Influence of Galactomannan on the Structure and Thermal Behaviour of Xanthan/Galactomannan Mixtures

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ABSTRACT

Mixed gels of xanthan gum and galactomannans (guar, whole and fractionated locust bean gum — LBG) were compared by means of oscillatory shear measurements. Whatever the LBG fraction, a synergistic maximum was observed when the ratio of xanthan to galactomannan was 1:1. However, the magnitude of this maximum varied with the LBG fraction used. The thermal behaviour of 1:1 xanthan/LBG fractions was characterized by cooling–heating cycles. A slight thermal hysteresis was systematically described for the several xanthan/LBG fraction systems. It was observed that the mannose to galactose (M/G) ratio of LBG fractions determined the sol–gel transition (gelation and melting temperature) of the xanthan/galactomannan mixed systems. From the galactomannan fine structure and thermorheological profiles it is evident that the higher the M/G ratio of galactomannan samples, the higher is the synergistic interaction as is also the transition temperature of the xanthan/LBG systems.

INTRODUCTION

Biopolymers are texture agents which have found widespread use in food and industrial formulations due to their ability to give very viscous solutions and gels at relatively low concentrations. Synergistic polysaccharide–polysaccharide interactions are attractive commercially and enjoy widespread technological applications. Expensive biopolymers are often replaced by cheaper alternative blends which may be used to generate new functionality in food ingredients. The texture characteristics of these mixed systems depend on several parameters,

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namely, temperature, total polymer concentration, ion concentration, ratio of the polysaccharides in the mixture and the total polymer concentration.

Galactomannan polysaccharides occur as reserve materials in a wide range of legume seeds. The primary source of these polysaccharides consists of a chain of (1 → 4)-β-D-mannopyranosyl units with attached (1 → 6)-α-D-galactose units. The quantity depends on the species from which the polysaccharide is extracted and varies from approximately 20% for locust bean gum (LBG) to about 33% for guar gum (GG) (Hui & Neukom, 1964). Both LBG and GG have found widespread use in the food industry due to their ability to form aqueous viscous solutions. The rheology of the galactomannans has been extensively studied (de Sabates, 1979; Doublier & Launay, 1981; Morris et al., 1981; Robinson et al., 1982; Fernandes et al., 1989). Of the two galactomannan samples, LBG has the lowest galactose content and is the least soluble. The heating of LBG aqueous dispersions up to 90°C is necessary to obtain a complete dissolution of the gum. By this means, LBG fractions were obtained with mannose to galactose (M/G) ratios increasing with the temperature of solubilization (Hui & Neukom, 1964; Gaisford et al., 1986; Silva & Gonçalves, 1990; Fernandes et al., 1991a; Mannion et al., 1992). Dea et al. (1977) using freeze-thaw cycles showed that LBG forms weak gels. These galactomannan gels showed no true melting point, however, on melting the structural integrity may be lost over a narrow range of temperature. Thus, 1% gels of LBG break down at 64–67°C, 0.75% at 60–65°C and 0.5% gels at 50–55°C. In contrast, GG showed no gel formation. The above authors proposed a structure for galactomannan gel which consists of the association of unsubstituted mannan backbone regions to form interchain junctions while the substituted regions were extensively hydrated.

Xanthan gum (XG) has a β-D-(1→4) linked glucan backbone with short trisaccharide side-chains consisting of α-D-mannose, β-D-glucuronic acid, and β-D-mannose on alternating glucose residues (Jansson et al., 1975). The mannose residue linking the side-chain is acetylated and the terminal mannose contains pyruvate groups approximately every other side-chain. The rheology of XG aqueous solutions has been attributed to the ordered macromolecular structure adopted which depends on the environmental conditions (Morris et al., 1977). XG has been shown to undergo a thermally induced conformational change which is sensitive to the ionic strength, and there is still debate as to whether the ordered structure adopted involves single or double helices (Morris et al., 1977; Southwick et al., 1982; Paoletti et al., 1983; Norton et al., 1984). Very recently, Gunning et al. (1993) by means of scanning tunneling microscopy studies of xanthan gum revealed aggregates of stiff, aligned rod-shapes for molecules with ‘diameters’ consistent with those expected for individual helices.

