

Rheological Characterization of Aqueous Polysaccharide Mixtures Undergoing Shear

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We studied the rheological properties of aqueous polysaccharide mixtures, prepared by blending two compatible biopolymers, i.e. sodium carboxymethylcellulose and xanthan, under destructive and non-destructive shear conditions, in order to evaluate synergistic/non-synergistic effects of mixed polysaccharide systems. The rheological experiments were carried out with the controlled stress rotational rheometer to detect the response of structured samples at low shear stresses. The flow behavior and the viscoelastic properties of polysaccharide systems under shear conditions were examined by applying continuous shear and oscillatory tests at ambient temperature. The empirical analysis of the flow behavior enabled us to evaluate the deviations in the zero shear viscosity, and the intensity of the shear-thinning behavior as determined for investigated binary mixtures, when compared to the flow behavior of pure component solutions. The mechanical properties of polysaccharide mixtures in the range of the linear viscoelastic response were analyzed with the generalized Maxwell model and the relaxation spectra were determined. The examined mixtures exhibited complex rheological behavior under the shear conditions, regarding the flow characteristics as well as the viscoelastic properties in the linear viscoelastic regime.

Keywords:

Aqueous polysaccharide mixtures, sodium carboxymethylcellulose, xanthan, rheology, shear flow, viscoelasticity

Introduction

Many polysaccharides play an important role in the field of science and technology due to their unique properties. These natural polymers are biodegradable, nontoxic, and widely available materials at low costs. They exhibit good compatibility and water solubility. The wide range of practical applications exploits the ability of polysaccharides to thicken or structure many times their own mass of water.¹ In this way biopolymers modify the properties of aqueous environment and control the rheology of hydrated systems.

Polysaccharides are widely used in food processing and preparation to stabilize emulsions and suspensions, and to improve the texture of food products. Within pharmaceutical and biomedical applications, biopolymers act as highly effective substances to control the release of a drug. Due to film-, membrane- and gel-forming properties, polysaccharides have found extensive applications for the immobilization of proteins, enzymes and animal cells, and act as important components in mem-

brane manufacturing. The water-retention properties improve the processing of ceramics² and the formulation of building materials in construction applications. The oil industry employs biopolymers due to their high swelling at low polymer concentrations, high efficiency as suspending agents, high shear thinning behavior and extreme compatibility with high concentrations of various salts and temperatures. Aqueous polysaccharide solutions can be successfully used as model fluids in order to simulate the complex rheological behavior of materials employed in various technological processes such as the mixing operation.^{3,4,5}

When different polysaccharides which exhibit a wide range of rheological properties, originating in peculiar structural properties, are mixed together, they are expected to have specific behavior, to improve the applicability of each separately used polysaccharide, and possibly to have cost advantages.^{2,6,7} In many cases, polysaccharide mixtures exhibit a behavior which is not simply the linear combination of individual contributions. In fact, by blending different polysaccharides with various structural properties, positive or negative effects can be observed.

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The biopolymer systems, investigated in our study, are aqueous mixtures of sodium carboxymethylcellulose (Na CMC) and xanthan. Separately used, both polysaccharides have found many practical applications. As physiologically harmless materials, they are widely used for pharmaceutical preparations, cosmetics, personal care products, and food products.^{1,8,9} Various technical applications can be found in oil field, agricultural, paint, and ceramic industry, and many other branches.^{1,10,11,12} The wide range of Na CMC applications involves a wide variety of technological processes, such as mixing, pumping, heating, cooling, and separation operations¹³. Both polysaccharides are common polymers used for turbulent flow experiments¹⁴ as well as for studying the effects of shear-dependent flow properties and viscoelasticity on the hydrodynamics in mixing operations, performed in the laminar flow regime.^{3,4} Aqueous Na CMC-xanthan mixtures have already found practical application as model fluids intended for studying power consumption in a double planetary mixer with non-Newtonian and viscoelastic materials⁵. By applying primary normal stress difference measurements, *Zhou et al.*⁵ noticed the non-linear effect of polymer concentration on the elasticity of fluids. As a possible reason for the significantly different behavior of one of the examined mixtures, they suggest the structural configuration of the specific mixture. Such deviations in the rheological behavior of mixed polysaccharides originate from the nature of each polymer in the mixture and various interactions which occur between polymer chains.

