include toy, small and large appliance, automotive, and cosmetic packaging. Applications exist in all industries for repair of all rubber and plastic parts, as well as some metal parts. The consumer market is a large volume user of CA adhesives for repairing everything in the home from wallpaper tears to broken toys to torn and false fingernails.

CA adhesive can be made from different acrylate monomers such as methyl, ethyl, butyl, isopropyl, and so on. These molecules differ in size and adhesives made from them, exhibiting different physical properties. Methyl is the smallest molecule and seems to work best on metal and rubber parts, whereas ethyl works best on plastic parts. Many modifications can be made to the monomers to alter or improve their properties as adhesives. They can be toughened with rubber or formulated to have low odor, resistance to thermal cycling, or less sensitivity to surface conditions, which tends to stabilize the adhesive and slows the cure.[18]

As with other acrylics, the monomers are liquids of low viscosity, which polymerize very easily in the presence of a slightly basic surface containing adsorbed water. Polymerization is ionic. The resulting polymers have different properties depending on the alkyl group. The methyl ester (methyl-2-cyanoacrylate) is the most commonly used compound. This material is formulated with a thickener (to prevent starved joints from being formed) and a plasticizer to make it more resistant to shock loading. The thickener can be a polymer of the same monomer. An essential feature is a stabilizer to prevent polymerization in the adhesive container, which is usually made of polyethylene.[20]

The polymerization of CAs is inhibited by low pH thus, it does not proceed satisfactorily on acid surfaces such as wood. The suggested incorporation of poly-*N*-vinyl pyridine or polyethyleneamine, or even simple amines, presumably serves the dual purpose of thickening the liquid and increasing the pH.

Adhesives based on higher homologs than the methyl form, such as ethyl or propyl forms, have been used for a number of years. These include the ethyl, propyl, and butyl esters of cyanoacrylic acid. Moisture resistance of the methyl-2-cyanoacrylate is only fair. Ethyl cyanoacrylate has been shown to form stronger bonds than the methyl form between several different types of plastic surfaces. The higher homologs, however, generally do not form bonds as strong as does the methyl form. The most important step in the successful application of a CA adhesive is the application of a thin adhesive film between two well-mated surfaces. The thinner the film is, the faster the rate of bond formation and the higher the bond strength. Bond strength is dependent on proper surface preparation.

In general, aging properties of the CAs are good. Rubber-to-rubber and rubber-to-metal bonds typically have endured outdoor weathering for more than 7 years. These bonds have also passed stringent water-immersion and salt-spray tests. Plastic-to-plastic and plastic-to-rubber bonds have aged satisfactorily for 3–5 years. Metal-to-metal bonds generally age rather poorly, except under special conditions where the minimal glue line is exposed to moisture. Solvent resistance is also generally satisfactory. Dilute-alkaline solutions weaken the bond considerably, whereas dilute-acid solutions weaken it to a lesser degree. Impact resistance is generally poor because of the thin, inflexible bond.

The above is especially true with two rigid substrates such as metals. The methyl cyanoacrylate bond melts at approximately 165 °C. Prolonged exposure to temperatures in this range results in a gradual but permanent breakdown of the bond. Generally, the upper temperature limit for continuous exposure is about 77 °C. At low temperatures, bonds remain intact at least to −54 °C. Grades of CAs with specialized improved properties are available. For example, one grade has improved heat resistance to 246 °C, high viscosity, and very fast setting ability.[21]

Among the advantages of the CAs are the following:

- Very fast bond formation
- High bond strength with thin glue line
- No added catalyst or mixing needed
- No solvent to evaporate during bond formation
- Contact pressure is usually sufficient

Table 14.1 Benefits and Limitation of Cyanoacrylate Adhesives[19]

Benefits	Limitations
• Excellent adhesion to a wide variety of substrates • Substrate variety • Simple cure mechanism • Rapid strength development • High strength possible on polyolefins and fluorocarbons using primers • Available in USP class VI compliant formulations • High shear strength • No measuring or mixing required	• Blooming/frosting • Difficult to cure fillet or exposed liquid adhesive without activator • Limited gap cure • Stress cracking could occur to some plastics • Soluble in polar solvents • Thermal and chemical stability not as good as with certain other structural adhesives • Unmodified formulations have low peel and impact strengths • Relatively high materials cost • Pungent odor associated with early formulations

- Very low shrinkage
- Economical because of minute quantities needed, although relatively expensive (Table 14.1).

The Loctite Corporation offers a rubber-toughened CA adhesive such as 380 Black Max®, which is reported to achieve improved strength, resiliency, and fast fixturing at the expense of a rather limited shelf life (about 4 months).[22] This adhesive cures to fixturing strength in 2 min with respect to most substrates. It reaches 80% strength in 24 h and full strength in 72 h (Table 14.2). On aluminum, its average strength is 16.6 MPa after full room temperature cure, versus 6.2 MPa for a typical epoxy adhesive and 3.8 MPa for “instant” adhesives. After 240 h of tensile-shear thermal-cycling tests, this adhesive improved its strength to 21.3 MPa for “instant” adhesive. Loctite claims that this adhesive is consistently 20 times stronger than epoxies on aluminum, 10 times stronger on neoprene, four times stronger on steel, and two times stronger on epoxy/glass after the tests. This adhesive is designed for assembly-line cure (Table 14.3).[23]

14.2.2 Medical Grade CA Adhesives

Butyl cyanoacrylate is an intermediate-length CA (Fig. 14.1) adhesive, and was the first product broadly used for closing cutaneous wounds. This compound has been approved for use in Europe and Canada as Histoacryl® Blue (trademark of Aesculap, Inc) and GluStitch® (trademark of GluStitch Inc.) for nearly 40 years. It was not, however, approved by the US FDA for use in the United States for a long time. In Europe, Canada, and Japan, it has been used for middle ear procedures to close cerebrospinal leaks, to repair incisions and lacerations, and to affix skin since the 1970s.[24–30]

Short-chain CAs (methyl, ethyl) are toxic to tissue; this, however, is not the case with butyl cyanoacrylate when applied topically. In an experimental model of incision wound healing in hamsters, butyl cyanoacrylate resulted in less inflammation than 4.0 silk sutures on histologic assessment.[25] Randomized clinical trials were conducted in a study of just fewer than 100 patients with facial lacerations suitable for tissue adhesive closure. The patients underwent wound closure using either butyl cyanoacrylate or octyl-2-cyanoacrylate (2-OCA), and results failed to reveal a difference in cosmetic outcome after 3 months. The ratings derived from photographs by a plastic surgeon using a visual analog scale.[31] A toxic reaction was prevented by taking precautions to prevent the adhesive from being trapped in the wound.[32] Owing to these concerns, *n*-butyl cyanoacrylate has been recently approved by FDA for use in the United States. In 2010, B. Braun manufactured Histoacryl®, which consists of *n*-butyl-2-cyanoacrylate. This sterile, liquid-topical skin adhesive is available in two formulations: Histoacryl® and Histoacryl® Blue.[33]

N-butyl cyanoacrylate (NBCA) is a liquid embolic material, in addition to being a tissue adhesive, that is approved by the USA FDA for use in embolization of cerebral arteriovenous malformations (AVM). It offers the advantages of low viscosity for easy injection through small catheters, but does not permeate all the way to the capillary level and thereby avoids tissue death.[34,35]

Table 14.2 Typical Performance of Cured Loctite 380 Cyanoacrylate Adhesive[22]

Adhesive properties	
After 24 h at 22 °C	
Lap-shear strength, ISO 4587, N/mm^2 (psi)	
Steel (grit-blasted)	26 (3770)
Aluminum (etched)	18 (2610)
ABS	>6 (>870)
PVC	>4 (>580)
Polycarbonate	>5 (>725)
Phenolic	10 (1450)
Neoprene	>10 (>1450)
Nitrile	>10 (>1450)
Tensile strength, ISO 6922	
Steel (grit-blasted), N/mm^2 (psi)	18.5 (2700)
After 48 h at 22 °C	
Lap-shear strength, ISO 4587	
Steel (grit-blasted), N/mm^2 (psi)	≥17.2[LMS] (≥2495)
Cured for 24 h at 22 °C, followed by 24 h at 121 °C, tested at 121 °C	
Lap-shear strength, ISO 4587	
Steel (grit-blasted), N/mm^2 (psi)	≥6.9[LMS] (≥1000)
Cured for 24 h at 22 °C, followed by 24 h at 121 °C, tested at 22 °C	
Lap-shear strength, ISO 4587	
Steel (grit-blasted), N/mm^2 (psi)	≥19.3[LMS] (≥2800)

LMS: Loctite material specification.

2-OCA has a longer chain than butyl cyanoacrylate. It was approved by the FDA in August of 1998 for use in the United States on certain types of lacerations. Its applications have been expanded and are now marketed as Dermabond® (a trademark of Ethicon, Inc, a Johnson & Johnson Company) topical skin adhesive for closure of lacerations and incisions in place of sutures or staples. In later years, a 2-OCA formulated for greater flexibility, Liquid Bandage, was approved for use in the over-the-counter market in the United States, for the purpose of treating minor cuts and abrasions.[36]

The longer side chain gives 2-OCA several potential advantages over shorter chain CAs. 2-OCA, for instance, produces a stronger bond and is more flexible than butyl cyanoacrylate. It has four times higher volumetric break strength than butyl cyanoacrylate.[32] With the increased strength and flexibility and reduced risk of tissue toxicity, 2-OCA is now widely used in the United States for closure of wounds. It is currently one of the best-selling bandage brands in the United States.

Here is an excerpt of a 2004, but useful, review of the tissue adhesives by Singer and Thode:[37]

> *Octylcyanoacrylate is a medical grade topical tissue adhesive that has been approved for closing surgical incisions and traumatic lacerations. We reviewed animal and human studies that evaluated its use for a variety of surgical indications and specialties. We also performed a meta-analysis of all clinical trials using octylcyanoacrylate. Data sources: Animal and human studies published in peer-reviewed articles as well as published abstracts. A search of Medline was performed*

using the MESH terms: tissue adhesives, cyanoacrylates, and octylcyanoacrylate. The current review and metanalysis demonstrate that octylcyanoacrylate can be used successfully in a wide variety of clinical and surgical settings for multiple types of wounds covering most of the surface of the human body.

Table 14.3 Bond Strength of Methyl or Ethyl Cyanoacrylate Adhesive as a Function of Substrate and Time[19]

Joint substrates	Age of bond	Shear strength, psi
Steel–steel	10 min	1920
	48 h	3300
Aluminum–aluminum	10 min	1480
	48 h	2270
Butyl rubber–butyl rubber	10 min	150*
SBR rubber–SBR runner	10 min	130
Neoprene–Neoprene	10 min	100*
SBR rubber–phenolic	10 min	110*
Phenolic–Phenolic	10 min	930*
	48 h	940*
Phenolic–aluminum	10 min	650
	48 h	920*
Aluminum–nylon	10 min	500
	48 h	950
Nylon–nylon	10 min	330
	48 h	600
Acrylic–acrylic	10 min	810*
	48 h	790*
ABS–ABS	10 min	640*
	48 h	710*
Polystyrene–polystyrene	10 min	330*
Polycarbonate–polycarbonate	10 min	790
	48 h	950*
Polyester glass–polyester glass	10 min	680

*Substrate failure.

14.2.3 Commercial Grades of CA Tissue Adhesives

Some of the manufacturers of CA tissue adhesives are listed below:

Company Name: AESCULAP, Inc.
Address: 3773 Corporate Pkwy
Center Valley, PA 18034, USA
Product: TISSUE ADHESIVE
Proprietary Device Name: HISTOACRYL® & HISTOACRYL BLUE® TOPICAL SKIN ADHESIVE
Website: http://www.aesculapusa.com

Company Name: CLOSURE MEDICAL CORP.
Address: 5250 Greens Dairy Rd.
Raleigh, NC 27616, USA
Product: TOPICAL TISSUE ADHESIVE
Proprietary Device Name: DERMABOND® TOPICAL SKIN ADHESIVE
Website: http://www.closuremed.com

Company Name: ETHICON, INC.
Address: Route 22 West.
Somerville, NJ 08876, USA
Product: TISSUE ADHESIVE
Proprietary Device Name: DERMABOND® TOPICAL SKIN ADHESIVE
Website: http://www.impactfs.com

Company Name: GEM S. r. l.
Address: Via dei Campi, 2 – PO Box 427
Viareggio, LU, 55049, Italy
Product: TISSUE ADHESIVE
Proprietary Device Name: Glubran2®
Website: http://www.gemitaly.it/web/en/glubran2.html

Company Name: HENKEL IRELAND LIMITED ELECTRONIC AND BIOMEDICAL FACILITY
Address: Whitestown, Dublin, 24 EI
Product: TISSUE ADHESIVE
Proprietary Device Name: INDERMIL® TISSUE ADHESIVE
Website: http://www.henkel.com/cps/rde/xchg/henkel_com/hs.xsl/indermil-17865.htm?automaticTransfer=3

Company Name: MEDISAV SERVICES, INC.
Address: 56 Elson St., #B
Markham, Ontario, L3S 1Y7 Canada
Product: TISSUE ADHESIVE FOR REPAIR OF MINOR CUTS & LACERATIONS

Proprietary Device Name: EPIDERMGLU®
Website: http://www.ethicon.com

Company Name: PRAXIS, LLC.
Address: 1110 Washington St.
Holliston, MA 01746, USA
Product: TISSUE ADHESIVE
Proprietary Device Name: PRAXI STAT®
Website: http://www.praxiscompanies.com

Company Name: SKINSTITCH CORP.
Address: 89 Old River Rd.
P.O. Box 179
Massena, NY 13662, USA
Product: TISSUE ADHESIVE FOR REPAIR OF MINOR CUTS & LACERATIONS
Proprietary Device Name: SKINSTITCH™
Website: http://www.skinstitch.com

CA tissue adhesives can be used vice sutures in a number of surgical procedures contributing to facilitating recovery and comfort.[38] They include the following:

1. Obstetrics and gynaecology surgeries, such as C-sections where excellent cosmetic outcomes are desired,[39] as well as enabling new mothers to shower immediately and move about without the discomfort of staples or sutures[40]
2. General surgeries such as many abdominal surgeries, back surgeries, and routine surgeries of the face, neck, arms, and legs[41]
3. Cardiovascular surgeries that may involve incisions in the arm or leg and chest[41]
4. Cosmetic surgery, particularly facial incisions, on areas such as the eyelid and the nose where suture removal can be painful. No stitches means no "suture marks"[42]
5. Sports surgery, involving lacerations that may need immediate attention, to help players to return to the game[43]

Dermabond® (2-OCA by Ethicon, a Johnson & Johnson Company), the latest in CA technology, has less toxicity and almost four times the strength of *N*-butyl-2-cyanoacrylate. Special plasticizers have been added to the formula to provide flexibility. It is marketed to replace sutures that are 5-0 or smaller in diameter for incision or laceration repair. Patients, especially children, readily accept the idea of being "glued" over traditional methods of repair.[44] This adhesive reaches maximum bonding strength within 2.5 min and is equivalent in strength to healed tissue at 7 days post-repair.[44]

Dermabond® (2-OCA) has been found to create[45] a microbial barrier over the wound and protect against the penetration of the following bacteria commonly associated with surgical site infections:

Staphylococcus aureus

Staphylococcus epidermidis

Enterococcus faecium

Escherichia coli

Pseudomonas aeruginosa

Dermabond® adhesives:[45]

1. Provide the strength of healed tissue at 7 days in less than 3 min
2. Offer three-dimensional strength that is at least three times stronger than *n*-butyl cyanoacrylate, another leading type of adhesive
3. Help protect and seal out bacteria that can lead to infection
4. Promote a moist wound-healing environment that has been shown to speed the rate of epithelialization
5. Cause less pain and relieve anxiety over sutures, particularly important for pediatric patients; have been found to be as safe and effective as conventional sutures with equivalent cosmetic results and
6. Save valuable clinical time in that they can be applied more quickly than sutures, eliminating the need for the following process:
    a. Injecting a local anesthetic into the wound
    b. Waiting for the anesthetic to numb the area
    c. Closing the wound with sutures
    d. Placing a dressing over the wound
7. Slough off naturally over time (usually 5−10 days), eliminating the need for a follow-up visit to remove stitches

14.2.4 Test Methods to Characterize Strength of Tissue Adhesives

The following four test methods are used[46] to provide a means for comparison of the adhesive strengths of tissue adhesives for use as surgical adhesives or sealants on soft tissue. These or equivalent methods may be used in support of the bench testing outlined above:

ASTM F2255-05 Standard Test Method for Strength Properties of Tissue Adhesives in Lap-Shear by Tension Loading

ASTM F2256-05 Standard Test Method for Strength Properties of Tissue Adhesives in T-Peel by Tension Loading

ASTM F2258-05 Standard Test Method for Strength Properties of Tissue Adhesives in Tension

ASTM F2458-05 Standard Test Method for Wound Closure Strength in Tissue Adhesives and Sealants.

14.2.5 Case Studies of Tissue Adhesives

In this section, examples of the use of tissue adhesives, namely CAs, in the closure of different types of lacerations and surgical incisions are discussed. In vitro and in vivo animal and human studies have been conducted to assess the efficacy and outcome of tissue adhesives as compared with traditional stitching.

14.2.5.1 Comparison of Effects of Suture and Tissue Adhesive on Bacterial Counts

In this study,[47] the effects of closing lacerations with suture or CA tissue adhesive on staphylococcal counts in inoculated guinea pig lacerations are investigated. Wounds closed with adhesive alone had lower counts than wounds containing suture material ($P < 0.05$). The results of a time-kill study were consistent with a bacteriostatic adhesive effect of the adhesive against *S. aureus*.

Another study used a well diffusion method to conclude that CA adhesive is bacteriostatic for gram-positive organisms.[48] Suture material also increases the risk of wound sepsis by serving as an adherent foreign body.[48,49] In contrast, *S. epidermidis* adheres to CA adhesive, which may thus promote wound infection.[50] The authors studied the difference in wound bacterial counts among the following wound closure methods (the terms are given in parentheses): use of a CA adhesive alone (glue), adhesive and subcutaneous suture (glue/SQ), skin suture alone (suture), and skin suture with subcutaneous suture (suture/SQ).

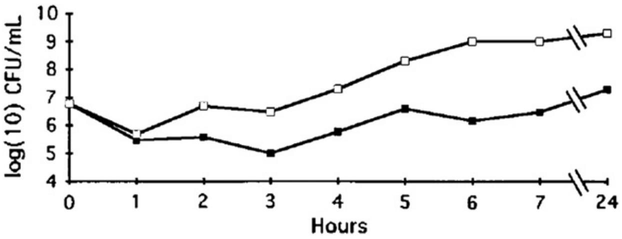


Figure 14.3 *S. aureus* kill curve. ■, cyanoacrylate adhesive; □, control.[47]

Four lacerations each, with a length of 3 cm, were made parallel to the spine to deep fascia. The lacerations were inoculated with *S. aureus* (ATCC 11632) and adjusted to a spectrophotometric absorbance of 0.138–0.139. Inocula were quantified at approximately 108 CFU/mL by standard microbiological methods. After inoculating the lacerations, the four wounds on each animal were approximated in one of four ways: (1) with Nexaband Liquid (*n*-butyl-2-cyanoacrylate and D and C violet number six dye) (glue), (2) with subcutaneous suture (i.e., intradermal stitches buried beneath the skin) followed by application of Nexaband Liquid (glue/SQ), (3) with simple skin suture (suture), or (4) with intradermal subcutaneous suture followed by simple skin suture (suture/SQ).

Table 14.4 summarizes the wound data. Any lacerations subjected to protocol abrogations were excluded. Wound bacterial counts for glue were significantly lower than those for glue/SQ, suture, and suture/SQ. A time-kill study of Nexaband with *S. aureus* was also performed according to National Committee for Clinical Laboratory Standards

Table 14.4 Bacterial counts for contaminated lacerations treated with tissue adhesive and suture[a,47]

Treatment method	Mean bacterial count ± SD[b]	95% confidence interval
Glue	1.78 ± 1.9	0.5–3.06
Glue/SQ	4.42 ± 1.92	3.1–5.7
Suture	3.72 ± 1.4	2.83–4.62
Suture/SQ	4.58 ± 1.43	3.67–5.49

[a] *The adhesive used was* n-*butyl-2-cyanoacrylate tissue adhesive: skin sutures were done with monofilament nylon, and subcutaneous sutures were done with braided absorbable suture.* [b] *Values are log10 conversions of CFU per gram of tissue.*

(NCCLS) guidelines.[51] Four drops of Nexaband, the approximate amount used to close each laceration, was suspended in Trypticase soy broth before vortexing. The results of the kill study are summarized in Fig. 14.3. Broth containing CA exhibited bacterial growth levels significantly lower than those of the control.

The study concluded that contaminated wounds sealed with CA alone have appreciably lower staphylococcus counts than lacerations containing suture material. The presence of suture material in some wounds may be the reason for this effect. Bacteriostatic behavior of the products containing CA may also be at work. However, no study has found any adhesive present in the wound after closure.

The microbiological permeability of CA compounds, using Liquiseal (MedLogic Global Ltd, Plymouth, United Kingdom) as an example, was studied[52] to verify its reported primary attribute as a compound that remains impervious to microorganisms and water for 1 week following application. The occlusive dressing used was OpSite (Smith & Nephew, London, United Kingdom), commonly used in surgical procedures. The methods used in the study are well established in the investigation of bacterial penetration through various materials.[53] The organisms selected were *S. aureus* and *E. coli*, both known to be common pathogens causing surgical site infections.

This study[53] demonstrated that, as a barrier to microbiological penetration, CAs are as effective as standard occlusive dressings. The limitations of the two types of dressing are similar; both have the potential to allow bacteria to travel around the edges of the dressing and potentially infect the wound. However, as suggested by Bady and Wongworawat, the adhesion that the CA compounds create to the skin is effective in preventing the translocation of microorganisms across the skin.[54]

14.2.5.2 Sutureless Anastomoses of Small and Medium Vessels

In a study conducted in China,[55] animal model was used to assess the efficacy of sutureless anastomoses using tissue adhesives. The two cut ends of the rabbit common carotid artery were sutured by three stitches with a 1208 interval circumferentially. Then two optional threads were pulled horizontally and 0.1 mL of CA adhesive was smeared on the attached surfaces of the two ends. The three stitches were removed after completion of anastomosis. The burst pressure of the anastomosis was measured and compared with that of a traditional sutured artery. The glued anastomosis was associated with a shorter completion time (8.25 ± 6.34 min vs. 20.67 ± 14.24 min, $P < 0.01$), less bleeding (3.17 ± 9.04 mL vs. 11.04 ± 16.28 mL, $P < 0.01$), and equivalent patency (93.8% vs. 87.5%, $P < 0.05$). The sutureless anastomosis was associated with less intimal thickening (decreased by 31.4%, 24.5%, 23.9%, and 31.9%, $P < 0.01$ compared with the traditional suture group at 1, 2, 4, and 12 weeks, respectively). The study concluded that glued anastomoses provide an effective, simple, and feasible way for anastomosing small or medium caliber vessels. This technique can also reduce intimal injury (i.e., to the inner lining of the vessels).

Another paper[56] presents the results of an experimental study of small arterial anastomosis, combining suture with the CA tissue adhesive. At the distal end of the vessel, two parallel incisions were made 180° apart from each other, and two sutures were placed passing from the proximal end to exit from the most distal part of the longitudinal incisions. The tissue adhesive was then applied to the proximal vessel, and the full-thickness vascular "lid" flap was closed over it on anterior and posterior surfaces. Eighty anastomoses were carried out at the left and the right femoral arteries of 40 Wistar rats. For all of the animals, conventional end-to-end anastomosis was carried out on the left side, and the lid technique was used on the right side. There was no statistically significant difference between the patency rates of the groups (two nonpatent in control and two in the study group) ($P > 0.05$), whereas significantly reduced operation time (mean 16.2 and 10.7 min in control and study groups, respectively) ($P < 0.0001$) and bleeding time (median 1.5 and 0.5 min in control and study groups, respectively) ($P < 0.0001$) were documented in the study group. Histopathological evaluation of both the patent and nonpatent vessels at day 21 revealed no signs of tissue toxicity or intraluminal adhesive leakage. In view of these data, the investigators concluded that using of CA tissue adhesive provides an effective and simple method for end-to-end anastomosis of small-size arteries.

Akhtar[57] has put forth contradictory studies regarding the toxicity and long-term effects of CA. He cites that Barbalinardo et al.[58] compared relative effectiveness of isobutyl-2-cyanoacrylate, fibrin adhesive, and oxidized regenerated cellulose by the application of these hemostatic agents to sources of point bleeding. They found in the meantime that hemostasis was shorter in CA group, but the reported inflammatory response that it induced, and its possible carcinogenicity, limited its availability for clinical use. Ellman et al.,[59] also using oxidized cellulose (Surgicel) as control, assessed two formulations of a new CA compound. Long-term graft patency was assessed angiographically at 4, 6, and 18 months. Tissue reaction at 2 weeks, and 1, 6, and 18 months was assessed grossly by vascular surgeons and microscopically by a blinded pathologist. There were no significant differences between groups with regard to graft patency. Histopathology showed mild to moderate tissue reaction at 2 weeks and 1 month in the CA groups compared with controls. Mild tissue reaction was seen at 6 and 18 months. Their conclusion was that the CA compound was an effective suture line sealant.

