



Influence of the concentration of polyols on the rheological and spectral characteristics of guar gum

Poliana Moser^{a,*}, Marinonio Lopes Cornelio^b, Vânia Regina Nicoletti Telis^a

^a Departamento de Engenharia e Tecnologia de Alimentos, Universidade Estadual Paulista, São José do Rio Preto, 15054-000, Brazil

^b Departamento de Física, Universidade Estadual Paulista, São José do Rio Preto, 15054-000, Brazil

ARTICLE INFO

Article history:

Received 20 October 2012

Received in revised form

13 February 2013

Accepted 18 February 2013

Keywords:

Apparent viscosity

Viscoelasticity

Polyols

Spectroscopy

Freezing

ABSTRACT

Polyols are widely used as sugar substitutes and provide texture to foods. Guar gum has many applications in food industry such as increasing product viscosity and improving texture. Knowledge of rheological properties of gum/polyol systems is important to permit replacing sugar while maintaining product texture. In this work, rheological properties of 0.1, 0.5 and 1 g/100 g guar solutions containing 10 and 40 g/100 g of maltitol, sorbitol, or xylitol were studied. The behavior of these mixtures was evaluated by steady and oscillatory shear measurements, and after a freezing/thawing cycle. Apparent viscosity of guar solutions increased with addition of polyols and with the increase in their concentrations, except for 40 g/100 g sorbitol addition to 1 g/100 g guar gum, in which the apparent viscosity decreased. Addition of polyols also increased the dynamic moduli of the systems. In mixtures of guar with 40 g/100 g polyol, the phase angle (δ) was below unity, but was dependent on frequency, which is characteristic of concentrated solutions with a certain degree of structuring. FTIR spectroscopy was studied to provide information on possible interactions between guar gum and polyols. Analyses carried out after freezing/thawing showed no changes in the viscoelastic behavior of the solutions.

© 2013 Elsevier Ltd. Open access under the [Elsevier OA license](http://www.elsevier.com/locate/elsevier).

1. Introduction

Sugar substitutes have received much attention recently due to the increasing worldwide demand for light and diet foods. These products are destined for individuals searching for low calorie food and/or those that attend specific diets, preventing or controlling common diseases such as diabetes. The absence of sugar in processed products alters moisture retention and other characteristics such as flavor, texture, color and aroma, making it difficult to obtain products similar to the conventional ones. In this case, ingredients that give body to the product must be used, substituting the volume and texture lost by removing sugar.

Polyols or sugar alcohols are hydrogenated carbohydrates that provide texture to foods, contributing to the nutritional value and flavor and showing organoleptic characteristics (Legaz & Vicente, 2005), and their use as sugar substitutes is widely recognized. The polyols used industrially include sorbitol and xylitol, which are monosaccharides, and maltitol which is a disaccharide. Recently the sugar alcohols have attracted consumers since they present multiple health benefits. They can be consumed by diabetics, are

non-cariogenic (Livesey, 2003) and have low calorie content (Siefarth et al., 2011). The polyols show a calorie content of 2.4 kcal/g, whereas the sugars and other carbohydrates show a value of 4 kcal/g (Zumbé, Lee, & Storey, 2001). They are considered to be GRAS (Generally Recognized as Safe) additives, and should be used at levels not exceeding those indicated in the GMP (Good Manufacturing Practices), since an excessive consumption can have a laxative effect and cause gastrointestinal disorders (Basu, Shivhare, Singh, & Beniwal, 2011).

Guar gum is a hydrocolloid extracted from the seed of a leguminous plant, *Cyamopsis tetragonolobus* (Gupta, Shah, Sanyal, Variyar, & Sharma, 2009). It is a galactomannan formed of linear chains of D-mannopyranosyl units connected to each other by β (1→4) bonds, and D-galactopyranosyl units connected to each other by α (1→6) bonds (Munhoz, Weber, & Chang, 2004). Guar is one of the most important thickeners used in food and drink industries (Richardson, Willmer, & Foster, 1998), since it produces highly viscous solutions even at low concentrations (Lapasin, Pricl, & Tracanelli, 1991), is cheap, and improves food stability (Bobbio & Bobbio, 1992). It is widely used in products such as salad dressings or as a suspension agent and crystallization inhibitor in ice-creams (Chenlo, Moreira, & Silva, 2011). It is also used in applications where viscosity control, suspension and body formation, as well as modification of texture, consistency or water retention are required.

* Corresponding author. Tel.: +55 17 81285070

E-mail address: polianamoser@yahoo.com.br (P. Moser).

The rheological behavior of guar gum solutions is pseudoplastic, showing good stability during freezing and thawing cycles. The effects of adding co-solutes such as sucrose, glucose, trehalose and sodium chloride on the steady-shear flow behavior of guar have been reported by various authors (Chenlo et al., 2011; Galmarini, Baeza, Sanchez, Zamora, & Chirife, 2011; Richardson et al., 1998). Mechanical spectra determined by small-amplitude oscillatory shear flow can also yield very useful information on the solution structure and the nature of the interactions between the biopolymer and other food constituents.

FTIR spectroscopy is widely used in food industry to provide valuable information on the structure and on concentration of chemical functional groups within the material. The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study.

Considering that other components present in a determined formulation can have a marked influence on the functional properties of hydrocolloids, studies on the interactions of the gums with co-solutes are of fundamental importance. Knowledge on such interactions may be useful to promote elaboration of healthy foods and which can attend the needs of individuals who have food restrictions, maintaining the sensory and technological properties of the product. Based on these considerations, the objective of this work was to study the interactions between polyols and guar gum by analyzing the rheological, also evaluating the systems after applying freezing and thawing cycles considering its potential use in ice cream or frozen desserts. Spectroscopic analyzes were performed to evaluate the structural changes of macromolecules depending on the composition of the systems.

2. Material & methods

2.1. Materials

The gum/polyol systems were prepared with different concentrations of guar gum (Plury Química Ltda, Diadema, Brazil), sorbitol (Corn Products Brasil, Mogi Guaçu, Brazil), maltitol and xylitol (Tovani Benzaquen, São Paulo, Brazil). In order to prevent microbial growth, 0.04 g/100 g of sodium azide (NaN₃) was added to all prepared samples (Pongsawatmanit & Srijunthongsiri, 2008).

