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, nontoxical, 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. 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 membrane manufacturing. The water-retention properties improve the processing of ceramics 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.

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. 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. Various technical applications can be found in oil field, agricultural, paint, and ceramic industry, and many other branches. The wide range of Na CMC applications involves a wide variety of technological processes, such as mixing, pumping, heating, cooling, and separation operations. Both polysaccharides are common polymers used for turbulent flow experiments 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. 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 materials. By applying primary normal stress difference measurements, Zhou et al. 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. 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. With higher polymer concentration the polymer-polymer interactions (entanglements) become the main factor influencing the rheology of the Na CMC solution. Above the overlap concentration, aqueous Na CMC solutions exhibit more marked shear-thinning flow behavior and viscoelastic properties 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.

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. 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. 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. Under small-deformation conditions, the weak gel behaves as a viscoelastic solid. 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.

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. 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. When the small-amplitude oscillatory shear technique is used, the sample is subjected to a sinusoidal shear strain, \( \gamma \), and the resulting oscillatory shear stress, \( \tau \), 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, \( \omega \), but in general it will be shifted by the phase angle, \( \delta \), with respect to the strain wave as described with the following mathematical expressions:

\[
\gamma = \gamma^0 \sin \omega t, \tag{1}
\]
\[
\tau = \tau^0 \sin (\omega t + \delta), \tag{2}
\]

where \( \gamma^0 \) is the shear strain amplitude, and \( \tau^0 \) 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:

\[
\tau = \gamma^0 G' \sin \omega t + \gamma^0 G'' \cos \omega t. \tag{3}
\]

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

\[
G^* = \frac{\tau^0}{\gamma^0} = G' + iG'' = \sqrt{G'^2 + G''^2}, \tag{4}
\]

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

\[
\frac{G''}{G'} = \tan \delta. \tag{5}
\]

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. Each Maxwell element has a characteristic relaxation time, \( \lambda \), defined as the ratio between the shear viscosity, \( \eta \), 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:

\[
\tau + \lambda \frac{d\tau}{dt} = \eta \gamma, \tag{6}
\]

where \( \tau \) is the shear stress, \( \lambda \) is the relaxation time, \( t \) is the time, \( \eta \) is the shear viscosity, and \( \gamma \) 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:

\[
G' (\omega) = G \frac{(\omega \lambda)^2}{1 + (\omega \lambda)^2}, \tag{7}
\]
\[
G'' (\omega) = G \frac{\omega \lambda}{1 + (\omega \lambda)^2}. \tag{8}
\]

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, \( \lambda_k \), and relaxation strengths, \( g_k \), within the model. The complete set of (\( g_k \), \( \lambda_k \)) is called the spectrum of the relaxation times. 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, \( \omega \):

\[
G' (\omega) = \sum_{k=1}^{N} g_k \frac{(\omega \lambda_k)^2}{1 + (\omega \lambda_k)^2}, \tag{9}
\]
\[
G'' (\omega) = \sum_{k=1}^{N} g_k \frac{\omega \lambda_k}{1 + (\omega \lambda_k)^2}. \tag{10}
\]

To fit our experimental data, we used a model with five Maxwell elements. First we selected a set of relaxation times, \( \lambda_k \), 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.
Experimental

Materials and preparation

Sodium carboxymethylcellulose (Na CMC), used in our study, with the trade name BLANOSE 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 \(4.35 \times 10^5\) 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\(^\circledR\), was supplied by CP Kelco. The lot number of xanthan sample used was 8LO680V.

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 °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 ± 0.3 °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 amplitude 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 regime\(^{8}\) (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
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 during 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
structure of the polysaccharide mixture at low shear is defined with the structural conditions of Na CMC. We assume that the concentration of xanthan molecules which are present as ordered helices and probably linked through intermolecular interactions, is too low to contribute to the entanglement structure formed by Na CMC polymer chains.