14.2.5.3 Tissue Adhesive as Dressing After Open Pediatric Urological Procedures

In 2003, there was an effectiveness study was conducted of 2-OCA (Dermabond® by Ethicon, Inc) tissue adhesive as a sole dressing after open pediatric urological procedures.[60] For a period of 6 months, February to August 2003, the investigators prospectively evaluated patients undergoing extragenital open and laparoscopic pediatric urological procedures at The Children's Hospital University of Colorado School of Medicine in Denver, Colorado. All open incisions were closed in layers using a final layer of self-absorbing subcuticular stitches for the skin before applying Dermabond® CA adhesive at the skin level alone. In laparoscopic cases, Dermabond® alone was applied to the port sites (3 mm or less in diameter) and instrument sites without any sutures beneath the skin. No adjuvant occlusive dressings were applied to any of these wounds. All patients were allowed to bathe and return to normal lifestyle activities immediately post-operation.

Another study involved 146 child patients with a total of 200 incisions (open 146, laproscopy 54). Of these children, 103 who had had 142 incisions returned for follow-up visits during the period of the study. Only one complication was identified. The subject, a 6-month-old infant, presented omental prolapse through the umbilical port (3-mm port), requiring urgent closure in the evening of surgery. There were no cases in which appreciable healing problems were identified by surgeon or parent examinations. No wound infection occurred. Dermabond® alone provides a simple coverage for a vast range of pediatric urological surgical wounds. Immediate bathing and return to normal lifestyle activities do not seem to affect the wound healing adversely as long as a simple skin barrier is applied to the wound sites.[60]

14.2.5.4 Tissue Adhesive Applications in Gastrointestinal (GI) Endoscopic Procedures

This section is based on a 2006 review paper by Ryou and Thompson.[61] CAs and other tissue adhesives can be applied locally for a variety of indications, including hemostatic, wound closure, and fistula repair. The main classes of tissue adhesives currently used in GI endoscopy include CAs, fibrin glues, and thrombin. The focus of this section is on applications of CAs.

14.2.5.4.1 Gastric Variceal Bleeding

Injection therapy with CAs is now the first-line of endoscopic intervention for bleeding gastric varices and secondary prevention of gastric variceal bleeds outside the United States.[62]

In a randomized controlled trial of 59 patients, CA injection of bleeding gastric varices was reported to be more effective and safer than band ligation. Both initial hemostatic rate and rebleeding rates were lower in the CA group compared with the band ligation group. Initial hemostatic rates were 87% in the CA group compared with 45% in the band ligation group ($P = 0.03$); rebleeding rates in the CA group were 31% compared with 54% in the band ligation group ($P = 0.0005$). Treatment-induced ulcer bleeding occurred in two patients (7%) in the CA group and eight patients (28%) in the band ligation group ($P = 0.03$). The number of blood transfusions required were also higher in the band ligation group than in the CA group (4.2 ± 1.3 vs. 2.6 ± 0.9 units, respectively) ($P < 0.01$).[63]

14.2.5.4.2 Esophageal Variceal Bleeding

Several randomized controlled studies have demonstrated that injection of CA is comparable with sclerotherapy in the endoscopic hemostasis of acute variceal bleeding and prevention of rebleeding.[64–66]

14.2.5.4.3 Peptic Ulcer Bleeding

In a randomized controlled trial comparing injection of CA and hypertonic saline for bleeding gastroduodenal ulcers, initial hemostasis was similar in both groups and the rebleeding rate was lower after CA injection.[67] There are no studies comparing glue injection to a combination of injection and cautery or application of clips, which are considered more effective than saline injection alone for the treatment of bleeding ulcers.

14.2.5.4.4 Bleeding From Other Sources

CA injection has been used successfully in the management of a few patients with Dieulafoy's lesions and bleeding tumors.[68,69] Dieulafoy's lesion is an uncommon cause of major gastrointestinal bleeding and may be difficult to recognize. It consists of an arteriole that protrudes through a tiny mucosal defect, usually within 6 cm of the gastroesophageal junction on the lesser curve of the stomach.[70]

14.2.5.4.5 Closure of Fistula

CAs have been shown to be successful in the closure of pancreatic fistulas, biliary fistulas,[71] and GI fistulas.[72] Seewald and coworkers[73] reported successful closure of pancreatic fistulas in 8 of 12 patients using endoscopic injection of Histoacryl® into the fistulous tract and endoscopic drainage. Seven of the eight successful patients required only one treatment over a median follow-up period of 21 months. Closure was temporary in two patients, unsuccessful in one patient, and there was one death within 24 h of treatment from pulmonary embolism.

Some complications have been described with the use of CAs such as systemic inflammatory reaction to foreign body (pain and fever, local tissue necrosis) and inflammatory reaction to foreign body (mediastinitis, esophageal pleural fistula, duodenal ulcer perforation, pancreaticoduodenal necrosis, inflammatory pseudotumor of pancreatic tail).[74−78] Other types of complications have also been reported.[79−83]

14.2.5.5 Tissue Adhesives in Topical Skin Wounds

There are over 7 million traumatic lacerations[84,85] in addition to tens of millions of surgical incisions annually in the USA. All require closure by surgeons, emergency physicians, and primary care practitioners.[86] These wounds and incisions have been traditionally closed with sutures, staples, or surgical tapes and, more recently, tissue adhesives. An ideal wound closure device is user friendly, quick, pain free, and results in excellent cosmetics, without device removal requirement, and is, of course is cost-effective.[87] None of the current closure devices possesses all these requirements. Topical CA tissue adhesives, however, have a number of the characteristics of an ideal wound closure device.

CA topical adhesives have some obvious benefits such as ease and pain-free application of the adhesive. Consequently, local anesthetics are unnecessary. In addition, because the CA adhesives slough off spontaneously within 5−10 days, no removal is required, which is a procedure that may be painful and threatening, especially to children. Although the cost of the CA adhesives is higher than for most sutures, a formal cost-effective analysis conducted several years ago that included the costs of the suture kits, suture removal kits, and dressing materials demonstrated that using adhesives actually reduces costs.[88] The use of topical CA adhesives also reduces the risks of needle sticks[89] and prevents the formation of suture marks on either side of the wound. Unlike suturing, which has a learning curve of up to 2 years,[90] proficiency at using CA adhesives is rapidly attained.[91] They also have the potential to save operative time, especially with longer incisions and lacerations. In surveys, most surgical patients prefer topical adhesives to sutures or staples.[92−94] In contrast, in a study of 724 emergency department patients, two thirds had a prior or current laceration; more patients preferred sutures to adhesives.[52] Surgical tapes offer many of the same advantages that the topical skin adhesives offer, and they are a reasonable alternative for closure of appropriate wounds.[31,39] Surgical tapes are easy to use, rapid, painless, and comfortable, do not require removal, and are less costly than any of the wound closure devices. However, because of their low-bursting strength and tendency to fall off, the use of surgical tapes is limited to simple, very low tension wounds. Furthermore, surgical tapes do not have microbial barrier properties. A summary of the advantages, disadvantages, and common indications for the various wound closure devices is presented in Table 14.5. A summary of potential pitfalls associated with the CAs, together with possible solutions, is presented in Table 14.6.

Table 14.5 Comparison of Wound Closure Devices[84]

	Sutures	Staples	Tapes	Adhesives
Advantages	Most meticulous approximation Great tensile strength Low dehiscence rate Time honored	Fast Good tensile strength Simple Lower issue reactivity Lower risk of needle stick	Fast Simple Inexpensive Minimal reactivity No risk of needle stick	Fast Simple No risk of needle stick No need for removal Microbial barrier
Disadvantages	Painful Prolonged learning curve Require removal May leave suture marks Risk of needle stick Most reactive	Less meticulous approximation Painful Require removal	Lowest tensile strength Highest risk of dehiscence No moisture resistance	Lower tensile strength than sutures Limited moisture resistance
Indications	Most incisions and lacerations	Long linear incisions and lacerations Scalp wounds	Linear low tension wounds and lacerations Fragile skin (flaps and skin tears) Wound support after suture/staple removal Under splints/casts	Linear low tension wounds and lacerations Fragile skin (flaps and skin tears) Under splints/casts
Contraindications	Infected or heavily contaminated wounds (all devices)	Inadequate hemostasis Complex irregular wounds	Inadequate hemostasis High tension Hear bearing area Uncooperative patients Circumferential use around digits Proximity to moist areas	Inadequate hemostasis High tension Hear bearing area Proximity to moist areas

14.2.5.6 Tissue Adhesive for Closure of Hernia Incisions

The study[95] intended to elucidate that suture-based permanent mesh fixation can be replaced by fixation with *n*-butyl-2-cyanoacrylate glue (Glubran® 2 by GEM S. r. l., Italy) for surgical repair of abdominal wall hernias. The aim was to investigate in the rat animal model, the efficacy of the use of a small amount of modified *n*-butyl-2-cyanoacrylate (Glubran® 2) in abdominal mesh fixation as a feasible alternative to sutures and staples. Glubran® 2 is a class III medical-surgical

Table 14.6 Potential Cyanoacrylate Pitfalls and Pearls[84]

Potential pitfall	Pearl
Runoff	Position wound horizontally Apply small amount of adhesive
Spillage into eyes	Cover eyelids with ointment and moist gauze Place patient in Trendelenburg for wound above eye and reverse Trendelenburg for wounds below eye Apply small amount of adhesive
Burning sensation	Apply small amount of adhesive Avoid pooling of adhesive Spread out evenly
Wound dehiscence	Avoid in high tension wounds unless in conjunction with deep tension relieving sutures, surgical tapes, and immobilization
Wound infection	Use proper wound preparation Avoid in wounds with high risk of infection
Adherence to wound	Apply small amount of adhesive Horizontal positioning of wound Alternate the hand used to appose wound edges before complete polymerization
Introduction of adhesive into wound	Ensure meticulous wound apposition Avoid pressing down on wound with applicator (glide over wound surface) Remove adhesive by applying ointment Removal may be facilitated by using substance containing isopropyl merystate (such as silver sulfadiazine)

product (for internal and external surgical use), which has outstanding hemostatic and adhesive properties and, once set, produces an effective antiseptic barrier against infectious agents or pathogens commonly found in surgical settings. At present, it is used in open and laparoscopic surgery, digestive tract endoscopy, interventional radiology, and vascular neuroradiology.

In 25 Wistar rats, two hernia defects (1.5 cm in diameter) per animal were created bilaterally in the midline of the abdominal wall. The peritoneum was spared. The lesions were left untreated for 10 days to achieve a chronic condition. The defects were then covered with TiMESH extra light (2 × 3 × 2 cm) and fixed by 30 μL of Glubran® 2 or traditional suture. The time points of sacrifice were 17 and 28 days, and 3, 4, and 5 months. At autopsy, histology and immunohistochemistry were performed to evaluate the inflammatory response and the presence of apoptotic cells, respectively. Mesh fixation was excellent in all samples at each time point. At application sites, the inflammatory reaction was mild, with a small number of macrophages and vascularized connective tissue present around glue and mesh threads. Glue residues were observed in histologic sections at each time point. No presence of apoptotic cells was found. This study demonstrated that Glubran® 2 can effectively replace traditional suture in mesh fixation without affecting tissue healing and determining a physiological inflammatory reaction at the abdominal wall site.

In conclusion, on the basis of these experimental results, the use of a right amount of Glubran® 2 can effectively replace traditional suture threads in fixing abdominal mesh, guaranteeing a long-term firm adhesion and without increasing inflammatory.

In another study,[96] the investigators compared the skin adhesive 2-OCA to subcuticular suture for the closure of pediatric inguinal hernia incisions to determine whether skin adhesive improves wound cosmesis, shortens skin closure time, and lowers operative costs. They prospectively randomized 134 children undergoing inguinal herniorrhaphy at CS Mott Children's Hospital of the University of Michigan to have skin closure with either skin adhesive ($n = 64$) or subcuticular closure ($n = 70$). Data collected included age, sex, weight, type of operation, total operative time, and skin closure time. Digital photographs of healing incisions were taken at the 6-week postoperative visit. The operating surgeon assessed cosmetic outcome of incisions using a previously validated visual analog scale, as well as an ordinate scale. A blinded assessment of cosmetic outcome was then performed by an independent surgeon comparing these photographs to the visual analog scale. Operating room time and resources use (i.e., costs) relative to the skin closure was assessed. Comparisons between groups were done using Student's t tests and χ^2 tests.

Children who enrolled in the study had a mean age of 3.7 ± 0.3 years and weighed 16 ± 0.8 kg. Patients were predominantly male (82%). Patients underwent one of three types of open hernia repair as follows: unilateral herniorrhaphy without peritoneoscopy ($n = 41$; 31%), unilateral herniorrhaphy with peritoneoscopy ($n = 55$; 41%), and bilateral herniorrhaphy ($n = 38$; 28%). Skin closure time was significantly shorter in the skin adhesive group (adhesive = 1.4 ± 0.8 min vs. suture = 2.4 ± 1.1 min; $P = 0.001$). Mean wound cosmesis scores based on the visual analog scale were similar between groups (adhesive = 78 ± 21; suture = 78 ± 18; $P = 0.50$). Material costs related to herniorrhaphy were higher for skin adhesive (adhesive = \$22.63 vs. suture = \$11.70; P b 0.001), whereas operating room time costs for adhesive skin closure were lower (adhesive = \$9.33 ± 5.33 vs. suture = \$16.00 ± 7.33; P b 0.001). Except for a 7% incidence of erythema in both groups, there were no complications encountered. In the meantime, the data from this trial suggest that skin adhesive wound closure in inguinal hernia repair is associated with a small reduction in operative time without effect upon total cost, complication rate, or cosmesis.

14.2.5.7 Use of Tissue Adhesive for Skin Closure in Plastic Surgery

Abdominoplasty and mammoplasty are cosmetic surgeries that demand relatively more time for skin closure.[97] Methods: Skin closure with 4.0 Mononylon (Ethicon) continuous subcuticular suture and with Dermabond® (Ethicon) (octylcyanoacrylate) was compared among 37 patients who had undergone body contouring surgery (23 abdominoplasties and 14 mammoplasties). Each side of the scar, randomly selected, was closed either with adhesive or suture. The time required for skin closure and the Aesthetic aspect of these scars were compared. Three observers evaluated the scars at 3, 6, and 12 months postoperatively using a categorical and a modified visual analog scale. Results: The average time for closure using suture was 7 min and 45 s for the abdominoplasty and 4 min and 25 s for the vertical incision of the mammoplasty. This was significantly different statistically, as compared with the 2 min required for polymerization of the skin adhesive. The mammoplasty and abdominoplasty scars showed no statistical difference at 3, 6, and 12 months according to both scales. The aesthetic aspects of the mammoplasty and abdominoplasty scars were similar on both sides at 3, 6, and 12 months. However, the adhesive allowed a shorter surgical time.

14.2.6 FDA and Tissue Adhesives

The FDA approval of several new CA tissue adhesives over the last decade has led to their increased use and popularity.[84] With the 2008 decision of an FDA expert panel to reclassify the CA topical skin adhesives from a class III device (that requires performance of a new clinical trial to receive approval) to a class II device (requiring demonstration of substantial equivalency to a currently approved predicate device), it is anticipated that many new CA adhesives will become available in the United States in the near future. We, therefore, think it is timely to review the properties, advantages, and indications for the various CA topical skin adhesive formulations and their clinical application for optimal use. See Appendix B for Guidance for Industry and FDA Staff—Class II Special Controls Guidance Document: Tissue Adhesive for the Topical Approximation of Skin.

14.3 Dental Applications of Adhesives

Dental adhesives are basically intended to provide retention to composite fillings or composite cements.[98] A good adhesive should not only withstand mechanical forces, particularly shrinkage stress from the lining composite, but should also be able to prevent leakage along the restoration's margins. Clinically, failure of restorations occurs more often because of inadequate sealing, with subsequent discoloration of the cavity margins, than because of loss of retention.[99,100]

Capability of dental adhesives is dependent on two conditions. First, the adhesive must bond to enamel and dentin, and second, the adhesive must adhere to the lining composite. The second condition has been shown to derive from a process of copolymerization of residual double bonds ($-C{=}C-$) in the oxygen inhibition layer. Bonding to enamel and dentin is believed to be by micromechanical adhesion as the main adhesive mechanism.[101] This happens by an exchange process during which inorganic tooth material is replaced by resin monomers that become interlocked in the retentions after polymerization.[102,103] Diffusion and capillarity are the primary mechanisms of micromechanical retention. Microscopically, this process is called "hybridization."[104] Composed of simple interlocking of resin in etch-pits in enamel, entanglement of resin within the exposed collagen lattice occurs in dentin. Self-etch adhesives (SEAs) with a mild (relatively high) pH do not now, however, completely expose collagen. An additional mechanism of ionic bonding of acidic monomers and calcium in hydroxyapatite was established in 2004,[105] which may explain the successful clinical performance of some of these mild SEAs.[106]

Some of the requirements of adhesive systems can be defined[98] using the knowledge of bonding mechanisms. Micromechanical interlocking occurs after consecutive demineralization, resin infiltration, and polymer setting. Consequently, adequately removing the smear layer together with demineralizing enamel and dentin to a small extent, good wetting, diffusion, penetration, and good polymerization of the resin components are all important. Chemical bonding can be achieved by adding specific monomers with affinity for hydroxyapatite. Finally, sufficient copolymerization between the adhesive and the lining composite provides good adhesion to the composite.

Chemical composition of adhesives selected is defined[98] such that the above mechanistic requirements may successfully be fulfilled. Even though dental adhesives can be classified into two main groups, that is, etch and rinse (E&Rs) and SEAs (Fig. 14.4), they all contain similar ingredients, irrespective of the number of containers required for a particular adhesive. Nevertheless, the proportional composition differs between the different classes of adhesives. Traditionally, adhesives contain acrylic resin monomers, organic solvents, initiators and inhibitors, and, sometimes, filler particles. It is obvious that every component has a specific function. Good insights into the chemical properties of adhesives' components are paramount to understanding or even predicting their behavior. Table 14.7 shows the various ingredients of dental adhesives.

Resin monomers in dental adhesives play a similar role to those of composites. Just as in composites, the cured resin in the adhesive forms a matrix that functions as a backbone, providing structural continuity and thus physico-mechanical properties such as

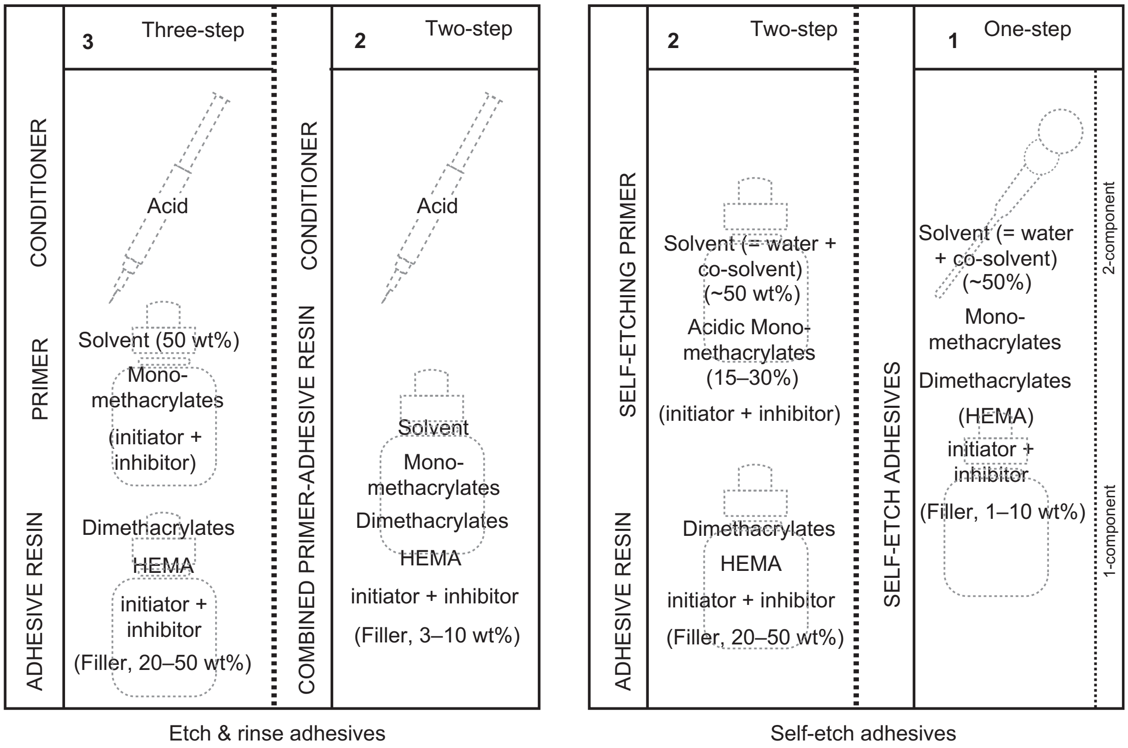


Figure 14.4 Classification of adhesives by Van Meerbeek et al.[101] Adhesives performance may differ significantly when the same components are present with different proportions of ingredients.

Table 14.7 Ingredients of Dental Adhesives[98]

Monomers
MAEPA: 2,4,6 trimethylphenyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate
MAC-10: 11-methacryloyloxy-1,10-undecanedicarboxylic acid
10-MDP: 10-methacryloyloxydecyl dihydrogenphosphate
MDPB: methacryloyloxydodecylpyridinium bromide
4-META: 4-methacryloyloxyethyl trimellitate anhydride
4-MET: 4-methacryloyloxyethyl trimellitic acid
MMA: methyl methacrylate
MMEP: mono-2-methacryloyloxyethyl phthalate (sometimes also called PAMA: phthalic acid monomethacrylate)
5-NMSA (or MASA): *N*-methacryloyl-5-aminosalicylic acid
NPG-GMA: *N*-phenylglycine glycidyl methacrylate
NTG-GMA: *N*-tolylglycine glycidyl methacrylate or *N*-(2-hydroxy-3-((2-methyl-1-oxo-2-propenyl)oxy)propyl)-*N*-tolyl glycine
PEGDMA: polyethylene glycol dimethacrylate
PEM-F: pentamethacryloyloxyethylcyclohexaphosphazene monofluoride
PENTA: dipentaerythritol pentaacrylate monophosphate
Phenyl-P: 2-(methacryloyloxyethyl)phenyl hydrogen phosphate
PMDM: pyromellitic diethylmethacrylate or 2,5-dimethacryloyloxyethyloxycarbonyl-1,4-benzenedicarboxylic acid
PMGDM: pyromellitic glycerol dimethacrylate or 2,5-bis(1,3-dimethacryloyloxyprop-2-yloxycarbonyl)benzene-1,4-dicarboxylic acid
Pyro-EMA: tetramethacryloyloxyethyl pyrophosphate
TCB: butan-1,2,3,4-tetracarboxylic acid di-2-hydroxyethylmethacrylate ester
TEGDMA: triethylene glycol dimethacrylate
TMPTMA: trimethylolpropane trimethacrylate
UDMA: urethane dimethacrylate or 1,6-di(methacryloyloxyethylcarbamoyl)-3,30,5-trimethylhexaan
Initiators and inhibitors
BHT: butylhydroxytoluene or butylated hydroxytoluene or 2,6-di-(tert-butyl)-4-methylphenol (inhibitor)
BPO: benzoylperoxide (redox initiator)
BS acid: benzenesulfinic acid sodium salt (redox initiator)
CQ: camphorquinone or camphoroquinone or 1,7,7-trimethylbicyclo-[2,2,1]-hepta-2,3-dione (photo-initiator)
DHEPT: *N*,*N*-di-(2-hydroxyethyl)-4-toluidine (co-initiator)
MEHQ: 4-methoxyphenol or monoethyl ether hydroquinone (inhibitor)
ODMAB: 2-(ethylhexyl)-4-(dimethylamino)benzoate (co-initiator)
TPO: Lucirin TPO, BASF (photo-initiator)
UV-9: 2-hydroxy-4-methoxybenzophenone (photo-initiator)
Fillers and silane coupling factors
Coupling factor A174: γ-methacryloxypropyltrimethoxysilane
F-PRG: full reaction type pre-reacted glass-ionomer fillers
NaF: sodium fluoride
Na_2SiF_6: disodium hexafluorosilicate

strength. Monomers are the most essential ingredient of the adhesive, because they are the key constituents of adhesives. There are two classes of monomers: cross-linking and functional monomers. Typically, the functional monomers only have one polymerizable group, whereas cross-linking monomers have two or more polymerizable groups such as vinyl linkages (−C═C−).[107] Functional monomers, in addition to polymerizable group, exhibit a particular chemical group, which the functional species that embodies the monomer-specific functions imparted to the polymer.

