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Short fiber reinforced composites for fused deposition modeling

Weihong Zhong [a,*], Fan Li [a], Zuoguang Zhang [a], Lulu Song [a], Zhimin Li [b]

[a] *Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, People's Republic of China*

[b] *Materials Engineering Program, Auburn University, Auburn, AL 36849, USA*

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Abstract

Addressed in this paper are critical material property issues related to the short fiber reinforced composite used in rapid prototyping and manufacturing (RP&M). Acrylonitrile–butadiene–styrene (ABS) copolymer has been a popular choice of material used in fused deposition modeling (FDM), a commonly used RP&M process. However, conventional ABS polymers in the filamentary form for FDM are known to be of low strength and hardness. In order to overcome this deficiency, ABS was modified by incorporating several different property modifiers including the short glass fiber, plasticizer, and compatibilizer. Glass fibers were found to significantly improve the strength of an ABS filament at the expense of reduced flexibility and handleability. The latter two properties of glass fiber reinforced ABS filaments were improved by adding a small amount of plasticizer and compatibilizer. The resulting composite filament, prepared by extrusion, was found to work well with a FDM machine.

Keywords: Composite; Fused deposition modeling; Short glass fiber; ABS

1. Introduction

Low-cost composite manufacturing technology has been an important research topic in the area of composite materials. A wide variety of composite processing methods have been developed, but most of these methods are of a long process cycle, laborious, and/or energy-intensive. The resulting high process costs have significantly constrained the scope of application for composites. Obviously, new and more effective manufacturing technologies for composites are highly desirable [1].

Rapid prototyping and manufacturing (RP&M) represents a group of novel manufacturing methods that entail building a 3-D object point by point and/or layer by layer. These methods are also commonly referred to as layer manufacturing (LM) and solid freeform fabrication (SFF) methods. A RP&M method normally begins with creating a computer aided design (CAD) or solid modeling file (e.g. in terms of the *.STL* format) to represent the object geometry, slicing this file into a multiple-layer data format (e.g. a CLI file format), and converting this layer-wise data into proper numerical control codes (e.g. CNC G- and M-codes). These codes are then used to control the X–Y–Z movements of a material-depositing nozzle and an object-supporting platform. When the nozzle is moved relative to the platform on an X–Y plane, a first layer of a solidifying material is dispensed from the nozzle and deposited onto a surface of the platform. Upon completion of the first layer, the nozzle is moved away from the platform by a predetermined distance in the Z-direction. A second layer of material is then deposited onto the first layer and adhered thereto. These procedures are then repeated to deposit a plurality of layers for building up the 3-D object.

Little has been done on the fabrication of SFF parts with high structural integrity [2–4]. Fiber reinforced composites are known to have great stiffness, strength, damage tolerance, fatigue resistance, and corrosion resistance. However, currently available SFF technologies, in their present forms, do not lend themselves to the production of continuous fiber composite parts. Some preliminary attempts have been made to use

* Corresponding author. Tel.: +86-10-82317122; fax: +86-10-82317127.

E-mail address: katiehong_2000@yahoo.com (W. Zhong).

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stereo lithography based techniques to fabricate both short and continuous fiber reinforced, UV-curable resins. In most cases, only composites with excessively low volume fractions of fibers were obtained and, hence, the resulting composites have exhibited low strength and stiffness. Furthermore, in such stereo lithography based techniques, only a laser- or UV-curable resin can be employed as the matrix material for a composite.

Modified laminated object manufacturing (LOM) has been used to prepare polymer matrix and ceramic matrix composites [5]. The process involves, for instance, feeding, laminating and cutting thin sheets of prepregs (pre-impregnated fiber preform) in a layer-by-layer fashion according to computer-sliced layer data representing cross sectional layers of a 3-D object. The process cycle typically consists of laminating a single sheet of prepreg to an existing stack, laser cutting the perimeter of the part cross section, and laser-dicing or 'cubing' the waste material. After all layers have been completed, the part block is removed from the platform, and the excess material is removed to reveal the 3-D object. This process results in large quantities of expensive prepreg materials being wasted.