The viscosity and viscoelastic properties of XG have been extensively studied (Dea et al., 1977; Morris et al., 1977; Cuvelier & Launay, 1986). XG, LBG and GG are used as thickeners. Mixtures of XG + LBG have been reported to form thermally reversible gels. Such properties have not been described in mixtures with GG. However, increases in viscosity have been reported (Tako & Nakamura, 1985; Shatwell et al., 1991b; Lopes et al., 1992), which suggests that some molecular interaction may arise in a mixture of XG + GG.

Much effort has been made to elucidate the synergistic interactions of XG/galactomannan blends. Various models for the mechanism of synergistic interac-
tions have been proposed (Dea & Morrisson, 1975; Dea et al., 1977; Morris et al., 1977). Early work suggested that a specific interaction occurred between the ordered XG molecule and the galactomannan chain (Dea & Morrisson, 1975; Dea et al., 1977; Morris et al., 1977; McCleary et al., 1979). It was shown that the observed synergistic interactions based on cooperative interaction depend on the M/G ratio and also on the fine structure of the galactomannan. Tako et al. (1984) reported that intermolecular interactions should occur between the XG side-chains and the galactomannan backbone, and that the molecules adopt the same ordered conformation as in the solid state. More recently, Cairns et al. (1986, 1987) by means of X-ray diffraction studies suggested that gel formation occurs only if XG is first disordered by heating above the order–disorder transition temperature with an interaction then occurring between the xanthan backbone in an extended two-fold cellulose-like conformation and LBG in a similar two-fold conformation. However, the necessity of heating above the order–disorder transition temperature to rearrange the junction zones between XG/galactomannan is still of considerable debate (Cuvelier & Launay, 1985, 1988; Cheeham & Mashimba, 1988; Cuvelier, 1988; Robinson, 1991; Shatwell et al., 1991a, c). Doublier and Llamas (1991) studied the rheological properties of XG/LBG or GG mixtures at a very low level of xanthan and, based on the mixing of non-interacting polysaccharides, they suggested that each XG and galactomannan (LBG and GG) macromolecules should be excluded from the volume occupied by the other. Very recently, Mannion et al. (1992) by means of rheological and ultracentrifugation studies on heated and unheated mixtures of XG with whole LBG and LBG fractions with different M/G ratios, suggested that XG and galactomannans may interact by two distinct mechanisms. One takes place at room temperature and yields weak but elastic mixed gels which are almost independent of the galactomannan M/G ratio, while the second requires heating of the gum mixture and is highly dependent upon the galactomannan M/G ratio. Nevertheless, in discussing the mechanism of gelation between the xanthan and LBG molecules, it is less clear how both polysaccharides behave in the vicinity of the sol–gel transition. In our work initially, xanthan/galactomannan (guar, whole and fractionated locust bean gum) at 1.0% (w/w) total polymer concentration were characterized using oscillatory shear measurements. The thermal behaviour of 1:1 XG/galactomannan mixtures at 1.0% by means of cooling–heating cycles (70°C → 25°C → 70°C) was observed. The overall objective was a better understanding of the role of the M/G ratio of galactomannans on the structure and in the formation of xanthan/galactomannan mixed gels.

MATERIALS AND METHODS

Materials

Two commercial guar and carob gums were kindly provided by SBI (France) and Indal (Portugal). The xanthan gum sample was kindly supplied by Jungbunzlauer Xanthan (Austria), and had an intrinsic viscosity $[\eta]=33$ dL/g (0.1 m NaCl) and pyruvate and acetate contents of 3.7% and 8.6%, respectively. Of the two galactomannans, only LBG had to be purified as described by
Fernandes et al. (1991a). The purified LBG was fractionated according to its solubility in water at temperatures of 10, 40, 60 and 80°C, and the procedure was carried out as described in Silva and Gonçalves (1990).

Methods

Analysis of galactomannan samples
The moisture and ash contents of the gums were obtained by standard methods. The M/G ratio was determined by GLC analysis of their alditol acetate derivatives (Blackney et al., 1983).

Preparation of the solutions
The galactomannan and xanthan gums were first dispersed in 0.1 M sodium chloride solution with moderate agitation for 1 h at room temperature, and then heated to 90°C for 30 min with continuous stirring at high shear rate. After cooling, the polysaccharide content was estimated using the phenol–sulphuric acid method of Dubois et al. (1956).

