Rheological behavior of binary and ternary mixtures of polysaccharides in aqueous medium

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Abstract
The rheological behavior of mixtures of xanthan with different galactomannans is examined to evaluate the influence of the structure of galactomannan and that of the mixture composition on the physical properties; the larger synergy is observed for locust bean gum in the presence of xanthan. It is also shown that pH has only a slight influence on the rheology down to pH = 3.59; at lower pH, the G' modulus decreases significantly.

Then, the behavior of xanthan–methylcellulose mixtures is studied, paying particular attention to the storage modulus (G') of the system, often equated to “gel strength”. The modulus values for direct dissolution of the two polysaccharides in 0.1 M NaCl show that xanthan and methylcellulose are incompatible. The rheological behavior observed is in agreement with DSC results which indicate that no specific interaction between the two polymers exists. However, upon increasing temperature, the modulus of methylcellulose increases substantially between 65 and 70 °C because of physical gelation and dominates the rheology of the mixtures. When temperature is decreased to 37 °C, the clear methylcellulose gel formed remains stable, still giving the main contribution to the overall rheology of the system. Finally, ternary systems are studied when xanthan is mixed with galactomannan and methylcellulose. In this case H-bonds involved in galactomannan–xanthan interaction break when temperature increases causing a decrease in rheological moduli which is then compensated by the gelation of methylcellulose giving an original large increase in moduli for the ternary systems. This can be interpreted as the presence of two independent but interpenetrating networks. The role of pH for these ternary systems is interesting: it is still dominated by methylcellulose and nearly independent of acidic pH (down to pH = 1.8).

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1. Introduction

Many papers exist in the literature that study the synergistic interactions that occur in systems containing different blends of polysaccharides. Some of these mixtures have been used for a long time in food and biomedical applications for their ability to form strong gels even at low concentrations. Systems containing xanthan in association with guar or locust bean gum or tara gum or alginates or cellulose ethers (hydroxypropylmethylcellulose, methylcellulose) have been especially used to prepare controlled release pharmaceutical tablets for drug delivery systems (Baichwal and Staniforth, 1991; Baichwal, Kao, & McCall, 2003; Ughini, Andreazza, Ganten, & Bresolin, 2004; Matthews, Stevens, Auffret, Humphrey, & Eccleston, 2005) as well as to modify the rheological properties of food systems for salad dressings, puddings, dietary fibers, etc. (Williams, Annable, Phillips, & Nishinari, 1994; Sanderson, 1982; Pettitt, 1982). Some of the most widely studied systems are galactomannan–xanthan mixtures and glucomannan–xanthan mixtures (Tako, 1991; Fitzsimons, Tobin, & Morris, 2008; Nishinari, 2000; Dea, Clark, & McCleary, 1986). The large increase in modulus and viscosity that occurs upon mixing of two such thickening polysaccharides gives origin to a physical gel based on cooperative H-bonds that form between the chains at ambient temperature; several types of interactions that may occur between main chains and/or side chains in xanthan/galactomannan mixtures and which lead to gel formation have been investigated and described by molecular modeling (Chandrasekaran & Radha, 1997). The gelation is strongly affected by the chemical structure of xanthan (especially its acetylation degree) and on the structure of the galactomannan or glucomannan including the galactose distribution along the
chain (hairy vs. non-hairy regions) and the mannose/galactose or mannose/glucose ratios (Chandrasekaran & Radha, 1997; Goycoolea, Foster, Richardson, Morris, & Giley, 1994; Goycoolea, Richardson, Morris, & Giley, 1995; Bresolin et al., 1997; Lopes, Andrade, Milas, & Rinaudo, 1992; Goycoolea, Milas, & Rinaudo, 2000; Goycoolea, Milas, & Rinaudo, 2001; Bresolin, Milas, Rinaudo, & Ganter, 1998; Bresolin, Milas, Rinaudo, Reicher, & Ganter, 1999; Cronin, Giannouli, McCleary, Brooks, & Morris, 2002). Two types of gel were recently described for the mixture xanthan/galactomannan: a low temperature one that forms around 20 °C in absence of external salt and especially with deacetylated xanthan; and a second one that forms around 50 °C after heating in presence of external salt (Goycoolea, Milas, & Rinaudo, 2000; Bresolin et al., 1998). A similar behavior was recently described for the glucomannan/xanthan mixture where a gel is also formed at room temperature (Fitzsimons, Tobin, & Morris, 2008) and appears to be in the form of a coupled network in which ordered conformation of the junction exists (Goycoolea, Milas, & Rinaudo, 2001; Bresolin et al., 1998).