Other SFF techniques that potentially can be used to fabricate short fiber- or particulate-reinforced composite parts include fused deposition modeling (FDM) and powder-dispensing techniques. The FDM process operates by employing a heated nozzle to melt and extrude out a material such as nylon, acrylonitrile–butadiene–styrene (ABS plastic), and wax. The build material is supplied in the form of a rod or filament. The filament or rod is introduced into a channel of the nozzle inside which the rod or filament is driven by a motor and associated rollers to move like a piston. The front end, near a nozzle tip, of this piston is heated to become melted; the rear end or solid portion of this piston pushes the melted portion forward to exit through the nozzle tip. The nozzle is translated under the control of a computer system in accordance with previously sliced CAD data to trace out a 3-D object point by point and layer by layer. In principle, the filament may be composed of a short fiber or particulate reinforcement dispersed in a matrix (e.g. a thermoplastic such as nylon). In this case, the resulting object would be a short fiber composite or particulate composite with improved properties. Presented in this paper are the results of a study on short fiber reinforced ABS polymers for use as a FDM feedstock material.

2. Experimental

2.1. Raw material

The raw materials used in this study were mainly ABS plastic (Qimei-757, Taiwan Qi Mei), short glass fiber reinforced ABS (GFABS-30, Beijing Chemistry Institution of the Ministry of Chemical Industry), LLDPE (0209, the Chemistry Institute of the Chinese Academy of Sciences; 7042, Qi Lu Petrochemicals) and Hydrogenated Buna-N. The ABS matrix in GFABS-30 was Qimei-757.

2.2. Equipment

A twin-screw extruder TE-34, made by Nanjing Ke Ya with a screw diameter (SD) of 34 mm and length/diameter (L/D) ratio of 34 was used. Also used was a single screw extruder with a screw diameter of 30 mm and length of 800 mm, respectively. A Model MEM-250 Multi-functional RP&M Machine was used in this study. This machine, developed by Tsinghua University in Beijing, China, provides both FDM and LOM functions in one machine. Controlled by a computer, the whole machine consists of two compartments: the upper one accommodating the motion control and linear motion device system and the lower one containing the part-building chamber. A German-made ZD-150 tensile test machine with a 100 kg load capacity was employed to measure the key mechanical properties of ABS plastics and their composites.

2.3. Sample preparation

The raw materials were mixed in the twin-screw extruder and then extruded and granulated into small pellets. The pellets were then fed into the single screw extruder and drawn into a filament form. The diameter of the filament was controlled to fall in the range of 1.75–1.90 mm by adjusting the rotational speed of the single screw and the filament-pulling speed of the tractor. The molding conditions of the single screw extruder in this experiment are listed in Table 1.

Table 1
Molding condition of single screw extruder

Temperature (°C)				Current intensity (A)	Rotational speed (r min^{-1})
Spray nozzle	Measuring section	Compressing section	Providing section		
200	270	24	140	3	140

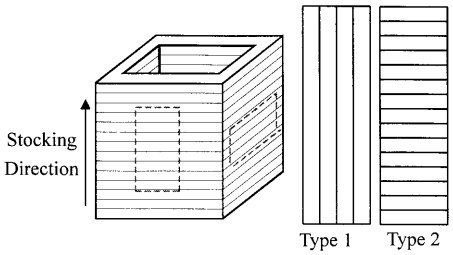

Fig. 1. Sketch of the samples.

The drawn filament was then wound up onto a drum and later fed into the MEM-250 operating in the FDM mode. The dispensing nozzle of MEM-250, under the control of a computer, was driven to build desired parts essentially point by point and layer by layer. The nozzle was controlled to move along a square route to form two sizes of square boxes or 'frames' (Fig. 1): 50 mm × 50 mm × 100 mm and 100 mm × 100 mm × 90 mm. The temperatures of the nozzle and the build chamber are 250 and 60°C, respectively. Two types of sample were machined from either frame, as indicated in Fig. 1. The direction of the sample length was parallel to that of the nozzle movement direction (parallel to the X–Y plane or layer plane) for Type 1 samples and was perpendicular for Type 2 samples (sample length is in the Z- or thickness direction). The samples are each 90 mm long and 20 mm wide with the thickness being equal to the diameter of the feedstock filament.

