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A rheological description of mixtures of a galactoxyloglucan with high amylose and waxy corn starches

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Abstract

A galactoxyloglucan hydrocolloid (HXG) was extracted with water from endosperms of seeds of *Hymenaea courbaril* and purified (18.5% yield). It contained galactose, xylose, and glucose in a ~1:3:4 molar ratio. HXG was mixed with a high amylose (66%) (CSM) and waxy corn starch (CSP). Each gel mixture, under static rheological conditions, showed an increase in the paste viscosity, when compared with those of starches or HXG alone. Dynamic rheological analysis showed an interaction occurred in the HXG–CSM mixture resulting in an increased thermal stability of its gel, when compared with that of CSM alone. © 2003 Published by Elsevier Science Ltd.

Keywords: Galactoxyloglucan; Starches; *H. courbaril*; Gels; Physicochemical interactions

1. Introduction

Starches have an enormous number of uses in the food industry and in other areas, including capacity of adhesion, binding, film-formation, gelling and thickening (Whistler & BeMiller, 1997). However, they have negative aspects such as syneresis, retrogradation, and on heating of granules with excess water, high viscosity during paste formation. This is often not desirable, and can be controlled by chemical modifications or mixing with hydrocolloids (Sudhakar, Singhal, & Kulkarni, 1996; Wurzburg, 1986; Yoshimura, Takaya, & Nishinari, 1999).

There are many reports on rheological properties resulting from interaction between starches and hydrocolloids (Abdulmola, Hember, Richardson, & Morris, 1996; Alloncle, Lefebvre, Llamas, & Doublier, 1989; Kulicke, Eidam, Kath, Kix, & Kull, 1995; Rayment, Ross-Murphy, & Ellis, 1995; Sudhakar et al., 1996; Yoshimura et al., 1999). However, there are only two specifically on the interaction between starch and galactoxyloglucan. Prabhanjan and Ali (1995) found that mixing of solutions of tamarind galactoxyloglucan and corn starch resulted in a high viscosity, an increase in pseudoplasticity and a decrease in the paste temperature. The level of carboxymethylation and hydroxypropylation of the galactoxyloglucan diminished the interaction. Yoshimura et al. (1999) showed by rheological analysis that the interaction did not exist but the hydrocolloid decreased the retrogradation and syneresis of the starch paste.

In our Carbohydrate Group, considerable attention has been paid to the galactoxyloglucan from the seeds of *Hymenaea courbaril*, which were obtained from different Brazilian locations and whose structure and properties have been determined (Freitas, 2000; Lima, Quoirin, Wollinger, Krüger, & Sierakowski, 2000; Lima, Reicher, Corrêa, Ganter, & Sierakowski, 1993; Lima, Rechia, Ganter, Reicher, & Sierakowski, 1995; Martin, 1999; Martin, Souza-Lima, Gorin, Reicher, & Sierakowski, 2000; Souza-Lima, 1997; Vargas-Rechia et al., 1998).

We now investigate some structural characteristics necessary to result in interaction between starches and our galactoxyloglucan. To this end, corn starches with a high (66%) and zero levels of amylose were utilized and the rheological characteristics of the mixtures compared.

2. Materials and methods

2.1. Plant material

Seeds of *H. courbaril* were harvested from the Foz do

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Table 1
Percentage chemical composition (g%) of galactoxyloglucan and corn starch samples

Samples	Carbohydrate[a]	Protein[b]	Moisture[c]	Ash[c]
HXG	81	2.00	15	0.40
CSM	91.5	0.19	8.5	0.045
CSP	89	0.26	9	0.04

[a] Method of Dubois et al. (1956).
[b] Method of Hartree (1972).
[c] Method of Zobel and Stephen (1996).

Chopin Forest Reserve, State of Paraná, Brazil. The galactoxyloglucan (HXG) was obtained by exhaustive aqueous extraction from pooled and milled *H. courbaril* seeds (40 g l^{-1} for each extraction process). The viscous extracts were purified by centrifugation at 30,200*g* and the supernatant sequentially passed through Millipore filter membranes with pore sizes of 3 and 0.8 μm.

Corn starch rich in amylose (CSM) and exclusively amylopectin (CSP) were supplied by Corn Products Brasil Ingredientes Industriais Ltda, Balsa Nova, State of Paraná, Brazil.