2.2. Sample preparation

The gum/polyol pairs were prepared based on the procedure described by Galmarini et al. (2011). The initial solutions were prepared containing twice the required concentration of each of the pure solute, and then mixed in equal amounts to obtain the desired final concentration of each gum/polyol pair, followed by agitation in magnetic stirrer for 1 h at room temperature. To complete hydration of the polymer, the solutions were allowed to rest for 12 h at 4 °C (Chenlo et al., 2011). Table 1 summarizes the concentrations of guar gum and the polyols in the final solutions.

2.3. Determination of the rheological properties

The rheological measurements were made using an AR-2000EX rheometer (TA Instruments, Delaware, USA) with cone and plate geometry and a gap of 52 μm. All the trials were carried out at a fixed temperature of 25 °C, controlled by a peltier system on the plate. All the analyses were carried out in triplicate.

2.3.1. Steady shear

The systems with the greater polyol concentration (40 g/100 g) were previously tested to evaluate their time dependence. For this

Table 1
Identification and composition of the guar gum and polyol samples.

Sample group	Sample code	Composition
Samples of pure solutes	G01, G05, G1	Samples of guar gum/water with 0.1, 0.5, or 1 g/100 g gum
	M10, M40	Samples of polyol/water with 10 or 40 g/100 g polyol.
	S10, S40	M = maltitol, S = sorbitol and X = xylitol, while the numbers refer to the polyol concentrations
	X10, X40	
Samples containing guar gum/polyol pairs	G01M10, G01M40	Samples of guar/maltitol/water, with 0.1, 0.5 or 1 g/100 g gum and 10 or 40 g/100 g maltitol
	G05M10, G05M40	Samples of guar/sorbitol/water, with 0.1, 0.5 or 1 g/100 g gum and 10 or 40 g/100 g sorbitol
	G1M10, G1M40	Samples of guar/xylitol/water, with 0.1, 0.5 or 1 g/100 g gum and 10 or 40 g/100 g xylitol
	G01S10, G01S40	
	G05S10, G05S40	
	G1S10, G1S40	
	G01X10, G01X40	
	G05X10, G05X40	
G1X10, G1X40		

purpose, three shear rate ramps were carried out in the following order: increasing–decreasing–increasing shear rate in the range from 1 to 500 s⁻¹. For all the systems, the area below the decreasing shear–rate curve (second ramp) practically coincided with that of the second increasing curve (third ramp), allowing to consider that after an initial fall in shear stress, the behavior of the samples stabilized. Based on these results, all the subsequent steady shear measurements were carried out using a decreasing shear rate ramp in the range from 500 to 1 s⁻¹.

Flow curves were obtained at 25 °C, and Newton, Ostwald-de-Waele, Herschel-Bulkley, Cross and Carreau models were tested to describing the flow behavior. The Cross model (Equation (1)), proposed by Cross (1965), resulted in adequate fittings.

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + k_{CR}\dot{\gamma}^n} \quad (1)$$

where η is the apparent viscosity (Pa s), η_0 and η_{∞} are the zero-shear rate and the infinite-shear rate viscosity (Pa s), respectively, k_{CR} (sⁿ) is relaxation time, $\dot{\gamma}$ the shear rate (s⁻¹), and n is dimensionless exponent.

The quality of fit was evaluated from the determination coefficient (R^2) and from the root mean square (RMS) of the residues (Telis, Lourençon, Gabas, & Telis-Romero, 2006).

2.3.2. Oscillatory shear

In order to determine the linear viscoelastic region, scans of increasing deformation were carried out in the range from 0.0001 to 100 at frequencies of 0.628 and 6.28 rad/s. Subsequent frequency scans were carried out in the range from 0.0628 to 10 rad/s, maintaining the deformation constant (5%) within the linear viscoelastic region. Mechanical spectra were obtained for the energy storage modulus (G'), dissipation modulus (G'') and phase angle (δ) as a function of the angular frequency (ω).

2.4. Freezing and thawing

Samples were frozen in a freezer at –38 °C for a 20 h period, and then thawed at room temperature. Oscillatory rheological trials were carried out on the samples before and after freezing/thawing.

2.5. FTIR spectroscopy

Samples were placed between two CaF₂ windows (Harrick model WFD-U25, U.S.A.), separated by a 6 μm spacer (Harrick

model MSP-6-M25, U.S.A.). Infrared spectra were measured with an NEXUS 670 FT-IR spectrometer (Nicolet, U.S.A.) purged with nitrogen (5 L/min). To obtain a high signal-to-noise ratio, 256 interferograms were averaged for each spectrum with a resolution of 4 cm^{-1} in the range of $3000\text{--}1200\text{ cm}^{-1}$, with 256 scans with resolution of 4 cm^{-1} .

The spectra subtraction was performed considering that the region between 2500 and 1800 cm^{-1} should be flattened consequently obtaining the polyol and guar absorptions independently. The influence of guar over the polyol was also taken into account doing a second type of subtraction from the system polyol, guar and water minus guar and water. From this result we search for the influence of guar on complex system. The baseline correction was also applied at both regions I and II and smoothing tools applied was Savitsky-Golay with 25 points.

2.6. Statistical analysis

The results for the dependence of G' and G'' on frequency (fit to the power law) before and after freezing were compared by Tukey's test at a level of significance of 5%, using the statistical software Minitab 15 (MINITAB, State College – PA, USA).

3. Results

3.1. Steady shear

Fig. 1 shows the variation in apparent viscosity with shear rate of guar gum solutions containing maltitol, sorbitol and xylitol in different concentrations. The effect of the polyols on the apparent

viscosity of the solutions varied as a function of the gum concentration. In the systems containing 0.1 and $0.5\text{ g}/100\text{ g}$ guar gum, the apparent viscosity of all the solutions increased with the polyol concentration, a result similar to that reported by Chenlo et al. (2011), for guar gum with sucrose and glucose.