POSS (Polyhedral Oligomeric Silsesquioxane Stabilized Pd) nanoparticulates: polyhedral oligomer silsesquioxanes functional monomers form linear polymers on polymerization, contrary to the cross-linkers that supply the linkages for cross-linked polymers. Compared with linear polymers, the latter have proven to exhibit better mechanical strength, and cross-linking monomers are, therefore, important to reinforcement of the adhesive resin.[107−110] Important characteristics of more common dental adhesive monomers are briefly covered in the following sections.[98]

14.3.1 Methacrylic Acid

Methacrylic acid (MA) is a strong irritant and is corrosive because of its strong acidity. It can also rapidly penetrate gloves and skin, causing allergic reactions. This monomer is, therefore, seldom added to adhesives. It is, however, most likely to be present to different extents in the majority of adhesive resins, thanks to the hydrolysis of the ester group in other monomers, as seen in Fig. 14.5. Hydroxy ethyl methacrylate (HEMA) hydrolyzes and generates MA. Hydrolysis of methacrylate monomers is a problem associated with self-etching adhesives that routinely contain water and have fairly low pH, both resulting in easy hydrolysis.[112]

14.3.2 Methyl Methacrylate

MMA, similar to MA, is one of the oldest monomers and is seldom and sporadically added to adhesives because of the risk of allergic reactions.[113] It is no longer used for cosmetic applications due to a ban. Its role in adhesives is limited to dissolution of other monomers.

14.3.3 Hydroxy Ethyl Methacrylate

HEMA is a small monomer with widespread use, not only in dentistry but also in medical applications. Its use is widespread because of its relatively good biocompatibility,[114] even though the uncured monomer is notorious for its high allergenic potential.[115,116] Unpolymerized HEMA appears as a fluid, which is quite soluble in water, ethanol, and acetone. HEMA is purported to evaporate from the adhesive solutions, although only in small amounts.[117] A key characteristic of HEMA is its hydrophilicity. Even though this monomer cannot be used as a demineralizing agent, its hydrophilicity makes it an excellent adhesion-promoting monomer.[118−122] By enhancing wetting of dentin, HEMA significantly improves bond strengths.[123,124] In monomeric and polymerized states, HEMA readily absorbs water. Water uptake adversely influences the mechanical strength of its HEMA copolymers; high amounts of HEMA result in flexible copolymers with inferior qualities. Homopolymer of HEMA is a flexible porous polymer.[125,126] As such, high concentrations of HEMA in an adhesive may have deteriorating effects on the mechanical properties of the resulting polymer.

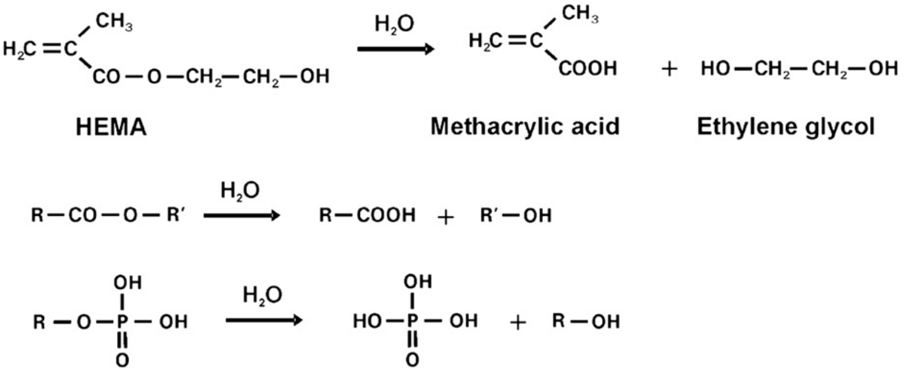


Figure 14.5 Hydrolysis of hydroxy ethyl methacrylate, an ester, and a phosphate.[98]

14.3.4 4-Methacryloyloxyethyl Trimellitic Acid

4-Methacryloyloxyethyl trimellitic acid (4-MET) is used both as an adhesion promoter and demineralizing monomer.[127,128] 4-MET is known to improve wetting to metals, such as amalgam[129] or gold.[130] Its popularity is partially due to its easy synthesizing method and broad availability. 4-MET is available in anhydride form [4-methacryloyloxyethyl trimellitate anhydride (4-META)], which is a crystalline powder. After addition of water to 4-META powder, hydrolysis reaction occurs rapidly to form 4-MET. The two carboxylic groups bonded to the aromatic ring increase acidity, and thus demineralizing properties and wetting. The aromatic group, however, is hydrophobic and moderates the acidity and the hydrophilicity of the carboxyl groups.[77]

14.3.5 4-Acryloyloxyethyl Trimellitate Anhydride

4-Acryloyloxyethyl trimellitate anhydride (4-AETA) differs from the structure of 4-META slightly, having an acrylate polymerizable group instead of a methacrylate group. The acrylate group is regarded as an advantage for polymerization because of its higher reactivity.[131] Apart from facilitating resin penetration into dentin, the highly reactive acrylate group of 4-AETA is regarded as an advantage for better polymerization.

14.3.6 10-Methacryloyloxydecyl Dihydrogenphosphate

10-Methacryloyloxydecyl dihydrogenphosphate (10-MDP) is a monomer that was originally synthesized by Kuraray (Osaka, Japan). Its main use is as an etching monomer, because of the dihydrogenphosphate group, which can dissociate in water to form two protons.[112] Structurally, the long carbonyl chain renders this monomer quite hydrophobic. Consequently, ethanol and acetone are the most suitable solvents for this monomer. It is clear that 10-MDP is relatively hydrolysis stable. Yoshida et al.[104] demonstrated that this monomer is capable of forming strong ionic bonds with calcium because of the low dissolution rate of its Ca salt in its own solution.

14.3.7 Other Monomers

These monomers include 11-methacryloyloxy-1,10-undecanedicarboxylic acid. This monomer is hydrophobic, which may be reflected in its limited dissolution in water. Another compound is 2-(methacryloyloxyethyl) phenyl hydrogenphosphate (Phenyl-P),[132,133] which was used as one of the first acidic monomers in self-etching primers. Two other monomers are phosphate: di-2-hydroxyethyl methacryl hydrogenphosphate (Di-HEMA-phospate) and 2-hydroxyethyl methacryl dihydrogenphosphate (HEMA-phosphate).[134] Dimethacrylates are cross-linking agents, and methacrylamide is an interesting matrix monomer because of its similarity to amino acids, of which collagen consists,[135] thus promoting the formation of hydrogen bonds between the carboxyl and amide groups of the monomer with the carboxyl groups of collagen.

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15 Adhesion Promoters

Peter G. Pape

15.1 General Concepts

Adhesion promoters, or coupling agents, are chemicals that act at the interface between an organic polymer and an inorganic substrate to enhance adhesion between the two materials. Organic and inorganic materials are very different in many ways, for example, compatibility, chemical reactivity, surface properties, and coefficient of thermal expansion, such that forming a strong adhesive bond between these two dissimilar materials is difficult. An adhesion promoter, in its optimal sense, will act effectively at the organic–inorganic interface to chemically and physically wed these dissimilar materials into a strong cohesive bond structure.

Other approaches to improve adhesion involve chemical modification of the polymer surface via oxidation with ozone or plasma, and physical abrasion of the inorganic substrate to increase the bonding surface area by altering the surface roughness. Although these approaches can enhance adhesion, the use of adhesion promoters will not only alter physical and chemical forces at the interface, but also provide a “glue,” or compatibility bridge, to give a much greater level of adhesion. Additionally, adhesion promoters can impart resistance to environmental and other destructive forces, such as heat and moisture, which often act on the bonded site to destroy adhesive strength.

Adhesion promoters are chemical materials that contain dual functionality in the molecular structure. A metallic central atom, such as silicon, zirconium, titanium, aluminum, or others, will give inorganic reactivity to the adhesion promoter, especially if methoxy, ethoxy, or hydroxyl groups are attached to the metal atom. An organofunctional group can also be attached to the metal atom through an alkylene, arylene, or other type of organic bridge, to give traditional organic reactivity to the adhesion promoter. The inorganic reactive groups can condense with themselves to give the adhesion promoter an oligomeric structure. An oligomeric adhesion promoter has dual- or multi-functionality and structural integrity, such that a stable chemical bond occurs between the dissimilar organic and inorganic surfaces to promote adhesion between the two dissimilar materials. This basic concept of the chemistry and action of adhesion promoters has allowed great advances in reinforced plastics, adhesive bonding, and compatibilization of different materials in a wide variety of applications.

Other types of reactive adhesion promoters that are not based on *inorganic* reactivity are also useful as compatibilizers for dissimilar polymeric materials. These adhesion promoters include reactive organic oligomers or polymers, such as thermoplastics polymers (polyethylene, polypropylene, etc.) grafted with organofunctional groups. Nonreactive adhesion promoters include block copolymers that function by having polymeric segments with solubility parameters that are matched to the components in order to be adhered or compatibilized and function by atomic interactions of van der Waals, dipole interaction, and other atomic forces.

Organosilane coupling agents are the predominant chemical type of adhesion promoter and, therefore, are here the main focus of discussion.

15.2 Silane Adhesion Promoters

15.2.1 Typical Silane-Coupling Agents

A silicon-based chemical that functions as an adhesion promoter, or as a coupling agent, has a general structure of four substituents attached to a single silicon atom. The most common structure has three inorganic–reactive alkoxy groups, methoxy or ethoxy, and one organic group (see Fig. 15.1), although sometimes it may contain only two alkoxy groups, one of the alkoxy groups being replaced by a methyl group.

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General Structure : $R_xSi(OR')_y$ x + y = 4

- **R= alkyl, aryl, or organofunctional group**
- **OR'= methoxy or ethoxy**
- **Examples:**

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2Si(OCH_2CH_3)_3$
(n-octyltriethoxysilane)

$H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$
(aminoethylaminopropyltrimethoxysilane)

Figure 15.1 General structure of silane-coupling agents.

The organic group is either reactive (amino, epoxy, methacrylate, etc.) or an unreactive (methyl, butyl, octyl, phenyl, etc.). Coupling agents, with several different organofunctional types, are commercially available. Typical commercial coupling agents are listed in Tables 15.1 and 15.2.

15.2.2 Silane Chemistry

Silicon is in the same family of elements as carbon in the periodic table, but silicon compounds exhibit significant differences in chemical reactivity compared to analogous carbon compounds. Similarly to carbon, silicon will conveniently bond to four substituents in its most stable state. However, silicon is more electropositive than carbon, does not form stable double bonds, and is capable of very special and useful chemical reactions that enhance its effectiveness as an adhesion promoter component. A silicon molecule that has dual reactivity can be synthesized; that is, both organic and inorganic reactivities can be synthesized into a single molecule. The unique nature of silane chemistry, to have both inorganic and organic reactivities in one molecular

Table 15.1 Silane-Coupling Agents—Part 1: Match Organic Group to Polymer Type

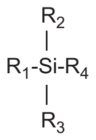
Chemical type	Chemical name	Polymer
Amine	Aminopropyltriethoxysilane	Acrylic, nylon, epoxy, phenolics, PVC, urethanes, melamines, nitrile rubber
Diamine	Diaminopropyltrimethoxysilane	Acrylic, nylon, epoxy, phenolics, PVC, melamines, urethanes, nitrile rubber
Methacrylate	3-Methacryloxypropyltrimethoxysilane	Unsaturated polyesters, acrylics, EVA, polyolefin
Epoxy	3-Glycidoxypropyltrimethoxysilane	Epoxy, PBT, urethanes, acrylics, polysulfides
Methyl	Methyltrimethoxysilane	Hydrophobing agent for mineral surfaces
Isobutyl	Isobutyltrimethoxysilane	Hydrophobing agent for mineral surfaces, masonry water repellent

Table 15.2 Silane-Coupling Agents—Part 2: Match Organic Group to Polymer Type

Chemical type	Chemical name	Polymer type/application
Phenyl	Phenyltrimethoxysilane	Hydrophobing , dispersing aid for mineral surfaces, blends, hydrophobe, thermal stability
Octyl	Octyltriethoxysilane	Hydrophobing for mineral surfaces; dispersion of minerals in polyolefins; masonry water repellent
Vinyl	Vinyltrimethoxysilane	Graft to polyethylene for moisture cross-linking, EPDM rubber, SBR, polyolefin
Chloroalkyl	3-Chloropropyltrimethoxysilane	Urethanes, epoxy, nylon, phenolics, polyolefins
Chloroalkyl	3-Chloropropyltriethoxysilane	Urethanes, epoxy, nylon, phenolics, polyolefins
Vinylbenzylamino	Vinylbenzylaminotrimethoxysilane	Epoxies for PCBs, polyolefins, all polymer types

structure together with the special chemistry of silicon, gives rise to the use of silane chemicals as coupling agents and adhesion promoters.

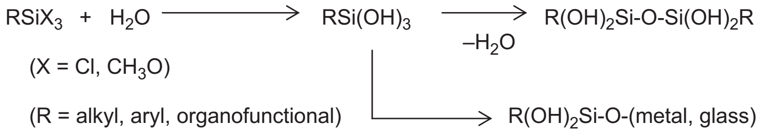
Monomeric silicon chemicals are known as silanes. A silane has the chemical formula **1** in which R_1, R_2, R_3, and R_4 can be the same substituent or four different substituents. The



$$\begin{array}{c} R_2 \\ | \\ R_1\text{-Si-}R_4 \\ | \\ R_3 \end{array}$$

1

electropositive nature of the silicon atom causes certain atoms or groups attached directly to silicon to be very reactive and exhibit inorganic rather than organic reactivity. Silane substituents, such as chlorine, amine, methoxy, acetoxy, or hydroxyl, are reactive with inorganic materials that contain hydroxyl groups, such as −Si−OH, −Al−OH, or metal−OH in glass, minerals, metals, and even water. A silanol, −Si−OH, or a silylamine, $-Si-NH_2$, is generally not stable and will condense rapidly to siloxane, −Si−O−Si−, or silazane, −Si−NH−Si−, respectively. A chlorosilane or a methoxysilane, $RSiX_3$, X=Cl or CH_3O, reacts with water (hydrolyzes) to give unstable silanetriol, $-Si(OH)_3$, condenses with a second silanetriol to form a siloxane, −Si−O−Si−, structure (Reaction (1)), or reacts with available metal hydroxyls on a metal or glass surface to form a silicon−oxygen−metal bond with the inorganic substrate (Reaction (2)).



(1)

(2)

To be classified as an *organo*silane, one of the silane substituents must be an organic group that is directly attached to silicon via a Si−C bond. Organic substituents attached to silicon are either nonreactive, such as methyl, ethyl, butyl, octyl, phenyl, and others, or organofunctional; that is, they contain an organic reactive group, such as amino, epoxy, methacrylate, sulfido, isocyanato, and so on. An organic spacer group usually separates the organofunctional group from the silicon atom. If the spacer group is at least three carbons in length, for example $-CH_2CH_2CH_2-$, then the organic reactivity of the organic group in the silane is similar to organic reactivity in carbon chemistry. If the spacer group is one or two carbons in length, then the silicon atom may influence the reactivity and change the chemistry of the organic group. Other reactive silanes, particularly vinyl silanes, $-Si-CH{=}CH_2$, and silicon hydrides, −Si−H, are useful reactive groups in silicon chemistry.

15.3 Adhesion Promoter Mechanism with Silanes

15.3.1 The Interphase Region

Silane-coupling agents will act in the interphase region, the area between an inorganic (such as glass, metal, or mineral) and an organic substrate (such as an organic polymer, coating, adhesive), and act as a bonding or bridging agent to improve the adhesion between the two dissimilar materials[1,2] (see Fig. 15.2). Modification of the interphase region produces other desirable changes: improve wet-out of the inorganic substrate by the polymer, improve dispersion of fillers in liquid polymers, reduce the viscosity of the uncured polymer−filler mixture, protect minerals against cleavage, heal flaws in the surface, and strengthen the polymer layer at the interface by interdiffusion with the coupling agent to form interpenetrating polymer networks (IPNs).

The interface (or interphase region) between a polymer and an inorganic substrate involves a complex interplay of physical and chemical factors related to adhesion, physical strength, and retention of properties of the product. Adhesive bonds are destroyed by migration of water into this interface to hydrolyze bonds and cause physical detachment.

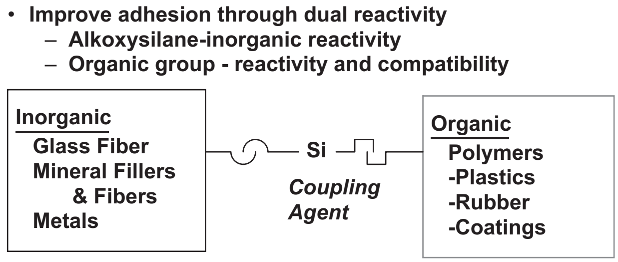


Figure 15.2 Silane-coupling agents—dual reactivity.

Silane-coupling agents have unique chemical and physical properties to not only enhance bond strength, but also to prevent debonding at the interface. In composites, often a 40% increase in flexural strength is obtained using silane-coupling agent. In coatings and adhesives, silane-coupling agents significantly increase bond strength and resistance to humidity and other adverse environmental conditions.

15.3.2 Bonding to the Inorganic Substrate

Silane-coupling agents, with their inorganic reactive groups on silicon, bond well to most inorganic substrates, especially when the substrate contains silicon, aluminum, or most heavy metals. The bond with the inorganic substrate forms very rapidly and dynamically in most situations. The alkoxy groups on silicon hydrolyze to silanols, either with added water or from residual water on the inorganic surface (Reaction (1)). The silanols coordinate with metal hydroxyl groups on the inorganic surface to from an oxane bond, with elimination of water (Reaction (2)). Studies of the mechanism of bond formation of silanes to inorganic substrates show covalent oxane bonds with silica and glass reinforcements.[3] Acids and bases catalyze both hydrolysis and condensation. It is estimated that a silanetriol, $R'Si(OH)_3$ (the intermediate generated by a trialkoxysilane coupling agent) has an equilibrium constant 10^3 more favorable toward bonding to a silica substrate than a coupling agent from a corresponding monoalkoxy silane.[4] Trialkoxysilanes have approximately a 10-fold equilibrium constant relative to dialkoxysilanes toward bonding to the inorganic substrate.

The condensation of silanols with other silanols at the interface gives a multimolecular structure of cross-linked siloxane. The cross-linked structure exists as multiple layers of siloxane, with a very tight siloxane structure existing close to the inorganic surface and a more diffuse structure away from the surface. This "grid" type of structure allows organic coatings to interpenetrate, or diffuse, into the siloxane structure to allow electrostatic forces of interpenetration, very powerful adhesive forces, to become part of the bonding mechanism. This type of IPN structure is shown in Fig. 15.3.[5]

Once the coupling agent is attached to an inorganic surface, that surface takes on the surface chemistry and surface reactivity characteristics of the organic group attached to the coupling agent. The treated surface exhibits the surface energy of the organic group, and the surface becomes reactive, as determined by the reactivity of the organofunctional group in the coupling agent. A silane surface modifier can be selected to give the surface whatever property is desired to transform the nature of the surface into that which is needed to allow optimization of the inorganic material for the intended use.

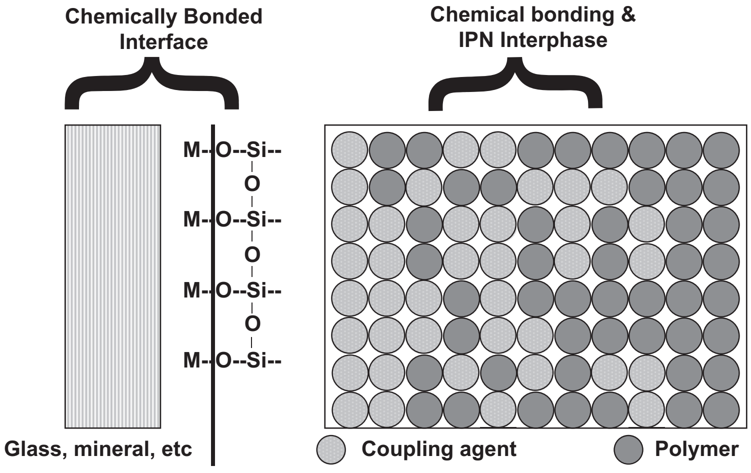


Figure 15.3 Interpenetrating network theory—bonding to polymers.

15.3.3 Bonding to the Organic Polymer

The interaction of the silane-coupling agent with the organic polymer is complex. For a thermoset polymer, the silane bonds to the polymer through chemical reactivities of both. The most important consideration is to match the reactivity of the coupling agent with that of the thermoset polymer.[6] Coupling agents are optimum when the organofunctional group participates in the curing mechanism or has some way of reactively attaching to the polymer structure in the final composite. For example, either an epoxysilane or an aminosilane can participate in the curing mechanism of an epoxy resin; a methacrylate silane bonds through free radical cross-linking during the cure of an unsaturated polyester resin in the composite; and phenolic resins have several different reaction modes so that several types of silanes (amino, epoxy, and chloroalkyl, for example) impart good properties to phenolic composites.

For thermoplastic polymers, especially polyethylene and polypropylene that lack reactivity on the polymer backbone, having covalent bonding to the polymer is difficult. However, good property improvements are obtained with silane-coupling agents in thermoplastic systems. In these cases, bonding is best explained by interdiffusion of the polymer into the layered siloxane network at the inorganic surface and formation of an IPN in the interphase region. Interdiffusion and cross-linking of silane adhesion promoters, as depicted in Fig. 15.3, were identified as the mechanism of adhesion of polyvinylchloride plastisols to silane-treated glass.[5] Such interdiffusion is an important factor in adhesion of thermoplastic elastomers to primers, comprising silane-modified tackifying resins,[7] primers used for bonding polyolefins,[8] silane-modified melamine resin primers for bonding engineering thermoplastics,[9] and silane-modified epoxy primers for bonding cross-linkable ethylene–vinyl acetate copolymers to surfaces in solar cell modules.[10] The solubility parameter of the organic group on the silane, if matched with that of the polymer, produces the beneficial effect of enhancing the interpenetration of the polymer.

Thermoplastic polyester resins, such as PET (polyethylene terephthalate) and PBT (polybutylene terephthalate), contain residual phenolic or carboxylic reactive sites that make epoxysilanes effective. Octyl and phenyl silanes are also used in combination with organofunctional silanes, for thermoset applications to improve dispersion of the resin by matching solubility parameters, increase hydrophobic character, and give greater resistance to attack of water in the interphase region. Aromatic structures in silane-coupling agents, such as phenylsilanes, impart increased heat resistance to the adhesive bond.

15.4 Optimizing Coupling Agent Performance

"Wet strength," the strength of the bond in a humid-aging environment, is often studied to evaluate the effectiveness of coupling agents. Physical properties, such as flexural strength of composites or a peel adhesion test for coatings and adhesives, are measured before and after a wet aging test. A test specimen is aged in warm or boiling water for 2, 4, or 24 h, for a week, or for longer. The length of time that a bond survives, or the coupling agent that gives the greatest retention of bond strength in the wet environment, gauges the effectiveness of a coupling agent.

The effect of the organic structure of the coupling agent in improving the flexural strength of a silica-reinforced unsaturated polyester composite is shown in Fig. 15.4. A significant increase in dry and wet strength of the composite, after aging for 24 h in boiling water, manifests when a coupling agent is used. The choice of a coupling agent with optimum reactivity and chemical structure optimizes the

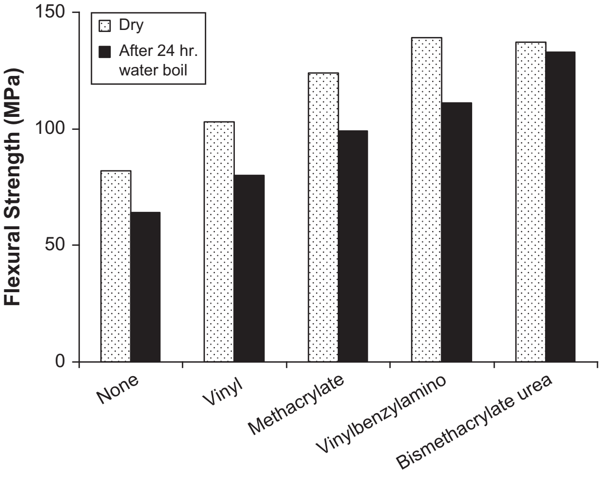


Figure 15.4 Silane organic group—effect on flexural strength of a silica–polyester composite.

retention of flexural strength. Two or more possible coupling agents can be effective in the same system, but often one gives the best combination of properties in the final bonded material.