Methylcellulose is a LCST polymer (the lower critical solution temperature (LCST) over which the phase separation occurs at 29 ± 2 °C) which gives a strong physical gel by itself upon heating above 50 °C; the gelation mechanism has been analyzed previously and the phase separation has been clearly demonstrated: a clear gel forms above 30 °C because of the interaction of the highly substituted zones on the cellulose backbone followed by a phase separation with formation of a turbid, stronger gel at temperatures above 50 °C (Hirrien, Chevillard, Desbrieres, Axosel, & Rinaudo, 1998; Vigouret, Rinaudo, & Desbrieres, 1996; Desbrieres, Hirrien, & Rinaudo, 1998a). The gelling occurs because of chain-to-chain hydrophobic interactions which are affected not only by the overall degree of substitution of cellulose but also by the distribution of methyl substituents along the cellulose backbone (Desbrieres, Hirrien, & Rinaudo, 1998b). Methylcelluloses are introduced in many pharmaceutical applications as viscosity modifiers (Matthews, Stevens, Auffret, Humphrey, & Eccleston, 2005; Corveley & Remon, 1999) or as food ingredients (Xue & Ngadi, 2007; Dikeman, Murphy, & Fahey, 2006), either alone or in combination with other polysaccharides.

The purpose of this work is to investigate the properties of binary mixtures composed of xanthan and galactomannan or methylcellulose; then the properties of ternary mixtures containing xanthan, galactomannan and methylcellulose are studied.

2. Experimental

The polysaccharides studied in this work are commercial samples used as received. Xanthan gum from Kelco (USA) has a degree of acetylation of 0.87 and of pyruvation of 0.57 per repeat unit as determined by NMR (Rinaudo, Milas, Lambert, & Vincendon, 1983); locust bean gum M200 (LBG galactomannan) with a mannose/galactose ratio of 3.6 was obtained from Rhodia (France); guar gum and tara gum (guar MLV and tara gum 100 respectively) were obtained from TIC Gums, Inc. (USA) and have a mannose/galactose ratio of 1.6 and 2.7 respectively; the composition is determined by 1H NMR in D2O in the presence of NaOD. Methylcellulose A4M Premium with an average degree of methylation (or degree of substitution DS) of 1.7 was received from Dow Chemical (USA).

Each polysaccharide solution is prepared by direct dissolution at ambient temperature in 0.1 M NaCl solution at a 6 g/L concentration. The solutions of different polysaccharides are mixed in controlled volume ratio when needed. The use of 0.1 M NaCl as solvent allows one to ignore the slight contribution (and variation) of xanthan counterions with dilution.

Proton NMR spectra were recorded at 85 °C with a Bruker Avance 400 spectrometer operating at 400.13 MHz. Polymer concentration adopted was around 3 mg/mL solvent in 0.5 mm o.d. tubes. Proton spectra are recorded with 4006 Hz spectral width, 32,768 data points, 4,089 s acquisition time, 64 scans and 10 s relaxation delay. 1H signal of the α-D-galactose unit is located at 4.9 ppm and that of the 1H of β-D-mannose unit at 4.6 ppm; their integrals allow to determine the M/G ratio.

Dynamic rheological measurements were performed with a controlled stress rheometer, model AR 1000 from TA Instruments, using a plate-cone geometry (4 cm diameter and 3°59’ angle cone) in a temperature range of 20–70 °C. Most isothermal runs were done at 37 °C, a reference temperature for applications in the body; variable temperature runs were performed at a temperature variation rate of 3 °C/min and controlled with the use of a Peltier plane. The strain % was selected to be in the linear domain. Samples were coated by a silicone oil film to prevent water evaporation during testing.