When dealing with samples containing $1\text{ g}/100\text{ g}$ gum, the behavior of the systems varied as a function of the concentration and type of added polyol. When added at a concentration of $10\text{ g}/100\text{ g}$, all the polyols caused an increase in apparent viscosity of the solutions. However, the addition of M40 or X40 did not modify the viscosity of G1 at shear rates below 50 s^{-1} , whereas addition of S40 did reduce the apparent viscosity of the gum. Milani and Koocheki (2011) evaluated the rheology of a yogurt ice cream with date syrup ($0, 25$ and $50\text{ g}/100\text{ g}$) added as a sugar substitute, and guar gum ($0, 0.1, 0.2$ and $0.3\text{ g}/100\text{ g}$) added as a fat substitute. Increasing concentrations of date syrup and guar gum led to increases in the viscosity of the ice cream, although the concentrations of gum used were below $0.5\text{ g}/100\text{ g}$. At this concentration, the results of the present study also indicated an increase in apparent viscosity with increase in concentration of the co-solutes.

At low shear rates, the typical Newtonian plateau was experimentally detected in the flow curves of guar/polyol systems. The plateau region, where viscosity has a constant value, decreased with increasing solute concentration. This behavior is in accordance with previous results reported to pure guar gum solutions (Chenlo, Moreira, & Silva, 2010).

Pure polyol solutions showed Newtonian behavior, in agreement with previously reported results obtained at room temperature (Lim, Seo, & Youn, 2004; Siefarth et al., 2011).

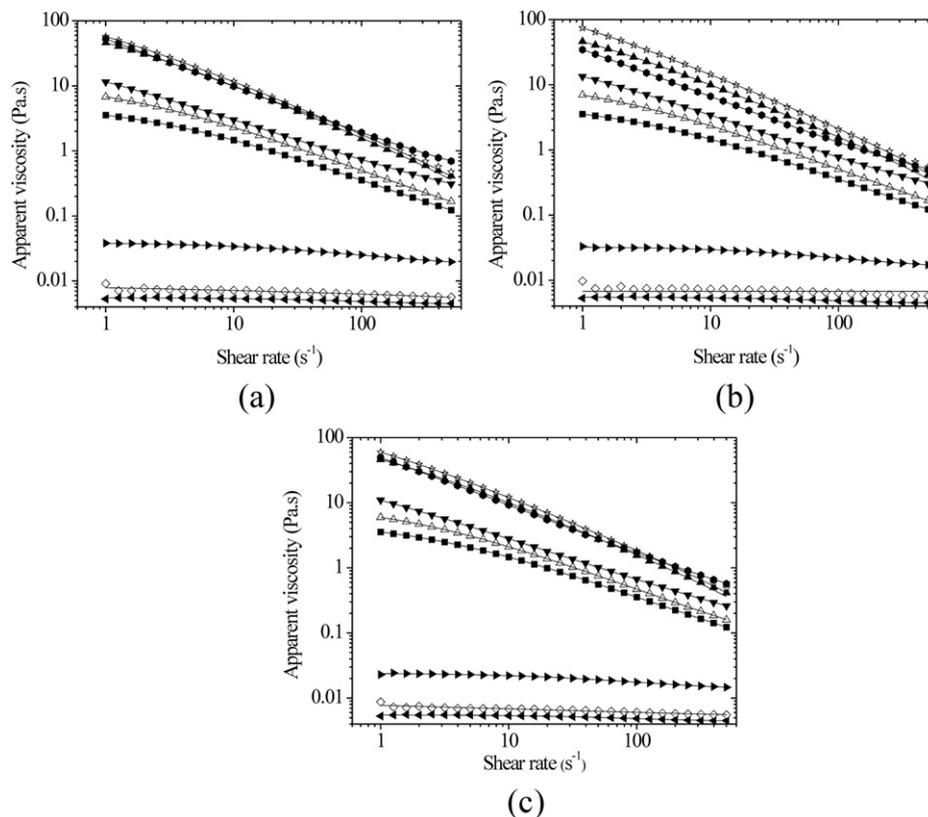


Fig. 1. Apparent viscosity predicted by the cross model for guar gum solutions with different concentrations of polyols: (a) maltitol; (b) sorbitol; and (c) xylitol: ◀ $0.1\text{ g}/100\text{ g}$ guar gum, ◇ $0.1\text{ g}/100\text{ g}$ guar gum + $10\text{ g}/100\text{ g}$ polyol, ▶ $0.1\text{ g}/100\text{ g}$ guar gum + $40\text{ g}/100\text{ g}$ polyol, ■ $0.5\text{ g}/100\text{ g}$ guar gum, △ $0.5\text{ g}/100\text{ g}$ guar gum + $10\text{ g}/100\text{ g}$ polyol, ▽ $0.5\text{ g}/100\text{ g}$ guar gum + $40\text{ g}/100\text{ g}$ polyol, ▲ $1.0\text{ g}/100\text{ g}$ guar gum, ☆ $1.0\text{ g}/100\text{ g}$ guar gum + $10\text{ g}/100\text{ g}$ polyol, ● $1.0\text{ g}/100\text{ g}$ guar gum + $40\text{ g}/100\text{ g}$ polyol.

The Cross equation was the best model for describing pseudo-plastic behavior of pure guar solutions and solutions of G01 with polyol (Table 2). The behavior of G05 and G1 solutions was different from the rheological profiles observed for the lower concentration of gum and the Cross model did not fit adequately to these flow curves. There was evidence of an apparent yield stress associated with particulate inclusions and this was also observed with the higher guar and polyol concentrations. These results are similar to those obtained in rheological studies of mixtures of guar galactomannan and insoluble particulate inclusions or 'fillers' (Rayment, Ross-Murphy, & Ellis, 1995, 1998, 2000). According to these authors this type of rheological behavior can be more easily described with inclusion a yield stress term (σ_0) modified Cross equation as follows:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + k_{CR}\dot{\gamma}^n} + \frac{\sigma_0}{\dot{\gamma}} \quad (2)$$

Table 3 shows the rheological parameters of the modified Cross model for solutions with 0.5 and 1.0 g/100 g concentrations of guar gum with polyols. In all systems the time constant increased significantly with increasing polyol concentration. Viscosity values at zero-shear rate also significantly increased with increasing guar and polyol concentration. In all systems the presence of 40 g/100 g polyol decreased the n value, demonstrating an increase in the degree of pseudoplasticity.