Adhesion can also be improved by using blends of silanes. A hydrophobic silane in combination with a hydrophilic silane often improves bonding and retention of wet strength, compared to using the hydrophilic silane alone. The hydrophobic nature of some silanes is listed in Tables 15.1 and 15.2. Phenyltrimethoxysilane, a hydrophobic silane, impels a significant improvement in adhesion of a urethane polymer to glass when blended with a hydrophilic diaminosilane, even though the aminosilane adhesion promoter alone is a good coupling agent for urethane polymers.[11] The data in Table 15.3 show that the bond of urethane to glass fails in boiling water after 2 h if the aminosilane alone is used, but total bonding is retained even after 5 h in boiling water when 90% phenylsilane is blended with the aminosilane.

Silane blends also can be used to increase the thermal stability of a silane for use in high-temperature polymers. Many reinforced plastics, such as polyimides, are fabricated at temperatures of 400 °C or higher, and adhesive bonds often must survive high-temperature environments. Standard aliphatic silane-coupling agents have adequate heat stability for fabrication temperatures up to about 250 °C, but they may decompose at higher temperatures. Certain aromatic functional silanes, such as an aminophenylsilane imidized with an aromatic anhydride, have outstanding heat stability, but they are not commercially available.

Table 15.3 Silane Blends—Adhesion of Urethane to Glass

Ratio of silanes	Adhesion to glass (N/cm)		
I/F in primer	Dry	2 h in boiling water	5 h in boiling water
Control	3.0	Nil	Nil
0/100	C	Nil	Nil
50/50	C	Nil	Nil
80/20	C	C	C
90/10	C	C	C
95/5	C	C	C
99/1	C	C	C

C = cohesive failure > 20 N/cm; I = phenyltrimethoxysilane; F = diaminopropyltrimethoxysilane.

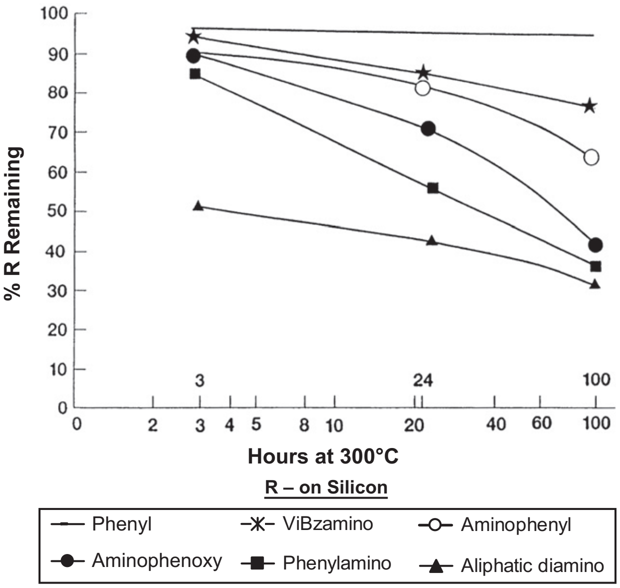


Figure 15.5 Stability of $RSiO_{3/2}$ in air at 300 °C.

The thermal stability of several commercial silanes was studied by determining isothermal weight loss of the hydrolyzed silsequioxane form of the silanes, $RSiO_{3/2}$, at 300 °C.[11] Figure 15.5 shows that the phenylsilyl structure has very good thermal stability, but the diaminosilane has poorer thermal stability. The vinylbenzylaminosilane has surprising good thermal stability. Phenyltrimethoxysilane blends, or vinylbenzylaminosilane, have been recommended for high-temperature applications.

A blend of 90% diaminosilane and 10% phenylsilane in fiberglass-reinforced polyimide, processed at 400 °C, was aged up to 2000 h at 260 °C. Flexural strength data in Table 15.4 show the improved thermal performance of the phenylsilane blend compared to a monoaminosilane, the standard coupling agent that had been used in that application.[12] In an analogous system, proprietary sizes were formulated with the more thermally stable vinylbenzylaminosilane and applied to a silicon carbide fiber—polyimide composite. The composite was aged at 315 °C for up to 1000 h. The proprietary sizes improved flexural strength after 1000 h compared to an epoxy-organic size that was normally used in such systems (see Table 15.5).

An increase in siloxane cross-linking in the interphase region also improves performance. A multifunctional cross-linking additive can be added as an

Table 15.4 Thermal Stability—S-Glass/Polyimide Laminates

Properties of laminates (MPa)	Coupling agents on glass	
	Blend 9/1, phenyl/ diamino silane	Monoamino silane
Flex. Str., initial	544	476
1000 h at 260 °C	409	258
2000 h at 260 °C	306	134

Phenylsilane = $PhSi(OMe)_3$; monoaminosilane = $(EtO)_3Si(CH_2)_3NH_2$; diaminosilane = $(MeO)_3Si(CH_2)_3NH(CH_2)_3NH_2$.

Table 15.5 Si-C Fiber/Polyimide Laminates—Retention of Strength at 315 °C

Silicon carbide	Flexural strength (MPa)			
Fiber size	Initial	100 h	500 h	1000 h
Epoxy organic	1480	1320	1000	610
DCC-1	2350	2320	1660	890
DCC-2	2120	2060	1670	980

DCC-1 and DCC-2 are proprietary—based on vinylbenzylaminosilane.

adhesion enhancer.[13] A hexafunctional methoxydisilane additive, $(CH_3O)_3SiCH_2CH_2Si(OCH_3)_3$, can be blended with conventional silanes. The data in Table 15.6 show that the cross-linking additive improves the adhesion of an epoxy film to glass compared to either a diaminosilane or an epoxysilane alone. Similarly, two silanes with organic functional groups that react with each other can be used to spur increased cross-linking. Pairings of aminosilane and epoxysilane, aminosilane and methacrylate silane, or chloroalkyl silane and an aminosilane, react jointly and in properly formulated amounts to give in situ formation of multifunctional alkoxy reactivity. Also, the use of tetraethoxysilane in a coupling agent formulation can increase cross-linking.

15.5 How to Choose a Silane-Coupling Agent

The nature of the organic group in the coupling agent is a key consideration when choosing a silane. With any silane-coupling agent, the three alkoxy groups on silicon should bond equally well to an inorganic substrate, but matching the organofunctional group on silicon with the polymer type of the resin bonded dictates which silane will be used in a particular application.

Several silanes are recommended for one polymer type. For example, the cure system for an epoxy resin, amine versus anhydride, high-temperature versus low-temperature cure, and aliphatic versus aromatic amine, often affects the performance of the coupling agent.

Table 15.6 Adhesion Enhancer/Cross-linker $(MeO)_3SiCH_2CH_2Si(OMe)_3$ Adhesion of Epoxy Film on Glass

Primer on glass	Curing agent type—hours to lose adhesion		
	Polyamide	DMP-30	DEH-24
None	<1	<1	<1
Diaminosilane alone	1	1	1
Blend 9:1:diaminosilane:enhancer	C	C	C
Epoxysilane	C	8	C
Blend 9:1:epoxysilane:enhancer	C	36	C
Blend 8:2:epoxysilane:enhancer	C	C	C

C = No failure after 1 week in 70°C water.

Table 15.7 Organosilanes—Applications

Chemical type	Chemical name	Coupling agent for polymer type/ application
Amine	Aminopropyltriethoxysilane	Acrylic, nylon, epoxy, phenolics, melamines, PVC, urethanes, nitrile rubber
Diamine	Diaminopropyltrimethoxysilane	Acrylic, nylon, epoxy, phenolics, melamines, PVC, urethanes, nitrile rubber
Methacrylate	3-Methacryloxypropyltrimethoxysilane	Unsaturated polyesters, acrylics, EVA, polyolefin
Epoxy	3-Glycidoxypropyltrimethoxysilane	Epoxy, PBT, urethanes, acrylics, polysulfides
Methyl	Methyltrimethoxysilane	Hydrophobing agent for mineral surfaces
Isobutyl	Isobutyltrimethoxysilane	Hydrophobing agent for mineral surfaces, Masonry water repellent
Phenyl	Phenyltrimethoxysilane	Hydrophobing, dispersing aid for minerals, blends with silanes/thermal stability
Octyl	Octyltriethoxysilane	Hydrophobing/dispersion of minerals in polyolefins, masonry water repellent
Vinyl	Vinyltrimethoxysilane	Graft to polyethylene for moisture cross-linking, EPDM rubber, SBR, polyolefin
Chloroalky	3-Chloropropyltrimethoxysilane	Urethanes, epoxy, nylon, phenolics, polyolefins
Chloroalkyl	3-Chloropropyltriethoxysilane	Urethanes, epoxy, nylon, phenolics, polyolefins
Vinylbenzylamino types	Vinylbenzylaminotrimethoxysilane	Epoxies for PCBs, polyolefins, all polymer

A list of silane-coupling agents and recommendations for their use in various applications is displayed in Table 15.7. A correlation exists between the chemical and physical characteristics of the coupling agent and the chemical and the physical characteristics of the polymer.

The same principles that are used in selecting a silane for reinforced plastics are used to select a silane for paints, inks, coatings, and adhesives (PICA). The chemical nature of the organic material used in the application is the major criterion that governs the effectiveness of a particular coupling agent as an adhesion promoter.

15.6 General Applications of Silane-Coupling Agents

Fiberglass-reinforced polyesters were developed in the 1940s and required an adhesion promoter to retain the physical strength of the composite during ambient aging. Other types of coupling agents, such as chrome complexes, were good coupling agents. But silane-coupling agents were developed to fill this need specifically, and they have proven to be the best adhesion promoters for these materials. Since then, other applications for adhesion promoters have been developed, including mineral-filled composites,

Table 15.8 Silane Applications

- Fiberglass cloth, mat, chopped glass (surface treatment) for *adhesion* in reinforced plastics (PCBs, auto, boats, tanks, etc.).
- Mineral (surface treatment) for *adhesion and/or dispersion* in reinforced plastics (auto, W&C, electronics, rubber/tires, etc.).
- Paints, inks, coatings, adhesives (primer or additive) to give *moisture resistant adhesion* to surfaces.
- Moisture *cross-linking* of polyethylene (Sioplas).

laminates for printed circuit boards, insulation fiberglass, silica-filled rubber tires, rubber insulation for wire and cable, adhesion promoters in PICA, and moisture-cured cross-linking systems for polyethylene. Various applications of silane-coupling agents are listed in Table 15.8.

15.7 Industry and Utility

15.7.1 Surface Treatment of Fiberglass

Glass fiber is a very hydrophilic material. It requires a protective coating to eliminate the degradative effects of moisture in a variety of applications, particularly when it is used as a reinforcement in polymeric composites. The natural chemistry of silanes is similar to the silicon chemistry of glass, and the favorable equilibrium of bonding silanes to glass surfaces designates them as being ideal for treatment thereof. Virtually all glass fiber for most applications requires a coupling agent to engender the glass fiber a viable material for intended applications. The fiberglass may be in the form of random glass matt, chopped strand, woven roving, continuous filament, or woven glass cloth; regardless of the form of the glass fiber, it must be treated with a coupling agent to render it useful as a reinforcement for polymers. The nature of the final application determines which type of silane is used and how the silane is applied in the process.

Other noncoupling benefits of silane adhesion promoters in composites are very important. These include the following: change in rheology of a filled system during processing, elimination of inhibition of cure caused by the reinforcement, better wet-out of the fiber, greater smoothness of the composite surface, increased clarity of a composite, and healing of flaws in glass fibers. A minuscule amount of coupling agent prompts a dramatic difference in the performance of the end product.

15.7.1.1 Fiberglass for Reinforced Plastics

The glass fiber that is used in reinforced plastics has a coupling agent on the surface. Fiberglass manufacturers apply a water-based "size" to it as the filaments are gathered into strands during the fiber-forming process. The formulation contains several ingredients, including a film-forming polymer, a glass lubricant, an antistatic agent, and other ingredients, but a critical component is 0.1%–0.5% silane-coupling agent. As the size is water-based (an important requirement by the fiberglass industry), any silane that is used must be dissolved in water. The addition of a silane to water generally gives a precipitated gel via hydrolysis and leads to the formation of insoluble hydrophobic siloxane structures. However, if the water is acidified to a pH of 4 with acetic or formic acid, a silane-coupling agent hydrolyzes and dissolves in water without gelling, especially at concentrations less than 5%. The low pH stabilizes the silanol species against condensation to allow the silane to dissolve and remain soluble. A higher pH of 5–6 is used in acid-sensitive epoxy silanes. Hydrophilic silanes, such as aminosilanes, form aqueous solutions at all pHs, but pH 4 is preferred for glass treatment to give correct orientation on the glass surface.[3]

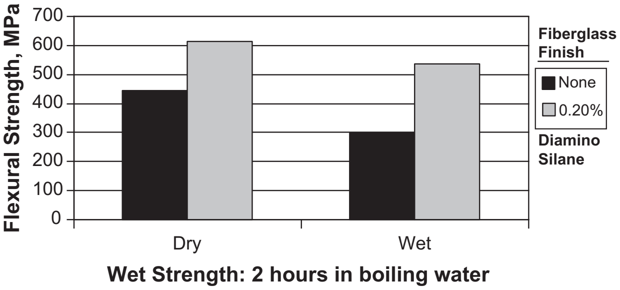


Figure 15.6 Fiberglass-reinforced phenolic laminate strength test.

The magnitude of the effect of a coupling agent regarding the improvement of strength properties of composites is usually significant (see Fig. 15.6). A fiberglass-reinforced phenolic composite with and without diaminopropyltrimethoxysilane on the glass surface was tested as prepared, and was also tested after immersion for 2 h in boiling water. Before aging, the flexural strength of the unaged composite showed a 38% increase with the silane versus without a silane; after aging, the sample without the silane lost 66% of its strength, whereas the silane-treated sample lost only 12% of its flexural strength. The wet strength properties represent an accelerated aging test comparable to long-term conditions in the environment.

The effect of the type of organic group in the silane-coupling agent is shown in Table 15.9. Epoxysilane and the vinylbenzylamino silane were used in fiberglass-reinforced epoxy composite formulations and the samples were aged in boiling water for 72 h.

Table 15.9 Coupling Agent—Organic Group Effect on Strength—Epoxy–Glass Laminate

Silane-coupling agent type	Flexural strength, MPa	
	Dry strength	Wet, 72 h in boiling water
None	394	221
Epoxy	605	476
Vinylbenzylamino	670	518

Both coupling agents gave a substantial increase in initial flexural strength and improved retention of strength after the aging test. That the performance of the vinylbenzylamino coupling agent improved maybe because the coupling agent has a complex chemical structure and cationic character to coat the glass fiber more efficiently, and it forms an IPN network with the thermoset polymer. It is also more hydrophobic than the epoxy silane and has a very reactive amine functionality to participate in the curing process.

15.7.1.2 Printed Circuit Board Applications

The printed circuit board industry is based largely on high-quality fiberglass-reinforced epoxy laminates that are made from layers of electronic-grade woven glass cloth and on which a silane size becomes the critical chemical component between the glass and the resin. The industrial requirement for better bonding of the epoxy resin to the glass surface increases as the density of holes that are drilled in a laminate for conductive sites increases. It is very important to eliminate failure along the glass fiber in the laminate.

The fiberglass that goes into printed circuit boards is processed in a different way than the conventional fiberglass for reinforced plastics. The fiberglass is first woven into a glass fabric with a starch size and lubricant on the surface. The starch is burned off and the silane is applied to the heat-cleaned woven glass fabric as, usually, the only ingredient on the glass cloth. The silane is applied from an acidified aqueous treating bath at a pH of 4 and at a treatment level of 0.1%–0.5%. The silane-treated woven glass cloth is dried, carefully inspected for flaws, and then supplied to laminators in the printed circuit board industry where lamination and fabrication of printed circuit boards are carried out.

The resins that are used in printed circuit board laminates determine the type of silanes that are used. High-performance epoxy resins are the most-used resins, so an epoxy compatible silane is required. Vinylbenzylaminosilane is used mostly for this application. Low ionic content (a low chloride level), ease of solubility in treatment baths, and minimization of agglomerates on the electronic glass surface to prevent flaws are important parameters in choosing a coupling agent.

For resin systems other than epoxy, or for other epoxy requirements, the glass weavers sometimes apply aminosilanes, epoxysilanes, and chloropropylsilanes.

15.7.1.3 Miscellaneous Fiberglass Applications

Other applications of fiberglass include insulation for construction applications, roofing shingles, and automotive insulation applications. These are not always composite applications, in the strictest sense, but still require a coupling agent to bond a resinous coating to the glass surface.

Insulation fiberglass for construction applications uses a phenolic binder to help retain the insulation value. An aminosilane, either a monoaminosilane or diaminosilane, can be mixed into an aqueous phenolic binder solution to bind the phenolic resin to the glass fiber surface. Without the silane present, the phenolic de-bonds during aging in the environment and causes the glass fiber to relax, so reducing the insulation value.

Fiberglass-based roofing shingles are similar to reinforced plastics' applications and require durable organic polymers to resist the sun and other degradative effects. Vinylbenzylaminosilane has been used in formulations to allow the products to meet the requirements of building codes and construction standards.

15.7.2 Surface Treatment of Minerals in Plastics

15.7.2.1 Nature of Bonding to Minerals

Mineral fillers require surface modification when used as reinforcements in plastics. Surface treatment improves mechanical strength and chemical

Table 15.10 Surface Treatment Benefits

- Mineral/Filler—0.1%–10% on filler (particle size = 0.1–50 μm)
  - – Plastics/rubber reinforcement
  - – Better filler wet-out and dispersion
  - – Lower viscosity of filled liquid resins
  - – Improved moisture resistance of composite
  - – Reduced cure inhibition of filler
  - – Improved electrical properties of filled polymer

resistance of composites by improving adhesion across the interface. Other benefits of surface treatment include improved dispersion of the mineral into polymeric media, lower viscosity of the mix, greater compatibility with the polymer, change of the mineral surface from hydrophilic to hydrophobic, improved electrical properties in a mineral-filled polymer system, and decreased cure inhibition of thermoset polymers. Some of these benefits are listed in Table 15.10.

In a mineral-filled composite, the interphase region between the polymer and filler involves the interplay of physical and chemical factors related to composite performance, including a tremendous mechanical stress of differential shrinkage during cure, wet-out and dispersion of the mineral in the polymer, protection of the filler against abrasion and cleavage during mixing, optimum alignment of polymer segments at the interface, and adhesion and an interfacial structure to generate the desired improved properties.

Mineral fillers usually contain silicon, aluminum, and other metallic elements in chemical structure such that metal hydroxyl groups on the surface are very hydrophilic in nature. Some of the more commonly used mineral fillers include silica, wollastonite, talc, mica, glass beads, and kaolin clay (see Table 15.11). The reactive sites on the filler surface can function in a manner similar to the silanol groups on fiberglass reinforcement that is chemically treated in a similar way (see Fig. 15.7). Treatment of the filler can make the surface either chemically reactive via an organofunctional silane, or it can make hydrophobic, organophilic, or hydrophilic, depending on the silane used. Some types of organosilanes and the characteristics of the organic group are listed in Table 15.12. Beyond these general characteristics of silanes, various silanes and polymer applications are catalogued in Table 15.7.

Table 15.11 Mineral–Filler Applications

Fillers	Comments
Kaolin clay	Reinforced nylon, wire, and cable (EPDM)
Talc	Stiffness, abrasion—polypropylene (auto)
Mica	Stiffness, polypropylene (auto)
Silica	Reinforced rubber, epoxy PCBs
Wollastonite	Reinforced plastics, coatings
Glass Fiber –Beads	Reinforced plastics
Aluminum trihydrate	Flame retardance
Magnesium hydroxide	Flame retardance
Crystobalite	Abrasion resistance/ plastics
Titanium dioxide	Plastics, colorant, filler

15.7.2.2 Methods of Applying Silanes to Minerals

Mineral fillers are often pretreated before compounding, but the silane is sometimes added to the filler–polymer mix during compounding (often referred to as in situ addition or integral blending).[14] Sometimes, additional coupling agent is added during compounding to enhance adhesion or to provide performance benefits.

Particulate fillers are pretreated with a silane by dry blending at room temperature or at elevated

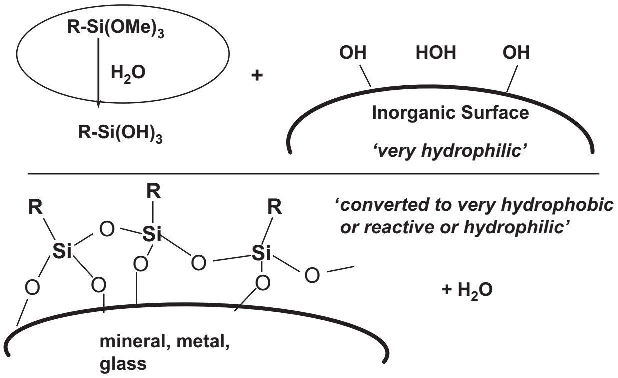


Figure 15.7 Silane bonding to inorganic surfaces.

Table 15.12 Organosilane Characteristics of R-Si $(OMe)_3$

R	Characteristics
• Me	Hydrophobic, organophilic
• Ph	Hydrophobic, organophilic
• *i*-Bu	Hydrophobic, organophilic
• Octyl	Hydrophobic, organophilic
• $-NH(CH_2)$ $3NH_2$	Hydrophilic, organoreactive
• Epoxy	Hydrophilic, organoreactive
• Methacryl	Hydrophobic, organoreactive

temperature. The filler surface may contain residual moisture to hydrolyze the silane, but sometimes water and/or an alcohol is added. A high-intensity mixer, such as an Henschel or Littleford Mixer, is used for the treatment process. Filler treatment may benefit from the addition of a trace of amine or titanate to catalyze the reaction with the filler surface.

At least a monolayer of silane is needed on the filler surface. In practice, about 1% silane is applied to the filler with a particle size of 1 μm, enough for several monolayers. Higher surface area fillers require higher levels of coupling agents. Figure 15.8 shows the effect of the level of silane treatment on several different fillers apropos of the flexural strength of a styrene–butadiene casting.

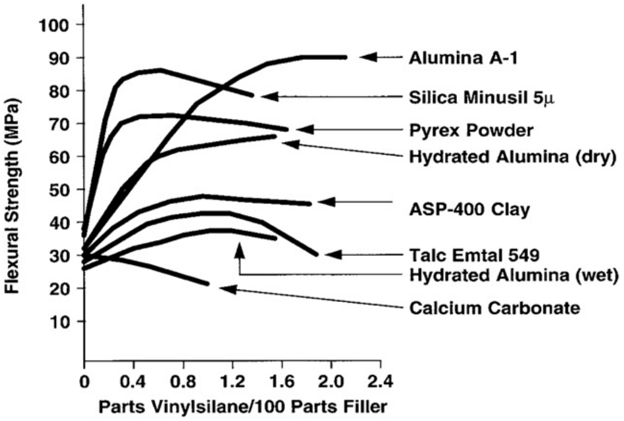


Figure 15.8 Silane treatment of fillers in a styrene–butadiene casting.

15.7.2.3 Effect of Silanes on Properties of Mineral-Filled Composites

A silane-coupling agent not only increases the flexural strength of a filler-resin composite, it also significantly lowers the viscosity of the uncured resin mix and allows for greater filler loadings and easier processing. An effect of silane on the viscosity of an uncured polymer–filler blend and on the flexural strength of the cured composite is exhibited in Fig. 15.9. The use of different types of silanes in the treatment process can significantly alter the effect on viscosity of the mix, and can alter the resulting flexural strength of the composite.

Conveyed in Fig. 15.10 are the benefits of silane filler treatment on the cure chemistry of a thermoset resin. The surface of the mineral filler can interfere with the curing chemistry and inhibit the cure. However, once the filler is treated with silane, the filler surface is changed chemically so that the inhibition of cure is minimized.

Electrical properties of filled resin systems are also improved by filler treatment. Filler particles are naturally hydrophilic via their metal hydroxide surfaces, and the particles naturally seek to agglomerate with each other, and so transport electrical charges through resin composite. Treatment with silane-coupling agent alters the chemistry of the filler surface, allow better dispersion of the filler throughout the resin matrix, and imparts improved electrical properties to the composite. Table 15.13 indicates the improved electrical properties of a quartz-filled epoxy resin system with 0.3% silane admixed into the formulation. Improved insulation values, including reduced dielectric constant and reduced dissipation factor, are also denoted.

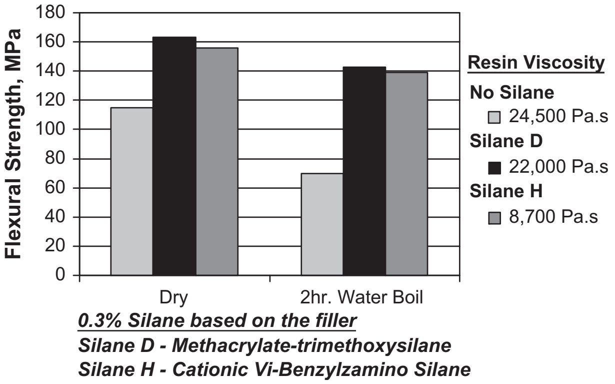
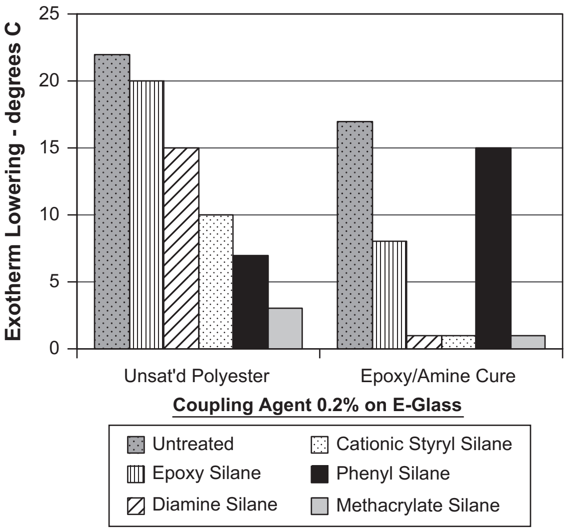


Figure 15.9 Viscosity and coupling effect—polyester castings with 50% silica.