DSC experiments were done in a SETARAM (France) DSCIII microcalorimeter in the same temperature range but with a rate of temperature change of 0.5 °C/min for the heating and cooling cycles.

3. Results and discussion

Many neutral polysaccharides which are rich in –OH groups are able to form tridimensional networks stabilized by H-bonds established between molecules (intra- and inter-chains but also..
with water molecules); these interactions are disrupted when temperature increases. In the experimental conditions adopted in this work, xanthan is known to adopt an ordered conformation (stabilized by intramolecular H-bonds) in an extended temperature range (Milas, Rinaudo, & Tinland, 1985; Milas, Rinaudo, Knipper, & Schuppiser, 1990; Chazeau, Milas, & Rinaudo, 1995). Galactomannan characteristics (mannose/galactose ratio) play a role on the viscosity of a semi-dilute solution (Petkowicz, Reicher, & Mazeau, 1998; Petkowicz et al., 1999; Kapoor, Milas, Taravel, & Rinaudo, 1994; Kapoor, Milas, Taravel, & Rinaudo, 1996; Kapoor et al., 1998; Ganter, Milas, & Rinaudo, 1992); these data were taken into account to discuss our results. It is known also that when xanthan is mixed with galactomannan in aqueous solutions, a gelation is observed, as extensively reported in the literature (Goycoolea, Milas, & Rinaudo, 2000; Bresolin et al., 1998, 1999); a high temperature gel (melting around 50 °C) is formed after heating the mixture around 70 °C and cooling it down in the presence of salt in the solution. This gel melts when the temperature increases as the cooperative network of H-bonds breaks. The distribution and number of galactose along the mannan backbone is important in the co-gel formation and the influence of M/G ratio will be tested by mixing guar (composition M/G approximately 2:1), tara (around 3:1), and LBG (around 4:1) gums with xanthan.

Water soluble methylcelluloses (with DS = 1.7 and a blockwise methyl groups distribution) are amphiphilic polymers and they associate via hydrophobic interactions in a two-step mechanism in aqueous solution when temperature increases. The characteristic temperatures for phase transition depend on the rate of temperature change; in addition, a large hysteresis is observed between strong gel formation on heating and its disruption on cooling as shown by rheology or DSC studies (Hirrien et al., 1998; Vigouret, Rinaudo, & Desbrieres, 1996; Desbrieres, Hirrien, & Rinaudo, 1998a; Desbrieres, Hirrien, & Rinaudo, 1998b).

However, the behavior of binary mixtures of xanthan and methylcellulose or ternary mixtures containing galactomannan, xanthan and methylcellulose has never been described in detail. Therefore, the objective of this study is to investigate the behavior of these mixed polysaccharides systems and to relate it with what was known previously about the different separated polymers.

3.1. Influence of temperature on the behavior of polysaccharide solutions

Examples of experimental data obtained for xanthan and galactomannan after direct dissolution or after heating to 70 °C and cooling down are given in Fig. 1. The values obtained for $G'(\omega)$ modulus after heating are slightly modified for xanthan (increasing

![Fig. 3. Dynamic rheology for methylcellulose in 0.1 M NaCl at 65 °C ($G'(\omega)$ $\bullet$; $G''(\omega)$ $\triangle$) and after cooling down to 37 °C ($G'(\omega)$ $\Delta$; $G''(\omega)$ $\triangledown$).](image)

![Fig. 4. DSC measured heat flow curves for methylcellulose at 6 g/L in 0.1 M NaCl upon heating and cooling at 0.5 °C/min.](image)
or decreasing in dependence on the degree of aggregation) but increases more clearly upon cooling for tara gum probably because of dissociation of aggregates and consequent increase in solubility. In Fig. 2, the influence of temperature is shown for xanthan and methylcellulose; a very small effect is observed on xanthan when compared with methylcellulose. The well known behavior of methylcellulose (M) with a large hysteresis in modulus is obtained with temperature cycling. A sharp increase in the \( G' \) modulus is observed when temperature increases above \( 55^\circ C \); the exact temperature for this physical transition may vary slightly, depending on the heating rate, as kinetic control plays a key role (Vigouret, Rinaudo, & Desbrieres, 1996; Desbrieres, Hirrien, & Rinaudo, 1998a). Upon subsequently decreasing temperature, methylcellulose \( G' \) decreases slowly at first and then more rapidly down to a final value that remains considerably higher than the starting value of \( 37^\circ C \). Fig. 3 confirms that a strong gel is formed on heating methylcellulose solution to \( 65^\circ C \) (with \( G' \) independent of the frequency in the range covered in this experiment and \( G' > G'' \)). On cooling to \( 37^\circ C \), \( G' \) remains larger than \( G'' \) and confirms the stability of the clear gel.