Preparation of mixed systems and gels
The mixed systems were prepared by mixing, at 90°C, solutions of galactomannan and xanthan gum in the desired ratio and total polymer concentration. The hot blend was heated for 15 min at a temperature of 90°C with continuous stirring at high shear rate. The hot mixture was then poured into glass moulds. Finally, the glass moulds were covered with parafilm to avoid dehydration problems. Then the blends were allowed to set for approximately 14 h, at 25°C, before use.

Rheological measurements
The viscosity of the dilute solutions was measured at 25°C. The intrinsic viscosity was evaluated from classical Huggins and Kraemer plots as described by Fernandes et al. (1991a).

Cooling–heating cycles. The hot mixture (90°C) was poured directly onto the plate of the controlled stress rheometer Carri-Med CS-100, at 70°C, and covered with light oil in order to eliminate dehydration problems. The storage modulus, $G'$, was obtained from temperature sweep experiments by cooling the mixed systems from 70°C to 25°C, and then heating to 70°C, at the rate of 1°C/min and at the fixed oscillatory shear measurement frequency of 1.0 Hz. A parallel plate geometry was used (gap 4 mm; plate diameter 6 cm) with radial grooves to avoid gel slippage. The strain amplitude was fixed at 0.02.

Kinetics of gelation. The hot mixture (90°C) was poured directly onto the plate of the rheometer (90°C). Then, a temperature of 25°C was automatically attained in a few seconds.

Mechanical spectra. The mechanical spectra of XG and of the whole LBG, at a temperature of 25°C, were obtained with the Carri-Med rheometer fitted with a cone and plate geometry (cone angle 4°C; diameter 5.0 cm), the strain amplitude was fixed at 0.05. In the characterization of the 1:1 XG/LBG
Fraction 60°C, temperatures of 58 and 54°C were attained at the rate of 1°C/min and the mechanical spectra were produced with parallel plate geometry using the same conditions indicated above for the cooling-heating cycles. The mechanical spectra were characterized by the storage modulus, \( G' \), and the loss modulus, \( G'' \), as functions of frequency in the range of 0.01–10 Hz.

The amplitudes of deformation used in this work were chosen in order to remain within the linearity limits of viscoelasticity.

**RESULTS**

The main physicochemical characteristics of the galactomannans are given in Table 1. Figure 1 shows the mechanical spectra, \( G'(\omega) \) and \( G''(\omega) \), of LBG and xanthan solutions at a concentration of 1.0%. Typically, the viscoelastic behaviour of the LBG solution can be ascribed to macromolecular solutions of polysaccharides, with \( G' > G'' \) for the high frequencies. In the case of XG solution, the difference in viscoelastic characteristics is clearly evident as

<table>
<thead>
<tr>
<th>Sample</th>
<th>( H_2O ) (%)</th>
<th>Ash (%)</th>
<th>Protein* (%)</th>
<th>( M/G )</th>
<th>( [\eta] )</th>
<th>( M_v )**</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBG</td>
<td>12.40</td>
<td>0.35</td>
<td>0.49</td>
<td>4.04</td>
<td>15.3</td>
<td>1.8 \times 10^6</td>
</tr>
<tr>
<td>GG</td>
<td>8.32</td>
<td>0.10</td>
<td>0.22</td>
<td>1.68</td>
<td>12.0</td>
<td>1.7 \times 10^6</td>
</tr>
</tbody>
</table>

*Kjeldahl determination according to Anderson (1986).

\( M/G \): mannose to galactose ratio.

\( [\eta] \): intrinsic viscosity in dL/g.

\( M_v \): viscosity average molecular weight from \([\eta]\) as described by Fernandes et al. (1991a).