Cure @ 115°C (epoxy) or 90°C (unsaturated polyester); 5g E-glass in 30 g resin

Figure 15.10 Resin exotherm lowering with silane-treated glass filler.

Silica-filled epoxy molding compounds use an epoxysilane for such a reason. In some cases, special epoxysilanes that have low chloride and low ionic content are used to further minimize negative effects on electrical properties.

Other filled resin systems that require a coupling agent include highly-filled sand cores with furan, urea–formaldehyde, urethane resins in the foundry industry, and highly-filled polymer concrete whereby polyester and epoxy binders are used to bond aggregate; and cultured marble, cultured onyx, and cultured granite are used, whereby a highly filled thermoset resin is used to bond calcium carbonate and aluminum trihydrate.

Table 15.13 Epoxy Resin–Quartz Filler–Electrical Properties versus Silane

Silane added	Dielectric constant		Dissipation factor	
	Initial	H_2O Boil	Initial	H_2O Boil
Unfilled resin	3.44	3.43	0.007	0.005
Quartz, no silane	3.39	14.60	0.017	0.305
Quartz/ epoxy-silane	3.40	3.44	0.01	0.024
Quartz/ amino-silane	3.46	3.47	0.013	0.023

Epoxysilane = 3-glycidoxypropyltrimethoxysilane; aminosilane = aminopropyltriethoxysilane; water boil = 72 h.

Polypropylene and polyethylene applications require the use of fillers in many applications to give desired properties, such as stiffness, impact strength, physical strength, and scratch and mar resistance. Talc, mica, kaolin clay, and titanium dioxide are used in polyolefins in large volumes. The filler can be treated with an octylsilane or phenylsilane to effect the filler in the polymer more dispersible. The low reactivity of polyolefins makes chemical bonding to the polymer very difficult. Maleated polyethylene or polypropylene adhesion promoters have been developed to yield improved bonding to fillers. The carboxy groups from the maleated polyolefin adhesion promoter can be used in combination with an aminosilane, offering good adhesion between the treated filler and the resin.[15] Combinations of aminosilanes and chlorinated paraffins also showed promise experimentally for adhesion of fillers to polypropylene.[16]

15.7.3 Mineral Fillers in Rubber Reinforcement

15.7.3.1 Rubber Tire Applications

Silica and kaolin clay can be treated with a mercaptosilane or polysulfidosilane to function adequately as a replacement for carbon-black reinforcement in sulfur-cured rubber applications. Carbon-black reinforced rubber is a huge industry, so the success of mineral-filled rubber has become a large application for silane-coupling agents. Organic rubber normally uses carbon-black filler, a natural reinforcing agent that does not require a coupling agent. Kaolin clay and silica fillers require a coupling agent that bonds the "unnatural" filler to the rubber polymer and enters into the sulfur-based curing mechanism.

The first silane applications in rubber tires used mercaptosilane to modify silica and clay fillers.[17] Commercial applications were limited to specialty areas, such as white sidewall components, some tread stocks, and some off-road tires, but processing and physical property deficiencies limited commercial applications. However, Degussa Corporation, which

Table 15.14 Ethoxy Silane Additives Used by the Rubber Industry

$(EtO)_3Si(CH_2)_3$–SS–$(CH_2)_3Si(OEt)_3$	Disulfidosilane (1)
Silane (1) blended 50% with carbon black	
$(EtO)_3Si(CH_2)_3$–SSSS–$(CH_2)_3Si(OEt)_3$	Tetrasulfidosilane (2)
Silane (2) blended 50% with carbon black	
$(EtO)_3Si(CH_2)_3$–SH	Mercaptosilane

Note: Sulfidosilanes (1) and (2) are polysulfide mixtures.

has been a filler manufacturer and supplier of silica for a variety of applications, developed a tetrasulfidodisilane, Si-69, which eventually led to the largest single application for a silane-coupling agent.[18] The new silane fit nicely into commercial rubber processing systems and allowed the new silica-reinforced rubber technology to become commercially successful. Silica-filled tires had several important advantages for autos compared to traditional carbon black tires: reduced rolling resistance, improved fuel economy, longer tire life via reduced wear and abrasion resistance, less heat generation, and improved grip and skid resistance on wet surfaces.

The tetrasulfidosilane is largely used, but other variations have been developed for the rubber industry (consult Table 15.14).

15.7.3.2 Wire and Cable Applications

Mineral-filled rubber formulations were developed for wire and cable applications in the 1960s where exceptional electrical resistance was needed to prevent electrical breakdown under high, humid-stress conditions. Carbon black is a conductive filler so the resulting rubber has poor insulation resistance properties. Silane-treated, mineral-reinforced rubber meets the strict electrical standards unattainable with a carbon black rubber. Kaolin clay and silica filler are the most-used "white" fillers, and treatment with amino-, vinyl-, and mercaptosilane coupling agents gives good electrical properties. Silane-treated kaolin clay has become the predominant filler for wire and cable insulation, with most applications using filler pre-treated with either a vinylsilane or a vinylsiloxane polymeric material.

Vinylsilane oligomers, such as partially hydrolyzed vinyltrimethoxysilane and vinyltrimethoxysilane and sometimes including dimethylsiloxy species in the structure, have been developed as premium treating liquids for kaolin clay reinforcements.[19] Silane additives, such as vinyltriethoxysilane or vinyl(tris-methoxyethoxy) silane, are often added during compounding to enhance properties.

15.7.4 Adhesion Promoters for PICA

Organofunctional silane-coupling agents function as adhesion promoters for PICA in a manner similar to that for fiberglass and mineral-filled composites. The general conditions are similar; that is, an organic polymer is bonded to an inorganic substrate. Bond failure mechanisms in PICA adhesion systems are similar to those in other adhesion promoter applications. Moisture attack in the bonded interfacial region is a leading cause of loss of adhesion. A silane-coupling agent, with its dual functionality, operates at the interface to induce improved adhesion when the bond is initially formed, and then to "protect" the bonded system from moisture-induced debonding and increase its useful life.

15.7.4.1 Choice of an Adhesion Promoter

Choice of the right coupling agent system for a PICA application requires similar thinking, as was discussed for reinforced plastics. If chemical reactivity is present in the polymeric component of the material bonded, then matching the reactivity of the silane-coupling agent with the reactivity in the polymer is essential. Correctly choosing a silane system in order to maximize interpenetration of the coating into the silane network is also important. Silane recommendations for various polymers, as presented in Table 15.7, are useful for PICA applications as well. Blends of silanes can be used to give increased hydrophobicity, increased cross-linking of the silane structure, and increased thermal stability to the adhesion promoter system.

15.7.4.2 Application Methods

Silane adhesion promoters are applied to PICA in two possible ways—adding as a primer on the substrate before the coating is applied or directly to the coating system. When used as a primer, the silane is diluted in a solvent and sprayed, dipped, or wiped onto the inorganic substrate. Various solvents can be used: methanol, ethanol, isopropanol, an ether glycol, or sometimes a mixture of solvents. Water, at levels of 1%−5%, is sometimes added to an alcohol solvent to promote hydrolysis of the silane during attachment to the surface. Water can also be used as the solvent if the coupling agent is an aminosilane, because aminosilanes are soluble in water.

The concentration of silane in the solvent during application as a primer controls the thickness of the silane coating on the surface. Poor adhesion is obtained if the silane coating is too thick. A thick, cross-linked silane oligomer is a weak layer and, in such a case, the bond fails in the silane layer. Poor adhesion is also obtained if the silane coating is too thin because not enough silane is present to generate improved bond strength and water resistance. A concentration of 0.5%−10% silane in solvent can be used in a primer, but usually levels of 2%−5% are used. The solvent can be allowed to evaporate at room temperature or the coated substrate can be heated to drive off solvent; however, heating above 125 °C cross-links the adhesion promoter and reduces interpenetration of the coating into the primer matrix to lessen the primer's effectiveness. Silane primers are applied as a much thicker coating on a surface than are comparable silane treatments on fiberglass or mineral surfaces for reinforcement applications.

15.7.4.3 Adhesion Promoter Benefits in Coatings

An example of silane benefits, when used as a primer, is shown in Table 15.15: urethane and epoxy paints were applied to aluminum surfaces using epoxysilane and aminosilane adhesion promoters to improve adhesion. The effects of degreasing and sandblasting the surface were compared to adhesion with the silanes.[20]

Alternatively, the adhesion promoter can be mixed directly into a PICA system to give "unprimed" adhesion. Silane levels of 0.5%−5%, usually about 2%, are added to a coating system. Some techniques that can be used to promote migration of the silane to the interface are as follows: partially pre-hydrolyzing the silane with water before adding it to the coating system so that the cross-linked silane becomes less soluble in the coating; modifying the cure system of the coating; or choosing the functionality of the coupling agent to minimize interaction of the silane with the polymer system. Plueddemann[21] compares the effectiveness of a series of silanes as primers and additives in bonding thermoplastic and thermoset coatings to glass.

Silane adhesion promoters have been studied for the corrosion protection of metal surfaces. The use of a silane cross-linking system (Table 15.6) in combination with sulfur silanes (Table 15.14) provided promising coating systems to replace toxic chromates in steel.[22] Similar corrosion protection was realized on cold-rolled steel, iron, aluminum, and aluminum alloy surfaces by treatment with the same cross-linker system but in combination with aminosilanes in the admixture.[23]

15.8 Nonsilane Adhesion Promoters

Adhesion promoter chemistries, other than those of silanes, have been extensively evaluated for many years. These materials use the same concepts as silane-coupling agents, but they are based on other metallic elements. They have inorganic reactivity on the metallic atom and contain organofunctional groups, such as methacrylate, carboxylate, and others, with dual- or multi-functionality built into the

Table 15.15 Effect of Surface Primer on Adhesion

Paint	Bond strength, paint to aluminum, silane	Surface preparation	Accelerated, weathering, adhesion
Urethane	None, none, Diamino (A)	Degreased, sandblasted, degreased	20, 95, 100
Epoxy	None, none, epoxy (D), diamino (A)	Degreased, sandblasted, degreased, degreased	70, 100, 100, 100

A—N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and D—3-glycidoxypropyltrimethoxysilane.

chemical structure to allot characteristics of dual reactivity, which silane-coupling agents possess.

Organo-titanates, organo-zirconates, and zircoaluminates have been advanced as adhesion promoters. Even so, they have not achieved the broad success that silane has achieved. In metal applications, the highly metallic nature of zircoaluminates promotes their reactivity with metal surfaces. Similarly, organo-titanates are well known as excellent wetting agents, they are able to function as adhesion promoters via chemical adhesion, and they provide more intimate contact between the adhesive or coating and the substrate.

Another family of adhesion promoters is based on the maleation of polypropylene, polyethylene, and other thermoplastic polymers. The polymer backbone in these coupling agents gives interpenetration into ethylene, propylene, or other thermoplastic polymers and adhesion to those polymers that occurs via van der Waals and other atomic forces. The carboxy group on the adhesion promoter allows for interaction and bonding to metals, mineral fillers, or glass, enabling adhesion to those materials.

Studies of maleated polypropylene in clay-based nanocomposities[24] suggest that the polar groups in the adhesion promoter (e.g., −OH, −COOH) intercalate between silicate layers, through hydrogen bonding or other chemical bonding, to the oxygen groups or negative charges in order to assist in exfoliation of the nanoclay reinforcement. In regular mineral-filled polyolefins, as was mentioned earlier,[15] the use of a maleated polyolefin in combination with an aminosilane produces a beneficial adhesion promoter for mineral- or glass-filled polypropylene and polyethylene.

Chlorinated polyolefins are used as adhesion promoters for coatings and inks on polyolefin plastics. They can be used as primers on polyethylene, polypropylene, or thermoplastic polyolefins (polypropylene−elastomer blends). They are used for the adhesion of paint to plastic surfaces in the automotive industry.

15.9 Sources of Adhesion Promoters

Silanes are manufactured globally. They have traditionally been manufactured in the United States, Europe, and Japan, and new manufacturing facilities in China and Korea supplement the global supply with high-quality products. The emergence of large-volume applications for silanes, especially in silica-filled rubber tires, has substantially increased the number of suppliers.

Silane adhesion promoters are available globally from several manufacturers including Dow Corning Corporation,[25] Degussa (now Evonik Degussa),[26] OSi Specialties (now Momentive Performance Materials),[27] Chisso Corporation,[28] Shin-Etsu Chemical,[29] KCC Silicones,[30] and several other Chinese suppliers such as Nanjing Capatue[31] and Wuhan University Silicone New Material Co., Ltd.[32]

Major suppliers of organo-titanates, organo-zirconates, and zircoaluminates are Kenrich Petrochemicals,[33] Manchem/FedChem,[34] and Wuhan University Silicone New Materials Co., Ltd.[32]

Maleated polyolefin adhesion promoters are available from Eastman Chemical[35] (Epolene®) and DuPont[36] (Fusabond®).

Chlorinated polyolefin adhesion promoters are available from Eastman Chemical[35] (CPO), Nippon Paper Chemical[37] (Superclon®), and DuPont[38] (Automotive Chemicals).

Other suppliers of adhesion promoters exist for the various types of adhesion promoters. All suppliers have websites on which product line lists, data sheets, Material Safety Data Sheets, and technical information are available. Of the various suppliers, the author's intent is not to favor or recommend one supplier over another.

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Appendix A Safety, Environmental, and Economic Aspects and Future Trends

A.1 Safety

Adhesives consist of a number of components as described in the earlier chapters, usually containing reactive chemicals. Adequate precautions must be taken when working with adhesives to prevent harmful exposure. Adhesive manufacturers are required by law to provide a material safety data sheet (MSDS) for each product that they sell. The MSDS must contain sufficient details about the composition, hazard rating, first aid measures, handling and storage, personal protection (exposure control), stability and reactivity, and toxicology of adhesives.

Anyone who plans to handle an adhesive must be familiar with the measures required to prevent or minimize exposure of personnel. In addition to volatile organic solvents and resins, adhesives may contain pigments, catalysts, stabilizer, extenders, and so on. Each of these components may possess hazardous properties individually or in combination with other materials. There are thousands of adhesive compounds on the market making it impractical to list the hazards of every one of them.[1] The current system of communication required by law is described below to allow the reader to decipher the safety information provided by adhesives manufacturers. This system is applicable to all chemicals.

Adhesives, as with other chemicals, must meet the standards of personal safety established by the Occupational Safety and Health Administration (OSHA).[2,3] The need to protect employees from the hazards of such chemicals led OSHA to issue the first Hazard Communication Standard (HCS) in 1983. The central idea of the HCS is the belief that workers who may be exposed to hazardous chemicals have a right to know about the hazards and how to work safely with the materials. As a result, the standard requires that chemicals manufacturers and importers evaluate all chemicals for hazards and that the information concerning those hazards be communicated downstream from the manufacturer to the employer and then to the employee.

The HCS has three basic requirements:

1. Chemicals manufacturers must review scientific evidence concerning the hazards of a material to determine if they are hazardous
2. The manufacturer must develop MSDSs and container labels that must be sent to downstream users
3. Employers must develop a written hazard communication program and provide information and training to employees about the hazards of chemicals found in the workplace

Hazardous Material Identification System (HMIS) helps to satisfy HCS requirements by providing a format for hazard determinations, offering a basic written hazard communication program and simplifying the employee training and information process.[2,3] HMIS provides clear, recognizable information to employees by standardizing the presentation of chemical information. This is accomplished by the use of color codes corresponding to the hazards of a product, assigned numeric ratings (Table A1) indicating the degree of hazard and alphabetical codes designating appropriate personal protective equipment (PPE) that employees should wear while handling the material. Of particular significance is inhalation and flammability risks encountered with solvent-based compositions.

Table A1 Numerical Hazard Code Versus Level

Number	Hazard level
0	Minimal hazard
1	Slight hazard
2	Moderate hazard
3	Serious hazard
4	Severe hazard

Table A2 Personal Protective Equipment Versus HMIS Letter Code

Letter designation	Required PPE
A	Safety glasses
B	Safety glasses and gloves
C	Safety glasses, gloves, and an apron
D	Face shield, gloves, and an apron
E	Safety glasses, gloves, and a dust respirator
F	Safety glasses, gloves, apron, and a dust respirator
G	Safety glasses, a vapor respirator
H	Splash goggles, gloves, apron, and a vapor respirator
I	Safety glasses, gloves, and a dust/vapor respirator
J	Splash goggles, gloves, apron, and a dust/vapor respirator
K	Airline hood or mask, gloves, full suit, and boots
L–Z	Custom PPE specified by employer

Volatility of the solvents selected for adhesive formulation is high to aid in its removal.

The lettering system in Table A2 indicates the level of PPE to be worn to work safely with a material. The original system traditionally provided letters of the alphabet corresponding to a specific grouping of PPE. However, this did not allow employers to customize their PPE recommendations. Now, employers who cannot find an appropriate grouping of PPE will be able to design their own custom set of equipment. Each of the individual PPE icons has been designated with a corresponding letter of the alphabet ranging from "m" to "z." An employer can list appropriate letters to customize the PPE required for handling a specific material. To facilitate this option, container labels have been revised to allow room for the additional codes in the PPE block of the label. Of course, employers who find the previous PPE groupings suitable for their workplaces can continue to use the standard codes.

Another feature that differs from the National Fire Protection Association (NFPA) label system is that HMIS allows an asterisk to designate a material as a carcinogen or for materials known to have an adverse effect on chronic exposure.[4] This designation would appear next to the numerical ranking within the blue health bar. This information is of great benefit to laboratory workers, as this is an indication of how the material will affect them in the long run. Recall that, in comparison, the NFPA rating indicates only the short-term or acute effects you might encounter in an emergency circumstance.

Adhesives, as with other chemicals, fall within the jurisdiction of a number of laws. Table A3 gives a list of acronyms and the full names of these legal acts. Table A4 decodes a number of other acronyms that may be encountered in MSDSs.

Care should be taken when applying adhesives. At the least, an air-filtering mask that is designed to provide protection from airborne particulates should be worn. Good ventilation is recommended for all adhesive applications. Ventilation hoods may be necessary for certain types of adhesives and building designs.

Additional protection may be required when applying water-based natural latex adhesives. Persons allergic to latex should not apply the product. Some carriers, such as formulations containing acetone, may have a low flash point, therefore requiring specialized fire detection and suppression equipment. Be sure to consult the manufacturer's MSDS for additional handling, storage, and application safety information. Insurance carriers are also good sources of information regarding proper use and ventilation of adhesive application areas.[5]

Table A3 Acronyms of Legal Acts Common in Material Safety Data Sheets

CEPA	Canadian Environmental Protection Act
CERCLA	Comprehensive Environmental Response, Compensations and Liability Act
CWA	Clean Water Act
RCRA	Resource Conservation and Recovery Act
SARA	Superfund Amendments and Reorganization Act
TSCA	Toxic Substances Control Act

Table A4 Acronyms Common in Material Safety Data Sheets

CAS	Chemical Abstracts Services
CFR	Code of Federal Regulations
DOT	Department of Transportation
DSCL	Dangerous Substances Classification and Labeling (Europe)
DSL	Domestic Substance List (Canada)
EEC/EU	European Economic Community/ European Union
EINECS	European Inventory of Existing Commercial Chemical Substances
HCS	Hazard Communication System
HMIS	Hazardous Material Information System
IARC	International Agency for Research on Cancer
LD_{50}/ LC_{50}	Lethal dose/concentration kill 50%
LDLo/ LCLo	Lowest published lethal dose/ concentration
NFPA	National Fire Prevention Association
NIOSH	National Institute for Occupational Safety and Health
NTP	National Toxicology Program
OSHA	Occupational Safety and Health Administration
PEL	Permissible exposure limit
STEL	Short-term exposure limit (15 min)
TDG	Transportation of Dangerous Goods (Canada)
TLV	Threshold limit value
TWA	Time weighted average
WHMIS	Workplace Hazardous Material Information System

A.2 Environmental Considerations

Adhesion requires the use of a variety of compounds that may be safe, hazardous, flammable, or form hazardous waste. Table A5 provides a partial list of some of the more commonly used chemicals. There has been extensive collaboration between the industry and the governmental environmental protection agencies to reduce all emissions. For instance, the Design for Environment (DfE) program in the Environmental Protection Agency's (EPA) Office of Pollution Prevention and Toxics has been a voluntary partnership with the industry to develop and distribute data on pollution prevention and environmental and human health risks on alternative chemicals, processes, and products. The DfE approach uses cleaner technologies substitute assessments (CTSAs) and life cycle tools to evaluate current and emerging technologies.[6,7]

Table A5 Commonly Used Compounds in the Adhesives Industry

Compound	**Use**
Toluene	Solvent
Xylene	Solvent
Methyl ethyl ketone	Solvent
Hexane	Solvent
Methylene chloride	Solvent
Trichloroethylene	Solvent
Perchloroethylene	Solvent
Chlorofluorocarbons	Solvent
Isocyanates	Adhesive ingredient
Di-2-ethylhexyl phthalate	Plasticizer
Antimony compounds	Flame retardant
Cadmium compounds	Pigment
Lead compounds	Pigment

The CTSA is a method of systematically evaluating and comparing human health and environmental risk, competitiveness (issues such as performance and cost), and resource requirements of the traditional and alternative chemicals, and manufacturing technologies to perform the same function. Furniture adhesives have utilized CTSA for assistance in decision-making to incorporate environmental concerns, performance, cost, and the selection of an adhesive technology. The adhesives that bond porous substrates are an example of the application of CTSA, where traditional solvent carriers were subjected to more stringent regulations.[8] New adhesive formulations, improved processes, and preventive measures have been developed to reduce environmental emissions and worker exposure without sacrificing the economics of the manufacturing.

Additional information can be obtained by contacting the US EPA (www.EPA.gov) or individual companies.

A.2.1 Environmental Trends

There are general trends in the adhesives industry in the United States and Europe. The goal is to reduce the environmental impact and hazards associated with the use of polymeric adhesives derived from petroleum. Simultaneously, there are market trends requiring higher performance from adhesive-bonded joints. The reconciliation of these two directions has required innovation in design and formulation of adhesives in which individual components are replaced or eliminated. Some of the individual directions to improve the environmental impact of adhesives are listed in Table A6.

Table A6 Environmentally Positive Directions in the Adhesives Industry

Replacement of organic solvents with water, especially chlorinated solvents
Aqueous emulsion polymerization to replace solvent-based polymerization
Surface treatment (modification) process development for waterborne adhesives
Development of solvent free, 100% solid adhesives
Development of safer cross-linking systems for 100% solid adhesives
Replacement of petroleum-derived polymers with bio-based alternatives
Examples include polylactic acid, polyhydroxyalkanoates, elastin, and soy protein derivatives (biodegradable)

A.3 Economics

Adhesives form the basis for a multibillion dollar industry with more than 750 companies competing for a share of the market. It is estimated that 50 of those companies are responsible for 50% of the sales dollars in the adhesives industry.[9]

Adhesives are extremely important components of most fabricated products. They play a functional role that is nearly always invisible. Because of their enabling role, users and consumers notice an adhesive only when it fails. The nature of the adhesives' functions has placed pressure on the prices of adhesives. The economics of nonspecialty adhesives have followed the path of other commodities. At the same time, performance requirements have escalated over time. A great deal of consolidation has been taking place among the manufacturers of adhesives (and sealants).

The Adhesive and Sealant Council, Inc. has published data for adhesives and sealants volume and value, summarized in Table A7. The data exclude adhesive used in plywood, particle board, other boards, foundry sand, and carpet backing. The US statistics including 2002 sales of major manufacturers are given in Tables A8−A11.