The peculiar behavior of methylcellulose is confirmed by DSC (Fig. 4) where a peak in heat flow occurs at \( 59.5^\circ C \) (formation of the turbid gel corresponding to a large increase in \( G' \)) upon heating, while upon cooling, the reverse transition occurs at \( 31.7^\circ C \) (gel–sol transition). In this case a clear gel is maintained at the desired temperature of \( 37^\circ C \) (see the shoulder in the thermogram) (Hirrien et al., 1998). No conformational change exists for xanthan in this temperature range as the molecule is stabilized in the helical conformation by the presence of an external salt in the solution and no particular features are observed in the thermogram.

3.2. Binary mixtures of xanthan–galactomannan

3.2.1. 50/50 weight % mixture characterization

Different 50/50 galactomannan/xanthan mixtures were prepared by dissolution at ambient temperature, heating, and then cooling down. Fig. 5 shows the \( G'(\omega) \) values for the xanthan solution and for galactomannan/xanthan mixtures at \( 37^\circ C \). Guar systems show \( G' \) values that remain smaller than the values of xanthan, even after heating. For the mixture with tara, there is only a small influence of the heating treatment and the values are near that of initial xanthan (even if tara gum solution has lower modulus, indicating some interaction with xanthan). \( G' \) modulus for the initial LBG/xanthan mixture is close to the xanthan values; when temperature increases, a decrease in \( G' \) (not shown) is attributed to heat induced intra- and inter-chain H-bonds breakage. These bonds reform with better cooperativity when temperature decreases (in relation with better solubility of galactomannan upon heating as discussed from Fig. 1), inducing a reinforced gel like behavior to the system. Another hypothesis should be that mixing at low temperature gives a dispersion of mixed gel particles which forms a continuous network after heating and cooling down. After heating and cooling down to \( 37^\circ C \), xanthan/LBG system shows \( G' \) modulus values substantially higher than xanthan alone and also than guar/xanthan or tara/xanthan mixtures. These results confirm, as previously mentioned in the literature, that LBG, which has the highest mannose/galactose ratio, forms the strongest gel-like structure with xanthan.

3.2.2. Influence of the mixture composition

The influence of the composition of the mixture was investigated for the tara gum/xanthan mixture: the two initial solutions are first mixed at \( 37^\circ C \), heated to \( 70^\circ C \) and then cooled down to \( 37^\circ C \). The values for the \( G' \) moduli at 1 Hz are given in Table 1. At \( 37^\circ C \), xanthan contribution dominates the mixture modulus (tara contribution being very low, \( G' = 0.33 \) Pa compared with xanthan \( G' = 11.7 \) Pa). In first approximation, calculated values based on additivity can be compared with experimental values; these values are compared in Table 1. \( G' \) experimental values at \( 37^\circ C \) obtained for compositions between 40 to 60% of tara gum are larger than calculated, reflecting tara/xanthan cooperative interactions. At \( 70^\circ C \), cooperative interactions are disrupted by temperature negative influence on H-bonds and all experimental values are lower than calculated indicating some incompatibility between the two polysaccharides. When the mixtures are returned to \( 37^\circ C \), a large increase in \( G' \) is observed with a maximum synergy for a tara/xanthan ratio of 60/40 w/w (largest difference between experimental and calculated values) indicating a reinforcement of the junctions in the physical network. This is slightly different than the optimal ratio obtained for different galactomannan/xanthan mixtures (usually given around 50/50 w/w in the literature).