Sodium carboxymethylcellulose (Na CMC) is a water-soluble derivative of biologically degradable natural polysaccharide cellulose, a fundamental component of plant cell walls. In aqueous solution it represents a complex rheological system, since it forms aggregates and associations, and hence higher level structures.¹⁵ At higher polymer concentrations, extended Na CMC chains start to overlap and undergo the coiling process, which causes formation of the network structure in the concentrated regime.¹⁶ With higher polymer concentration the polymer-polymer interactions (entanglements) become the main factor influencing the rheology of the Na CMC solution.⁸ Above the overlap concentration, aqueous Na CMC solutions exhibit more marked shear-thinning flow behavior and viscoelastic properties^{8,13,17} and can be seen as entanglement polymer solutions. The polymer concentration, temperature, salt content, the presence of surfactants, and the molecular structure have a considerable effect on the rheological properties of Na CMC.^{8,13,16,17,18}

Xanthan, an anionic exocellular microbial polysaccharide, is produced by the bacterium

Xanthomonas campestris. Its primary structure consists of a linear cellulosic backbone with trisaccharide sidechains, attached to alternating backbone residues.¹ The semi-flexible xanthan molecule undergoes a conformation transition from an ordered double helix to a random coil when heated, depending on the ionic strength of the solution.¹⁹ With the polymer in a water-soluble ordered form, aqueous solutions in semi-dilute and concentrated regime generally have high viscosity at low shear rates and show characteristic weak gel properties even at low polymer concentrations.^{20,21,22} Under small-deformation conditions, the weak gel behaves as a viscoelastic solid.¹ As the deformation increases, the weakly formed three-dimensional network breaks down and the material starts to flow. The rupture of weak junctions upon shear, and their restoration upon the cessation of shear, could account for xanthan thixotropy. The double-stranded helix formation stabilizes xanthan self-association, and is responsible for the insensitivity of the viscosity to salt and pH changes.²³

The objective of this paper is to present the rheological characterization of aqueous Na CMC-xanthan mixtures under destructive and nondestructive shear conditions in order to evaluate synergistic/non-synergistic effects of blended polymers. Biopolymer mixtures used in our study were prepared by blending two polysaccharides with different rheological properties. The microbial polysaccharide xanthan, exhibiting weak gel properties in aqueous solutions, was added to Na CMC at different mass fractions, in order to investigate the differences in the rheological behavior of aqueous Na CMC-xanthan mixtures in concentrated regime, when the mass ratio of blended polymers changes. The examined mixtures exhibit complex rheological behavior under shear conditions, regarding the flow characteristics as well as the viscoelastic properties in the linear viscoelastic regime. Due to the complex rheological behavior of examined mixtures, indicating that these systems can be regarded as structured liquids, special attention was paid to measurements of the response at low stresses by using a sensitive controlled-stress rheometer.

Phenomenological modeling of linear viscoelastic properties

The quantitative interpretation of the rheological data, obtained with experimental tests, requires description of the rheological response by using mathematical model, providing different parameters with various physical meanings. The rheological models, based on the phenomenological approach, have been developed to achieve maximum agree-

ment between the predicted and experimental rheological properties of a fluid, by taking into account only the principles of continuum mechanics, regardless of structural characteristics.¹ Despite the fact that for structured systems, such as weak gels, satisfactory rheological modeling has not been developed yet due to their peculiar structural characteristics and physical properties, we examined the linear viscoelastic properties by using the generalized Maxwell model, based on the phenomenological approach.

A number of small-deformation experiments are used to measure the linear viscoelastic response of the material.^{24,25} When the small-amplitude oscillatory shear technique is used, the sample is subjected to a sinusoidal shear strain, γ , and the resulting oscillatory shear stress, τ , is measured. As a response of the material to the oscillating strain input, the shear stress will also oscillate sinusoidally at the same oscillation frequency, ω , but in general it will be shifted by the phase angle, δ , with respect to the strain wave as described with the following mathematical expressions:²⁵

$$\gamma = \gamma^\circ \sin \omega t, \quad (1)$$

$$\tau = \tau^\circ \sin(\omega t + \delta), \quad (2)$$

where γ° is the shear strain amplitude, and τ° is the shear stress amplitude. By decomposing the stress wave into two waves of the same frequency, two dynamic moduli, the storage modulus, G' , and the loss modulus, G'' , are introduced:

$$\tau = \gamma^\circ G' \sin \omega t + \gamma^\circ G'' \cos \omega t. \quad (3)$$