When the Na CMC-xanthan mixture is subjected to higher shear stresses, the shear viscosity of the mixture decreases more rapidly compared to pure Na CMC solution. The latter observation shows that the structure of the mixture is more sensitive to higher stresses than the structure of pure Na CMC.

At higher mass fractions of xanthan (above 0.5), the zero-shear viscosity has significantly higher values, indicating that by the additional formation of the network structure xanthan helices contribute to higher resistance to flow. Under the conditions of flow regime, the shear-thinning behavior becomes slightly more pronounced. The zero-shear viscosity reaches almost the same value as with the pure xanthan solution when the weight fraction of xanthan increases to 0.75, and the intensity of the shear-thinning behavior is similar as for the xanthan solution. The structure of the mixture breaks down at much lower shear stresses and the ‘up flow curve’ passes over two flow regimes. In the intermediate region of the examined shear stresses, the Na CMC fraction significantly influences the flow pattern of the mixture. At high shear stresses the flow behavior is again similar to that of the pure xanthan solution.

In order to evaluate the synergistic/non-synergistic effect of the Na CMC-xanthan mixtures in terms of flow behavior, the experimental data were empirically analyzed in two flow regimes. The zero shear viscosity of the Na CMC-xanthan mixtures is lower than it would be expected from the linear relationship drawn through the flow behavior of pure components (considering $\eta_0$ or $\log \eta_0$ vs. mixture composition), indicating that the structure of the mixture is less resistant to flow.

The intensity of the shear thinning behavior was quantitatively examined by applying the empirical parameter $\Delta \log (\eta)/\Delta (\log \tau)$. This empirical parameter is a measure of decrease of the shear viscosity within the shear stress range, limited with two values of shear stress. The lower limit is the critical shear stress above which shear viscosity decreases sharply, and is determined as the shear stress at which shear viscosity decreases by 5 %. The upper limit is chosen as the maximum shear stress experimentally reached for all examined systems and has the value of 40 Pa. As shown in Figure 3, a smooth non-linear increase of intensity of the shear-thinning behavior for the Na CMC-xanthan mixtures, is observed.

The synergistic effect of the Na CMC-xanthan mixtures, observed as deviations from the flow behavior of pure polysaccharide components, can be explained in terms of specific molecular interactions between unbranched Na CMC chains and multi-stranded helices of xanthan.

When Na CMC chains dominate in the Na CMC-xanthan mixture, the rheological properties are ruled more pronouncedly by the properties of Na CMC as a continuous phase. At higher mass fractions of xanthan, more progressive shear-thinning behavior of the Na CMC-xanthan mixture is observed and the ‘up flow curves’ exhibit a double-step behavior, indicating different regimes in the structural breakdown due to the shear action.

![Figure 3](image.png)
The heterogeneous nature of the polysaccharide dispersion is reflected in a progressive disruption of the weakly structured network of gel regions, surrounded by entangled Na CMC chains, which occur at lower stresses than observed for the pure xanthan solution, indicating that the structure of the polysaccharide mixture has weaker character than that of the pure xanthan solution. Further increase of the shear stress causes a formation of smaller flow units, having the ability to flow. With increasing mass fraction of Na CMC, the rheological properties are governed by the surrounding medium, in which small gel regions of xanthan are dispersed.

Viscoelastic properties under oscillatory shear conditions

The linear viscoelastic properties of aqueous Na-CMC-xanthan mixtures at a total polymer mass fraction of $w = 1.0\%$ were examined by applying oscillatory tests under small-deformation conditions which preserve the structure of the material.