According to the Adhesive and Sealant Council, Inc. (ASC) (www.Adhesives.com), the global marketplace can be viewed as consisting of three classes of

Table A8 US Volume and Sales of Adhesives and Sealants in 2002 (on a Wet Basis)[10]

Product	Volume (million metric tons)	Sales (billion $)
Adhesive	2.6	7.1
Sealant	0.23	1.2

Table A7 Global Volume and Sales of Adhesives and Sealants in 2002 (on a Wet Basis)[10]

Region	Volume (million metric tons)	Sales (billion $)	Market share (%)
North America	3.09	9.07	34.5
Western Europe	2.55	7.50	28.3
Asia Pacific (including India)	2.40	6.45	25.7
Rest of the World	1.02	4.11	11.5
Total	9.06	27.13	100

Table A9 Major US Manufacturers' Sales of Adhesives and Sealants in 2002 (on a Wet Basis)[10]

Company	Sales (million $)
Henkel/Loctite	740
H. B. Fuller	470
National Starch	360
Bostik Findley	270
3M	266
Sovereign	209
Forbo	195
Rohm and Haas	189
Borden	185
GE Silicones	180

Table A10 US Market Segments Shares (%) of Adhesives and Sealants (on a Wet Basis)[10]

Market segment	2002	2005 (estimate)
Conversion/ packaging	53	54
Construction	15	15
Assembly	8	8
Woodworking	9	8
Transportation	4	4
Consumer	3	3
Footwear	<0.5	<0.5
Sealants	8	8

Table A11 US Share (%) of Adhesives Types (on a Wet Basis)[10]

Adhesive type	2002	2004 (estimate)
Water base	55.2	55.7
Hot melt	19.5	20
Solvent	14.9	13.9
Reactive	6.8	6.8
Other	3.6	3.6
Total volume (million metric tons)	2.59	2.70 (+4.2%)

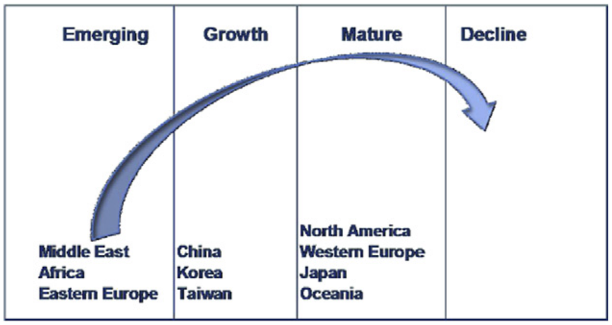


Figure A1 Global adhesive and sealant industry market life cycle chart 2003–2007.[11]

players on a country-by-country basis according to their market participation and economic development. These include the following:

- *Industrialized* (North America, Western Europe, Japan, Australia, New Zealand)
- *Newly Industrialized* (most of Latin America, South Korea, Taiwan, Singapore)
- *Emerging* (Central and Eastern Europe, China, all the rest)

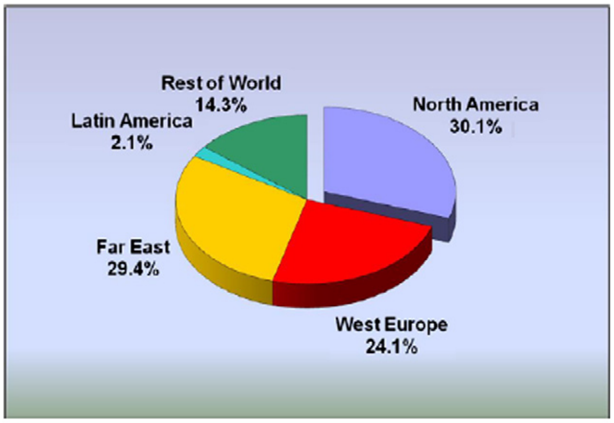
Market life cycle for various economies is shown in Fig. A1.

The industrialized category represents more than 63% of the adhesives and sealants demand and controls nearly 70% of their production. The relative market share of demand by economic level and region is shown in the next two charts. This is a change from 2005 indicating the high growth of the emerging and newly industrialized economies and their taking of market share from the industrialized countries. Figures A2 and A3 also take into account the economic slowdown in industrialized countries after the September 2008 financial crisis.

A.4 Future Trends

The trends in adhesives are influenced by a number of factors that influence a number of other industrial commodities. Globalization, technological maturity, and increased government regulations have been the key drivers of adhesives trends.

Globalization has intensified competition and pressure on adhesive prices because of the lower cost of production in developing regions of the world. Customers and capital markets are becoming



2007 World Total Demand:

Figure A2 Global adhesives and sealants industry by region, 2007 percent share of demand million pounds.[11]

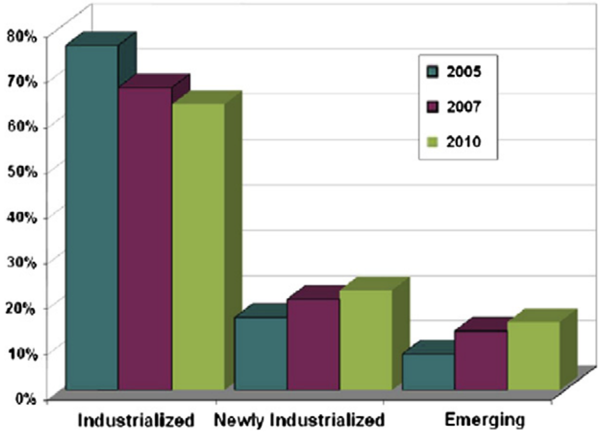


Figure A3 Global adhesives and sealants industry market by economic category, 2007–2010 [share of demand (million pounds)].[11]

increasingly more global. A great deal of consolidation has taken place in the adhesives industry. Further mergers and acquisitions can be expected in the future, thus reducing the number of suppliers and enlarging new companies.

Research activity has slowed down in the industry because of technological maturity in traditional adhesives development. The industry is attempting to revive research by focus on process technology know-how and newer approaches such as nanotechnology. Trade associations, including the ASC, are engaged in leading renewal initiatives. ASC is an excellent source for information and data about the trends in the adhesives industry.

New regulations have focused on environmental emissions and waste disposal. These trends have been ongoing in North America, Europe, and Japan for decades. A more recent phenomenon is the start of promulgation of similar rules in the developing regions, especially China.

Waterborne systems have been dominating the North American market for decades.[12] The share of solvent-based systems has decreased significantly since the 1980s. The decrease in the demand has been modest (10%–15%). The consumption of solvents has decreased much more significantly by conversion from low to high solids formulas. The one-part adhesives (nonvolatile), including epoxies, cyanoacrylates, and urethanes, have made large inroads nearly tripling their share of the market in the last two decades.

A major opportunity for growth is the replacement of mechanical fasteners by adhesive bonds. Structural adhesives are the existing products that serve this market segment. The key to success in fastener applications is acceptance by end users, mainly because of the concern about reliability and reparability of adhesive bonds.

A.4.1 Green Adhesives

IntertechPira has conducted a study of green adhesives, the excerpts of which have been recounted here.[13] Even though natural adhesives currently make up about 5% of the total adhesive market, this percentage could be actually misleading, because many natural raw materials are used as additives and modifiers in petroleum-based adhesive formulations. On an overall raw materials basis, natural components account for about 30% of all components used in adhesive formulations. With regard to future market trends, IntertechPira expects the natural adhesive market to grow slightly faster than the overall adhesives market in the period of 2007–2017, with the annual growth rate of all adhesives conforming to the regional increase in gross domestic product.

Starch derivatives make up the majority of the natural adhesives that are used today, with approximately 65% of all natural adhesives based on starch derivatives, that is, pure starch, modified starch, and dextrin. IntertechPira forecasts that starch and other plant-derived adhesives will experience single digit growth rates in the range of 3%–4% over the next 10 years, compared with the 2.7% growth rate expected for all adhesives and the 3.1% growth rate expected for all natural adhesives.

With regard to starch adhesives, the bulk of development is expected to come from thermoplastic starches that can be used as hot-melt adhesives or transformed into waterborne dispersions. For other plant derivatives such as soy and castor oil, a significant development effort is taking place in the manufacture of polyols for use primarily in polyurethane adhesives and sealants. Similarly, derived waxes are also being used as plasticizers in hot-melt adhesive formulations. For natural adhesives that are based on cellulose derivatives, tree resins and their by-products, as well as natural rubber, low growth rates are envisaged, whereas the market for advanced bio-based adhesives is still in the early stages of development.

According to IntertechPira, new bio-based adhesives must be cost-competitive and provide performance-based properties that are equivalent to those of conventional adhesives. As of today, advanced bio-based adhesives are a small, almost insignificant, part of the overall market, with the study projecting that the market share of bio-based polymers will continue to remain negligible, that is, in the order of 1%−2% over the next few years and in the 1%−4% range by 2020, with price and competitive performance playing a key role in this regard.

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Guidance for Industry and FDA Staff

Class II Special Controls Guidance Document: Tissue Adhesive for the Topical Approximation of Skin

Document issued on: May 30, 2008

This document supersedes Cyanoacrylate Tissue Adhesive for the Topical Approximation of Skin – Premarket Approval Applications (PMAs), dated February 13, 2004

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U.S. Department of Health and Human Services
Food and Drug Administration
Center for Devices and Radiological Health

Plastic and Reconstructive Surgery Devices Branch
Division of General, Restorative, and Neurological Devices
Office of Device Evaluation

Contains Nonbinding Recommendations

Preface

Public Comment

Written comments and suggestions may be submitted at any time for Agency consideration to the Division of Dockets Management, Food and Drug Administration, 5630 Fishers Lane, Room 1061, (HFA-305), Rockville, MD, 20852. Alternatively, electronic comments may be submitted to http://www.regulations.gov. When submitting comments, please refer to the exact title of this guidance document. Comments may not be acted upon by the Agency until the document is next revised or updated.

Additional Copies

Additional copies are available from the Internet at: http://www.fda.gov/cdrh/ode/guidance/1630.pdf. You may also send an e-mail request to dsmica@fda.hhs.gov to receive an electronic copy of the guidance or send a fax request to 240-276-3151 to receive a hard copy. Please use the document number **1630** to identify the guidance you are requesting.

Class II Special Controls Guidance Document: Tissue Adhesive for the Topical Approximation of Skin

This guidance represents the current thinking of the Food and Drug Administration (FDA) on this topic. It does not create or confer any rights for or on any person and does not operate to bind FDA or the public. You can use an alternative approach if the approach satisfies the requirements of the applicable statutes and regulations. If you want to discuss an alternative approach, contact the FDA staff responsible for implementing this guidance. If you cannot identify the appropriate FDA staff, call the appropriate number listed on the title page of this guidance.

B.1 Introduction

This guidance document was developed as a special control to support the reclassification of tissue adhesive for the topical approximation of skin into class II (special controls). The device is intended for topical closure of surgical incisions, including laparoscopic incisions and simple traumatic lacerations that have easily approximated skin edges. This guidance document does not apply to tissue adhesives for nontopical uses.

On August 25, 2006, the General and Plastic Surgery Devices Panel unanimously recommended that the tissue adhesive for the topical approximation of skin be reclassified into class II with special controls. This guidance is issued in conjunction with a *Federal Register* notice announcing the reclassification of this device type.

Following the effective date of a final rule reclassifying the device type, any firm submitting a 510(k) for a tissue adhesive for the topical approximation of skin will need to address the issues covered in the special control guidance document. However, the firm need only show that its device meets the recommendations of the guidance document or in some other way provides equivalent assurances of safety and effectiveness.

FDA's guidance documents, including this guidance, do not establish legally enforceable responsibilities. Instead, guidances describe the Agency's current thinking on a topic and should be viewed only as recommendations, unless specific regulatory or statutory requirements are cited. The use of the word *should* in Agency guidances means that something is suggested or recommended but not required.

B.1.1 The Least Burdensome Approach

The issues identified in this guidance document represent those that we believe should be addressed before your device can be marketed. In developing the guidance, we carefully considered the relevant statutory criteria for Agency decision-making. We also considered the burden that may be incurred in your attempt to follow the guidance and address the issues we have identified. We believe that we have considered the least burdensome approach to resolve the issues presented in the guidance document. If, however, you believe that there is a less burdensome way to address the issues, you should follow the procedures outlined in the "A Suggested Approach to Resolving Least Burdensome Issues" document. It is available on our Center web page at http://www.fda.gov/cdrh/modact/leastburdensome.html.

B.2 Background

FDA believes that special controls, when combined with the general controls, will be sufficient to provide reasonable assurance of the safety and effectiveness of the tissue adhesive for the topical approximation of skin. Thus, a manufacturer who intends to market a device of this generic type must (1) conform to the general controls of the Federal Food, Drug, and Cosmetic Act (the Act), including the premarket notification requirements described in 21 CFR 807 Subpart E, (2) address the specific risks to health associated with the tissue adhesive for the topical approximation of skin identified in 21 CFR 878.4010(a), and (3) obtain a substantial equivalence determination from FDA prior to marketing the device.

This special controls guidance document identifies the classification regulation and product code for the tissue adhesive for the topical approximation of skin (please refer to Section B.4). In addition, other sections of this special controls guidance document list the risks to health identified by FDA and describe measures that, if followed by manufacturers and combined with the general controls, will generally address the risks associated with tissue adhesives for the topical approximation of skin and lead to a timely 510(k) review and clearance. This document supplements other FDA guidance documents regarding the content requirements of a 510(k) submission. You should also refer to 21 CFR 807.87, the guidance, Format for Traditional and Abbreviated 510(k)s,[1] and the section of CDRH's Device Advice, How to Prepare a 510(k) Submission.[2]

As described in the guidance entitled, The New 510(k) Paradigm – Alternate Approaches to Demonstrating Substantial Equivalence in Premarket Notifications; Final Guidance,[3] a manufacturer may submit a Traditional 510(k) or has the option of submitting either an Abbreviated 510(k) or a Special 510(k). FDA believes an Abbreviated 510(k) provides the least burdensome means of demonstrating substantial equivalence for a new device, particularly once FDA issues a class II special controls guidance document. Manufacturers considering certain modifications to their own cleared devices may lessen the regulatory burden by submitting a Special 510(k).

B.3 The Content and Format of an Abbreviated 510(k) Submission

An Abbreviated 510(k) submission must include the required elements identified in 21 CFR 807.87, including the proposed labeling for the device sufficient to describe the device, its intended use, and the directions for its use. In an Abbreviated 510(k), FDA may consider the contents of a summary report to be appropriate supporting data within the meaning of 21 CFR 807.87(f) or (g); therefore, we recommend that you include a summary report. The report should describe how this special controls guidance document was used during the device development and testing and should briefly describe the methods or tests used and a summary of the test data or description of the acceptance criteria applied to address the risks identified in this document, as well as any additional risks specific to your device. This section suggests information to fulfill some of the requirements of section 807.87 as well as some other items that we recommend you to include in an Abbreviated 510(k).

B.3.1 Coversheet

The coversheet should prominently identify the submission as an Abbreviated 510(k) and cite the title of this special controls guidance document.

B.3.2 Proposed labeling

Proposed labeling must be sufficient to describe the device, its intended use, and the directions for its use (21 CFR 807.87(e)). (Please refer to Section B.13 for specific information that should be included in the labeling for devices of the types covered by this guidance document.)

B.3.3 Summary report

We recommend that the summary report contain a:

Description of the device and its intended use: We recommend that you describe the performance specifications and, when appropriate, include detailed, labeled drawings of the device. (Please refer to Section B.6 for specific information that we recommend you to include in the device description for devices of the type covered by this guidance document.) You should also submit an "indications for use" enclosure.[4]

Description of device design requirements: We recommend that you include a brief description of the device design requirements.

Identification of the risk analysis method: We recommend that you identify the risk analysis method(s) you used to assess the risk profile, in general, as well as the specific device's design and the results of this analysis. (Please refer to Section B.5 for the risks to health generally associated with the use of this device that FDA has identified.)

Discussion of the device characteristics: We recommend that you discuss the device characteristics that address the risks identified in this class II special controls guidance document, as well as any additional risks identified in your risk analysis.

Description of the performance aspects: We recommend that you include a brief description of the test method(s) you have used or intend to use to address each performance aspect identified in Sections B.6–B.12 of this class II special controls guidance document. If you follow a suggested test method,

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[1] http://www.fda.gov/cdrh/ode/guidance/1567.html.

[2] http://www.fda.gov/cdrh/devadvice/314.html.

[3] http://www.fda.gov/cdrh/ode/parad510.html.

[4] http://www.fda.gov/cdrh/ode/indicate.html for the recommended format.

you may cite the method rather than describing it. If you modify a suggested test method, you may cite the method but should provide sufficient information to explain the nature of and reason for the modification. For each test, you may either (1) briefly present the data resulting from the test in clear and concise form, such as a table or (2) describe the acceptance criteria that you will apply to your test results.[5] (See also 21 CFR 820.30, Subpart C—Design Controls for the Quality System Regulation.)

Reliance on standards: If any part of the device design or testing relies on a recognized standard, we recommend that you include either:

- a statement that testing will be conducted and meet specified acceptance criteria before the product is marketed or
- a declaration of conformity to the standard.[6]

Because a declaration of conformity is based on results from testing, you cannot properly submit a declaration of conformity until you have completed the testing the standard describes. For more information, refer to the FDA guidance document, Use of Standards in Substantial Equivalence Determinations; Final Guidance for Industry and FDA, http://www.fda.gov/cdrh/ode/guidance/1131.html.

If it is not clear how you have addressed the risks identified by FDA or additional risks identified through your risk analysis, we may request additional information about aspects of the device's performance characteristics. We may also request additional information if we need it to assess the adequacy of your acceptance criteria. (Under 21 CFR 807.87(l), we may request any additional information that is necessary to reach a determination regarding substantial equivalence.)

As an alternative to submit an Abbreviated 510(k), you can submit a Traditional 510(k) that provides all the information and data required under 21 CFR 807.87 and described in this guidance. A Traditional 510(k) should include all your methods, data, acceptance criteria, and conclusions. Manufacturers considering certain modifications to their own cleared devices should consider submitting Special 510(k)s.

The general discussion above applies to any device subjected to a special controls guidance document. The following is a specific discussion of how you should apply this special controls guidance document to a 510(k) submission for a tissue adhesive for the topical approximation of skin.

B.4 Scope

The scope of this guidance document is limited to tissue adhesives for the topical approximation of skin as described below in proposed 21 CFR 878.4010(a). The product code associated with this device is MPN (tissue adhesive for the topical approximation of skin).

B.4.1 Section 878.4010 Tissue adhesive

(a) Tissue adhesive for the topical approximation of skin

  (1) Identification: A tissue adhesive for the topical approximation of skin is a device intended for topical closure of surgical incisions, including laparoscopic incisions, and simple traumatic lacerations that have easily approximated skin edges. Tissue adhesives for the topical approximation of skin may be used in conjunction with, but not in place of, deep dermal stitches.

  (2) Classification: Class II (special controls). The special control for this device is FDA's "Class II Special Controls Guidance Document: Tissue Adhesive for the Topical Approximation of Skin." See § 878.1(e) for the availability of this guidance document.

(b) Tissue adhesive for nontopical use

  (1) Identification: A tissue adhesive for nontopical use, including adhesives intended for use

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[5] If FDA makes a substantial equivalence determination based on acceptance criteria, the subject device should be tested and shown to meet these acceptance criteria before being introduced into interstate commerce. If the finished device does not meet the acceptance criteria and, thus, differs from the device described in the cleared 510(k), FDA recommends that submitters apply the same criteria used to assess modifications to legally marketed devices (21 CFR 807.81(a)(3)) to determine whether marketing of the finished device requires clearance of a new 510(k).

[6] See required elements for a declaration of conformity to a recognized standard [Screening Checklist for All Premarket Notification (510(k)) Submissions], http://www.fda.gov/cdrh/ode/reqrecstand.html.

in the embolization of brain arteriovenous malformation or for use in ophthalmic surgery, is a device used for adhesion of internal tissues and vessels and does not include the use as described in point (a) of this section.

(2) Classification: Class III (premarket approval). As of May 28, 1976, an approval under section 515 of the act is required before this device may be commercially distributed. See § 878.3.

Tissue adhesives for nontopical use include tissue adhesive for use in embolization of brain arteriovenous malformation (product code KGG) and tissue adhesive for ophthalmic use (product code LZQ) remain in class III and continue to require premarket approval. Nonadhesive agents, including injectable embolic agent (product code MFE), are not within the scope of this guidance and continue to require premarket approval. This guidance also does not address liquid bandage devices, which are used to cover openings in the skin, as a dressing for burns or as topical skin protectants (product codes KMF and NEC) classified in 21 CFR 880.5090. For information regarding these devices, please contact the Plastic and Reconstructive Surgery Devices Branch of the Division of General, Restorative and Neurological Devices. This guidance also does not address tissue adhesives used as a dental cement. These devices are classified under 21 CFR 872.3275, product code EMA.

Devices used as an adjunct to standard methods of achieving hemostasis in open surgical repair of large vessels such as the aorta, femoral, and carotid arteries (product code MUQ) are also not within the scope of this guidance and continue to require premarket approval. For information regarding these devices, please contact the Peripheral Vascular Devices Branch of the Division of Cardiovascular Devices at 240-276-4141.

B.5 Risks to Health

In the table below, FDA has identified the risks to health generally associated with the use of the tissue adhesive for the topical approximation of skin device addressed in this guidance document. The measures recommended to mitigate these identified risks are given in this guidance document, as shown in the table below. We recommend that you also conduct a risk analysis, before submitting your 510(k), to identify any other risks specific to your device and include the results of this analysis in your 510(k). If you elect to use an alternative approach to address a particular risk identified in this guidance document, or have identified risks additional to those in this guidance document, then you should provide sufficient detail to support the approach you have used to address that risk.

Identified risk	**Recommended mitigation measures**
Unintentional bonding or product leaks into eyes	Section B.7. Bench Testing Section B.13. Labeling
Wound dehiscence	Section B.7. Bench Testing Section B.8. Shelf Life Testing Section B.10. Animal Testing Section B.13. Labeling
Adverse tissue reaction and chemical burns	Section B.9. Biocompatibility Section B.10. Animal Testing
Infection	Section B.7. Bench Testing Section B.12. Sterility
Applicator malfunction	Section B.7. Bench Testing
Delayed polymerization	Section B.7. Bench Testing Section B.10. Animal Testing

B.6 Device Description

FDA recommends that you identify your device by the regulation and product code described in Section B.4 and include the information discussed below.

Tissue adhesives polymerize at room temperature in an exothermic reaction on contact with a small amount of water or a basic fluid to form strong adhesive bonds with a variety of substrates. Various formulations can be manufactured that vary in viscosity, setting time, bond strength, degradation rate, and other physical and mechanical properties. Because these properties define the adhesive performance and utility of the final product, your description should discuss the molecular composition and structure of your compound. Products that include biological or drug components are generally considered by the agency to be combination products. For advice about the appropriate regulatory pathway, please contact the Office of Combination Products at 301-427-1934.[7]

FDA recommends that you identify all materials used to comprise the finished device. FDA recommends that you provide a Certificate of Analysis or a Material Safety Data Sheet for each chemical included in the device.

a. Chemistry: We recommend that you provide the following information for chemicals included in your device:
  - chemical name
  - chemical abstracts service number
  - trade name
  - structural formula
  - molecular formula and molecular weight
  - source and purity

b. Material characteristics of the adhesive: We recommend that you provide the following information about the device, including your test methods:
  - viscosity determination[8]
  - analysis of residual content of the components of bulk formation by, for example, gas chromatography, nuclear magnetic resonance, or mass spectrometry
  - purity
  - moisture determination
  - setting time determination[9]
  - physical and mechanical testing (see Section B.7)
  - shelf life determination (see Section B.8)
  - sterility (see Section B.12)

B.7 Bench Testing

B.7.1 Adhesive Strength

FDA recommends that you conduct mechanical testing to evaluate the ability of the polymerized adhesive to provide enough bond strength to hold the wound edges together without manual approximation. We recommend that you evaluate the following key adhesive properties of the polymerized adhesive in accordance with appropriate testing on your device:

- tensile strength
- tensile or overlap shear strength
- peel adhesion strength
- impact strength

The following four test methods are intended to provide a means for comparison of the adhesive strengths of tissue adhesives for use as surgical adhesives or sealants on soft tissue. These or equivalent methods may be used in support of the bench testing outlined above:

- ASTM F2255-05 Standard Test Method for Strength Properties of Tissue Adhesives in Lap-Shear by Tension Loading
- ASTM F2256-05 Standard Test Method for Strength Properties of Tissue Adhesives in T-Peel by Tension Loading
- ASTM F2258-05 Standard Test Method for Strength Properties of Tissue Adhesives in Tension

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[7] Office of Combination Products, see http://www.fda.gov/oc/combination/.

[8] Viscosity of the liquid adhesive in the final product is a primary indicator of the stability of the subject device. As cyanoacrylate formulations age, the viscosity increases because of the transition of the monomer into a polymer. This, in effect, reduces the concentration of monomer and can affect the adhesive bond formed with underlying tissue. Also, if viscosity is too great, then it will be difficult to express it through applicator tip. In other words, the ease of expression is affected by the stability of the viscosity of the final product.

[9] Setting time is the amount of time required for the device to polymerize sufficiently for the wound edges to stay together without assistance. The setting time is also an indicator of the time needed to achieve maximum temperature from the introduction of the product formulation from the applicator to the test device. The stability of the final product influences the setting time. The instructions to the physician regarding application of the product are based on setting time.