For samples G1, G1M10, G1S10 G1X10 the parameter infinite shear rate viscosity (η_{∞}) resulted in negative values during fitting. In order to eliminate this inconsistency we decided to establish a fixed value for this parameter and only adjust the additional fitting parameters. The criterion adopted to set the value of consisted in assuming a linear relationship between and guar concentration for each polyol concentration.

3.2. Oscillatory shear

The samples of guar 0.1 g/100 g, pure and with polyols, did not present viscoelastic behavior, as shown in Fig. 2, which shows the variations in the energy storage modulus (G') and the phase angle (δ) as a function of the angular frequency, obtained with a 5% deformation amplitude. Nevertheless, the rheological measurements carried out in 0.5 and 1 g/100 g guar solutions provided evidence that the presence of polyols, and the increase in their concentrations, increased the values of G' , resulting in more structured systems.

A variation in the storage modulus was shown to exist as a function of angular frequency for all the samples, showing behavior closer to that of a concentrated solution than a true gel. In a certain way this behavior was already expected, since guar gum does not form a gel in solution, being used as a thickener and stabilizer (Dziejak, 1991). On the other hand, as the concentration of the polyols increased in the solution, the dependence of the G' moduli

on the frequency decreased, indicating greater structuring of the systems.

The addition of polyols decreased the values for the phase angle as compared to the values obtained with the pure gum (G05 and G1), suggesting an increase in system elasticity, which behavior became less similar to that of a liquid and closer to that of a gel. The increase in system structuring was not proportional to the gum/polyol concentrations in the system.

The solutions containing 0.5 g/100 g guar gum, pure or with 10 g/100 g of any of the polyols, presented $\delta > 1$, which is characteristic of a dilute solution. With the addition of 40 g/100 g of any of the polyols, there was a change to $\delta < 1$, although the curves corresponding to the G05 systems were less dependent on frequency than those obtained with samples of G1. This is further evidence that the addition of 40 g/100 g polyol to solutions that already contain 1 g/100 g hydrocolloid creates a competitive effect for the water available in the system, resulting in less structured systems.

The systems containing G1, pure and with polyols, showed liquid-like behavior at low frequencies ($G'' > G'$) and solid-like behavior ($G' > G''$) at higher frequencies, passing through a cross-over ($G' = G''$). The cross-over moves to lower frequencies with increasing system concentration, indicating the behavior of a highly concentrated solution, as shown in Fig. 3 for solutions of guar gum added with maltitol. Chenlo et al. (2010) reported similar results to guar gum.

Dynamic rheological measurements were made by Evageliou, Kasapis, and Hember (1998), in systems composed of 0.5 g/100 g k-carrageen and high glucose syrup concentrations at a temperature of 5 °C, and the addition of 60 g/100 g glucose syrup resulted in an increase in system firmness. Doyle, Giannouli, Martin, Brooks, and Morris (2006), investigated the effect of high sorbitol concentrations (40–60 g/100 g) in the cryo-gelatinization of galactomannan (1 g/100 g). The gel strength showed an increase and subsequent reduction with increasing polyol concentration, the maximum strength being attained with 50 g/100 g sorbitol.

Comparing Fig. 2a and b, it can be seen that the values reached for G' were slightly higher for maltitol than for sorbitol. The systems containing xylitol presented results very similar to those obtained with sorbitol, the corresponding data being shown in Fig. 4, which also shows the effect of freezing/thawing on the solutions.

The dependence of G' and G'' on the frequency can be described by a power law-type equation, as shown in equations (3) and (4) (Kim & Yoo, 2006; Rao, 1999; Wang et al., 2008):

$$G' = k'\omega^{n'} \quad (3)$$

Table 3

Rheological parameters of the modified cross model (Equation (2)) for solutions with 0.5 and 1.0 g/100 g concentrations of guar gum pure and with maltitol, sorbitol and xylitol.

Sample code	η_0 (Pa.s)	k_{CR} (s ⁿ)	n (-)	η_{∞} (Pa.s)	σ_0 (Pa)	R^2	RMS %
G05	5.175	0.356	0.74	0.016	0.003	1	21.56
G1	76.4	1.112	0.83	0.031	9.474	0.999	10.46
G05M10	11.511	0.647	0.75	0.021	0.090	1	8.56
G05M40	14.764	0.873	0.73	0.153	3.7	0.999	3.08
G1M10	88.028	1.169	0.84	0.05	16.278	1	1.47
G1M40	108.107	3.867	0.71	0.181	23.189	1	26.04
G05S10	12.202	0.687	0.75	0.017	0.013	1	7.73
G05S40	46.866	3.622	0.72	0.098	0.010	0.999	26.14
G1S10	99.165	1.052	0.85	0.02	26.071	1	0.72
G1S40	107.833	5.499	0.73	0.175	10.531	0.999	26.97
G05X10	9.8174	0.571	0.75	0.023	0.018	1	11.48
G05X40	28.992	3.205	0.67	0.063	1.798	0.999	25.71
G1X10	96.403	1.245	0.84	0.022	15.788	1	2.32
G1X40	57.235	1.306	0.79	0.306	23.373	0.999	28.07

Table 2

Rheological parameters of the cross model (Equation (1)) for solutions with 0.1 g/100 g guar gum pure and with maltitol, sorbitol and xylitol.

