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Thermal, Mechanical, and Molecular Relaxation Properties of Frozen Sucrose and Fructose Solutions Containing Hydrocolloids

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Abstract Model frozen systems formulated with 20wt% sucrose or fructose and with the addition of 0.3 or 0.5wt% of xanthan gum (XG), guar gum (GG), locust bean gum (LBG), or a 50wt% mixture of XG and LBG were studied by differential scanning calorimetry, dynamic mechanical analysis, and ^{1}H-pulsed nuclear magnetic resonance. Melting onset of either the sucrose or fructose model systems was not affected by the addition of hydrocolloids. As expected, ice content was lower in fructose than in sucrose systems. Addition of hydrocolloids had no effect on ice content, except when the blend of XG and LBG was added to the fructose system, where ice content was significantly diminished. Hydrocolloids decreased molecular mobility for both frozen sucrose or fructose solutions, especially for the addition of XG/LBG blend. Relaxation times and storage modulus of the frozen systems with added hydrocolloids were significantly lower than the control frozen sugar solutions.

Keywords Stabilized sugar systems · Hydrocolloids · Rheology · Molecular mobility · NMR · Differential scanning calorimetry

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Introduction

Food materials stored at subzero temperatures may contain an unfrozen phase that can participate in or support several deleterious reactions such as structural collapse, crystal growth, and enzymatic activity, consequently reducing the overall textural and quality attributes of the product. High molecular weight polysaccharide stabilizers are added at low concentrations to frozen foods such as ice cream to suppress ice crystal growth (recrystallization) during storage.[1,2] However, there is no consistent evidence for the mechanism by which stabilizers suppress recrystallization in frozen systems.

Sahagian and Goff[3] suggested that stabilizer action may evolve from modification of the kinetics and specifically the rheological and viscoelastic response of the system at subzero temperatures. Martin et al.[4] reported that although stabilizers had a significant effect on the matrix viscosity, their effect was not associated with a change in overall diffusion properties of either the water or the sugar molecules. Thus, it is interesting to perform further studies to obtain a better understanding of the function of polysaccharides in frozen products.

The ice quantity present in a frozen system is related to both the final temperature attained and the system composition. In carbohydrate–water systems, once all freezable water becomes separated as ice during freezing, a freeze-concentrated matrix surrounds the ice crystals. Maximum ice formation is attained by slow freezing and annealing at a temperature close to the glass transition, T'_g, of the maximally freeze-concentrated matrix. At this condition, the unfrozen matrix obtained contains maximum solute concentration. At temperatures below T'_g, this concentrated matrix undergoes a glass transition, changing from a highly viscous, rubbery state to a vitreous state. The temperature at which the glass transition takes place in this matrix, T'_g, depends only on the composition of the system and not on its thermal history.

In rheological measurements at low deformation, viscoelasticity is measured below the yield point and any permanent strain remains upon complete release of stress. This region in which the applied stress was not excessive enough to damage the internal structure of the sample is commonly referred to as the linear viscoelastic region (LVR).[5] From dynamic mechanical analysis (DMA), fundamental rheological properties (complex viscosity E^*, storage modulus E', and loss modulus E'') of the product can be obtained. The strain response E^* can be broken into its elemental components: E', which is the ratio of the applied stress that is in phase with the strain, which means it is an expression of the magnitude of the energy stored in the material or recoverable per deformation cycle; and E'', which is the ratio of the applied stress that is out of phase with the strain, meaning that it is a measurement of the energy lost as viscous dissipation per deformation cycle. Two phases control the viscoelastic properties of frozen sugar solutions: ice crystals and cryo-concentrated phase. In this study, we analyzed the effect of macromolecules on ice quantity and molecular mobility of water in the cryo-concentrated phase and related these results with the rheological behavior of systems.

Differential scanning calorimetry (DSC) is a useful technique used to locate glass transition temperatures and to measure the heat involved in thermal transitions. Through enthalpy values it is possible to determine the quantity of ice formed in a certain process. It was reported that many systems containing low molecular weight carbohydrates present two successive steps in the DSC thermograms;[6,7] these two successive steps were interpreted in different ways. Slade and Levine[8] reported that this feature in frozen sugar aqueous solutions represents two successive glass transitions corresponding to different glassy domains: the dilute bulk glass with a lower value of T_g (first step) and the freeze concentrated glass with a higher value of T_g (second step) called T'_g. In more complex aqueous model systems containing proteins–sugars, polysaccharides–sugars, and other components, multiple T'_g values were attributed to the coexistence of two distinct aqueous glasses.[8] However, other authors proposed a different interpretation of this phenomenon. Simatos and Blond[6] considered that the two step increase in heat capacity is representative of a single glass transition with associated relaxation and the second step of the glass transition is superimposed to ice melting. Shalaev and Franks[9] reported that this second step contains a contribution because of heat absorption that accompanies the melting of ice, followed by the dilution of the supersaturated solution phase and associated enthalpy changes. In these previous studies,[6–9] T'_g would be closer to the lower temperature value corresponding to the first heat capacity change.