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**Fig. 1.** Mechanical spectra of xanthan gum and LBG solutions at 1.0% ((□) \( G' \); (■) \( G'' \)-LBG; (○) \( G' \); (●) \( G'' \)-xanthan gum).
xanthan shows little frequency dependence of $G'$ and $G''$ in contrast to LBG. Moreover, $G'$ is higher than $G''$ over the whole frequency range investigated, and such viscoelastic properties appear to respond to the definition of a weak gel according to Clark and Ross-Murphy (1987). It should be noted that the downturn of $G'$ at low frequencies means that the relaxed modulus should be zero, as expected for a macromolecular solution (Doublier, 1994). Whether or not properties such as those depicted in Fig. 1 are typical of a weak gel and not of a macromolecular solution with long relaxation times is a matter of debate. Further studies are needed to elucidate the structural organization of xanthan molecules. The different viscoelastic properties between LBG and XG systems may be related to a higher stiffness of the XG chains which adopt a helical conformation and thus are much more rigid than the random-coil LBG molecules. The macromolecular characteristics of the LBG fractions obtained by temperature fractionation are shown in Table 2. Four fractions were obtained with $M/G$ ratios increasing with the temperature of solubilization. As expected, there is a good correlation between the solubilization temperature and the $M/G$ ratio of galactomannan samples (Hui & Neukom, 1964). The intrinsic viscosity which is an indirect measure of molecular weight and chain extension (Sabater de Sabates, 1979) varied between 10^{-9} and 14^{-9} dL/g. These results are consistent with those of Gaisford et al. (1986), Silva and Gonçalves (1990) and Mannion et al. (1992). Figure 2 shows typical kinetics of gelation at a temperature of 25°C for the 1% total polymer 1:1 XG/LBG mixed systems prepared using both the 10°C and 60°C LBG fractions. For both mixed systems, it is clearly seen that the gel maturation proceeded quickly: 60 min and 90 min were required in order to reach a steady value of about 230 Pa for the 1:1 XG/LBG F10°C blend and of about 550 Pa for the 1:1 XG/LBG F60°C mixture, respectively. In general, the variation in $G'(ω)$ is quite similar for the two mixed systems, however, the $G'$ value for the 1:1 XG/LBG F60°C blend is about twice that of the 1:1 XG/LBG F10°C mixture. In the case of $G''(ω)$ variation, no differences are seen between the two mixed systems; moreover, the $G''$ values are almost identical at around 40–50 Pa. It is important to note that the elastic character of the gel is more pronounced in the case of 1:1 of XG/LBG F60°C mixed gel ($\tan δ = 0.1$) than in the case of the 1:1 XG/LBG F10°C mixed system ($\tan δ = 0.2$). Certainly, this fact reflects the direct effect of the $M/G$ ratio of the

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M/G$</th>
<th>$η$</th>
<th>Huggins constant</th>
<th>$G'$ at 1:1</th>
<th>$Hz^1$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBG F10°C</td>
<td>2.89</td>
<td>10.9</td>
<td>0.79</td>
<td></td>
<td>232</td>
</tr>
<tr>
<td>LBG F40°C</td>
<td>3.78</td>
<td>11.0</td>
<td>0.83</td>
<td></td>
<td>423</td>
</tr>
<tr>
<td>LBG F60°C</td>
<td>4.16</td>
<td>14.6</td>
<td>0.92</td>
<td></td>
<td>557</td>
</tr>
<tr>
<td>LBG F80°C</td>
<td>4.84</td>
<td>14.9</td>
<td>0.78</td>
<td></td>
<td>666</td>
</tr>
</tbody>
</table>

*M/G: mannose to galactose ratio.*

$[η]$: intrinsic viscosity.