Sample Code	η_0 (Pa.s)	k_{CR} (s ⁿ)	n (-)	η_{∞} (Pa.s)	R^2	RMS %
G01	0.0055	0.0136	1.03	0.0043	0.974	1.41
G01M10	0.0074	0.0139	1.06	0.0054	0.963	4.25
G01M40	0.0390	0.0177	0.73	0.0157	0.999	17.21
G01S10	0.0075	0.0122	1.06	0.0055	0.957	4.74
G01S40	0.0328	0.0164	0.83	0.0146	0.998	9.71
G01X10	0.0070	0.0128	1.04	0.0053	0.999	4.25
G01X40	0.0241	0.0147	0.80	0.0127	0.996	9.19

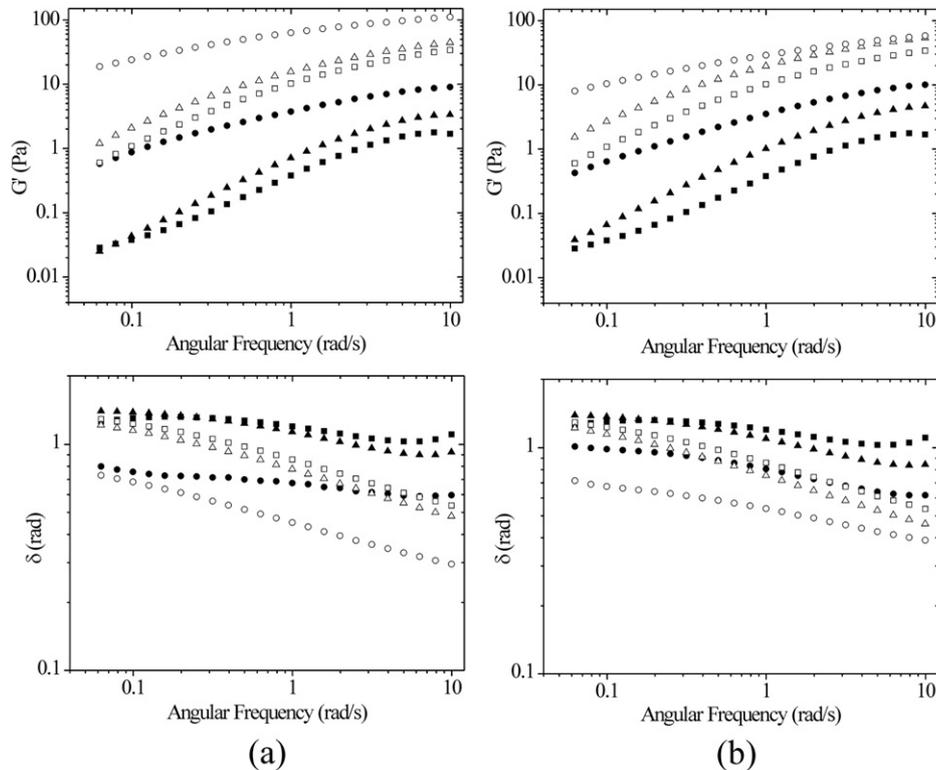


Fig. 2. Variation in G' and $\tan \delta$ with angular frequency for guar gum with different concentrations of (a) maltitol; (b) Sorbitol; ■, □ pure guar gum; ▲, Δ guar gum + 10 g/100 g polyol; ●, ○ guar gum + 40 g/100 g polyol; filled symbols = 0.5 g/100 g guar gum; empty symbols = 1.0 g/100 g guar gum.

$$G'' = k''\omega^{n''} \quad (4)$$

where k' and k'' are constants, n' and n'' are the frequency exponents, and ω the angular frequency.

The magnitude of k' increased with increasing polyol concentration. At the same time, the increase in polyol concentration reduced the values of n' and n'' (Table 4), indicating reduced dependence of the G' and G'' values of the systems on frequency.

3.2.1. Freezing and thawing

Fig. 4 shows the dependence of G' and G'' as a function of frequency for the guar and xylitol systems before freezing and after

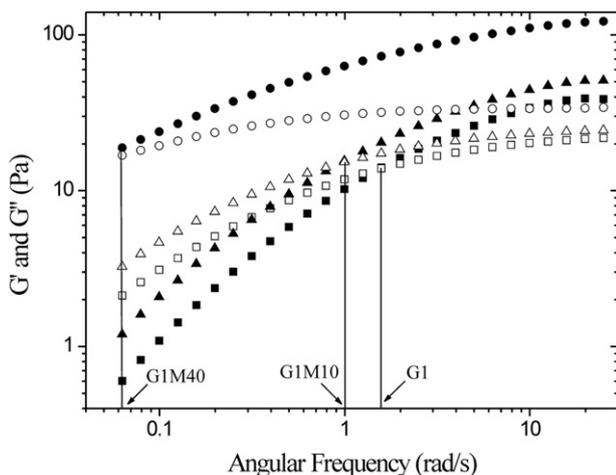


Fig. 3. Cross-over frequency ($G' = G''$) for 1 g/100 g guar gum (■, □), 1 g/100 g guar gum + 10 g/100 g maltitol (▲, Δ), and 1 g/100 g guar gum + 40 g/100 g maltitol (●, ○); filled symbols = G' ; empty symbols = G'' .

the freezing and thawing cycle. After freezing/thawing the G05 solution showed a slight loss in elasticity with a slight reduction in G' . In general the polyols helped preserve the structure of the guar after freezing.

The systems G05M10 and G05X10 presented a slight increase in the values for G' and G'' in relation to G05, showing that these polyols contributed to an increase in elasticity. At the same time, the addition of 40 g/100 g of the polyols to G1 resulted in slight reductions in the values obtained for G' after freezing. In all the other systems studied, the freezing/thawing cycle applied had no effect on the viscoelasticity of the materials.

Table 5 illustrates the dependence of the G' and G'' of the systems on the frequency after the freezing and thawing cycle, as described by equations (3) and (4), and shows the fitting parameters for these equations. When comparing the slope values (n' and n'') of the curves and the constants k' and k'' obtained for samples before freezing and after freezing/thawing (Table 4), there were no significant differences at the 5% level as a result of the freezing and thawing cycle.