2.2. Chemical analysis

Total carbohydrate was assayed by the phenol–H_2SO_4 method, with a necessary modification for starch samples (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956), protein by the method of Hartree (1972), ash and moisture by that of Zobel and Stephen (1996), and amylose content was by the method of Chrastil (1987).

^{13}C and ^{1}H NMR spectra were obtained using a BRUKER, model AVANCE-DRX-400 instrument, using D_2O as solvent for the galactoxyloglucan and DMSO-d_6 for starch samples. All analyses were carried out at 60 °C and chemical shifts are in ppm based on that of acetone, as internal standard (δ 30.2).

Monosaccharide contents of starches were determined on complete acid hydrolysis with M TFA at 100 °C for 5 h (Adams, 1965). The solutions were evaporated to a residue, which was repeatedly dissolved in H_2O and evaporated. For the galactoxyloglucan, better quantitation was obtained as follows. The polysaccharide was dissolved and partially hydrolyzed with H_2SO_4–H_2O (1:1, v/v) at 4 °C for 1 h, H_2O added to give a dilution of 8% and complete hydrolysis effected at 100 °C for 5 h. The solution was neutralized ($BaCO_3$), the suspension filtered and the filtrate evaporated to dryness (Selvendran, March, & Ring, 1979). The products from each hydrolysis procedure were reduced with $NaBH_4$ and acetylated with pyridine–Ac_2O (1:1 v/v) for 12 h at 25 °C (Wolfrom & Thompson, 1963). The resulting alditol acetates were analysed by GLC using an HP model 5890-2, with a DB-225 capillary column at 220 °C, a flame ionization detector at 250 °C, and nitrogen as carrier gas.

2.3. Average molar mass (M_w) and R_g

The d*n*/d*c* of the galactoxyloglucan was determined using a Waters differential refractometer, model 2410 at a wavelength of 546 nm, the concentrations used being 1.0; 0.5; 0.25 and 0.125 g l^{-1} (filtered by Millipore filter 0.45 μm). The ratio of refractive index to concentration gives the constant d*n*/d*c* that is used to calculate the molar mass.

Aqueous solutions of galactoxyloglucan (0.5 g l^{-1}) were filtered through a 0.22 μm pore Millipore filter and injected into a GPC having 2000, 500, 250 and 120 ultragel columns. Detection was carried out using the above Waters refractometer and a DAWN DSP-F Wyatt Technology model controlled at a light scattering multiangle of 632.8 nm. The eluent was 0.5 g l^{-1} aq. sodium nitrite containing 200 ppm of sodium azide at a flux of 0.6 ml min^{-1}.

2.4. Syneresis

Syneresis in the samples was estimated using a centrifuge tube of 10 ml capacity with a graduated scale of 0.1 ml. A Fanem centrifuge, model 208, was used at 1800 rpm for 30 min. After 1, 24, 48 and 72 h of refrigeration, syneresis was determined by the ratio of separated water after centrifugation to the initial volume of liquid (10 ml) (Zheng & Sosulski, 1998).

2.5. Rheological properties

For rheological analyses, the galactoxyloglucan (5 g l^{-1}) was solubilised over 16 h in distilled H_2O at 25 °C. Samples of starch alone were solubilised in closed tubes at 96 ± 1 °C for 30 min and the solutions cooled to 5 °C and maintained over periods of 1, 24, 48 and 72 h. Each mixture of CSM or CSP (40 g l^{-1}) with HXG (10 g l^{-1}), at a v/v mixture of 1:1, was prepared with or without heating at 96 °C for 30 min, and then maintained at 5 °C for 24 h.

Non-oscillatory analyses were performed with a model LV DV-III Brookfield rheometer fitted with cone and plate geometry. The apparent viscosity was determined at a shear rate of 1.5 s^{-1}. The temperature of the systems was controlled with a model TC-500 Brookfield circulatory bath.

Oscillatory analyses were carried out using a model RS 75 Haake Rheometer with a C-60/2° sensor. For constant temperature studies at 25 °C was controlled with a model BC-5 Haake bath and with variation of temperature was achieved with a Peltier system with heating (20–90 °C) and cooling gradients (90–20 °C) at a rate of 0.033 °C s^{-1}.