3. Results and discussion

3.1. Basic requirements of the material for RP&M

The materials for use in RP&M must meet the design and application requirements of the intended products and, in the meantime, be compatible with the RP&M process. For FDM, specifically, the materials must exhibit certain thermo-physical, mechanical, and layer-stacking characteristics.

The requirements on thermo-physical properties include a proper range of melting and solidification temperatures, low coefficient of thermal expansion, minimal shrinkage, high heat resistance, no or few volatile molecules (when the material is in the liquid state), and no phase transformation in the solid state. On the one hand, the melting point should not be too low in order for the material to have a high softening point (or heat distortion temperature). On the other hand, the melting point should not be too high to avoid a high processing temperature. Generally, a part-building zone temperature of 70–100°C is preferred. The suitable solidification temperature range is preferably 5–10°C below the softening point. There is amorphous part as well as crystalline part in a semi-crystalline polymer. The solid to liquid transformation of the amorphous part is a gradual process without a definitive temperature point. The commonly used term 'softening point' is a critical temperature in the transformation. A lower thermal expansion is essential to achieving the part dimensional accuracy. The amount of linear shrinkage in a part between the build temperature and the end-use temperature should be less than 1%.

Key mechanical properties of a RP&M material include strength, stiffness, ductility and flexibility. In the process of FDM, the material needs to be fabricated into a filament form. The drawn filaments were fed into the nozzle of MEM-250 as the feedstock material with the leading portion of the filament being melted before exiting the orifice of the dispensing nozzle. The solid portion of the filament, being driven by a set of rollers, acted as a piston to push the fused material out of the nozzle orifice. Therefore, the material needs an adequate strength, ductility and flexibility. At the same time, to keep the surface quality of the parts the material also requires enough rigidity to prevent the surface from wearing and tearing.

The raw material for the FDM process is normally a thermoplastic and the process can be realized by the solid-to-liquid transformation of the thermoplastics inside the nozzle. Proper rheological properties are needed; i.e. a low viscosity after the filament is liquefied. A lower viscosity makes it easier for the nozzle to dispense the polymer melt. The deposited material must be capable of solidifying in a relatively short time in order to achieve a good build speed. However, a sufficient amount of time is needed to allow a solidifying layer to well adhere to a previously deposited layer. In addition, the solidification process should result in minimal internal stress in the part.

3.2. Modifications of ABS composites

According to the above requirements, ABS, an engineering plastic, was selected as the raw material in the present study due to its ready availability in the market and good balance of processing and performance properties. Its softening point is approximately 100°C, which could meet the heat-resistance requirement of the FDM parts. ABS begins to flow at about 200°C so the part-building temperature does not have to be too high. ABS begins to decompose at approximately 250°C. Thus, there is a disparity of 50° between the flowing temperature and the decomposing temperature. This makes the actual heating temperature range wide enough to allow for a wide processing window in which the material can be heated to flow properly without decomposing. Besides, ABS has good mechanical properties and fluidity. Pure ABS, however, still exhibited

excessively large shrinkage, resulting in less-than-satisfactory part accuracy.

In order to improve the properties of ABS, short glass fiber was added as a reinforcement. Compared with pure ABS, the strength of short glass fiber reinforced ABS composite (GFABS-30) was significantly increased, and both the softening temperature and the heat distortion temperature were increased as well. In the meantime, the shrinkage was decreased and the surface rigidity was improved, but the surface toughness was compromised. This composite could not be made into a continuous filament wound on a cylindrical drum because it became brittle after being extruded and cooled to room temperature. This brittleness makes it impossible to feed GFABS-30 into the FDM machine. To improve its toughness, the approach of changing the fiber content in the composite was attempted. Glass fiber reinforced ABS composites with a glass fiber (GF) content of 15, 20 and 25% were obtained by adding pure ABS into GFABS-30 which had a GF content of 30%. The toughness of the resulting composites was similar to that of GFABS-30, indicating that this method was not feasible.