3.3. FTIR spectroscopy

From a first-order perspective, the idea of the quantitative aspects of the group frequencies carries through for most functional groups, and the overall spectrum is essentially a composite of the group frequencies, with band intensities in part related to the contribution of each functional group in the molecule. This assumes that the functional group does give rise to infrared absorption frequencies, and it is understood that each group has its own unique contribution based on its extinction coefficient (or infrared absorption cross-section) (Coates, 2000).

Fig. 5 shows a set of vibrations in two specific regions, 1600–1200 cm^{-1} (region I) and 3000–2600 cm^{-1} (region II). The first region represents the deformation of $\delta(\text{CH})$ and $\delta(\text{CH}_2)$ groups and

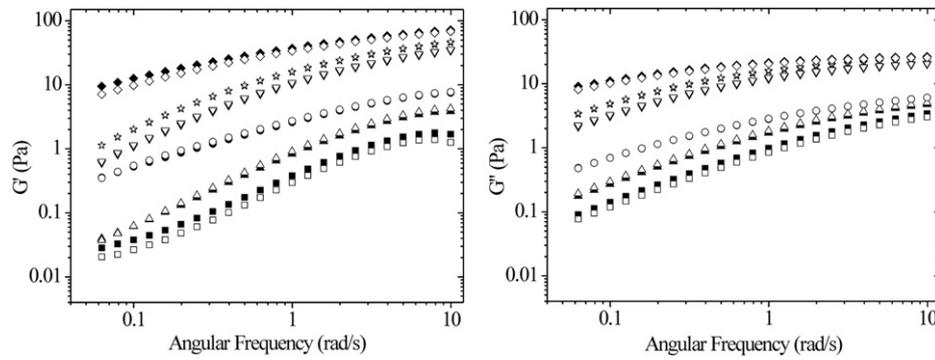


Fig. 4. Effects of freezing/thawing on the values of G' and G'' ; ■, □ 0.5 g/100 g guar gum, ▲, △ 0.5 g/100 g guar gum + 10 g/100 g xylitol, ●, ○ 0.5 g/100 g guar gum + 40 g/100 g xylitol, ▼, ▽ 1 g/100 g guar gum, ★, ☆ 1 g/100 g guar gum + 10 g/100 g xylitol; ◆, ◇ 1 g/100 g guar gum + 40 g/100 g xylitol; filled symbols represent solution before freezing and empty symbols after freezing/thawing.

the second region the major contribution comes from stretching ν (CH) (Mishra & Sen, 2011; Zhang & Han, 2006). According to the infrared spectra, the absence of the band displacement indicates that the vibrational mode is not affected by the presence of guar. On the other hand, the spectral intensity increases in the presence of guar gum, independently of the polyol investigated.

4. Discussion

All the systems evaluated presented pseudoplastic behavior, that is, the apparent viscosity decreased as the shear rate increased. According to Barnes et al., (1989), this occurs due to orientation of the molecules in the direction of flow, and the break-up of aggregates, decreasing the resistance to movement.

The plateau region decreased with increasing concentration, which is due to the decreasing rate of entanglement formation at higher concentrations, as well as with the increasing rate of entanglements disruption that occurs with increasing shear rate (Chenlo et al., 2010).

In the system containing G01 and G05, the apparent viscosity of all the solutions increased with the polyol concentration. This increase in viscosity is associated with synergistic effects: the viscosity increases with the solids content due to the increase in molecular interactions, particle format, electro-viscous effects and the formation of an interfacial film (Maskan & Gogus, 2000; Rao, 1999). In the samples containing G1, the behavior of the systems varied as a function of the concentration of the type of polyol added. The addition of 40 g/100 g sorbitol reduced the apparent viscosity of the gum, what could be attributed to inhibition of the polymer–polymer association by bonding of the polyol molecules to the polymeric chains (Doyle et al., 2006). According to Oliani and

Bobbio (1981), variations in the viscosity of gums in the presence of sugars are associated with the reduction in free water available for interaction with the hydrocolloid.

The time constant to Cross model increased with increasing gum concentration and polyols. The higher dependence on concentration of the time constants could be attributed to a more limited molecular motion due to the higher degree of entanglement (Yoo, Figueiredo and Rao, 1994).

The determination of the dynamic moduli can indicate changes in the structures of macromolecule solutions with greater precision. The presence of polyols, and the increase in their concentrations resulted in more structured systems. Guar gum showed viscoelastic behavior strongly influenced by high polyol concentrations (40 g/100 g), which could be connected to the fact that the strength and density of the hydrogen bonds increased, due to a smaller distance between the molecules (Chen & Dickinson, 2000). Bayarri, Durán, and Costell (2004) reported an increase in G' for k-carrageen gels in the presence of sucrose, suggesting that the presence of sugar increased and stabilized the number of junction zones between the polymer chains. The dependence of G' and G'' on the frequency can be described by a power law-type equation. The magnitude of k' increased with increase in polyol concentration and this increase could be attributed to an increase in viscoelasticity of the gum/polyol system (Kim et al., 2006).

In solutions containing 0.5 g/100 g guar, polyols helped to preserve the structure of the gum after freezing. By interacting with the polyols, the gums are kept more elastic and are not influenced by the freezing process, which is an important result for the food industry, as it indicates a higher stability of systems. In solutions

Table 4
Power law fitting parameters for Equations (3) and (4) before freezing.

Sample code	k' (Pa.s ^{n'})	n' (–)	K'' (Pa.s ^{n''})	n'' (–)
G05	0.455	0.65	0.971	0.57
G1	9.968	0.57	10.556	0.33
G05M10	0.812	0.68	1.467	0.51
G05M40	3.621	0.44	2.796	0.37
G1M10	14.708	0.52	13.474	0.29
G1M40	59.280	0.30	28.438	0.11
G05S10	1.126	0.67	1.878	0.49
G05S40	3.454	0.51	3.365	0.36
G1S10	18.492	0.50	16.276	0.27
G1S40	27.785	0.35	16.024	0.21
G05X10	0.937	0.67	1.627	0.50
G05X40	2.152	0.51	2.271	0.42
G1X10	14.867	0.52	13.713	0.29
G1X40	35.087	0.34	19.550	0.17

Table 5
Power law fitting parameters for Equations (3) and (4) after the freezing/thawing cycles.