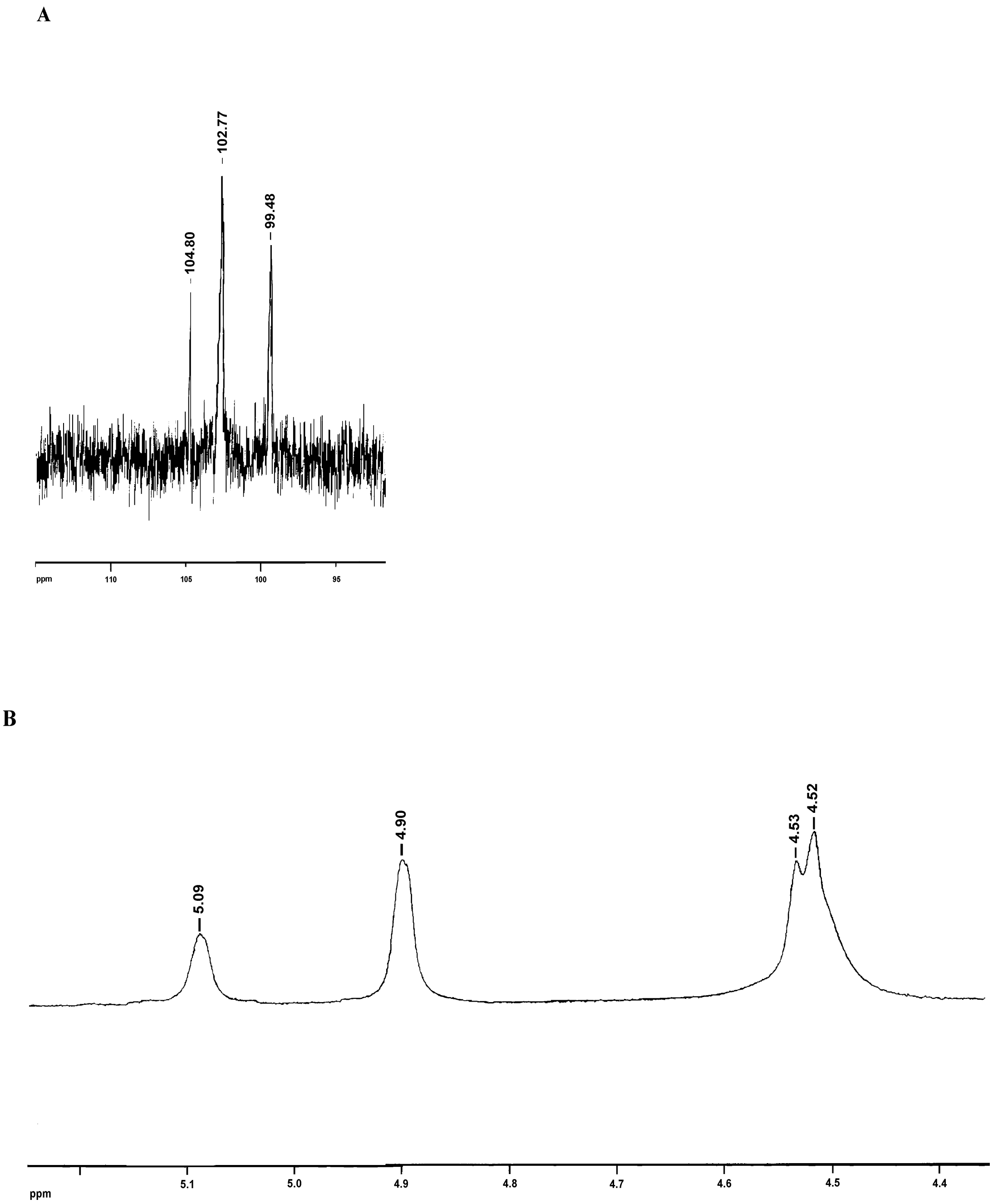

Fig. 1. Anomeric region of ^{13}C (1A) and ^{1}H NMR (1B) spectra of the galactoxyloglucan of *Hymenaea courbaril* in D_2O at 60 °C (δ in ppm).