In the rubbery state, at temperatures above T'_g, many processes or reactions in foods are controlled by diffusion. Diffusion-limited phenomena, such as crystallization, may determine product acceptability because they commonly lead to textural changes. When there is sufficient molecular mobility, deteriorative changes may reduce the shelf life of the product. Therefore, molecular mobility is a critical aspect during storage of foods at low temperatures. For example, Hagiwara et al.[10] recently reported that ice recrystallization rate in frozen sugar solutions without added stabilizers can be explained well by the different diffusion rates of water molecules in unfrozen phase. Nuclear magnetic resonance (NMR) is a noninvasive technique that was used extensively to evaluate water mobility and dynamics in sucrose and food systems at ambient temperature. Recently, NMR techniques were also applied to investigate molecular mobility of sugar solutions at subzero temperature.[4,10] However, only a limited number of NMR studies focusing on the crystallization process or second order phase behavior at subzero temperatures were performed. Determination of relaxation properties of protons dispersed within the unfrozen phase, from measurement of the ^{1}H spin–spin (T_2) relaxation time, may provide insight into the molecular mobility and nature of the system.[11]

The purpose of this study was to evaluate the effect of guar gum (GG), xanthan gum (XG), locust bean gum (LBG), and mixtures of LBG and XG on the viscoelastic properties of frozen rubbery sucrose and fructose solutions at subzero temperatures by DMA and to study the effect of the mentioned hydrocolloids in molecular mobility as determined by NMR. Glass transition temperature T'_g of the maximally freeze-concentrated matrices and the amount of ice formed were determined by DSC.

Materials and methods

Model system preparation

Sucrose solutions at concentrations of 10 or 20 g/100 g solution were prepared in distilled water alone (control samples) and with 0.3 or 0.5 g/100 g solution of XG, LBG, GG, and a blend of XG and LBG (1:1). All materials were analytical grade (Sigma-Aldrich, St Louis, MO, USA). Sugar stabilizer blends were slowly added to water under constant stirring and heated to 40 °C. Upon complete dissolution of the sugars, the solutions were cooled to −7 or −15 °C and aged for 12 h before being analyzed for rheological behavior.

Dynamic mechanical analysis (DMA)

Complex, storage, and loss moduli were measured by small-amplitude dynamic measurements using DMA in a DMA 7e PerkinElmer analyzer (PerkinElmer, Chicago, IL, USA) with Pyris™ software for Windows. Compression experiments were performed in a parallel plate system of 10-mm in diameter. Calibrations for height, force, eigendeformation (eigenvalue of the deformation), and temperature of the DMA were performed before the study. The equipment calibration was checked before each use with a 10-mm quartz cylinder for height and a steel cylinder for eigendeformation. The sugar solutions were placed in 10-mm cylindrical tubes made of wax paper, which were filled up to 8-mm in height. Samples were stored at −7 or −15°C overnight before measuring. To determine the LVR for these systems, a static force scan from 0.5 to 20 kPa was performed. The static and dynamic forces per area selected for the LVR were lower than the stress corresponding to the yield point, which was 14 kPa. A dynamic test from 0.5 to 4 kPa with an increasing rate of 0.5 kPa/min at a frequency of 1 Hz and a strain of 0.0001 was done to put the probe in touch with the sample surface. Values of moduli were obtained for a frequency scan from 1 to 10 Hz using a fixed stress value of 2.0 kPa dynamic force and 2.5 kPa static force. E'' describes the viscous behavior, E' the elastic or solid-like behavior, and E^* the general viscoelastic behavior of the materials. Results are the average of four runs.