Sample code	k' (Pa.s ^{n'})	n' (–)	K'' (Pa.s ^{n''})	n'' (–)
G05	0.370	0.64	0.848	0.58
G1	10.484	0.57	11.007	0.33
G05M10	0.974	0.67	1.661	0.50
G05M40	1.954	0.55	2.300	0.42
G1M10	14.509	0.52	13.376	0.29
G1M40	57.670	0.30	27.344	0.12
G05S10	1.210	0.67	1.980	0.48
G05S40	3.644	0.49	3.378	0.36
G1S10	18.230	0.50	16.106	0.27
G1S40	25.833	0.36	15.588	0.22
G05X10	1.021	0.68	1.754	0.50
G05X40	2.706	0.50	2.637	0.40
G1X10	15.256	0.52	14.172	0.29
G1X40	31.428	0.37	18.697	0.18

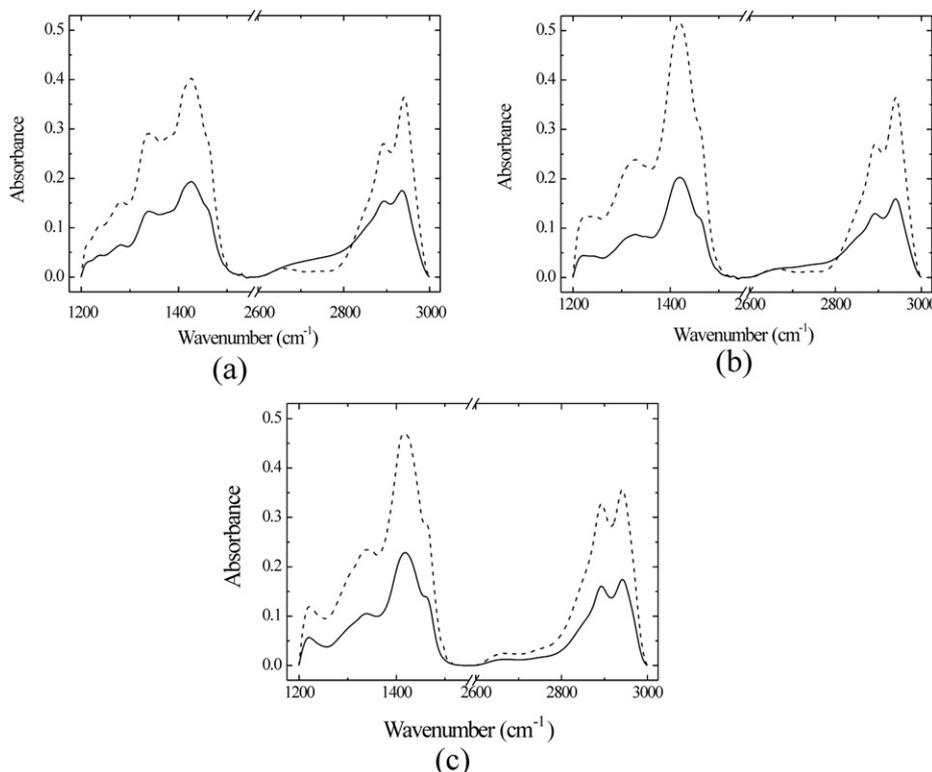


Fig. 5. Infrared absorption spectrum to pure polyols (—) and system containing guar with (a) maltitol, (b) sorbitol, (c) xylitol (---).

containing 1 g/100 g guar with polyols the freezing/thawing cycle did not modify the structure of the macromolecules in solution, which presented the same values for energy storage and dissipation moduli, and the same dependence on the frequency.

The spectroscopic analysis showed that the presence of guar in the polyol solutions made the competition for water more restricted, influencing the intensity of the spectra; such increment indicates that polyol molecules interacted with each other more efficiently than before.

5. Conclusions

An increase in polyol concentration raised the apparent viscosity of the solutions containing 0.1 and 0.5 g/100 g guar gum, whereas in the systems containing 1 g/100 g gum, a higher polyol concentration influenced the viscosity negatively. The viscoelastic behavior of the guar gum was strongly influenced by the polyol concentration, resulting in more elastic systems. In the 0.5 g/100 g guar gum solution, the polyols helped preserve the gum structure after freezing, whereas in the other hydrocolloid/polyol concentrations, the freezing/thawing cycle did not modify the structure of the macromolecules in solution. The vibrational mode of the polyols has not been altered in the presence of guar, but the intensity of the spectra increased, independent of the studied polyol.