3. Results and discussion

3.1. Chemical and physicochemical analysis of galactoxyloglucan and starches

Milled endosperms of *H. courbaril* seeds were subjected to aqueous extraction at 25 °C, and after purification using Millipore filters, a water-soluble galactoxyloglucan (HXG) was obtained (18.5% yield). The starches CSM and CSP contained 66% and zero amylose, respectively. The composition of the starches and HXG, in terms of carbohydrate, protein, ash and moisture, is summarized in Table 1.

The starches contained exclusively glucose. Comparison of the ^{13}C NMR spectra of CSM and CSP in DMSO-d_6 showed only one C-1 signal (δ 101.54) for CSM and a small additional signal from CSP at δ 100.94, due to 6-*O*-substitution.

The ^{13}C NMR spectrum of HXG in deuterium oxide contained signals at δ 104.8, 102.77 and 99.48, which can be assigned to C-1 of β-D-Gal*p*, β-D-Glc*p*, and α-D-Xyl*p* units, respectively. In the C-6 region, the signal at δ 67.15 arose from 6-*O*-substituted β-D-Glc*p* units, while that at δ 61.14 was from unsubstituted units. The areas of the C-1 signals showed Gal, Xyl, and Glc to be present in a ~1:3:4 molar ratio (Fig. 1(A)), a value that agreed with those of H-1

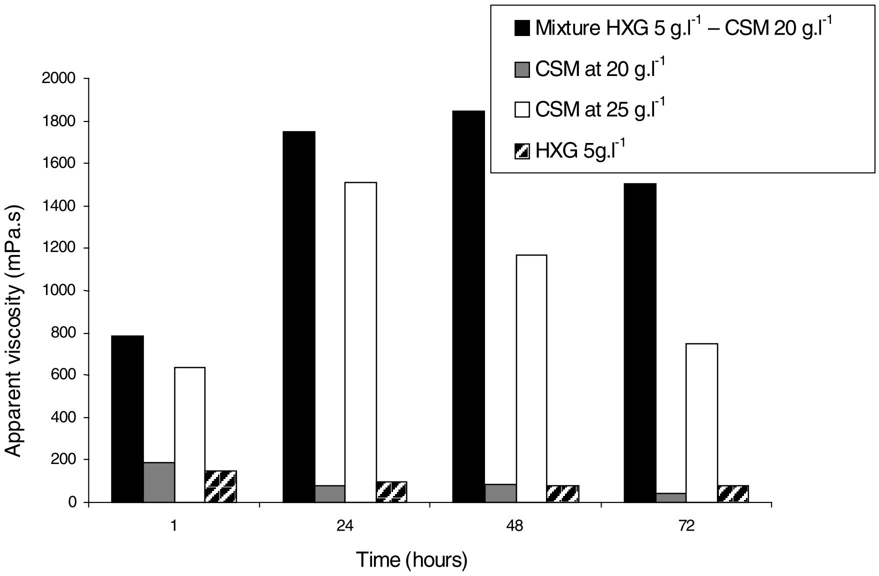

Fig. 2. Effect of storage time at 5 °C on the apparent viscosity of various solutions, involving CSM.

signals in the ^{1}H spectrum, although some overlapping was present (Fig. 1(B)), and the ratio obtained on acid hydrolysis.

The galactoxyloglucan had an intrinsic viscosity of 700 ml g^{-1} in water and an average molar mass (M_w) obtained by gel permeation (GPC), detected by refractive index and light scattering, of 1.44×10^6 g mol^{-1} and R_g of 75.8 nm. The degree of polydispersion was 1.7 and the d*n*/d*c*, determined experimentally for the macromolecule, was 0.113 ml g^{-1}.

3.2. Rheological properties of starches and starch–galactoxyloglucan mixtures

In order to check that gelling of the starches rich in amylose and amylopectin was complete the samples were treated for 15, 30 and 60 min at 96 ± 1 °C. No difference was found between the pastes obtained after 30 and 60 min of heating (data not shown). The paste-forming temperature for the starch alone and in the presence of galactoxyloglucan was determined by rheology, using a constant frequency of 1 Hz and by measurement of the G' value as a function of the temperature. No appreciable difference in the gelatinization temperature (~70 °C) was observed (data not shown).