The storage modulus, G' , and the loss modulus, G'' , are the real and the imaginary component of the complex modulus, G^* , respectively:

$$G^* = \frac{\tau^\circ}{\gamma^\circ} = G' + iG'' = \sqrt{G'^2 + G''^2}, \quad (4)$$

and the ratio between the dynamic moduli can be written as follows:

$$\frac{G''}{G'} = \tan \delta. \quad (5)$$

When the mechanical properties of the material are experimentally determined, the linear viscoelastic behavior can be analyzed by using a proper mechanical model. The generalized Maxwell mechanical model can be represented as a parallel series of Maxwell elements, consisting of linear springs and dashpots.²⁶ Each Maxwell element has a characteristic relaxation time, λ , defined as the ratio between the shear viscosity, η , and the elastic modulus, G . In the linear viscoelastic region, where

the strain of a particular material varies linearly with the stress, the response of a single Maxwell element can be written in a differential form:^{25,27}

$$\tau + \lambda \frac{d\tau}{dt} = \eta \dot{\gamma}, \quad (6)$$

where τ is the shear stress, λ is the relaxation time, t is the time, η is the shear viscosity, and $\dot{\gamma}$ is the shear rate. By using a single Maxwell element to describe the linear viscoelastic response of the liquid under oscillatory shear conditions, the frequency-dependent dynamic moduli can be mathematically expressed as follows:

$$G'(\omega) = G \frac{(\omega\lambda)^2}{1 + (\omega\lambda)^2}, \quad (7)$$

$$G''(\omega) = G \frac{\omega\lambda}{1 + (\omega\lambda)^2}. \quad (8)$$

The rheological behavior of many liquids in the linear viscoelastic regime is often too complex to be successfully described by using a single Maxwell element model. Therefore, the generalized Maxwell model is frequently used to describe the linear viscoelastic response of the liquid. When the model is described in terms of a discrete set of Maxwell elements, it is possible to incorporate a discrete range of relaxation times, λ_k , and relaxation strengths, g_k , within the model. The complete set of (g_k, λ_k) is called the spectrum of the relaxation times.²⁷ If the generalized Maxwell model with a limited number of Maxwell elements is used to describe the dynamic response of the viscoelastic liquid in the linear viscoelastic regime, the discrete relaxation spectra can be determined from experimentally obtained dependencies of the storage modulus, G' , and the loss modulus, G'' , on the oscillation frequency, ω :²⁵

$$G'(\omega) = \sum_{k=1}^N g_k \frac{(\omega\lambda_k)^2}{1 + (\omega\lambda_k)^2}, \quad (9)$$

$$G''(\omega) = \sum_{k=1}^N g_k \frac{\omega\lambda_k}{1 + (\omega\lambda_k)^2}. \quad (10)$$

To fit our experimental data, we used a model with five Maxwell elements. First we selected a set of relaxation times, λ_k , evenly spaced on a log scale, i.e. one per decade, and then we ran the fitting procedure to determine the relaxation strengths, g_k , using the least-squares regularization method that minimizes the sum of squared relative deviations between the calculated values and the experimental data.²⁵

Experimental

Materials and preparation

Sodium carboxymethylcellulose (Na CMC), used in our study, with the trade name BLANO-SE® 7HF cellulose gum, is a commercial product of Aqualon France, Hercules. Determined by the producer, the molar mass of this purified Na CMC powder is $4.35 \cdot 10^5 \text{ g mol}^{-1}$, with the degree of substitution in the range of 0.65–0.90, pH of 6.5–8.5, and sodium fraction of 7.0–8.9 %. Its purity is 99.5 % minimum. Xanthan, known as KELTROL®, was supplied by CP Kelco. The lot number of xanthan sample used was 8LO68OV.

Water-based salt-free solutions of Na CMC and xanthan (X), having a polymer mass fraction of $w = 1.0 \%$ were prepared by dissolving a known amount of polymer powder in distilled water at room temperature. All samples were stirred by hand for few minutes and stored in a refrigerator at $4 \text{ }^\circ\text{C}$ in covered glass beakers, allowing the powder to hydrate for several days to ensure that the sample had completely dissolved.

The mixtures of Na CMC-xanthan (CX) with a variable mass ratio between two polymers and a constant total polymer mass fraction of $w = 1.0 \%$ were prepared by blending appropriate amounts of the two polysaccharide solutions at room temperature. The rheological behavior of aqueous Na CMC-xanthan mixture was investigated in three different mass ratios.

During the mixture preparation, the storage period, and the measurements no stability problems occurred.

Measurement techniques

The rheological measurements used in this study were carried out by using a HAAKE RS 150 controlled stress rheometer. A cone and plate geometry of the sensor system was used to ensure a constant shear rate in the sample. The cone diameter was 60 mm, with the cone angle of 2° . All experiments were carried out at a temperature of $20 \pm 0.3 \text{ }^\circ\text{C}$. The temperature was externally controlled by circulator HAAKE DC5-K20.