3.2.3. Role of pH on rheological behavior of xanthan–galactomannan mixture

Because of the different pH conditions existing in the different parts of the human gastrointestinal tract, it is important to evaluate the rheological behavior of potential delivery systems at different pHs, and especially in an acidic environment similar to what is found in the stomach. Swelling degree and gel strength have been found in the stomach. Swelling degree and gel strength have a profound effect on release rate, especially in the presence of food, and it is important to understand and predict behavior of systems based on these polymers when designing a delivery system. Therefore, the testing medium pH was adjusted by successive additions of controlled amounts of HCl to simulate the dosage form presence in different parts of the GI tract.

![Graph](image_url)

**Fig. 5.** Influence of heating process on rheological properties of xanthan/galactomannan (1/1) mixtures at 6 g/L in comparison with xanthan (○). \( G'(\omega) \) values are given at \( 37^\circ C \) before (open symbols) and after (closed symbols) heating up to \( 70^\circ C \) in 0.1 M NaCl. Guar/xanthan (■); tara/xanthan (▲, ▼); LBG/xanthan (●, ◆).

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>( G'(\text{Pa}) ) at 1 Hz, ( 37^\circ C )</th>
<th>( G'(\text{Pa}) ) at 1 Hz, ( 70^\circ C )</th>
<th>( G'(\text{Pa}) ) at 1 Hz on return at ( 37^\circ C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthan</td>
<td>11.17</td>
<td>5.94</td>
<td>12.46</td>
</tr>
<tr>
<td>Tara gum</td>
<td>0.33</td>
<td>~0</td>
<td>0.70</td>
</tr>
<tr>
<td>T/X 20/80</td>
<td>9.05</td>
<td>9.00</td>
<td>3.62</td>
</tr>
<tr>
<td>T/X 40/60</td>
<td>8.54</td>
<td>6.83</td>
<td>2.05</td>
</tr>
<tr>
<td>T/X 50/50</td>
<td>8.02</td>
<td>5.75</td>
<td>1.67</td>
</tr>
<tr>
<td>T/X 60/40</td>
<td>5.96</td>
<td>4.67</td>
<td>0.88</td>
</tr>
<tr>
<td>T/X 80/20</td>
<td>2.47</td>
<td>2.50</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Exp. – values are the experimental determination; Calc. – values are the calculated values by additivity of the values obtained for the two separated components.
Fig. 6 shows the pH effect on the modulus of a 50/50% mixture of xanthan and locust bean gum at 37 °C after direct dissolution in 0.1 M NaCl, and after heating to 70 °C and cooling down to 37 °C. The $G_0$ values obtained for this system are usually higher after heating and do not vary much at pH above 3.59 (heated mixture at pH = 4.55 overlaps with the initial solution) but strongly decrease at lower pH where xanthan ionization and electrostatic inter-chain repulsions decrease. At low pH, xanthan helical conformation is stabilized and, because of its larger resistance to unfolding, does not allow LBG chains to bind effectively to xanthan, thus negatively affecting the galactomannan–xanthan secondary interaction and hastening gel collapse. Therefore, a consequent reduction in system viscosity and especially its modulus is observed as pH decreases. Such a decrease in the viscosity of xanthan/LBG at pH < 3.5–5 was described by Pramoda and Lin (1979) and more recently also discussed by Agoub, Smith, Giannouli, Richardson, and Morris (2007); it was shown that the temperature for gelation on cooling is progressively depressed for pH lower than 4.25 and that gelation is suppressed at pH = 2.5 in agreement with the stabilized conformation of xanthan at low pH.

3.3. Binary mixtures of xanthan–methylcellulose

3.3.1. 50/50 weight % mixture characterization

Fig. 7 shows the influence of temperature on $G'$ modulus for a 50/50 methylcellulose/xanthan mixture. Modulus increases sharply with temperature up to 70 °C. In this case, a large hysteresis is observed between the heating and cooling process as imposed by methylcellulose contribution (compare with Fig. 2). For this mixture, during the decreasing temperature cycle, $G'_0$ modulus remains nearly constant between 65 and 45 °C, with a slight maximum at about 50 °C. The original $G'_0$ (u) values at 37 °C for the initial mixture are low and depend on the frequency, while at 70 °C a large increase is observed, as well as frequency independence, confirming methylcellulose gel formation. Interestingly, upon returning to 37 °C, modulus remains higher than for the initial solution because of the presence of the clear methylcellulose gel (Fig. 8).