The effect of HXG on the apparent viscosity of mixtures with CSM and CSP is shown in Figs. 2 and 3, respectively. The value of apparent viscosity at 1.5 s^{-1} was greater for both mixtures, the increase being the greatest after 20 h storage at 5 °C of CSM and CSP solutions at a concentration

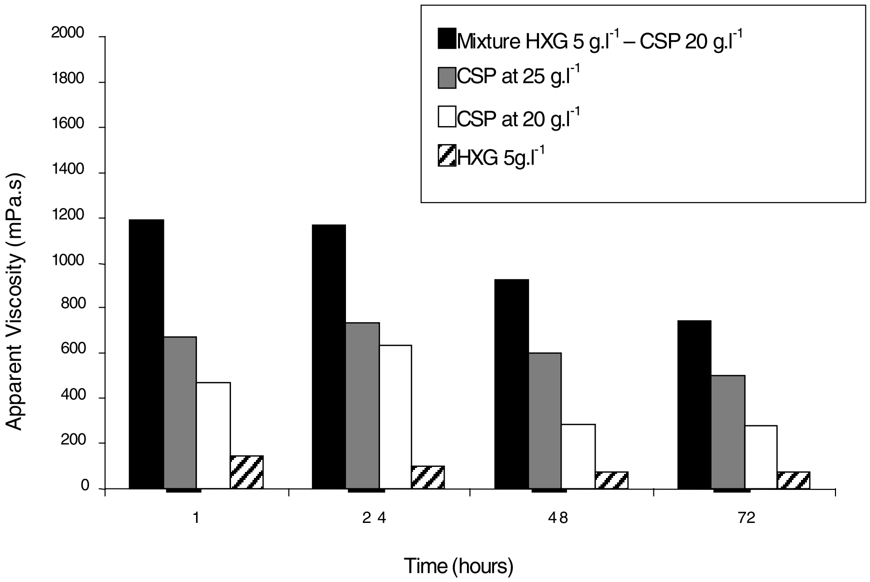

Fig. 3. Effect of storage time at 5 °C on the apparent viscosity of various solutions, involving CSP.

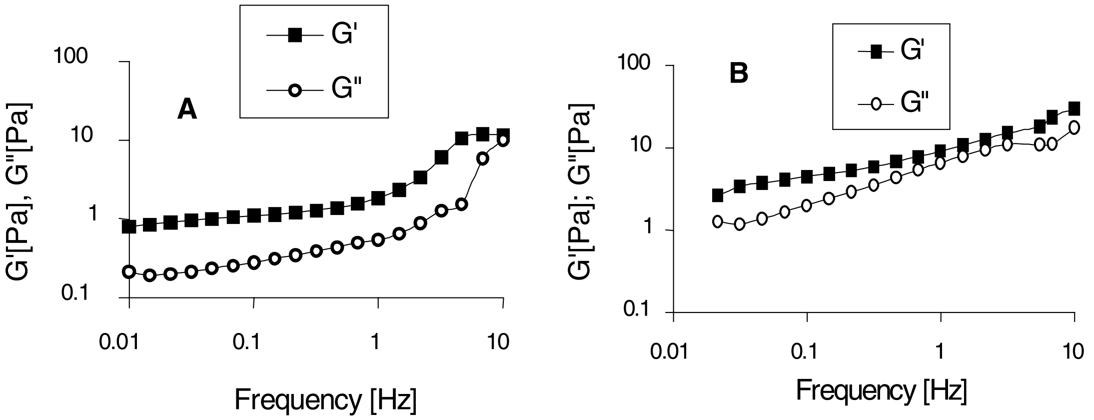

Fig. 4. Frequency dependence of the storage (G'), loss modulus (G'') at stress 0.1 Pa for: (A) CSM (25 g l^{-1}) and (B) the HXG (5 g l^{-1})–CSM (20 g l^{-1}) mixture heated together.

of 25 g l^{-1}. Therefore, in later experiments, comparative analysis were carried out after 24 h of cooling. However, increases in viscosity values, over those of CSP and CSM alone, after all times of cooling were found. In terms of the effect of the galactoxyloglucan on syneresis in high-amylose starch, after 1 h of refrigeration, the starch alone showed 30 and 60% of syneresis at concentrations of 25 and 20 g l^{-1}, respectively, these values being reduced to 6.25 % in the mixture (data not shown).