As a large deformation technique, the continuous-shear experiments were applied to determine the flow behavior under destructive shear conditions when the structure of the material is broken down.

The viscoelastic response of aqueous polysaccharide systems was examined by carrying out oscillatory measurements. The stress-sweep tests at a frequency of 1 Hz enabled us to follow the behavior of dynamic moduli, while the shear stress ampli-

tude was changing in order to determine the limit of linear viscoelastic response.

Hence, the mechanical spectra in the range of the linear viscoelastic regime, when non-destructive shear conditions enable the material to preserve the structure, were obtained with frequency tests at a constant strain amplitude of 3 %.

Results and discussion

Flow behavior under shear conditions

The first part of our paper represents the results of the continuous-shear experiments under the conditions of large shear deformations for aqueous Na CMC-xanthan mixtures at total polymer mass fraction of $w = 1.0 \%$. The experimental tests were repeated at least two times, and the results found to be reproducible in the range of experimental error.

The Na CMC-xanthan mixtures exhibit complex time-dependent non-Newtonian flow behavior of the shear-thinning type, as shown in Figure 1. Pure Na CMC solution exhibits the first Newtonian plateau at low shear-stresses and moderate shear thinning time-independent flow behavior (Figure 1a), whereas pure xanthan solution shows a significant effect of shear history and more pronounced shear thinning behavior (Figure 1b). At low shear conditions, the ‘up flow curve’ of the xanthan solution exhibits the first Newtonian plateau and high values of shear viscosity, indicating strong resistance of the material to flow, while the ‘down flow curve’ indicates continuously decreasing viscosity (Figure 1b). The ‘up flow curve’ and the ‘down flow curve’ represent the viscosity as a function of increasing and decreasing shear stress, respectively. As the shear stress increases, a strong decrease of shear viscosity is detected in a narrow shear stress range. Such behavior of the xanthan solution shows existence of a three-dimensional network structure, consisting of long polymer chains associated into higher level structural formations as observed for weak gels,^{19,20} while the Na CMC solution behaves as an entanglement polymer solution in a concentrated regime⁸ (Figure 2).

Under destructive shear conditions our attention is primarily focused on the effect of the shear action during dynamic process of the structural breakdown in the samples. The flow behavior of aqueous Na CMC-xanthan mixtures when the shear stress increases (‘up flow curves’) is illustrated in Figure 1a. When xanthan at mass fraction of 0.25 is present in the Na CMC solution, the zero-shear viscosity remains unchanged, while the shear-thinning behavior becomes more pronounced at higher shear stresses. The presence of xanthan at mass fraction