3.3.2. Influence of the mixture composition

The effect on rheology of mixtures with different xanthan/methylcellulose ratios was studied first at 37 °C, then at 65 and 70 °C in separate experiments before returning to 37 °C. On the same systems, DSC was performed for the different ratios; Fig. 9 shows that nearly no modification occurs in the position of the two DSC peaks (compared to methylcellulose alone in solution; Fig. 4). DSC analysis provides the heat flow curve with characteristic peaks...
at temperatures independent from the composition but with enthalpy $E$ directly proportional to the methylcellulose weight fraction ($E \sim 20$ J per gram of methylcellulose).

At $37^\circ$C, directly after mixing, $G'$ values at 1 Hz are lower than predicted for additivity (straight line), and show incompatibility between the two molecules (Fig. 10A). After heating at 65 or $70^\circ$C, $G'$ modulus increases dramatically in proportion to the amount of methylcellulose in the mixture, which imposes its behavior (Fig. 10B). A loose gel like structure forms after decreasing temperature back to $37^\circ$C and additivity is now observed (linear behavior), although the two polymers remain independent (as concluded from the DSC experiments) with the contribution of methylcellulose clear gel increasing proportionally to its weight fraction (Fig. 10C). No difference is now observed between samples heated to 65 or $70^\circ$C.

Fig. 11 shows the effect of temperature cycling on $G'$ for few samples. The hysteresis becomes significant as soon as the content in methylcellulose increases above 20%. Methylcellulose/xanthan mixtures with composition ratios (weight %) from 20/80 to 80/20 show similar behavior in the intermediate temperature range. In addition, methylcellulose has the strongest effect on the overall system behavior not only at high temperature, but also after cooling back to $37^\circ$C.

These results suggest that: (1) that the overall behavior of the xanthan/methylcellulose system is controlled by methylcellulose
after a first heating because of the formation of a methylcellulose hydrophobic interactions based physical gel; and (2) and that there is no specific interaction between xanthan and methylcellulose. Then, methylcellulose forms its own loose network independently from xanthan and xanthan is embedded in the clear gel of methylcellulose. This behavior is quite opposite from that of the LBG/xanthan mixtures, where a strong interaction between the two polysaccharides exists and where a cooperative gel based on H-bonds forms at lower temperature.

3.4. Ternary mixtures

3.4.1. Influence of the composition on the behavior of ternary mixtures

The study on the binary mixtures suggests that a ternary mixture of methylcellulose, galactomannan and xanthan may have unexpected and interesting properties such as higher viscosity and modulus than xanthan alone (xanthan is known to be more viscous and to have a higher $G'$ modulus than other comparable water soluble polymers separately) and with properties that also vary less when temperature changes. Furthermore, the xanthan/galactomannan thermoreversible gelling behavior can be counteracted by the introduction of methylcellulose which forms its own hydrophobic network when temperature increases and still remains active upon returning to 37 °C.

To test this hypothesis, different methylcellulose (M)/locust bean gum (L)/xanthan (X) mixtures were prepared in the following ratios: MLX 5/5/5, MLX 2/8/8 and MLX 8/2/2 (the numbers are proportional to the volume of 6 g/L solution in the mixtures). The $G'$ moduli for the different mixtures are compared with initial xanthan after direct dissolution at 37 °C in Fig. 12.

The xanthan/locust bean gum/galactomannan mixture (MLX 2/8/8) modulus nearly overlaps xanthan alone in the range studied while the methylcellulose rich mixture (MLX 8/2/2) shows much higher modulus than methylcellulose alone but smaller than for xanthan alone. This indicates that all three polymers contribute to various extents to the overall system behavior. A few experimental values are given in Table 2 where the composition of mixtures is expressed in weight % including a mixture with tara gum showing a similar effect. Fig. 13 shows the influence of temperature on the modulus of the different mixtures tested. During the return cycle, the MLX mixtures moduli remain nearly constant from 65 down to 45 °C. These unexpected results thus show how even a small addition of methylcellulose to the xanthan/LBG system (MLX 2/8/8 or 20 g of methylcellulose solution added to 160 g of the LBG/X (50/50) mixture) can substantially improve overall system performances (higher $G'$ and lower variation). As shown in Fig. 14, at high temperature, $G'$ modulus of the mixture MLX 2/8/8 is lower than after return to 37 °C; methylcellulose has not had a significant influence on the predominant xanthan/LBG synergism upon return to lower temperatures. In contrast, the methylcellulose rich mixture (MLX 8/2/2) has $G'$ modulus higher at high temperature than on return.