In the dynamic rheological analyses, the viscoelastic behavior was determined for starches and HXG–starch mixtures over a frequency range of 0.01–10 Hz. Linear G^* and deformations of less than 5% were observed under stresses of less than 0.4 Pa. Fig. 4 shows the variation of G' and G'' as a function of frequency under a stress of 0.1 Pa at 25 °C for the HXG (5 g l^{-1})–CSM (20 g l^{-1}) CSM (25 g L^{-1}) and HXG (5 g L^{-1})–CSM (20 g L^{-1}) mixture.

These rheograms show that mixing increased the G' value five-fold at all the chosen frequencies, but that the ratio G''/G'(tan δ), was higher for starch alone (0.28 at 1 Hz): in the mixture, tan δ was 0.54 at the same frequency.

A similar experiment depicted in Fig. 4 was carried out, but without heating CSM and HXG together. The results in Fig. 5 show that this did not apparently give rise to an increase in the interaction.

The dynamic viscosities (η^*) of the HXG–CSM mixture, together, and CSM alone, are presented in Fig. 6. One can observe that the values of η^* for mixtures are 5–6 times greater than for the starch rich in amylose, even at a greater concentration, under practically all the frequencies studied, and that the viscosity decayed linearly.

The unusual frequency behavior, presented in Figs. 4 and 6 at above ~2 Hz can be attributed to the presence of suspended solids, signifying that the amylose was probably retrograded. Another important observation was that this effect was less pronounced for the mixture.

Experiments to determine the interaction capacities of corn starches and HXG were also carried out on a mixture of HXG and CSP. The linear viscoelastic region for CSP (25 g l^{-1}) and CSP (20 g l^{-1})–HXG (5 g l^{-1}) mixture was determined using a stress sweep of 0.088–1 Pa at frequencies of 0.01, 0.1, 1, and 10 Hz. The constant G^* and low deformation (±5%) at all of these frequencies was determined under stresses lower than 0.3 Pa. Thus, the value chosen was 0.1 Pa for CSP and the mixture. The influence of frequency on the G' and G'' values over the mixture range is shown in Fig. 7. It shows that the gel formed on cooling over

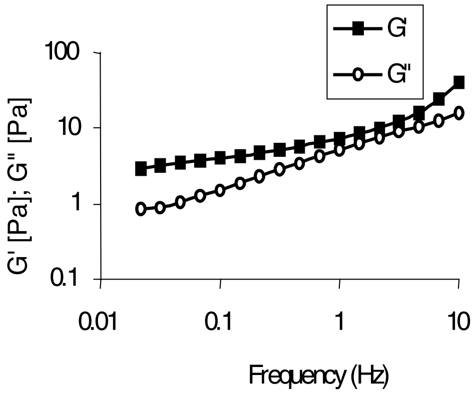

Fig. 5. Frequency dependence of storage (G') and loss modulus (G'') for the HXG (5 g l^{-1})–CSM (20 g l^{-1}) mixture not heated together.

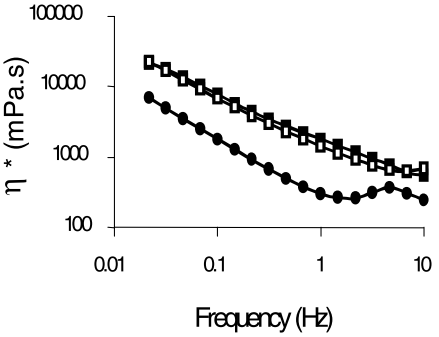

Fig. 6. Frequency dependence of dynamic viscosity (η^*) on: (•) CSM (25 g l^{-1}), (■) the HXG (5 g l^{-1})–CSM (20 g l^{-1}) mixture heated together, and (□) the mixture not heated together.