$G'$: storage modulus of 1:1 XG/LBG fraction mixtures at 10%.
galactomannan samples on the elastic properties of the XG/galactomannan mixed gels. It should be said that the present data were obtained from measurements at a fixed frequency (1 Hz) while a better understanding of the gel maturation process would require the description of the entire mechanical spectra at any time. In Fig. 3, mechanical spectra of 1:1 XG/LBG fraction mixed gels, that aged during 14 h before the rheological measurements, are presented at a temperature of 25°C. It is clearly seen that there is a direct relation between $G'(\omega)$ and the M/G ratios of LBG fractions. In contrast, this relation is not evident for $G''(\omega)$. Also here it is apparent that the elastic behaviour of the several 1:1 XG/LBG fraction mixed gels increases linearly with the M/G ratio of galactomannans, while the viscous behaviour remains
almost the same for all the mixed systems. It is noteworthy that the dependency of \( G' \) on frequency decreases with an increase in the M/G ratio of LBG fractions present in the XG/galactomannan mixtures. Thus, the storage modulus of the 1:1 XG/LBG 10°C and 40°C fractions mixtures appear to be much more dependent on frequency rather than the other 1:1 XG/LBG 60°C and 80°C fraction mixed gels. In general, \( G'' \) is almost constant from the low frequencies up to 0.3–1 Hz and then shows an increase up to the higher frequencies, for all mixed systems. The \( G' \) values obtained for XG/LBG fractions and XG/GG systems at a frequency of 1.13 Hz are plotted against the XG/galactomannan ratio at the 1.0% total polymer concentration in Fig. 4. Whatever the LBG fraction, it is seen that a synergistic maximum was obtained for the mixing ratio of 1:1 xanthan/galactomannan. Figure 4 shows that a similar pattern of \( G' \) versus mixing ratio of xanthan/galactomannan was obtained for all XG/LBG fraction gels, while GG did not display a maximum at a 1:1 mixing ratio. The values of \( G' \) of 1:1 XG/LBG fraction mixed gels obtained from dynamic measurements are also presented in Table 2. As expected, there is a linear relationship between the M/G ratio of galactomannans and the \( G' \) maximum obtained at the 1:1 XG/galactomannan mixing ratio. In fact, a linear relation between the maximum synergism \( (G'_{\text{max}}) \) and the galactose content of galactomannan samples was found which can be described by the following equation:

\[
G'_{\text{max}} = -425 + 228(M/G)
\]

with a correlation factor of 0.99. Clearly, the synergistic effects that take place in the xanthan/galactomannan mixed gels, taken as the \( G'_{\text{max}} \), are ruled by the galactomannan M/G ratio. However, the molecular weight of LBG fractions appear not to interfere with the rigidity of the established mixed gel network. Despite the similarities in molecular weights between 10 and 25°C LBG fractions \( ([\eta] = 11 \text{ dL/g}) \) and also between the 60 and 80°C LBG fractions

![Figure 4](image-url)

**Fig. 4.** Effect of the xanthan/galactomannan ratio on the storage modulus \( (G') \) of mixed gels at 1.0% and at a temperature of 25°C. Frequency: 1.13 Hz (□) \( G'^{-1}\)-XG/guar gum; (○) \( G'^{-1}\)-XG/LBG fraction 10°C; (■) \( G'^{-1}\)-XG/LBG fraction 40°C; (△) \( G'^{-1}\)-XG/LBG fraction 60°C; (△) \( G'^{-1}\)-XG/LBG fraction 80°C.
Xanthan/galactomannan mixtures ([η] = 15 dL/g), this fact is not reflected in the $G'$ maximum value obtained for each XG/LBG fraction mixed gel, since this value increases linearly with the M/G ratio of galactomannans. These results are in good agreement with those of Mannion et al. (1992). However, the $G'$ values obtained for the 1:1 XG/LBG fractions in the present work are significantly lower than those described by the latter authors. This fact can be simply explained by structural differences between the xanthan gums used, namely in their molecular weights.

In order to determine the gelation ($T_g$) and melting ($T_m$) temperatures of 1:1 XG/galactomannan mixtures at 1.0%, cooling–heating cycles were carried out using oscillatory shear measurements at a fixed frequency of 1 Hz. The mixed systems were cooled from 70°C to 25°C and then reheated. In Figs 5 and 6 the variation of $G'$ as a function of temperature for the 1:1 XG/LBG fractions and GG mixtures during the cooling and heating, respectively, is presented. In the present study the sol–gel transition was defined by the departure point of the plots of $G'$ versus temperature. We choose this criterion because, at a frequency of 1 Hz and at temperatures between 60 and 70°C, the $G'$ modulus was always higher than the $G''$ modulus. This way it was not possible to take the sol–gel transition as typically defined by the cross-over of the $G'-G''$ moduli, as described in the case of physical gels by Cuvelier and Launay (1990) and Lin et al. (1991). This situation is clearly described by the mechanical spectra of 1:1 XG/LBG F60°C mixture at temperatures of 58°C and 54°C (Fig. 7). $G'> G''$ over almost the whole frequency range, with the exception at a frequency of 0.01 Hz. Apparently, $G''$ tends to be higher than $G'$ below 0.01 Hz. Such a behaviour may appear to respond to the definition of a weak gel. However, it was verified that this mixed dispersion flows freely at 58–60°C and for this reason it cannot be considered as a gel. It seems like the time-scale investigated could be considered as relatively narrow. This way, the mechanical spectrum observed may be regarded as that of a macromolecular solution with the $G'-G''$