First the limit of the linear viscoelastic response was determined by carrying out stress-sweep tests at a constant frequency of 1 Hz. Figure 5 represents the shear strain amplitude dependence of the dynamic moduli of aqueous polysaccharide systems used in our study. At low shear strain amplitudes pure Na CMC solution exhibits the loss modulus, $G''$, slightly higher than the storage modulus, $G'$, while for the xanthan solution the elastic response predominates over the viscous one (Figure 5a). As the shear strain amplitude increases, the dynamic response becomes non-linear and the decrease of the moduli occurs. A significantly different behavior is observed for the loss modulus, $G''$, of the pure xanthan solution above the critical strain amplitude which determines the transition from the linear to the nonlinear regime. As shown in Figure 5a, a slight increase of the loss modulus, $G''$, is observed, followed by a continuous decrease which is less pronounced than the decrease of the storage modulus, $G'$. Such behavior is often found for weak gel structures.1,28

When xanthan is blended with Na CMC, the characteristic behavior of the loss modulus, exhibited by pure xanthan solution, disappears, as can be noticed in Figure 5b. The analysis of the strain amplitude independent dynamic moduli for Na CMC-xanthan mixtures, within the linear viscoelastic regime shows that smaller mass fractions of xanthan (up to 0.5) reduce both moduli, with a stronger effect observed for the loss modulus. The lowest values of both moduli, $G'$ and $G''$, are observed when xanthan is present in the Na CMC-xanthan mixture at a mass fraction of 0.5. As the mass fraction of xanthan increases above 0.5, a slight increase of the loss modulus and a significantly stronger increase of the storage modulus, are observed.

Figures 6 and 7, indicating not-linear variation of $G_0^*$ and $\delta_0$ with the mixture composition, show that the synergistic effect of the Na CMC-xanthan
mixtures is also observed for rheological properties measured under non-destructive shear conditions. The complex modulus, $G^*$, determined for the Na CMC-xanthan mixtures, is lower than expected, and simultaneously slightly higher values of the phase angle, $\delta$, are observed for the Na CMC-xanthan mixtures.

By analyzing the results of oscillatory stress-sweep tests for all examined polysaccharide systems, the strain amplitude of 3% was chosen to apply in the frequency-sweep tests. Figure 8 represents the mechanical spectra of pure Na CMC and pure xanthan solution used in our study as obtained by applying the frequency-sweep experiments in the linear viscoelastic regime at a constant shear strain amplitude of 3%. The strong frequency dependence of dynamic moduli as observed for the Na CMC solution with the viscous component, exceeding the elastic one in the whole frequency range examined, indicates that the Na CMC solution behaves as an entangled polysaccharide solution. The xanthan solution exhibits the viscoelastic
properties usually observed for weak gel systems: the elastic response predominates over the viscous one, both dynamic moduli show only slight variation with oscillation frequency, and the frequency dependencies of dynamic moduli become parallel.\textsuperscript{20,21}

When xanthan is added to the Na CMC solution, the mechanical spectra change significantly, indicating the transition from the entangled polymer solution to a structured system (Figure 9). By increasing the mass fraction of xanthan, the dynamic moduli become less frequency-dependent and the elastic contribution gradually prevails over the viscous one.

At a mass fraction of 0.25, xanthan slightly reduces the loss modulus in the whole frequency range examined, as well as the storage modulus at high frequencies, while at low frequencies the storage modulus slightly increases (Fig. 9a). The presence of xanthan in Na CMC solution is first noticeable in the low frequency range where both dynamic moduli become less dependent on the oscillation frequency. When xanthan is present at a mass fraction of 0.5, the intersection of dynamic moduli occurs, the elastic response exceeds the viscous one in the range of low frequencies, and the loss modulus becomes less frequency-dependent at low frequencies (Fig. 9b). At an even higher mass fraction of xanthan, i.e. 0.75, two intersection points of dynamic moduli are detected with the storage modulus slightly higher than the loss modulus in the frequency range between the crossing points (Fig. 9c).
The formation of structured polysaccharide system, when xanthan is present in the Na CMC solution, can be experimentally verified by the application of the Cox-Merz empirical rule. This rule states that for polymer solutions the values of complex viscosity, \( \eta^* \), obtained from low-amplitude oscillatory measurements which preserve intermolecular association, and the corresponding values of steady shear viscosity, \( \eta_s \), from rotational measurements where the network structure is disrupted, should be equal at equal low values of frequency and shear rate. The comparison between the shear viscosities and the corresponding complex viscosities of the examined polysaccharide systems is presented in Figure 10. The pure Na CMC solution used in our study obeys the Cox-Merz rule as observed for entanglement polymer solutions (Figure 10a), while the pure xanthan solution exhibits a complex viscosity higher than the shear viscosity, indicating a weak gel structure of the xanthan solution (Figure 10e).1,20,21 The deviation from the Cox-Merz rule becomes noticeable when the Na CMC-xanthan mixtures exhibit a double-step flow behavior. The observed deviation from this empirical rule indicates that xanthan induces formation of weakly structured material.