Differential scanning calorimetry

Thermograms were obtained with a Pyris 1 PerkinElmer calorimeter (PerkinElmer) and Pyris™ software for Windows. The DSC was calibrated with indium and mercury standards before analysis. Dry nitrogen gas was used to purge the thermal analysis system, and a mechanical cooler was used to cool the system. A small aliquot of each solution (10–20 μl) was sealed into aluminum pans (TA Instruments, New Castle, DE, USA) and placed in the DSC. An empty pan was used as reference. The following temperature protocol was used: samples were cooled at 5°C/min from 25 to −60°C, and held at −60°C for 60 min before being heated at 5°C/min from −60 to 10°C. Changes in heat flow during melting were recorded. Figure 1 shows analysis of a typical DSC thermogram (20% sucrose sample).Similar to previous studies,[6–9] two stepwise changes in the baseline (C_p change) were observed at low temperatures, followed by the endothermic peak corresponding to ice melting. As mentioned previously, there is still some debate about how to interpret such DSC scans for determining T'_g. However, in this study, our intent was only to measure the effects of solutes on ice content, which was determined as the area under the endothermic peak. For this purpose, the midpoint of the second (higher temperature) baseline shift was used as the onset of the melting peak. The midpoint was taken as the peak temperature of the first derivative of the thermal scan, as shown in Figure 1. Because annealing was not performed, maximal ice formation may not have been attained; however, preliminary trials with and without annealing did not result in significant differences in ΔH. All determinations were performed in triplicate and the average values were used to calculate ice content.

Pulsed nuclear magnetic resonance

Spin–spin relaxation times (T_2) were measured using the Carr–Purcel–Meiboon–Gill pulse sequence with an interpulse spacing of 200 μs. Typically, eight transients were averaged for each temperature and the decay envelopes were fitted to biexponential behavior. If all water in the system is as ice, no signal is observed in this assay because nuclei are immobilized. If water is partly unfrozen, it is enough to reduce the bipolar enhancement and give a signal that decays with time. The following equation was fitted to spin–spin relaxation data.[12]

$$I = A_1 \exp(-t/T_{21}) + A_2 \exp(-t/T_{22}) \quad (1)$$

where I represents protons signal intensity, proportional to water quantity in the sample. The term with the lower relaxation time (T_{21}) corresponds to the protons in the less mobile water fraction. A_1 is the signal intensity of protons in T_{21} state. The term with the major relaxation time (T_{22}) corresponds to the more mobile water fraction. A_2 is the signal intensity of protons in T_{22} state. To obtain the parameters that gave the best fit to Eq. 1, the nonlinear section of the Systat software was used (SYSTAT, CA, USA).

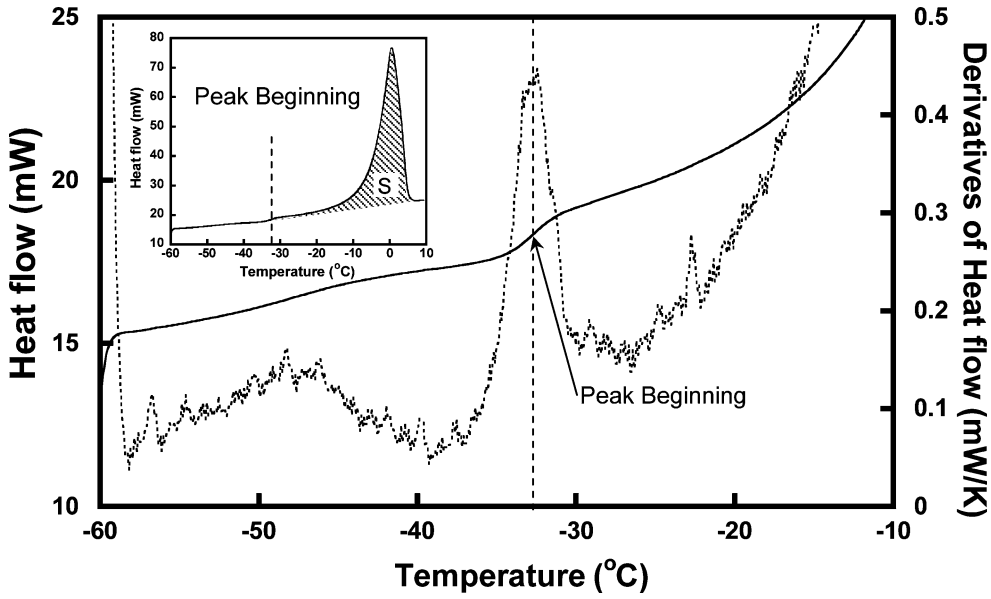

Fig. 1. Typical DSC thermogram to evaluate freezable water content. Sample: 20wt% sucrose. The inset shows whole DSC thermogram. The shaded area S was used to calculate amount of freezable water. The solid line represents original DSC heat flow data. The dotted line is the derivatives of the heat flow data that was used for determination of beginning of peak

About 5 ml of samples was placed in NMR tubes. Tubes were immersed in a bath at −15 or −7°C and kept for 30 min to get a homogeneous freezing before measuring. All determinations were performed in duplicates. As an example, T_2 average values of 20wt% sucrose or fructose solutions and with the addition of 0.5wt% of hydrocolloids crystallized at −15°C, which are reported in Table 3.