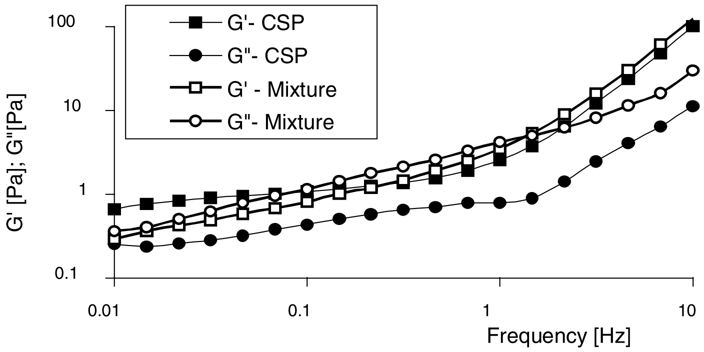

Fig. 7. Frequency dependence of storage (G') and loss modulus (G'') at stress 0.1 Pa on CSP (25 g l^{-1}) and HXG (5 g l^{-1})–CSP (20 g l^{-1}) mixture, prepared by heating.

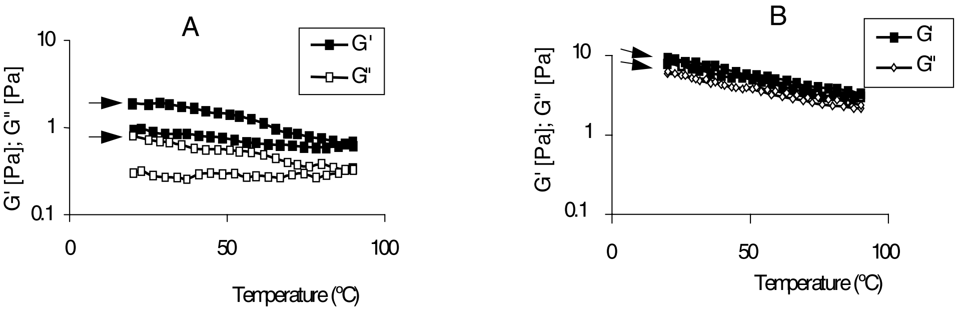

Fig. 8. Temperature dependence of storage (G') and loss modulus (G'') at 1 Hz and deformation of 5% on: (A) CSM at 25 g l^{-1} and (B) CSM (20 g l^{-1})–HXG (5 g l^{-1}) mixture prepared by heating. (→) shows the initial heating program.

24 h at 5 °C of the CSP solution (25 g l^{-1}) did not occur for the CSP (20 g l^{-1})–HXG (5 g l^{-1}) mixture, but that the storage moduli (G') are similar for CSP alone and the mixture. The greater difference is in the loss modulus (G'') that increased substantially when the mixture was examined. Thus, HXG does not apparently interact to the same degree with CSP than the amylose-rich CSM, showing that part of the branched molecule did not contribute (Fig. 4(B)).

3.3. Effect of temperature on the viscoelastic behavior of the gels

The rheogram depicted in Fig. 8(A) shows that with CSM at a concentration of 25 g l^{-1}, the gel did not melt, but that a proportionally greater decrease in G' and G'' occurred. Fig. 8(B), corresponding to the CSM (20 g l^{-1})–HXG (5 g l^{-1}) mixture, shows that melting did not occur, but that the variation of G' and G'' was less than that shown in Fig. 8(A). The G' and G'' values are also greater for the mixture at all temperatures. The tan δ values are shown in Fig. 9 for CSM alone and the mixture.

These results show that the G''/G' ratio did not vary appreciably on increasing and decreasing of temperature, but that the values of tan δ are greater for CSM alone at 25 g l^{-1} concentration. This indicates that the starch gel is stronger than that formed by the mixture. On the other hand, the constant values observed for tan δ demonstrate that the interaction of CSM with the hydrocolloid HXG increased the thermal stability of the gel, consistent with a stabler interaction.

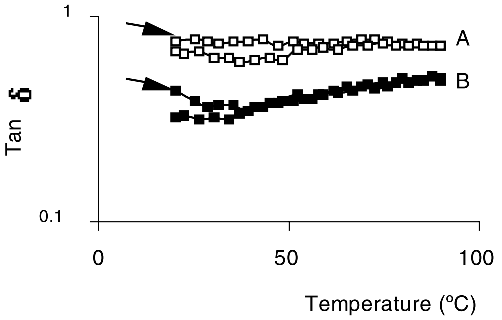

Fig. 9. Temperature dependence of tan δ on: (A) CSM (20 g l^{-1})–HXG (5 g l^{-1}) mixture and (B) CSM alone (25 g l^{-1}), prepared by heating. At 1 Hz and deformation of 5%. (→) shows the initial heating.