References

- Barnes, H. A. (1989). Shear-thickening ("Dilatancy") in suspensions of non-aggregating solid particles dispersed in Newtonian liquids. *Journal of Rheology*, 33(2), 329–366.
- Basu, S., Shivhare, U. S., Singh, T. V., & Beniwal, V. S. (2011). Rheological, textural and spectral characteristics of sorbitol substituted mango jam. *Journal of Food Engineering*, 105(3), 503–512.
- Bayarri, S., Durán, L., & Costell, E. (2004). Influence of sweeteners on the viscoelasticity of hydrocolloids gelled systems. *Food Hydrocolloids*, 18(4), 611–619.
- Bobbio, P. A., & Bobbio, F. Q. (1992). *Introdução à Química de Alimentos* (2th ed.). São Paulo: Varela.
- Chen, J., & Dickinson, E. (2000). On the temperature reversibility of the viscoelasticity of acid-induced sodium caseinate emulsion gels. *International Dairy Journal*, 10(8), 541–549.
- Chenlo, F., Moreira, R., & Silva, C. (2010). Rheological properties of aqueous dispersions of tragacanth and guar gums at different concentrations. *Journal of Texture Studies*, 41(3), 396–415.
- Chenlo, F., Moreira, R., & Silva, C. (2011). Steady-shear flow of semidilute guar gum solutions with sucrose, glucose and sodium chloride at different temperatures. *Journal of Food Engineering*, 107(2), 234–240.
- Coates, J. (2000). Interpretation of infrared spectra, a practical approach. In R. A. Meyers (Ed.), *Encyclopedia of analytical chemistry* (pp. 10815–10837). Chichester: John Wiley & Sons Ltd.
- Cross, M. M. (1965). Rheology of non Newtonian fluids: a new flow equation for pseudoplastic systems. *Journal of Colloid Science*, 20(5), 417–437.
- Doyle, J. P., Giannouli, P., Martin, E. J., Brooks, M., & Morris, E. R. (2006). Effects of sugars, galactose content and chainlength on freeze–thaw gelation of galactomannans. *Carbohydrate Polymers*, 64(3), 391–401.
- Dziezak, J. D. (1991). A focus on gums. *Food Technology*, 45(3), 117–120, 122–124, 126, 128, 130–132.
- Evageliou, V., Kasapis, S., & Hember, M. W. N. (1998). Vitrification of k-carrageenan in the presence of high levels of glucose syrup. *Polymer*, 39(17), 3909–3917.
- Galmarini, M. V., Baeza, R., Sanchez, V., Zamora, M. C., & Chirife, J. (2011). Comparison of the viscosity of trehalose and sucrose solutions at various temperatures: effect of guar gum addition. *LWT – Food Science and Technology*, 44(1), 186–190.
- Gupta, S., Shah, B., Sanyal, B., Variyar, P. S., & Sharma, A. (2009). Role of initial apparent viscosity and moisture content on post irradiation rheological properties of guar gum. *Food Hydrocolloids*, 23(7), 1785–1791.
- Kim, C., & Yoo, B. (2006). Rheological properties of Rice starch–xanthan gum mixtures. *Journal of Food Engineering*, 74(1), 120–128.
- Lapasin, R., Prici, S., & Tracanelli, P. (1991). Rheology of hydroxyethyl guar gum derivatives. *Carbohydrate Polymers*, 14(4), 411–427.
- Legaz, M. E., & Vicente, C. (2005). Sugar alcohols. *Carbohydrates*, 427–439.
- Lim, Y. M., Seo, D., & Youn, J. R. (2004). Rheological behavior of dilute bubble suspensions in polyol. *Korea-Australia Rheology Journal*, 16(1), 47–54.
- Livesey, G. (2003). Health potential of polyols as sugar replacers, with emphasis on low glycaemic properties. *Nutrition Research Reviews*, 16(2), 163–191.
- Maskan, M., & Gogus, F. (2000). Effect of sugar on the rheological properties of sunflower oil–water emulsions. *Journal of Food Engineering*, 43(3), 173–177.
- Milani, E., & Koocheki, A. (2011). The effects of date syrup and guar gum on physical, rheological and sensory properties of low fat frozen yoghurt dessert. *International Journal of Dairy Technology*, 64(1), 121–129.
- Mishra, S., & Sen, G. (2011). Microwave initiated synthesis of poly-methylmethacrylate grafted guar (GG-g-PMMA), characterizations and applications. *International Journal of Biological Macromolecules*, 48(4), 688–694.

- Munhoz, M. P., Weber, F. H., & Chang, Y. K. (2004). Influência de hidrocolóides na textura de gel de amido de milho. *Ciência e Tecnologia de Alimentos*, 24(3), 403–406.
- Oliani, V., & Bobbio, P. A. (1981). Viscosity of a galactomannan from delonix regia comparative study with carrageenan, carboxymethylcellulose, locust and guar gum. *Ciência e Tecnologia Alimentos*, 1(2), 85–91.
- Pongsawatmanit, R., & Srijunthongsiri, S. (2008). Influence of xanthan gum on rheological properties and freeze-thaw stability of tapioca starch. *Journal of Food Engineering*, 88(1), 137–143.
- Rao, M. A. (1999). *Rheology of fluids and semisolids foods: Principles and applications*. Gaithersburg: Aspen Publication.
- Rayment, P., Ross-Murphy, S. B., & Ellis, P. R. (1995). Rheological properties of guar galactomannan and rice starch mixtures-I. Steady shear measurements. *Carbohydrate Polymers*, 28(2), 121–130.
- Rayment, P., Ross-Murphy, S. B., & Ellis, P. R. (1998). Rheological properties of guar galactomannan and rice starch mixtures-II. Creep measurements. *Carbohydrate Polymers*, 35, 55–63.
- Rayment, P., Ross-Murphy, S. B., & Ellis, P. R. (2000). Effect of size and shape of particulate inclusions on the rheology of guar galactomannan solutions. *Carbohydrate Polymers*, 43(1), 1–9.
- Richardson, P. H., Willmer, J., & Foster, T. J. (1998). Dilute solution properties of guar and locust bean gum in sucrose solutions. *Food Hydrocolloids*, 12(3), 339–348.
- Siefarth, C., Tyapkova, O., Beauchamp, J., Schweiggert, U., Buettner, A., & Bader, S. (2011). Influence of polyols and bulking agents on flavor release from low-viscosity solutions. *Food Chemistry*, 129(4), 1462–1468.
- Telis, V. R. N., Lourençon, V. A., Gabas, A. L., & Telis-Romero, J. (2006). Drying rates of Rubi grapes submitted to chemical pretreatments for raisin production. *Pesquisa Agropecuária Brasileira*, 41(3), 503–509.
- Wang, Y., Wang, L. J., Li, D., Özkan, N., Chen, X. D., & Mao, Z. H. (2008). Effect of flaxseed gum addition on rheological properties of native maize starch. *Journal of Food Engineering*, 89(1), 87–92.
- Yoo, B., Figueiredo, A. A., & Rao, M. A. (1994). Rheological properties of mesquite seed gum in steady and dynamic shear. *Lebensmittel-Wissenschaft und-Technologie*, 27(2), 151–157.
- Zhang, Y., & Han, J. H. (2006). Plasticization of pea starch films with mono-saccharides and polyols. *Journal of Food Science*, 71(6), 253–261.
- Zumbé, A., Lee, A., & Storey, D. (2001). Polyols in confectionery: the route to sugar-free, reduced sugar and reduced calorie confectionery. *British Journal of Nutrition*, 85(1), 31–45.