Another approach was then attempted by adding LLDPE into GFABS-30 to improve the ductility and flexibility. The experimental results have indicated that LLDPE, a flexible linear polymer, is an effective toughening agent for GFABS-30. In the present experiments, four compositions, designated as 1#, 2#, 3# and 4# (Table 2), were formulated. In these compositions the weight contents of GF were 10.2 and 13.2%. Different LLDPE grades (7042 and 0209 from two different suppliers), each with two different proportions of LLDPE in the short fiber composite, were used. In this way, composite filaments were extruded successfully. The appearance and toughness of the composite filaments made from 1# were found to be better than those of the other three compositions. However, the content of LLDPE in 1# was only 10%, while that of other three was up to 30%. This difference might be ascribed to the limited compatibility between LLDPE and the ABS composite host. LLDPE could be well mixed with ABS when the LLDPE content was only 10%. Higher LLDPE contents than 30% appeared to result in extensive phase separation between the LLDPE-rich phase and the ABS matrix, which had a detrimental effect on the appearance and the ductility of the filaments. Microscopy observations on the cross section of the filament indicated that the surface and the core of the drawn filament were separated into two layers in Samples 2#, 3# and 4#.

To overcome this incompatibility problem, hydrogenated Buna-N was added to the mixture systems in compositions 6# and 7#. On the one hand, there are butadiene (B) and acrylonitrile (A) groups in Buna-N, which are structurally similar to ABS. On the other hand, the main-chain structure of hydrogenated Buna-N is $-(CH_2)_n-$, which is structurally similar to LLDPE. Therefore, hydrogenated Buna-N could serve as a compatibilizer between LLDPE and ABS, which significantly improved the properties of the composite systems. The surface and core areas of the filament were no longer separated. Both the toughness and appearance of the filament were also improved, even when the content of GF was further increased. From the appearance the filaments of the seven compositions studied, one could not observe any significant difference in filament quality between the composite samples containing different trades of LLDPE.

Ethylene-ethyl-acrylate (EEA), an elastomer, did not have any obvious effect on the properties of the resulting composites. Possibly due to its lubricity, the wax used in the composite systems makes the material extrusion through the nozzle more easily.

Figs. 2–5 show representative SEM pictures of the cross sections of the filaments prepared from compositions 1#, 2# and 6#, 7#, respectively. To prepare appropriate SEM samples, the filament was soaked in liquid nitrogen to freeze the structure so that the filament could be broken in a brittle fashion.

Table 2
Modified formula of GFABS[a]

No. formula	Raw material						
	GFABS-30 (g)	ABS (g)	LLDPE (g)	PE (wax) (g)	Hydrogenated Buna-N (g)	EEA (g)	Weight content of GF (%)
1#	440	440	100 (0209)	20	–	–	13.2
2#	340	340	300 (0209)	20	–	–	10.2
3#	340	340	300 (7042)	20	–	–	10.2
4#	340	240	300 (7042)	20	–	100	10.2
5#	–	880	100 (0209)	20	–	–	0
6#	440	430	100 (0209)	20	10	–	13.2
7#	600	270	100 (0209)	20	10	–	18.0

[a] The content of GF is received by the grams of GFABS-30 times 30% (g GF) and then divided by the whole grams of the system because there is 30% of glass fiber in weight in GFABS-30.

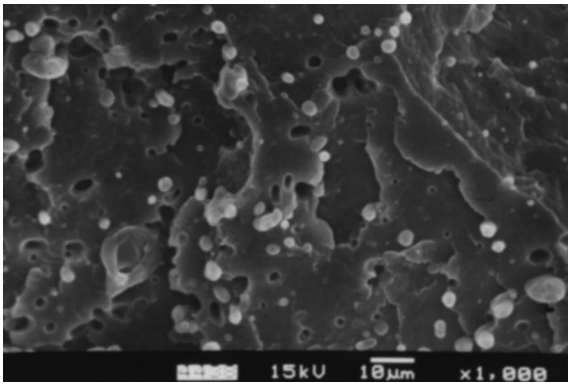

Fig. 2. Cross section of the filament from system 1 # by SEM.