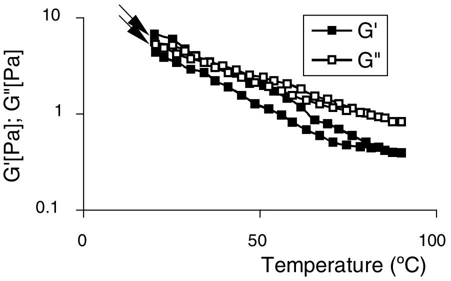

Fig. 10. Temperature dependence of storage (G') and loss modulus (G'') for the CSM (20 g l^{-1})–HXG (5 g l^{-1}) mixture, not heated. At 0.1 Hz and deformation of 5%.

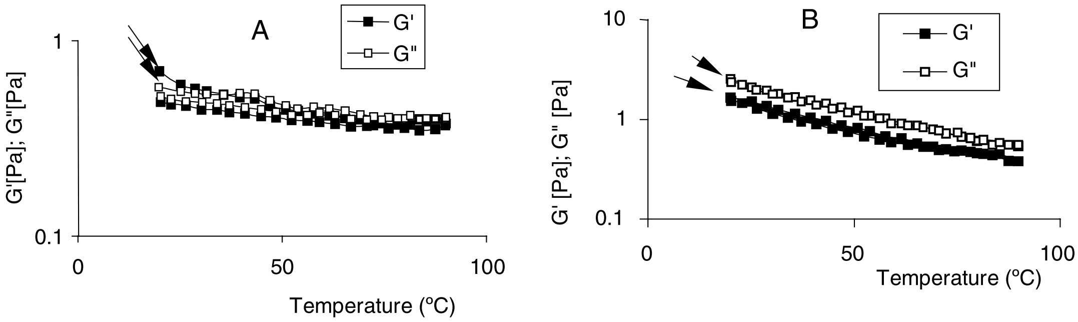

Fig. 11. Temperature dependence of storage (G') and loss modulus (G'') for: (A) CSP at 25 g l^{-1} and (B) CSP (20 g l^{-1})–HXG (5 g l^{-1}) mixture, prepared by heating. At 1 Hz and deformation of 5%.

Fig. 10 shows the temperature dependence of the CSM (20 g l^{-1})–HXG (5 g l^{-1}) mixture, prepared without heating of HXG with CSM together. The values of G' and G'' are identical at 35 °C in the heating program and the values of G'' became greater than G' at 39 °C, indicating melting. Thus, the presence of the hydrocolloid HXG, when mixed with the high amylose starch CSM, increased the thermal stability of the gel.

Apparently, heating of the amylose-rich starch together with the HXG is necessary to give rise to a stable complex (Figs. 8 and 10). This could be through conformational modifications of the amylose (folding) resulting in a stable interaction with galactoxyloglucan.

Fig. 11(A) and (B) shows the temperature dependence of gels formed by CSP alone (25 g l^{-1}) and the weak gel formed by the mixture of CSP (20 g l^{-1})–HXG (5 g l^{-1}), respectively. Fig. 11(A) indicates that the gel formed by CSP alone at 25 g l^{-1} melted at ~30 °C, and the structure was not regenerated on cooling. In addition, the mixture did not show hysteresis on cooling, but at the frequency employed (1 Hz), G'' was greater than G' at all temperatures. At this frequency, both G' and G'' values of the mixture are greater than those for CSP alone at 25 g l^{-1}.

4. Conclusions

Rheological measurements show that CSM and CSP interact with HXG. In both cases, an increase in the viscosity occurs, when compared with those of HXG or starches alone, due to interaction with the hydrocolloid. Oscillation experiment showed the interaction occurred to a greater degree with CSM, which contains 66% of linear amylose, when compared with CSP, whose amylose content is zero. With the latter, there was an increase in the loss modulus (G''), generating a weak gel. The presence of the hydrocolloid in the CSM–HXG mixture, increased the thermal stability of the gel, an indication of stable interactions.

Acknowledgments

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