Results

Differential scanning calorimetry

As discussed previously, Figure 1 shows the analysis of a typical thermogram of a sucrose–water solution. The midpoint of the small baseline shift just before the large ice-melting endotherm was taken as the onset point of melting. The midpoints of these transitions were located at −32.6°C for sucrose solutions and at −42.2°C for fructose solutions. These values were consistent with T'_g values (midpoint) quoted by Slade and Levine[13] (sucrose −32°C, fructose −42°C) and the T'_m melting (onset) values quoted by Roos[14] (sucrose −34°C, fructose −46°C).

It was reported that polysaccharides could restrict molecular mobility by elevating T'_g and thus slowing down ice crystal growth.[15] In our systems, the addition of XG, GG, or LBG in 0.3 or 0.5wt% to sucrose or fructose solutions did not modify the transition used as onset temperature of melting (as defined above). Table 1 shows the percentage of formed ice (with respect to total water) for the 20wt% sucrose and fructose solutions with and without addition of 0.5wt% of LBG, GG, XG, or a 1:1 blend of XG/LBG. Sucrose solutions with and without hydrocolloids had higher proportions of ice than fructose–water systems with

Table 1 Percentage of frozen water for the 20wt% sucrose and fructose solutions with and without addition of 0.5wt% of gums

Sample	Heat of ice melting ΔH (Joules per gram of sample)	Ice content (gram per gram of sample)	Frozen water (ice per total water weight percent)
Sucrose 20wt%	217.9±1.2	0.65±0.01	81.25±0.88[a]
With 0.5wt% GG	215.9±1.3	0.65±0.01	81.76±0.89[a]
With 0.5wt% LBG	216.1±1.6	0.65±0.02	81.76±0.89[a]
With 0.5wt% XG	214.8±1.3	0.64±0.01	80.50±0.89[a]
With XG 0.25 and LBG 0.25wt%	213.3±2.3	0.63±0.01	80.31±0.89[a]
Fructose 20wt%	204.1±4.0	0.61±0.01	76.73±1.26[b]
With 0.5wt% GG	202.5±2.1	0.61±0.01	76.73±0.15[bc]
With 0.5wt% LBG	201.8±3.5	0.60±0.02	75.47±1.54[bc]
With 0.5wt% XG	203.0±0.9	0.61±0.00	76.73±0.00[bc]
With XG 0.25 and LBG 0.25wt%	194.8±1.4	0.58±0.01	72.95±0.89[cd]

Latent heat of ice melting ΔH_m=334 J/g
GG = Guar gum, XG = xanthan gum, LBG = locust bean gum
Values without the same superscript letter in the same column are significantly different (P<0.05).

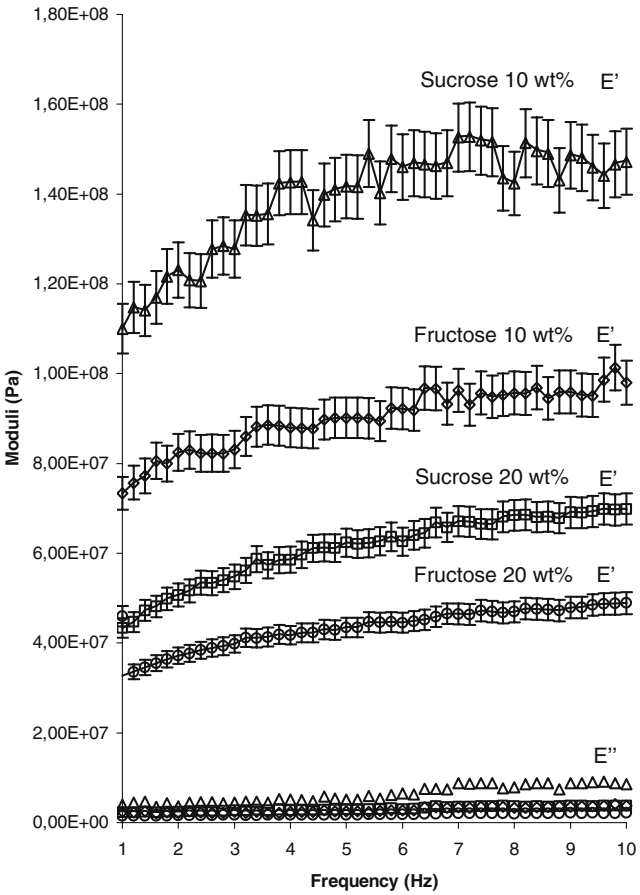

Fig. 2. Effect of the kind of sugar and solution concentration on storage (E', symbols) and loss (E'') modulus values (E'' values not distinguished for each condition because all were very low) measured for 10 and 20wt% sucrose or fructose solutions (control samples), crystallized quiescently at −15°C, during a frequency scan from 1 to 10 Hz. Samples were kept at −15°C overnight before analysis. Data are average of four runs