![Fig. 5. $G'$ variation as a function of temperature (on cooling) for 1:1 XG/LBG fractions 10, 40, 60 and 80°C and GG at 1.0%. Frequency: 1.0 Hz (--; --) $G'-XG/guar gum; (\Delta) G'-XG/LBG fraction 10°C; (+) G'-XG/LBG fraction 40°C; (△) G'-XG/LBG fraction 60°C; (▲) G'-XG/LBG fraction 80°C.](image-url)
Fig. 6. $G'$ variation as a function of temperature (on heating) for 1:1 XG/LBG fractions 10, 40, 60 and 80℃ and GG at 1-0%. Frequency: 1-0 Hz (⋯) $G'$-XG/guar gum; (△) $G'$-XG/LBG fraction 10℃; (+) $G'$-XG/LBG fraction 40℃; (□) $G'$-XG/LBG fraction 60℃; (▲) $G'$-XG/LBG fraction 80℃.

Fig. 7. Mechanical spectra of 1:1 XG/LBG fraction 60℃ at 1-0% and at temperatures of 58 and 54℃ (●) $G'$; (○) $G''$-54℃; (■) $G'$; (□) $G''$-58℃.

cross-over point occurring at frequencies < 0-01 Hz. In fact, this viscoelastic behaviour is somehow between those displayed in Fig. 1 for both polysaccharides alone, and can simply be ascribed by different molecular mobilities of the XG and LBG macromolecules. In contrast, at 54℃, the mechanical spectrum was typical of a weak gel with $G' > G''$, thus indicating that the system is already beyond the gel point. The data of Fig. 7 are in good agreement with the departure point of $G'$ in Fig. 5 for the same XG/LBG fraction mixture ($T_g = 55-56℃$) suggesting that this temperature is close to the gel point. It is to
Xanthan/galactomannan mixtures

TABLE 3
Parameters Related to the Sol–Gel Transition

<table>
<thead>
<tr>
<th>Sample</th>
<th>M/G</th>
<th>( T_g ) (°C)(^a)</th>
<th>( T_m ) (°C)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBG F10°C</td>
<td>2.89</td>
<td>48–49</td>
<td>54–55</td>
</tr>
<tr>
<td>LBG F40°C</td>
<td>3.78</td>
<td>50–51</td>
<td>56–57</td>
</tr>
<tr>
<td>LBG F60°C</td>
<td>4.16</td>
<td>55–56</td>
<td>61–61</td>
</tr>
<tr>
<td>LBG F80°C</td>
<td>4.84</td>
<td>59–60</td>
<td>66–67</td>
</tr>
</tbody>
</table>

\(^a\) \( T_g \): gelation temperature.
\(^b\) \( T_m \): melting temperature.

be noted that we did not apply the same kind of approach to the gel melting. However, it seems reasonable to assume that the melting process should present an identical evolution as in the case of the gel point. In general, the pattern of cooling and melting curves for 1:1 XG/LBG fraction mixed systems were identical (Figs 5 and 6) and as expected, reflects the effect of the M/G ratios of the different galactomannan fractions. Thus was detected an increase in the transition temperatures also of \( G' \) values at 25°C. On heating, a slight hysteresis was systematically observed for all the XG/LBG fraction mixtures which was characterized by an increase in the \( T_m \) values of about 4–6°C over the \( T_g \) values (Figs 5 and 6). The gelation and melting temperatures are listed in Table 3. The \( T_g \) and \( T_m \) values increase quite clearly with a decrease in galactose content of the galactomannan fraction. In contrast, no transition was found for the 1:1 XG/GG blend. These results are quite consistent with those of McCleary et al. (1984). Cuvelier (1988) working in equilibrium conditions did not find a thermal hysteresis for the XG/LBG mixed systems. However, in our case the hysteresis (5°C) was systematically observed for all XG/LBG fraction mixtures (Figs 5 and 6). Certainly, this hysteresis can be explained by the non-equilibrium conditions that were used during the cooling–heating cycles (i.e. the rate of 1°C/min).