The mechanical properties of the examined polysaccharide systems, experimentally determined in the range of linear viscoelastic response, were successfully interpreted by the generalized Maxwell model with five Maxwell elements (Equations 9 and 10) as presented in Figures 8 and 9. We used the least-squares regularization method to fit the experimental data with the model, and the relaxation spectra as presented in Figure 11 were determined. Tables 1 to 5 report the values of the relaxation times, \( \lambda_k \), and the relaxation strengths, \( g_k \), as obtained by fitting the mechanical spectra with the model. The zero-shear viscosity, \( \eta_0 \), resulting from the relaxation spectra, and the average relaxation time, \( \langle \lambda \rangle \), have been calculated according to the formulas:29

\[
\eta_0 = \sum_k g_k \lambda_k, \tag{11}
\]

\[
\langle \lambda \rangle = \frac{\sum_k g_k \lambda_k^2}{\sum_k g_k \lambda_k}, \tag{12}
\]

and the values of \( \eta_0 \) and \( \langle \lambda \rangle \) for examined systems are presented in Tables 1 to 5.

The calculated values of \( \eta_0 \) are in good agreement with experimental results. Both \( \eta_0 \) and \( \langle \lambda \rangle \) exhibit non-linear variation with the mixture composition. As the mass fraction of xanthan increases in biopolymer mixtures, the relaxation spectra are

| Table 1 – The relaxation spectrum for \( w = 1.0 \% \) aqueous Na CMC solution at \( 20 \pm 0.3\,^\circ\text{C} \) \( (\langle \lambda \rangle = 4.92 \, \text{s} \), \( \eta_0 = 3.26 \, \text{Pa} \cdot \text{s} ) \) |
|---|---|---|
| \( k \) | \( \lambda_k \) / s | \( g_k \) / Pa |
| 1 | 1.36 \times 10^{-3} | 83.7 |
| 2 | 1.36 \times 10^{-2} | 21.9 |
| 3 | 1.36 \times 10^{-1} | 5.74 |
| 4 | 1.36 \times 10^{0} | 0.737 |
| 5 | 1.36 \times 10^{1} | 0.0795 |

| Table 2 – The relaxation spectrum for aqueous Na CMC-xanthan mixture at mass fraction of xanthan 0.25 and total polymer fraction of \( w = 1.0 \% \) at \( 20 \pm 0.3\,^\circ\text{C} \) \( (\langle \lambda \rangle = 19.8 \, \text{s} \), \( \eta_0 = 4.60 \, \text{Pa} \cdot \text{s} ) \) |
|---|---|---|
| \( k \) | \( \lambda_k \) / s | \( g_k \) / Pa |
| 1 | 3.28 \times 10^{-3} | 51.8 |
| 2 | 3.28 \times 10^{-2} | 8.71 |
| 3 | 3.28 \times 10^{-1} | 2.31 |
| 4 | 3.28 \times 10^{0} | 0.208 |
| 5 | 3.28 \times 10^{1} | 0.0824 |