- ASTM F2458-05 Standard Test Method for Wound Closure Strength in Tissue Adhesives and Sealants

B.7.2 Degradation Rate

Degradation rate is an indicator of the possible toxicity of an adhesive material. The hydrolytic degradation of an adhesive material, such as cyanoacrylate, to smaller oligomers involves a hydrolysis reaction and release of formaldehyde. In the case of cyanoacrylate adhesives, formaldehyde as a by-product of hydrolytic degradation and the resultant cytotoxic or histotoxic effects have been reported and documented in research and medical journals. Specifically, the degradation products of cyanoacrylate adhesives could accumulate in tissues and lead to significant histotoxicity characterized by both acute and chronic inflammation. The literature shows that the rate of formation of the formaldehyde decreases with increase in the length of alkyl groups and the molecular weight of the cyanoacrylate polymers.[10]

Accordingly, FDA recommends that you provide hydrolytic degradation study data to identify the amount of any by-products of material decomposition. To identify the amount of any by-products of material decomposition, we recommend that the hydrolytic degradation study monitor the amounts of:

- formulation additives
- monomer impurities
- degradation products

We recommend that you report results for these by-products of material decomposition present in saline extract at 50 °C for a period of 15 days via gas and/or liquid chromatography. The analytical procedure should be sensitive to the parts per million (ppm) levels.

B.7.3 Heat of Polymerization Study

Polymerization of an adhesive material, such as cyanoacrylate, is generally an exothermic reaction. The amount of heat generated is governed by the rate of curing (polymerization) and the thickness of the device applied to the surgical site. The heat generated can create a sensation of warmth or heat and cause discomfort in the patient. Therefore, we recommend that you provide the heat of polymerization data and the method used to determine the heat of polymerization.

B.7.4 Other Mechanical Testing

Your submission should include additional mechanical testing of the applicator functionality appropriate to the design of your applicator and its components.

B.8 Shelf Life Testing

We recommend that you conduct shelf life testing to support the expiration date in the labeling of your device. Stability studies should monitor the critical parameters of your final finished device to assure adequate device performance during its entire shelf life.[11] We recommend that your testing include parameters such as the following:

- purity of the materials
- water content
- setting time (in seconds)
- viscosity [in centipoises (cps)]
- color
- sterility

We recommend that you perform stability testing on representative aged samples at time zero and at several intervals during the real-time study. For example, for a 12-month real-time stability study, we recommend that you place samples of the finished, packaged device on stability trials at the storage temperature recommended in your labeling. We recommend that you test the device at 1, 3, 6, 9, and 12-month intervals to assess the stability at each of these points.

Accelerated shelf life testing should be supported and validated by real-time shelf life testing. The validity of the accelerated stability testing relies on

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[10] Quinn JV. *Tissue Adhesives in Clinical Medicine*. 2nd ed. Hamilton, Ontario: BC Decker Inc.; 2005.

[11] After you qualify the package configuration, we recommend that you assess the initial integrity of your final finished package and its ability to maintain that integrity. You should document the assessment in your design history file (see 21 CFR 820.30).

the assumption that the mechanisms of product inactivation and decomposition remain the same at elevated temperatures that simulate testing at lower temperatures for longer times according to the assumptions of thermodynamics. However, because there is no validated accelerated testing method and because of the reactive nature of polymers such as cyanoacrylates, the usefulness of predicting expiration date from accelerated stability studies remains unclear. Thus, the validity of an accelerated stability study is generally confirmed by a real-time stability study performed at the labeled product storage temperature(s). Therefore, if you include accelerated shelf life testing, you should also include information that demonstrates the role of accelerated stability testing in predicting the expiration date. We recommend that you discuss various inactivation and decomposition pathways for polymerization as a function of time. We also recommend that the results of real-time stability studies illustrate the value of accelerated stability testing in predicting an expiration date of 1 year or more.

B.9 Biocompatibility

FDA recommends that you conduct biocompatibility testing as described in the FDA-modified Use of International Standard ISO-10993, Biological Evaluation of Medical Devices Part-1: Evaluation and Testing for breached or compromised surface with blood contact.[12]

As a note, the subchronic implantation study duration should mimic the proposed use of the material. The test material should be implanted at or near the proposed site of use. You should monitor systemic toxicity, as well as local effects at the application site. You should also assess macroscopic pathology and histopathology.

B.10 Animal Testing

In addition to the biocompatibility testing described above, we recommend that you provide additional animal testing of your topical tissue adhesive to address the issues discussed below.

Inflammation and the replacement of soft tissue with fibrous tissue are expected outcomes of the normal healing process. Therefore, FDA recommends that you conduct animal studies to evaluate the potential for delayed healing using histopathology. We also recommend that your animal studies demonstrate that the fumes given off by the product itself and fumes that arise during polymerization will not cause chemical burns.

FDA recommends that you assess the performance characteristics of the device in the appropriate animal model(s). FDA generally recommends a porcine model; however, other models may be more appropriate for your device. The study should represent the method of application that will be employed in clinical use. You should compare the amount of the product used in the animal study to the amount given in your instructions for use. You should also provide a brief discussion of the rationale for and the limitations of the animal model used.

B.11 Clinical Studies

In accordance with the act, FDA will rely upon well-designed bench and/or animal testing rather than requiring clinical studies for new devices unless there is a specific justification for asking for clinical information to support a determination of substantial equivalence. Although, in general, clinical studies will not be needed for most tissue adhesive for the topical approximation of skin devices, FDA may recommend that you collect clinical data for a tissue adhesive for the topical approximation of skin with:

- material formulations dissimilar from designs or material formulations used in legally marketed tissue adhesives for the topical approximation of skin
- new technology, that is, technology different from that used in legally marketed tissue adhesives for the topical approximation of skin
- indications for use dissimilar from a legally marketed tissue adhesive for the topical approximation of skin

FDA will always consider alternatives to clinical testing when the proposed alternatives are supported by an adequate scientific rationale. The Plastic and

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[12] http://www.fda.gov/cdrh/g951.html.

Reconstructive Surgery Devices Branch is available to discuss any questions about clinical testing before you initiate your studies. If a clinical study is needed to demonstrate substantial equivalence (i.e., conducted prior to obtaining 510(k) clearance of the device), the study must be conducted under the Investigational Device Exemptions (IDE) regulation, 21 CFR Part 812. FDA believes that this device is a significant risk device as defined in 21 CFR 812.3(m).[13] In addition to the requirement of having a FDA-approved IDE, sponsors of such trials must comply with the regulations governing institutional review boards (21 CFR Part 56) and informed consent (21 CFR Part 50).

B.12 Sterility

FDA recommends that you provide sterilization information in accordance with the Updated 510(k) Sterility Review Guidance K90-1.[14] The device should be sterile with a sterility assurance level (SAL) of 1×10^{-6}.

B.13 Labeling

The 510(k) must include labeling in sufficient detail to satisfy the requirements of 21 CFR 807.87 (e). The following suggestions are aimed at assisting you in preparing labeling that satisfies the requirements of 21 CFR 807.87(e).[15]

B.13.1 Prescription Use

As a prescription device under 21 CFR 801.109, this device must bear the following caution statement: "Caution: Federal law restricts this device to sale by or on the order of a physician."

B.13.2 Instructions for Use

We recommend that you include the following information in your instructions for use:

- adequate information on contraindications, warnings, and precautions to address the identified risks to health
- a clear explanation of the device's technological features and how it is to be used on patients
- labeling instructions to mitigate the risks to health shown in Section B.5 of this document

We recommend that you provide detailed instructions for wound preparation and device application. The instructions should also describe techniques for tissue separation and device removal in the event of inadvertent bonding.

B.13.3 Warnings

The labeling should also include warnings that address the use of the device near the eye. For example:

> *When closing facial wounds near the eye with a tissue adhesive for topical approximation of skin, position the patient so that any runoff of adhesive is away from the eye. The eye should be closed and protected with gauze. Prophylactic placement of petroleum jelly around the eye, to act as a mechanical barrier or dam, can be effective at preventing inadvertent flow of adhesive into the eye. Use of tissue adhesive near the eye has inadvertently caused some patients' eyelids to be sealed shut. In some of these cases, general anesthesia and surgical intervention has been needed to open the eyelid.*

B.13.4 Precautions

We recommend that the labeling provide precautions about the inappropriate use of these devices, for example:

Tissue adhesives for the topical approximation of skin should not be used:

- in the presence of infection
- in the presence of ongoing bleeding
- in the presence of incomplete debridement
- on mucosal or hair-covered surfaces

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[13] See Significant Risk and Nonsignificant Risk Medical Device Studies, http://www.fda.gov/oc/ohrt/irbs/devices.html#risk.

[14] http://www.fda.gov/cdrh/ode/guidance/361.html.

[15] Although final labeling is not required for 510(k) clearance, final labeling must comply with the requirements of 21 CFR Part 801 before a medical device is introduced into interstate commerce. In addition, final labeling for prescription medical devices must comply with 21 CFR 801.109. Labeling recommendations in this guidance document are consistent with the requirements of part 801.

Tissue adhesives for the topical approximation of skin should also not be used on wounds that are as follows:

- wet
- dirty
- complex
- not easily approximated
- nonacute
- poorly perfused
- located in areas where device runoff into unintended sites cannot be prevented

In addition, the labeling should address potential interference with adherence to skin, for example:

> *The tissue adhesive will not adhere to skin precoated with petroleum jelly. Therefore, avoid using petroleum jelly on any skin area where tissue adhesive is intended to adhere.*

Glossary

A-stage: An early stage in the reaction of certain thermosetting resins in which the material is fusible and still soluble in certain liquids. Sometimes referred to as Resol. (See also B-stage and C-stage.)

Abhesive: A material that is adhesive-resistant and applicable as a nonsticking surface coating; release agent.

Adhere, v: To cause two surfaces to be held together by adhesion (q.v.). To be in a state of adherence.

Adherence: The state in which two surfaces are held together by interfacial forces.

Adherend: A body that is held to another body by an adhesive (a narrower term than substrate, q.v.).

Adhesion: The state in which two surfaces are held together by interfacial forces that may consist of valence forces, or interlocking action, or both. (See also adhesion, mechanical and adhesion, specific.) The state in which two surfaces are held together by chemical, or physical forces, or both, with the aid of an adhesive. The attraction between substances, when they are brought into contact, makes it necessary to do work to separate them.

Adhesion, mechanical: Adhesion between surfaces in which the adhesive holds the parts together by interlocking action. (See also adhesion, specific.)

Adhesion, specific: (sometimes called adhesion, molecular). Adhesion between surfaces that are held together by valence forces of the same type as those that give rise to cohesion. (See also adhesion, mechanical.)

Adhesive: A substance capable of holding materials together by surface attachment. Adhesive is the general term and includes, among others, cement, glue, mucilage, and paste (q.v.). All these terms are used interchangeably. Various descriptive adjectives are applied to the term to indicate characteristics such as physical form, chemical type, materials bonded, and conditions of use. A substance capable of bonding materials together by adhesion. Any material that causes one body to stick or adhere to another.

Adhesive, anaerobic: An adhesive that cures spontaneously in the absence of oxygen and catalyzed by metallic ions. An adhesive that cures only in the absence of air after being confined between assembled parts. An example is dimethacrylate adhesive used for bonding assembly parts, locking screws and bolts, retaining gears and other shaft-mounted parts, and sealing threads and flanges.

Adhesive, assembly: An adhesive that can be used for bonding parts together, such as in the manufacture of a boat, airplane, and furniture. This term is commonly used in the wood industry to distinguish such adhesives, formerly called "joint glues," from those used in making plywood, sometimes called "veneer glues." It is applied to adhesives used in fabricating finished structures or goods, or subassemblies thereof, as differentiated from adhesives used in the production of sheet materials, such as plywood or laminates.

Adhesive, bonded: (Note the comma, meaning bonded adhesive and not adhesive bonded.) A solvent solution of resins, sometimes containing plasticizers, which dries at room temperature.

Adhesive, cold-setting: An adhesive that sets at temperatures below 68 °F (20 °C).

Adhesive, contact: An adhesive that is apparently dry to the touch and that will adhere to itself instantaneously on contact; also called contact bond adhesive. An adhesive applied to both adherends and allowed to become dry, which develops a bond when the adherends are brought together without sustained pressure.

Adhesive, dispersion (or emulsion): A two-phase system with one phase (the adhesive material) in a liquid suspension.

Adhesive, encapsulated: An adhesive in which the particles or droplets of one of the reactive components are enclosed in a protective film (microcapsules) to prevent cure until the film is destroyed by suitable means.

Adhesive, film: An adhesive in film form, with or without a carrier, usually set by means of heat and pressure. The main advantage is uniformity of glue line thickness.

Adhesive, film-supported: An adhesive material incorporating a carrier that remains in the bond when the adhesive is employed. The carrier support material is usually composed of organic and/or inorganic fibers, which may be in woven form.

Adhesive, film-unsupported: An adhesive material in film form without a carrier support.

Adhesive, foamed: An adhesive, the apparent density of which has been decreased substantially by the presence of numerous gaseous cells dispersed throughout its mass.

Adhesive, foaming: An adhesive designed to foam in situ, after application, to provide extensive gap-filling properties.

Adhesive, gap-filling: An adhesive subject to low shrinkage in setting, employed as sealant.

Adhesive, heat-activated: A dry adhesive that is rendered tacky or fluid by application of heat, or heat and pressure, to the assembly.

Adhesive, heat-sealing: A thermoplastic film adhesive that is melted between the adherend surfaces by heat application to one or both of the adjacent adherend surfaces.

Adhesive, hot-melt: An adhesive that is applied in a molten state and forms a bond on cooling to a solid state. A bonding agent that achieves a solid state and resultant strength by cooling, as contrasted with other adhesives that achieve the solid state through evaporation of solvents or chemical cure. A thermoplastic resin that functions as an adhesive when melted between substrate and cooled.

Adhesive, hot setting: An adhesive that requires a temperature at or above 212 °F (100 °C) to set it.

Adhesive, intermediate-temperature setting: An adhesive that sets in the temperature range from 87 °F to 211 °F (31−99 °C).

Adhesive, latex: An emulsion of rubber or thermoplastic rubber in water.

Adhesive, multiple-layer: A film adhesive, usually supported with a different adhesive composition on each side, designed to bond dissimilar materials such as the core-to-face bond of a sandwich composite structure.

Adhesive, one-component: An adhesive material incorporating a latent hardener or catalyst activated by heat. Usually not only refers to thermosetting materials but also describes anaerobic, hot-melt adhesive, or those dependent on solvent loss for adherence. Thermosetting one-component adhesives require heat to cure.

Adhesive, pressure-sensitive: A viscoelastic material that, in solvent-free form, remains permanently tacky at room temperature. Such material will adhere instantaneously and tenaciously to most solid surfaces with the application of very slight manual pressure. These adhesives are frequently used on tapes. An adhesive that, in the dry state, is aggressively and permanently tacky at room temperature and firmly adheres to a variety of dissimilar surfaces on contact without the need for more than finger or hand pressure.

Adhesive, room-temperature setting: An adhesive that sets in the temperature range from 68 °F to 86 °F (20−30 °C), in accordance with the limits for standard room temperature specified in ASTM Methods D618.

Adhesive, separate-application: An adhesive consisting of two parts, one part being applied to one adherend and the other part to the other, the two then being brought together to form a joint. Acrylics are examples of this type.

Adhesive, solvent: An adhesive having a volatile organic liquid as a vehicle. This term excludes water-based adhesives.

Adhesive, solvent-activated: A dry adhesive or adherend that is rendered tacky just prior to use by the application of a solvent.

Adhesive spread: See spread.

Adhesive, structural: A bonding agent used for transferring required loads between adherends exposed to service environments typical for the structure involved. An adhesive of proven reliability in engineering structural applications in which the bond can be stressed to a high proportion of its maximum failing load for long periods without failure. A material employed to form high-strength bonds in structural assemblies that perform load-bearing functions, and which may be used in extreme service conditions, for example, high- and low-temperature exposure.

Adhesive, two-component: An adhesive supplied in two parts that are mixed before application. Such adhesives usually cure at room temperature.

Adhesive, warm-setting: A term that is sometimes used as a synonym for intermediate-temperature-setting adhesive (q.v.).

Amylaceous, adj: Pertaining to, or of, the nature of starch; starchy.

Anodize: To coat a metal with a protective film by subjecting it to electrolytic action as the anode of a cell.

Assembly (for adhesive): A group of materials or parts, including adhesive, that has been placed together for bonding or that has been bonded together.

Autoclave: A closed container that provides controlled heat and pressure conditions.

B-stage: An intermediate stage in the reaction of certain thermosetting resins in which the material softens when heated to a rubbery state and swells when in contact with certain liquids but may not entirely fuse or dissolve in some of the solvents that will dissolve resins in the A-stage. The resin in an uncured thermosetting adhesive is usually in this stage. Sometimes referred to as Resitol.

Backing: The flexible supporting material for an adhesive. Pressure-sensitive adhesives are commonly backed with paper, plastic films, fabric, or metal foil; heat-curing thermosetting adhesives are often supported on glass cloth backing.

Bag molding (blanket molding): A method of molding or bonding, involving the application of fluid pressure, usually by means of air, steam, water, or vacuum, to a flexible cover which, sometimes in conjunction with the rigid die, completely encloses the material to be bonded.

Bag, vacuum: A flexible bag in which pressure may be applied to an assembly inside the bag by means of evacuation of the bag.

Binder: A component of an adhesive composition that is primarily responsible for the adhesive forces that hold two bodies together.

Bite, n: The penetration or dissolution of adherend surfaces by an adhesive.

Blister: An elevation of the surface of an adherend, somewhat resembling in shape of a blister on the human skin; its boundaries may be indefinitely outlined, and it may have burst and become flattened. A blister may be caused by insufficient adhesive, inadequate curing time, temperature or pressure, or trapped air, water, or solvent vapor.

Blocked-curing agent: A curing agent or hardener rendered unreactive, which can be reactivated as desired by physical or chemical means.

Blocking: An undesired adhesion between touching layers of a material, such as occurs under moderate pressure during storage or use. An unintentional adherence between materials.

Blushing: The condensation of atmospheric moisture at the bond line interface.

Body: The consistency of an adhesive, which is a function of viscosity, plasticity, and rheological factors.

Bond, n: The union or joining of materials by adhesives. The attachment at the interface between an adhesive and an adherend.

Bond, v: To unite or join materials by means of an adhesive.

Bond line: See glue line.

Bond strength: The unit load (force) supplied in tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly, with failure occurring in or near the plane of the bond (the interface). The term adherence (q.v.) is frequently used in place of bond strength.

Bond, structural: See structural bond.

Building construction, panel, and floor covering: adhesive Any non-aerosol, one-component adhesive that is designed or labeled for the installation, remodeling, maintenance, or repair of (a) structural and building components that include, but are not limited to, beams, trusses, studs, paneling (drywall or drywall laminates, fiberglass reinforced plastic (FRP), plywood, particle board, insulation board, predecorated hardboard or tileboard, etc.), ceiling and acoustical tile, molding, fixtures, countertops or countertop laminates, cove or wall bases, and flooring or subflooring or (b) floor or wall coverings that include, but are not limited to, wood or simulated wood covering, carpet, carpet pad or cushion, vinyl-backed carpet, flexible flooring material, nonresilient flooring material, mirror tiles and other types of tiles, and artificial grass. “Construction, panel, and floor covering adhesive” does not include “floor seam sealer.”

C-stage: The final stage in the reaction of certain thermosetting resins in which the material is relatively insoluble and infusible. Certain thermosetting resins in a fully cured adhesive layer are in this stage. Sometimes referred to as resite.

Catalyst: A substance that markedly speeds up the cure of an adhesive when added in minor quantity compared with the amounts of the primary reactants. A material that promotes cross-linking in a polymer or accelerates drying.

Caul, n: A sheet of material employed singly or in pairs in hot or cold pressing of assemblies being bonded. Cauls are used to protect the faces of the assembly, or the press platens, or both against marring and staining to prevent sticking, to facilitate loading, to impart a desired surface tension or finish, or to provide uniform surface distribution. Cauls may be made of any suitable material, such as aluminum, stainless steel, hardboard, fiberboard, or plastic. The length and width dimensions are generally the same as those of the platen of the press where it is used.

Cement, n: See adhesive and solvent cement. A synonym for adhesive; a mixture of water with finely powdered lime and clay, which hardens and adheres to suitable aggregates to form concrete or mortar; an inorganic paste with adhesive properties.

Cement, v: To bond with a cement.

Cohesion: The state in which the particles of a single substance are held together by primary or secondary valence forces. In adhesives, cohesion is the state in which the particles of the adhesive or adherend are held together.

Cold pressing: A bonding operation in which an assembly is subjected to pressure without the application of heat.

Collagen: The protein derived from bone and skin used to prepare animal glue and gelatin.

Colophony: The resin obtained from various species of pine trees.

Condensation: A chemical reaction in which two or more molecules combine with the separation of water or some other simple compound. If a polymer is formed, the process is called polycondensation.

Consistency: That property of a liquid adhesive by virtue of which it tends to resist deformation. Consistency is not a fundamental property but is composed of viscosity, plasticity, and other phenomena. The term is usually applied to materials whose deformations are not proportional to applied stresses.

Contact adhesive: A nonaerosol adhesive that (a) is designed for application to both surfaces to be bonded together, (b) is allowed to dry before the two surfaces are placed in contact with each other, (c) forms an immediate bond that is impossible, or difficult, to reposition after both adhesive-coated surfaces are placed in contact with each other, and (d) does not require sustained pressure or clamping of surfaces after the adhesive-coated surfaces have been brought together using sufficient momentary pressure to establish full contact between both surfaces. "Contact adhesive" does not include rubber cements that are primarily intended for use on paper substrates. Contact adhesive also does not include vulcanizing fluids that are designed and labeled for tire repair only.

Contact adhesive—general/regular purpose: Any contact adhesive that is not defined as "Contact adhesive special purpose."

Contact adhesive—special purpose: A contact adhesive that (a) is used to bond melamine-covered board, unprimed metal, unsupported vinyl, Teflon, ultrahigh-molecular-weight polyethylene, rubber, high-pressure laminate or wood veneer 1/16 in or less in thickness to any porous or nonporous surface and is sold in units of product, less packaging, that contain more than eight fluid ounces or (b) is used in automotive applications that are (1) automotive under-the-hood applications requiring heat, oil, or gasoline resistance or (2) body-side molding, automotive weather-strip or decorative trim.

Contact angle: The angle between a substrate plane and the free surface of a liquid droplet at the line of contact with the substrate.

Contact bonding: The deposition of cohesive materials on both adherend surfaces and their assembly under pressure.

Copolymer: See polymer, copolymerization, and polymerization.

Core: The honeycomb structure used in sandwich panel construction; innermost portion of a multilayer adherend assembly.

Corrosion: The chemical reaction between the adhesive or contaminant and the adherend surfaces, due to reactive components in the adhesive film, leading to deterioration of the bond strength.

Cottoning: The formation of web-like filaments of adhesive between the applicator and the substrate surface.

Coverage: The spreading power of an adhesive over the surface area of the adherend.

Crazing: Fine cracks that may extend in a network on, under the surface of, or through a layer of adhesive.

Creep: The dimensional change with time of a material under load, following initial instantaneous elastic or rapid deformation. Creep at room temperature is sometimes called cold flow.

Cross-linking (crosslinking): The union of adjacent molecules of cured adhesive (often existing as long polymer chains) by catalytic or curing agents.

Cure, v: To change the physical properties of an adhesive, usually thermosetting, by chemical reaction, which may be condensation, polymerization, vulcanization, or cross-linking. It is usually accomplished by the action of heat and catalyst, alone or in combination, with or without pressure.

Cure (curing) temperature: The temperature to which an adhesive or an assembly is subjected to cure the adhesive.

Cure (curing) time: The period of time necessary for an adhesive or an assembly to cure under specified conditions of temperature, pressure, or both.

Curing agent (hardener): A substance or mixture of substances added to an adhesive to promote or control the curing reaction. An agent that does not enter into the reaction is known as a catalytic hardener or catalyst. A reactive curing agent or hardener is generally used in much greater amounts than a catalyst and actually enters into the reaction.

Degrease: To remove oil and grease from adherend surfaces.

Delamination: The separation of layers in a laminate because of failure of the adhesive, either in the adhesive itself or at the interface between the adhesive and the adherend.

Dextrin: A water-based product derived from the acidification and/or roasting of starch.

Dielectric curing: The use of a high-frequency electric field through a joint to cure a synthetic thermosetting adhesive. A curing process for wood and other nonconductive joint materials. Curing results from the heat generated by the resonance of the molecules within the adhesive because of the imposed field.

Diluent: An ingredient usually added to an adhesive to reduce the concentration of bonding materials. A liquid additive whose sole function is to reduce the concentration of solids and the viscosity of an adhesive composition. Also called thinner that is deprecated by some workers.

Diluent, reactive: A low-viscosity liquid added to a high-viscosity solvent-free thermosetting adhesive that reacts chemically with the adhesive during curing. The advantage of lowered viscosity is gained with minimum loss of other properties.