<table>
<thead>
<tr>
<th>Reference and mixture</th>
<th>$G'$ (Pa) at 1 Hz</th>
<th>$G'$ (Pa) at 1 Hz, 65 or 70 °C</th>
<th>$G'$ (Pa) at 1 Hz, return at 37 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMX 2-2-8</td>
<td>11.39</td>
<td>23.90</td>
<td>19.34</td>
</tr>
<tr>
<td>16.6/16.6/66.6</td>
<td>11.90</td>
<td>17.74</td>
<td>27.27</td>
</tr>
<tr>
<td>MLX 2-2-2</td>
<td>11.90</td>
<td>34.19</td>
<td>19.17</td>
</tr>
<tr>
<td>66.6/16.6/16.6</td>
<td>4.36</td>
<td>18.77</td>
<td>18.40</td>
</tr>
<tr>
<td>MLX 2-8-8</td>
<td>11.39</td>
<td>23.90</td>
<td>19.34</td>
</tr>
<tr>
<td>11.1/44.4/44.4</td>
<td>11.90</td>
<td>34.19</td>
<td>19.17</td>
</tr>
<tr>
<td>MLX 5-5-5</td>
<td>11.90</td>
<td>23.90</td>
<td>19.34</td>
</tr>
<tr>
<td>33/33/33</td>
<td>4.36</td>
<td>18.77</td>
<td>18.40</td>
</tr>
</tbody>
</table>

T = tara gum; M = methylcellulose; X = xanthan; L = locust bean gum.
3.4.2. Influence of pH on rheology of ternary mixture

A mixture made of equal amounts of methylcellulose, xanthan and locust bean gum (MXL 1/1/1) was prepared and studied at 37 °C; then, each mixture was heated up to 65 °C. As shown in Fig. 15, at 37 °C, the pH has only moderate influence on the rheology of the mixtures which is dominated by methylcellulose. Before heating, modulus remains fairly constant as pH decreases and quite higher than a comparable XG/LBG system (see Fig. 6); after heating, G' modulus increases significantly and still remains fairly constant even as pH drops as low as pH = 1.45.

4. Conclusion

This paper describes the solution behavior of binary mixtures of galactomannan/xanthan and methylcellulose/xanthan at various temperatures in 0.1 M NaCl solutions, used to screen the long range electrostatic interaction between xanthan chains and to stabilize the helical conformation of xanthan. The usual behavior of galactomannan/xanthan systems is observed with a more efficient role of locust bean gum rather than tara or guar gums on the xanthan/galactomannan theroreversible gel performances. The synergy is maintained at pH above 3.5 although G' modulus decreases significantly with pH down to pH = 1.8.

DSC and rheology studies on the xanthan/methylcellulose mixtures, show that, while there is an incompatibility and lack of synergy between the two polymers at 37 °C, upon heating, methylcellulose forms its own network based on hydrophobic interactions independently from xanthan; methylcellulose contribution dominates the rheological behavior of the mixtures even when temperature returns down to 37 °C. This behavior is opposite to that of the well known xanthan/galactomannan mixture which forms a synergistic, H-bond based network at 37 °C which disappears reversibly upon heating.

Surprisingly, in ternary mixtures of xanthan, galactomannan and methylcellulose, the overall rheological properties remain fairly constant in an extended temperature range after a first heating up to 65 or 70 °C because the thermal behavior of methylcellulose and galactomannan/xanthan complex compensate, avoiding decrease in system performances. A similar behavior is observed in acidic medium, where G' modulus remains nearly constant down to pH = 1.45. These ternary mixtures may be of interest for applications in controlled release dosage forms or food applications where hydrophilic gels with good thermal and pH stability are required.

References