| Table 3 – The relaxation spectrum for aqueous Na CMC-xanthan mixture at weight fraction of xanthan 0.5 and total polymer concentration of \( w = 1.0 \% \) at \( 20 \pm 0.3\,^\circ\text{C} \) \( (\langle \lambda \rangle = 32.4 \, \text{s} \), \( \eta_0 = 12.1 \, \text{Pa} \cdot \text{s} ) \) |
|---|---|---|
| \( k \) | \( \lambda_k \) / s | \( g_k \) / Pa |
| 1 | 3.78 \times 10^{-3} | 44.3 |
| 2 | 3.78 \times 10^{-2} | 6.35 |
| 3 | 3.78 \times 10^{-1} | 1.84 |
| 4 | 3.78 \times 10^{0} | 0.180 |
| 5 | 3.78 \times 10^{1} | 0.272 |

| Table 4 – The relaxation spectrum for aqueous Na CMC-xanthan mixture at weight fraction of xanthan 0.75 and total polymer concentration of \( w = 1.0 \% \) at \( 20 \pm 0.3\,^\circ\text{C} \) \( (\langle \lambda \rangle = 21.9 \, \text{s} \), \( \eta_0 = 33.6 \, \text{Pa} \cdot \text{s} ) \) |
|---|---|---|
| \( k \) | \( \lambda_k \) / s | \( g_k \) / Pa |
| 1 | 2.44 \times 10^{-3} | 57.7 |
| 2 | 2.44 \times 10^{-2} | 6.54 |
| 3 | 2.44 \times 10^{-1} | 3.60 |
| 4 | 2.44 \times 10^{0} | 0.993 |
| 5 | 2.44 \times 10^{1} | 1.23 |

| Table 5 – The relaxation spectrum for 1.0 wt. % aqueous xanthan solution at \( 20 \pm 0.3\,^\circ\text{C} \) \( (\langle \lambda \rangle = 46.9 \, \text{s} \), \( \eta_0 = 112.9 \, \text{Pa} \cdot \text{s} ) \) |
|---|---|---|
| \( k \) | \( \lambda_k \) / s | \( g_k \) / Pa |
| 1 | 5.19 \times 10^{-3} | 31.0 |
| 2 | 5.19 \times 10^{-2} | 4.59 |
| 3 | 5.19 \times 10^{-1} | 3.38 |
| 4 | 5.19 \times 10^{0} | 1.83 |
| 5 | 5.19 \times 10^{1} | 1.95 |
shifted towards longer relaxation times and the relaxation strengths become less dependent on the relaxation time. We noticed that the presence of xanthan in the Na CMC-xanthan mixtures contributes to the appearance of higher values of relaxation strengths at long relaxation times.
As for the flow behavior of the Na CMC-xanthan mixtures, also the synergistic effect, observed in the viscoelastic behavior of biopolymer mixtures under small-amplitude oscillatory shear, can be explained through the formation of small gel regions of xanthan, dispersed in the entanglement polymer solution of Na CMC (Figure 4).

When Na CMC is blended with xanthan, even at very low mass fractions, the gel character of the mixture becomes weaker than in the pure xanthan solution, but the elastic component of the response still predominates over the viscous one. As explained above, the presence of the entanglement polymer solution of Na CMC, which surrounds the gel regions of xanthan, inhibits the formation of extended junction zones and induces the formation of polysaccharide dispersion.

At low mass fractions of Na CMC in the sample composition, the concentration of small gel clusters of xanthan is high enough to form a structure of weak gel, reflecting in a slightly stronger elastic response compared to the viscous one. With increasing mass fraction of Na CMC, the viscous component of the dynamic response predominates over the elastic one, indicating that the linear viscoelastic behavior is ruled by the entanglement solution of Na CMC, which surrounds the gel regions of xanthan. The synergistic effect of the Na CMC-xanthan mixtures shows the minimum in the complex modulus when the mass ratio between Na CMC and xanthan changes. The increase of the mass fraction of Na CMC up to 0.5 leads to the minimum value of both dynamic moduli, i.e. lower than the values of both pure polysaccharide components.