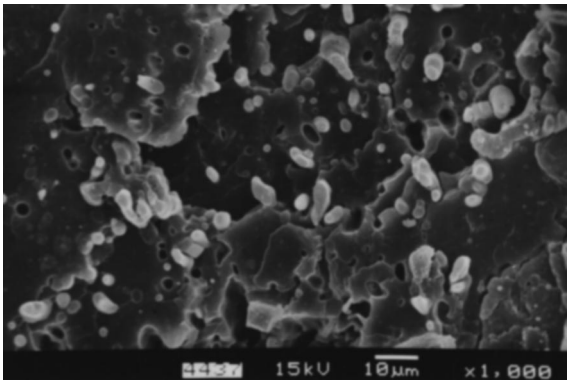

Fig. 3. Cross section of the filament from system 2 # by SEM.

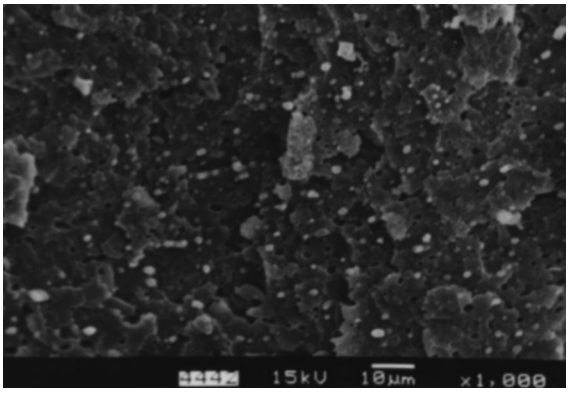

Fig. 4. Cross section of the filament from system 6 # by SEM.

In these micrographs, white LLDPE phases were found to be dispersed in the black ABS matrix. Compared with the phase morphology in Figs. 4 and 5 for the composite compositions containing the interfacial compatibilizer, Hydrogenated Buna-N, the LLDPE phase particles in Figs. 2 and 3 are much larger in sizes. In particular, the length of LLDPE phase particles is up to 10 μm in Fig. 3 which shows the phase morphology of Composition 2 # with a LLDPE content of 30%. By contrast, Figs. 4 and 5 demonstrate that the compatibility between ABS and LLDPE increases significantly and the dispersion of LLDPE is more uniform after the compatibility agent is added to the material system. Hence, the surface quality and mechanical properties of Compositions 6 # and 7 # are better than those of 1 # and 2 # .

3.3. Mechanical properties of the modified GFABS samples made by FDM

Two types of tensile samples were made from the modified GFABS by FDM. Type 1 was used to measure the longitudinal strength of glass fiber reinforced ABS to assess the effect of modifications. The tensile strength of Type 2 samples was used to mainly determine the adhesive strength between the composite layers. In order to reduce the effect of the clamping force from the clamp on the precision of the test results, a layer of adhesive tape was adhered onto the clamped part of the sample and a layer of rubber was adhered onto the rim of the clamp. The frictional coefficient between the sample and the clamp rim was also increased in this way. Besides, the distribution of the clamping force is more even because the rubber reduces the stress concentration on the sample.

From Tables 2 and 3, it can be found that the strength of the modified GFABS is markedly higher than that of the unmodified counterpart. Moreover, the strength of GFABS is much higher than that of ABS when Type 1 samples were tested. The data of Type 2 samples show that the properties of the modified materials are much higher than those of the unmodified

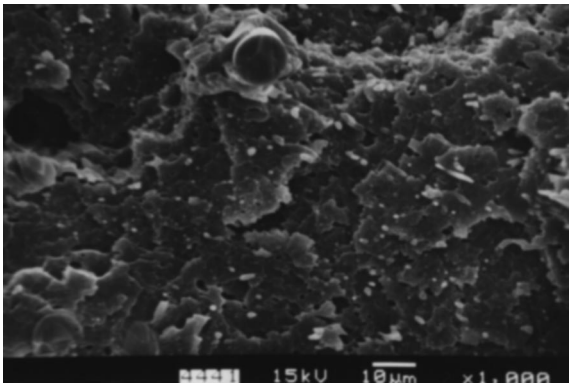

Fig. 5. Cross section of the filament from system 7 # by SEM.

Table 3
Tensile strength of GFABS composites by FDM

No. formula	Type of sample				
	1 #	2 #	5 #	6 #	7 #
Type 1 (kg)	38.93	29.16	24.50	52.37	58.60
Type 2 (kg)	1.19	0.72	12.25	8.81	11.15

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