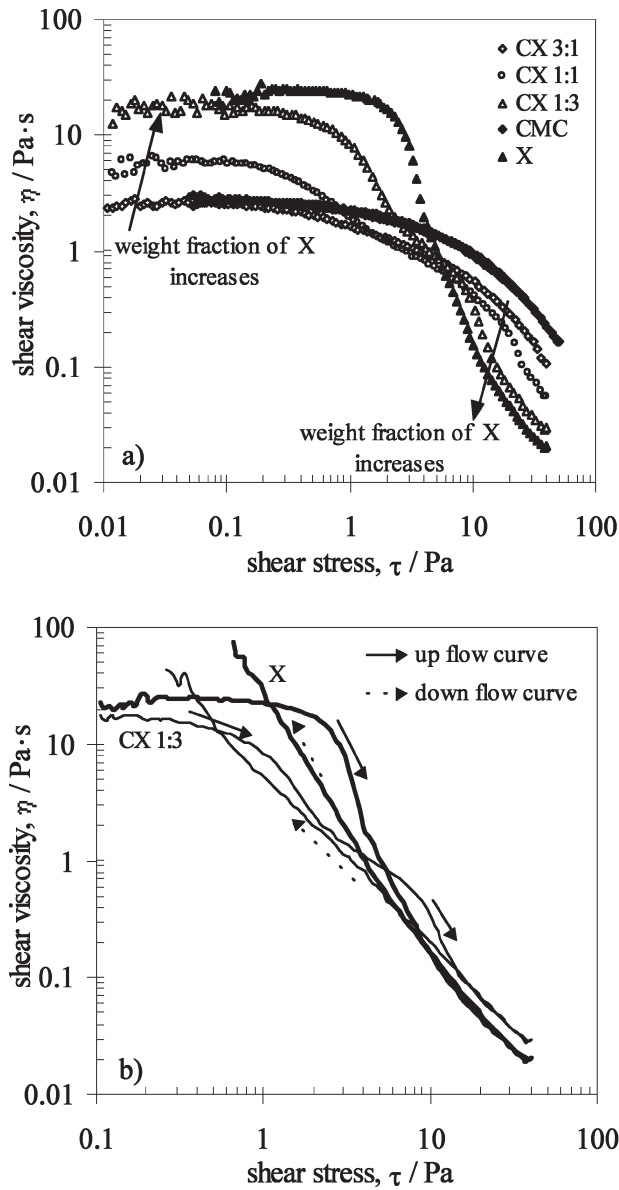


Fig. 1 – The flow behavior of pure Na CMC solution (CMC), pure xanthan solution (X), and aqueous Na CMC-xanthan mixtures (CX) at different mass ratios and a total polymer mass fraction of $w = 1.0\%$, determined at temperature of $20 \pm 0.3^\circ\text{C}$ and represented as a) up flow curves, b) up and down flow curves

of 0.25 only enhances the shear-thinning behavior, without changing the type of the ‘up flow curve’, which is controlled by Na CMC properties. As the mass fraction of xanthan increases up to 0.5, the zero shear viscosity increases, and the ‘up flow curve’ changes its shape more pronouncedly. It seems that the gradual decrease of shear viscosity with increasing shear stress passes over two flow regimes. With a further increase of mass fraction of xanthan the effect is even more pronounced. Figure 1b illustrates the ‘up and down flow curves’ (i.e. the shear stress first increases and then decreases dur-

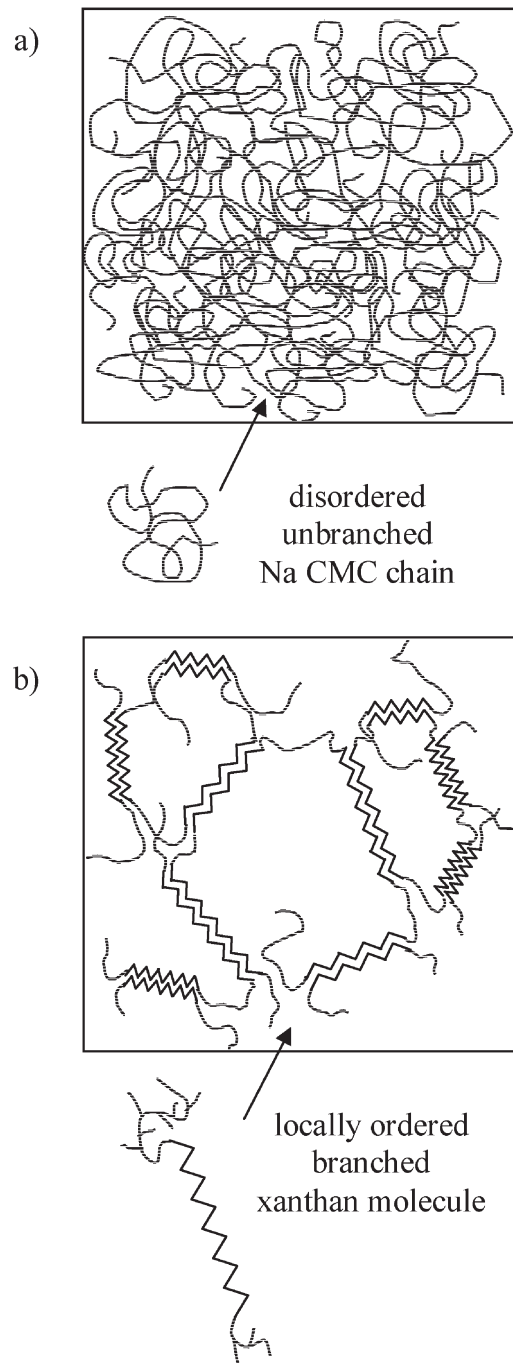


Fig. 2 – Schematic representation of the structural conditions of a) concentrated Na CMC solution, b) weak gel network of xanthan.

ing experimental test). A double S-shape of the flow curves found for the mixtures is only observed with the ‘up flow curves’, indicating that two flow regimes of the Na CMC-xanthan mixtures originate in two structural mechanisms and are not caused by slippage effects.

We can conclude that at low shear stresses the presence of small quantities of xanthan (up to mass fraction of 0.25) doesn’t change the flow properties of the Na CMC solution, which shows that the

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