DISCUSSION

Oscillatory shear measurements have been extensively used by several authors to investigate the gelation of XG/galactomannan or glucomannan mixtures (McCleary et al., 1984; Tako et al., 1984; Cuvelier, 1988; Tako, 1991; Williams et al., 1991). Williams et al. (1991) described a good correlation between the transition temperature obtained by differential scanning calorimetry (DSC) and electron spin resonance spectroscopy and the evolution of \( G' \) as a function of the temperature. Cuvelier (1988) by interpretation of the mechanical spectra of XG/LBG systems suggested that XG–XG and XG–LBG interactions could take place. Recently, Doublier and Llamas (1991) also by means of rheological experiments conducted on XG/galactomannan mixtures have suggested that galactomannan–galactomannan interactions can take place. According to Dea et al. (1977), the melting temperature of an LBG gel at 0.5% is about 50–55°C. The LBG concentration of 0.5% corresponds to the same galactomannan
concentration present in a 1:1 XG/LBG mixture at 1.0%. Apparently, there is an interesting coincidence between the \( T_g \) values of the several XG/LBG fraction systems that are around 50–60°C and the \( T_m \) (50–55°C) of a LBG gel at 0.5%. Cuvelier (1988) and Williams et al. (1991) by means of DSC measurements have studied the gelation of XG/LBG systems. The latter authors obtained too broad a peak on the DSC cooling curves for the XG/LBG mixed systems which was ascribed to a poor resolution of the experiment while the former author, working in experimental conditions close to those used in the present work (0.8% total polymer concentration; 1:1 mixing ratio; 0.1 M NaCl), described two peaks very well defined at 50°C and 70°C. According to this author one peak (50°C) could be related to the XG/LBG interactions and the other one (70°C) could be attributed to LBG-LBG aggregation. This fact can at least show that the galactomannan should play a crucial role in the process of XG/LBG gel formation.

From the rheological data and transition temperatures here presented it is evident that the higher the M/G ratio of galactomannan samples the higher is the synergistic interaction. Moreover, the M/G ratio of the galactomannan also determines the \( T_g \) at which the XG/galactomannan mixed system initiates gelation. In the case of carrageenans the sol to gel transition is instantaneous and results directly in gel formation (Rochas & Rinaudo, 1982; Fernandes et al., 1991b, 1993). While the xanthan molecules in a helix form adopt a more rigid conformation, they do not gel (Morris et al., 1977). In the case of \( \kappa \)-carrageenan/galactomannan mixtures the gelation temperature depends exclusively on the ionic content and \( \kappa \)-carrageenan concentration and not on the M/G ratio of the galactomannan used (Fernandes et al., 1991b, 1992). In contrast, in the case of xanthan/galactomannan mixtures the gelation temperature is directly related to the M/G ratio of the galactomannan. The higher the galactomannan M/G ratio the higher is the \( T_g \) of the XG/galactomannan mixed system. This way the LBG appears to be the primary initiator of gelation of XG/LBG mixed systems. This mechanism of gelation is thus different from that described for \( \kappa \)-carrageenan/LBG mixed systems (Cairns et al., 1987; Fernandes et al., 1992). Thus, the additional effect of LBG in the XG/LBG mixed gels, at the sol to gel transition, is in the initiation of the medium structure formation following a mechanism which is likely the same as that observed in synergistic interactions between XG and LBG. The results obtained support the interaction mechanism between xanthan and LBG previously proposed. However, this is not clearly the case with XG/GG systems. Thermorheological measurements on these polymer mixed systems allowed us to correlate the temperature dependence of their structural development and suggest possible molecular mechanisms. However, it is necessary to be cautious when interpreting thermorheological profiles in terms of molecular mechanisms. Other supporting evidence is needed. Nevertheless, studies on the viscoelastic characteristics of biopolymers as the temperature increases and decreases allows an assessment of their performances as ingredients in food systems which undergo thermal treatment.

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REFERENCES