Doctor bar or blade: A scraper mechanism that regulates the amount of adhesive on the spreader rolls or on the surface being coated. A mechanism (bar or blade) on application equipment for spreading a material evenly on the application rolls or on the surface being coated, thereby controlling its thickness.

Doctor roll: A roller mechanism that revolves at a different surface speed, in a direction opposite to that of the spreader roll, resulting in a wiping action to control the amount of adhesive supplied to the spreader roll.

Double spread: See spread.

Dry, v: To change the physical state of an adhesive or an adherend by the loss of solvent constituents by evaporation, absorption, or both.

Elasticity, modulus of: The ratio of stress to strain in elastically deformed material.

Elastomer: A macromolecular material that, at room temperature, is capable of recovering substantially in size and shape after removal of deforming force.

Emulsion: A stable dispersion of two or more immiscible liquids held in suspension by small percentages of substances called emulsifiers.

Extender: A substance, generally having some adhesive action, added to an adhesive to reduce the amount of the primary binder required per unit area. Another function is to reduce costs. Such materials also improve void-filling properties and reduce crazing.

Failure, adherend: Joint failure by cohesive failure of the adherend.

Failure, adhesive: Rupture of an adhesive bond at the interface between the adhesive and the adherend. Rupture of an adhesive bond in which the separation appears visually to be at the adhesive/adherend interface.

Failure, cohesive: Rupture of an adhesive bond in such a way that the separation appears to be within the adhesive. Rupture of an adhesive bond in which the separation appears visually to be in the adhesive or in the adherend.

Failure, contact: The failure of an adhesive joint, as a result of incomplete contact during assembly, between adherend and adhesive surfaces or between adhesive surfaces.

Failure, wood: The rupturing of wood fibers in strength tests on bonded specimens, usually expressed as the percentage of the total area involved that shows such failure. This is a form of adherend failure.

Fatigue: A condition of stress from repeated flexing or impact force on the adhesive—adherend interface; weakening of material caused by repetitive loading and unloading.

Faying surface: The surface of an adherend that makes contact with another adherend.

Feathering: The tapering of an adherend on one side to form a wedge section, as used in a scarf joint.

Filler: A relatively nonadhesive substance added to an adhesive to improve its working properties, permanence, strength, or other qualities.

Filler sheet: A sheet of deformable or resilient material that, when placed between the assembly to be bonded and the pressure applicator or when distributed within a stack of assemblies, aids in providing uniform application of pressure over the area to be bonded.

Fillet: That portion of an adhesive that fills the corner or angle formed where two adherends are joined. The term for junction of the outer skin and inner core in honeycomb assemblies.

Flow: Movement of an adhesive during the bonding process before the adhesive is set. (See also cold flow under creep.)

Gel, n: A semisolid system consisting of a network of solid aggregates in which liquid is held.

Gel, v: To reach a gel condition or state.

Gelation: Formation of a gel.

General purpose adhesive: Any nonaerosol adhesive designed for use on a variety of substrates. "General purpose adhesive" does not include (a) contact adhesives; (b) construction, panel, and floor covering adhesives; (c) adhesives designed exclusively for application on one specific category of substrates (i.e., substrates that are composed of similar materials, such as different types of metals, paper products, ceramics, plastics, rubbers, or vinyls); or (d) adhesives designed exclusively for use on one specific category of article (i.e., articles that may be composed of different materials but perform a specific function, such as gaskets, automotive trim, weather-stripping, or carpets).

Glue, n: Originally, a hard gelatin obtained from hides, tendons, cartilage, bones, and so on of animals. Also, an adhesive prepared from this substance by heating with water. Through general use, the term is now synonymous with the term "adhesive." However, the term is most commonly used for wood adhesives.

Glue line (bond line): The layer of adhesive that attaches two adherends. The interface between an adhesive and an adherend.

Green strength (grab): The ability of an adhesive to hold two surfaces together when first brought into contact and before the adhesive develops its ultimate bonding properties when fully cured.

Gum: Any of a class of colloidal substances exuded by or prepared from plants. Sticky when moist, they are composed of complex carbohydrates and organic acids that are soluble or swell in water.

Hardener: A substance or mixture of substances added to an adhesive to promote or control the curing reaction by taking part in it by catalysis or cross-linking. The term is also used to designate a substance added to control the degree of hardness of the cured film.

Heat reactivation: The use of heat to effect adhesive activity, for example, hot-melt adhesive; completion of the curing process of a B-staged resin.

Heat seal: The use of heat reactivation to prepare a joint with a thermoplastic material present, as a thin layer, on the adherends, bringing adherend surfaces to their melting point and bonding under pressure.

Heteropolymerization: See polymerization.

Honeycomb core: A sheet material, which may be metal, foamed into cells (usually hexagonal) and used for sandwich construction in structural assemblies, especially in aircraft construction.

Impact shock: See strength, impact.

Inhibitor: A substance that slows down a chemical reaction. Inhibitors are sometimes used in certain adhesives to prolong storage or working life.

Interface: The contact area between adherend and adhesive surfaces.

Jig. A: Form used to hold a bonded assembly until the adhesive has cured. A supporting frame for the production of laminate shapes under pressure.

Joint: The location at which two adherends are held together with a layer of adhesive.

Joint, butt: A joint made by bonding two surfaces that are perpendicular to the main surface of the adherends.

Joint, lap: A joint made by placing one adherend partly over another and bonding together the portions of the adherends. Double lap joints involve the overlapping by opposing faces of one adherend.

Joint, scarf: A joint made by cutting away similar segments of two adherends at an angle less than 45° to the major axis of two adherends and bonding the adherends with the cut areas fitted together to be coplanar.

Joint, starved: A joint that has an insufficient amount of adhesive to produce a satisfactory bond. This condition may result from too thin a spread to fill the gap between the adherends, excessive penetration of the adhesive into the adherend (when porous), too short an assembly time, or the use of excessive pressure.

Laminate, n: A product made by bonding together two or more layers of material or materials.

Laminate, v: To unite layers of material with adhesive.

Laminate, cross, n: A laminate in which some of the layers of material are oriented at right angles to the remaining layers with respect to the grain or strongest direction in tension.

Laminate, parallel, n: A laminate in which the grain of all layers of material are oriented approximately parallel to each other. A laminate in which all the layers of material are oriented approximately parallel with respect to the grain or strongest direction in tension.

Latex: A stable dispersion of a polymeric material in an essentially aqueous medium.

Legging: The drawing of filaments or strings when adhesive-bonded substrates are separated.

Mastic: A high-viscosity, low-cost adhesive, either latex or solvent based, used in industrial applications, such as in applying wall boards and floor tiles. Mastics are applied by knife, trowel, or pressure guns and become immobile on loss of solvent or water.

Matrix: The part of an adhesive that surrounds or engulfs embedded filler or reinforcing particles and filaments.

Modifier: Any chemically inert ingredient added to an adhesive formulation that changes its properties.

Modulus: See elasticity, modulus of and rigidity, modulus of.

Monomer: A relatively simple compound that can react to form a polymer.

Mucilage: An adhesive prepared from a gum and water. Also, in a more general sense, a liquid adhesive that has a low order of bonding strength. Mucilages are used in schools and offices for applications usually involving paper products.

Newtonian fluid: A fluid in which the shearing rate is directly proportional to the applied torque.

Novalak: A phenolic-aldehydic resin that, unless a source of methylene groups is added, remains permanently thermoplastic.

Open time: See open assembly time under time, assembly.

Paste, n: An adhesive composition having a characteristic plastic-type consistency, that is, a high order of yield value, such as that of an adhesive prepared by heating a mixture of starch and water and subsequently cooling the hydrolyzed product.

Penetration: The passage of an adhesive into an adherend.

Permanence: The resistance of an adhesive bond to deteriorating influences.

Photographing: See telegraphing.

Pick-up roll: A spreading device where the roll for picking up the adhesive runs in a reservoir of adhesive.

Plasticity: A property of adhesives that allows the material to be deformed continuously and permanently without rupture on the application of a force that exceeds the yield value of the material.

Plasticizer: A material, such as a high-boiling point organic solvent, incorporated in an adhesive to increase its flexibility, workability, or distensibility. The addition of the plasticizer may cause a reduction in melt viscosity, lower the temperature of the second-order transition, or lower the elastic modulus of the solidified adhesive.

Polycondensation: See condensation and polymer.

Polymer: A compound formed by the reaction of simple molecules having functional groups that permit their combination to proceed to higher molecular weights under suitable conditions. Polymers may be formed by polymerization (addition polymers) or polycondensation (condensation polymers). When two or more different monomers are involved, the product is a copolymer.

Polymerization: A chemical reaction in which the molecules of a monomer are linked together to form large molecules whose molecular weight is a multiple of that in the original substance. When two or more different monomers are involved, the process is called copolymerization or heteropolymerization.

Porosity: The ability of an adherend to absorb an adhesive.

Postcure, v: To expose an adhesive assembly to an additional cure, following the initial cure, for the purpose of modifying specific properties.

Postvulcanization bonding: Conventional adhesive bonding of previously vulcanized elastomeric adherends.

Pot life (working life): The period of time during which an adhesive or resin prepared for application after mixing with catalyst, solvent, or other compounding ingredients remains usable. The effective working time for an adhesive after preparation; interval before the adhesive system becomes unusable through an increase in viscosity or curing.

Prebond treatment: See surface preparation.

Pressure-sensitive adhesives (PSAs): Adhesive materials that bond to adherend surfaces at room temperature immediately as low pressure is applied. Adhesives that require only pressure application to effect permanent adhesion to an adherend.

Primer: A coating applied to a surface of an adherend prior to the application of an adhesive to improve adhesion and/or durability of the bond.

Qualification test: A series of tests conducted by the government procuring activity, or an agent thereof, to determine conformance of materials, or materials systems, to the requirements of a specification, which normally results in a Qualified Products List (QPL) under the specification. Qualification under a specification generally requires conformance to all tests in the specification. It may, however, be limited to conformance to a specific type, or class, or both.

QPL: See qualification test.

Release agent: An adhesive material that prevents bond formation.

Release paper: A sheet, serving as a protectant, or carrier, or both, for an adhesive film or mass that is easily removed from the film or mass prior to use.

Resin: A solid, semisolid, or pseudosolid organic material that has an indefinite and often high molecular weight, exhibits a tendency to flow when subjected to stress, usually has a softening or melting range, and usually fractures conchoidally. A liquid resin is an organic polymeric liquid that, when converted to its final state for use, becomes a resin.

Resinoid: Any of the class of thermosetting synthetic resins, either in their initial temporarily infusible state or in their final infusible state.

Resite: An alternative term for C-stage (q.v.).

Resitol: An alternative term for B-stage (q.v.).

Resol: An alternative term for A-stage (q.v.).

Retrogradation: A change of starch pastes from low to high consistency on aging.

Rigidity, modulus of: Modulus of Rigidity (or Shear Modulus) is the coefficient of elasticity for a shearing force. It is defined as “the ratio of shear stress to the displacement per unit sample length (shear strain)”.

Rosin: A resin obtained as a residue in the distillation of crude turpentine from the sap of the pine tree (gum rosin) or from an extract of the stumps and other parts of the tree (wood rosin).

Sagging: Run or flow-off of adhesive from an adherend surface because of the application of excess or low-viscosity material.

Sandwich panel: An assembly that is composed of metal skins (facings) bonded to both sides of a lightweight core.

Sealant: A gap-filling material to prevent excessive absorption of adhesive or penetration of liquid or gaseous substances.

Sealant/caulking compound: Any product with adhesive properties that is designed to fill, seal, waterproof, or weatherproof gaps or joints between two surfaces. “Sealant and caulking compound” does not include roof cements and roof sealants, insulating foams, removable caulking compounds, clear/paintable/water resistant caulking compounds, floor seam sealers, products designed exclusively for automotive uses, or sealers that are applied as continuous coatings. Sealant and caulking compound also does not include units of product, less packaging that weigh more than one pound and consist of more than 16 fluid ounces. For the purposes of this definition only, “removable caulking compounds” means a compound that temporarily seals windows or doors for 3−6-month time intervals, and “clear/paintable/water resistant caulking compounds” means a compound that contains no appreciable level of opaque fillers or pigments, transmits most or all visible light through the caulk when cured, is paintable, and is immediately resistant to precipitation on application.

Self-vulcanizing, adj: Pertaining to an adhesive that undergoes vulcanization without the application of heat.

Service conditions: The environmental conditions to which a bonded structure is exposed, for example, heat, cold, humidity, radiation, and vibration.

Set, v: To convert an adhesive into a fixed or hardened state by chemical or physical action, such as condensation, polymerization, oxidation, vulcanization, gelation, hydration, or evaporation of volatile constituents. The term is most commonly used with thermoplastic adhesives, unless a chemical process, such as polymerization, is involved.

Shear, tensile: The apparent stress applied to an adhesive in a lap joint.

Shelf life: See storage life.

Shortness: A qualitative term that describes an adhesive that does not string cotton or otherwise form filaments or threads during application.

Shrinkage: The volume reduction occurring during adhesive curing, sometimes expressed as a percentage volume or linear shrinkage; size reduction of adhesive layer due to solvent loss or catalytic reaction.

Single-spread: See spread.

Sizing: The process of applying a material on a surface to fill pores and thus reduce the absorption of the subsequently applied adhesive or coating, or to otherwise modify the surface properties of the substrate to improve the adhesion. Also, the material used for this purpose. The latter is sometimes called size.

Skinning: The formation of a dry surface layer (skin) on an adhesive coating following too rapid evaporation of the solvent vehicle.

Slip: The ability of an adhesive to accommodate adherend movement or repositioning after application to adherend surfaces.

Slippage: The movement of adherends with respect to each other during the bonding process.

Slip sheet interliner: A sheet or film used to cover an adhesive during handling; protective film for a film adhesive.

Softener: A plasticizing additive to reduce adhesive embrittlement; component of elastomeric films to increase their flexibility.

Solids content: The percentage by weight of the nonvolatile matter in an adhesive.

Solvent bonding: See solvent welding.

Solvent cement: An adhesive utilizing an organic solvent as the means of depositing the adhesive constituent. An adhesive that dissolves the plastics being joined, forming strong intermolecular bonds, and then evaporating. An adhesive made by dissolving a plastic resin or compound in a suitable solvent or mixture of solvents. The solvent cement dissolves the surfaces (of the pipe and fittings) to form a bond between the mating surfaces, provided that the proper cement is used for the particular materials and proper techniques are followed.

Solvent cement joint: A joint made by using a solvent cement to unite the components.

Solvent cementing: See solvent welding.

Solvent joint: A joint made by using a solvent to unite the components.

Solvent reactivation: The application of solvent to a dry adhesive layer to regenerate its wetting properties.

Solvent welding (solvent bonding or solvent cementing): The process of joining articles made of thermoplastic resins by applying a solvent capable of softening the surfaces to be joined and pressing the softened surfaces together. Adhesion is attained by means of evaporation of the solvent, absorption of the solvent into adjacent material, and/or polymerization of the solvent cement. ABS, acrylics, cellulosics, polycarbonates, polystyrenes, and vinyls are plastics that may be joined in this way. The formation of a joint in which a self-bond between the polymeric components is promoted by the temporary presence of a solvent in the absence of an extraneous adhesive.

Spread (adhesive spread): The quantity of adhesive per unit joint area applied to an adherend, usually expressed in points of adhesive per thousand square feet of joint area. (1) Single spread refers to the application of adhesive to only one adherend of a joint. (2) Double spread refers to application of adhesive to both adherends of a joint.

Squeeze-out: Excess adhesive pressed out at the bond line because of the pressure applied in the adherends.

Stabilizer: An adhesive additive that prevents or minimizes change in properties, for example, by adherend absorption, demulsification, or rapid chemical reaction.

Storage life: The period of time during which a packaged adhesive can be stored under specified temperature conditions and remain suitable for use. Sometimes called shelf life. Refrigerated storage often extends storage life considerably.

Strength, cleavage: The tensile load expressed as force per unit of width of bond required to cause cleavage separation of a test specimen of unit length.

Strength, dry: The strength of an adhesive joint determined immediately after drying under specified conditions or after a period of conditioning in the standard laboratory atmosphere.

Strength, fatigue: The maximum load that a joint will sustain when subjected to repeated stress application after drying or after a conditioning period under specified conditions.

Strength, impact: Ability of an adhesive material to resist shock by a sudden physical blow directed against it. Impact shock is the transmission of stress to an adhesive interface by sudden vibration or jarring blow of the assembly, measured in work units per unit area.

Strength, longitudinal shear (lap-joint strength): The force necessary to rupture an adhesive joint by means of stress applied parallel to the plane of the bond.

Strength, peel: The force per unit width necessary to bring an adhesive to the point of failure and/or to maintain a specified rate of failure by means of a stress applied in a peeling mode.

Strength, shear: The resistance of an adhesive joint to shearing stresses; the force per unit area sheared, at failure.

Strength, tensile: The resistance of an adhesive joint to tensile stress; the force per unit area under tension, at failure.

Strength, wet: The strength of an adhesive joint determined immediately after removal from a liquid in which it has been immersed under specified conditions of time, temperature, and pressure. The term is commonly used to designate strength after immersion in water. In latex adhesives, the term is also used to describe the joint strength when the adherends are brought together with the adhesive still in the wet state.

Stringiness: The property of an adhesive that results in the formation of filaments or threads when adhesive transfer surfaces are separated. Transfer surfaces include rolls, picker plates, stencils, and so on. The complete break off of adhesive film when it is divided between transfer rollers, stencils, picker plates, and so on; uneven transfer of an adhesive to an adherend surface.

Structural adhesive: See adhesive, structural.

Structural bond: A bond that stresses the adherend to the yield point, thereby taking full advantage of the strength of the adherend. On the basis of this definition, a dextrin adhesive used with paper (e.g., postage stamps and envelopes), which causes failure of the paper, forms a structural bond. The stronger the adherend, the greater the demands placed on the adhesive. Thus, few adhesives qualify as "structural" for metals. A further requirement for a structural adhesive is that it be able to stress the adherend to its yield point after exposure to its intended environment.

Substrate: A material on the surface of which an adhesive-containing substance is spread for any purpose, such as bonding or coating. A broader term than adherend (q.v.).

Surface preparation (surface treatment): A physical or chemical preparation, or both, of an adherend to render it suitable for adhesive joining. The term prebond treatment is sometimes used but is deprecated.

Syneresis: The exudation by gels of small amounts of liquid on standing.

Tack: The property of an adhesive that enables it to form a bond of measurable strength immediately after adhesive and adherend are brought into contact under low pressure.

Tack, aggressive: See tack, dry.

Tack, dry, n: The property of certain adhesives, particularly nonvulcanizing rubber adhesives, to adhere on contact to themselves at some stage in the evaporation of volatile constituents, even though they seem dry to touch. Sometimes called aggressive tack. The self-adhesion property of certain adhesives that are touch-dry (a stage in the evaporation of volatile constituents).

Tack-dry (tacky-dry), adj: The state of an adhesive that has lost sufficient volatiles (by evaporation or absorption into the adherend) to leave it in the required sticky (tacky) condition.

Tackifier: An additive intended to improve the stickiness of a cast adhesive film, usually a constituent of rubber-based and synthetic resin adhesives.

Tack range (tack stage): The period of time in which an adhesive will remain in the tacky-dry condition after application to an adherend under specified conditions of temperature and humidity.

Tacky-dry: See tack-dry. Tape. A film form of adhesive that may be supported on carrier material.

Teeth: The resultant surface irregularities or projections formed by the breaking of filaments or strings that may form when adhesive-bonded substrates are separated.

Telegraphing: A condition in a laminate or other type of composite construction in which irregularities, imperfections, or patterns of an inner layer are visibly transmitted to the surface. Telegraphing is occasionally referred to as photographing. The visible transmission of faults, imperfections, and patterned striations occurring in an inner layer of a laminate structure.

Temperature, curing: The temperature to which an adhesive or an assembly is subjected to cure the adhesive. The temperature attained by the adhesive in the process of curing; it (adhesive curing temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly curing temperature).

Temperature, drying: The temperature to which an adhesive on an adherend, or in an assembly, or the assembly itself, is subjected to dry the adhesive. The temperature attained by the adhesive in the process of drying it (adhesive drying temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly drying temperature).

Temperature, maturing: The temperature, for a given time and bonding procedure, which produces required characteristics in components bonded with ceramic adhesives.

Temperature, setting: The temperature to which an adhesive or an assembly is subjected to set the adhesive. The temperature attained by the adhesive in the process of setting (adhesive setting temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly setting temperature).

Tests, destructive: Tests involving the destruction of assemblies to evaluate the maximum performance of the adhesive bond.

Tests, nondestructive: Inspection tests for the evaluation of bond quality without damaging the assembly, for example, ultrasonics and visual inspection.

Thermoplastic, adj: Capable of being repeatedly softened by heat and hardened by cooling.

Thermoplastic, n: A material that will repeatedly soften when heated and harden when cooled.

Thermoset (thermosetting), adj: Having the property of undergoing a chemical reaction by the action of heat, catalysis, ultraviolet light, and so on, leading to a relatively infusible state.

Thermoset, n: A material that has the property of undergoing or has undergone a chemical reaction by the action of heat, catalysis, ultraviolet light, and so on, leading to a relatively infusible state.

Thinner, n: A volatile liquid added to an adhesive to modify the consistency or other properties. See diluent.

Thixotropic, adj: A term applied to materials having the property of thixotropy (q.v.).

Thixotropy: A property of adhesive systems of thinning upon isothermal agitation and thickening upon subsequent rest. A property of materials that display a reduction in viscosity when a shearing action is applied. Some adhesive systems become thinner in consistency on agitation and thicker again when left undisturbed.

Time, assembly: The time interval between the spreading of the adhesive on the adherend and the application of pressure, or heat, or both, to the assembly. For assemblies involving multiple layers or parts, the assembly time begins with the spreading of the adhesive on the first adherend. Assembly time is the sum of the open and closed assembly times. Open assembly time is the time interval between the spreading of the adhesive on the adherend and the completion of assembly of the parts for bonding. During this period, the adhesive-coated surfaces are exposed to the air before being brought into contact. Closed assembly time is the time interval between completion of assembly of the parts for bonding and the application of pressure, or heat, or both, to cure or set the adhesive.

Time, curing: The period of time during which an assembly is subjected to heat or pressure, or both, to cure the adhesive. Further cure may take place after removal of the assembly from the conditions of heat, or pressure, or both.

Time, drying: The period of time during which an adhesive on an adherend or an assembly is allowed to dry with or without the application of heat, or pressure, or both.

Time, joint conditioning: The time interval between the removal of the joint from the conditions of heat, pressure, or both, used to accomplish bonding and the attainment of approximately maximum bond strength. Sometimes called joint aging time.

Time, setting: The period of time during which an assembly is subjected to heat, pressure, or both, to set the adhesive.

Vehicle: The carrier medium (liquid) for an adhesive material that improves its ease of application to adherends; solvent component of an adhesive.

Viscosity: The ratio of the shear stress existing between laminae of moving fluid and the rate of shear between these laminae. A fluid exhibits newtonian behavior when the rate of shear is proportional to the shear stress. A fluid exhibits non-newtonian behavior when an increase or decrease in the rate of shear is not accompanied by a proportional increase or decrease in the shear stress. A measure of the resistance to flow of a liquid. For newtonian liquids, the shear rate is proportional to the shear stress between laminate of moving fluid; for non-newtonian liquids, it is not proportional.

Viscosity coefficient (coefficient of viscosity): The shearing stress that is tangentially applied will induce a velocity gradient. A material has a viscosity coefficient of one poise when a shearing stress of one dyne per square centimeter produces a velocity gradient of 1 cm/s/cm.

Vulcanization: A chemical reaction in which the physical properties of a rubber are changed in the direction of decreased plastic flow, less surface tackiness, and increased tensile strength by reacting it with sulfur or other suitable agents. The cross-linking of an adhesive material by means of heat or catalysis; the chemical reaction of rubber with sulfur or other agents to alter its physical properties, for example, to cause less tackiness, reduced plastic flow, and increased tensile strength.

Vulcanize, v: To subject to vulcanization (q.v.).

Warp, n: A significant variation from the original, true, or plane surface of a material. A distortion of an adherend surface.

Webbing: Filaments or threads that may form when adhesive transfer surfaces are separated. Transfer surfaces may be rolls, picker plates, stencils, and so on.

Weldbonding: A process in which a joint is formed by spot welding through an uncured adhesive bond line, or by flowing an adhesive into a spot-welded joint.

Wetting: The process in which a liquid spontaneously adheres to and spreads on a solid surface. A surface is said to be completely wet by a liquid if the contact angle is zero, and incompletely wet if it is a finite angle. Surfaces are commonly regarded as unwettable if the angle exceeds 90°.

Wood veneer: A thin sheet of wood, generally within the thickness range of 0.01−0.25 in (0.3−6.3 mm), to be used in a laminate.

Working life: See pot life.

Yield value: The stress, either normal or shear, at which a marked increase in deformation occurs without an increase in load.

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