The reason for such behavior can be a combination of two possible molecular mechanisms. As already proposed, the presence of unbranched Na CMC chains in the Na CMC-xanthan mixtures seems to inhibit the formation of extended junction zones and hence the weak gel character of the examined mixtures. At a specific mass ratio of blended polymers, small gel clusters of xanthan can prevent formation of Na CMC entanglements, resulting in the minimum of the complex modulus. When the mass fraction of Na CMC in the mixture increases, the concentration of gel regions becomes low enough to inhibit the formation of entanglements, and the viscoelastic properties of the polysaccharide dispersion are governed by the entanglement solution of Na CMC.

As the mechanical spectra show, the three-dimensional network structure of small gel regions of xanthan in the solution of entangled Na CMC macromolecules as the surrounding medium exists only at very low frequencies, indicating that such a weak structure can easily be disrupted.

Conclusions

The rheological behavior of aqueous polysaccharide mixtures, consisting of sodium carboxymethylcellulose and xanthan at a total polymer concentration of \( w = 1.0\% \) was extensively studied under the conditions of shear flow and by applying small-amplitude oscillatory tests in order to follow the changes in rheological responses due to the structural rearrangements in biopolymer binary mixtures.

As the origin of the synergistic effects of the Na CMC-xanthan mixtures, observed in terms of flow behavior and linear viscoelastic properties, we propose the existence of aqueous Na CMC-xanthan mixtures as polysaccharide dispersions, with small gel clusters of xanthan dispersed in the entanglement solution of Na CMC. When xanthan is present at low mass fractions, the concentration of gel regions is low and the rheology is ruled by the surrounding medium, i.e. the Na CMC solution. With increasing mass fraction of xanthan the formation of the weakly structured system is governed by concentrating the gel clusters of xanthan, surrounded with entangled Na CMC chains. The weakly formed structure of the examined biopolymer mixtures has a heterogeneous character and the formation of the three-dimensional network structure is possible only at small deformations and low frequencies. It can easily be disrupted and when sub-
jected to large deformations, the presence of smaller flowing units enables flowing. When Na CMC-xanthan mixtures are subjected to large shear conditions, a complex shear-thinning behavior is observed. At low shear stresses the mixed systems exhibit lower zero-shear viscosity than the xanthan solution and at higher shear stresses a more intense shear-thinning behavior than the Na CMC solution is observed.

The heterogeneous character of the investigated polysaccharide mixtures can easily be recognized also under non-destructive conditions of oscillatory shear. As the dynamic rheological properties at a constant frequency show, the minimum values of dynamic moduli are found for the Na CMC-xanthan mixture at a 1:1 mass ratio of blended polymers, whereas the phase angle continuously decreases when the mass fraction of xanthan in the mixture increases. The critical strain amplitude, characterizing the limit of the linear viscoelastic regime, is found to be lower for the mixtures than for pure solutions of Na CMC and xanthan. The mechanical spectra and the calculated relaxation spectra of the examined polymer systems and, finally, the comparison of the rheological data according to the Cox–Merz rule, suggest the structural conditions of the Na CMC-xanthan mixtures as explained above.

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Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$G_k$</td>
<td>relaxation strength of $k$-th Maxwell element, Pa</td>
</tr>
<tr>
<td>$G$</td>
<td>elastic modulus, Pa</td>
</tr>
<tr>
<td>$G'$</td>
<td>storage modulus, Pa</td>
</tr>
<tr>
<td>$G''$</td>
<td>loss modulus, Pa</td>
</tr>
<tr>
<td>$G^*$</td>
<td>complex modulus, Pa</td>
</tr>
<tr>
<td>$G_0$</td>
<td>complex modulus in the linear viscoelastic regime, Pa</td>
</tr>
<tr>
<td>$t$</td>
<td>time, s</td>
</tr>
<tr>
<td>$w$</td>
<td>concentration, %</td>
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</table>

Greek symbols

<table>
<thead>
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<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>shear strain, %</td>
</tr>
<tr>
<td>$\gamma^o$</td>
<td>shear strain amplitude, %</td>
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<tr>
<td>$\gamma$</td>
<td>shear rate, s$^{-1}$</td>
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</tbody>
</table>

References