or without hydrocolloids ($P<0.05$). The addition of gums up to 0.5wt% had no effect on ice formation in sucrose solutions ($P<0.05$). However, the addition of 0.5wt% of the 1:1 blend of XG and LBG to fructose solution significantly ($P<0.05$) diminished ice content. Lower values of ice contents were obtained at −7°C (data not shown) with the same pattern as at −15°C.

Rheological behavior

Storage modulus is essentially a measure of the elasticity or solid-like character of a system. From the ice content (Table 1) it may be expected that storage modulus (E') was higher for sucrose than fructose solutions. Figure 2 shows the effect of the sugar (sucrose or fructose) and concentration on the values of storage (E') and loss (E'') moduli as a function of frequency at −15°C. The expected results were obtained. Sucrose solutions had E' values higher than fructose solutions for the same sugar concentration. The slope of E' with frequency was also higher, indicating a more solid-like behavior. In addition, E' values were higher for lower sugar concentration (more ice formation). E' was about three times E''. E^* showed the same behavior as E' (not shown), which means that for these systems elastic behavior prevails over viscous behavior.

The effects of addition of 0.3% gum to a 20wt% sucrose or fructose solutions on E' values as a function of frequency at −7°C are shown in Figures 3 and 4, respectively. In the same way, one would expect E' modulus values to be similar for all gums except for the 50wt% blend XG and LBG added to fructose solutions. However, as shown in Figures 3 and 4, the addition of gums decreased the E'

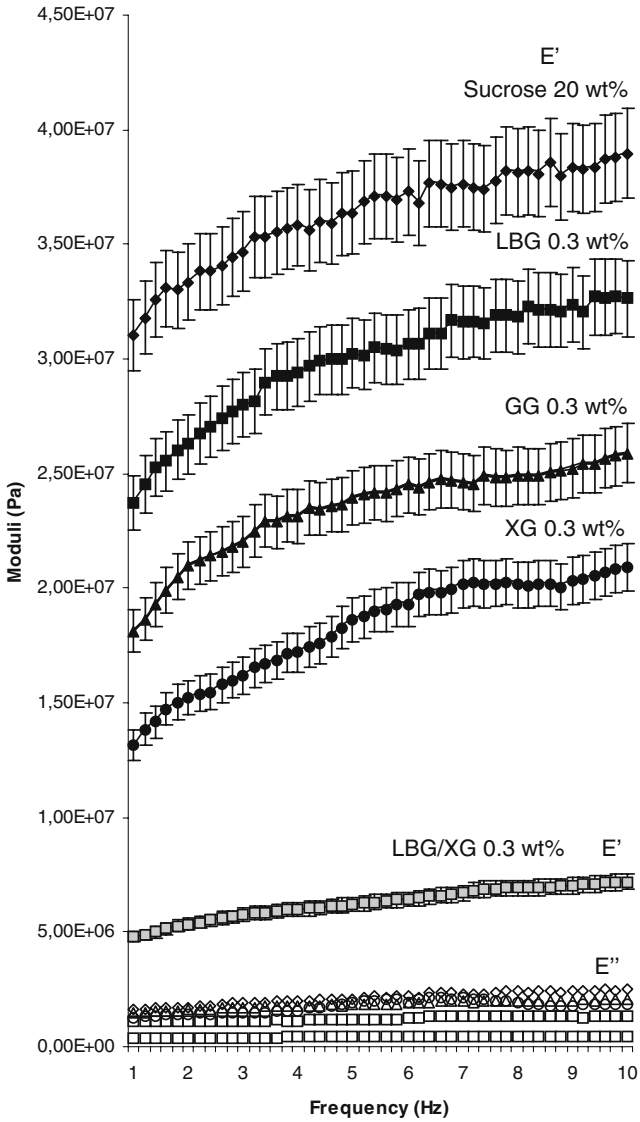

Fig. 3. Effect of the addition of 0.3wt% of guar gum (GG), xanthan gum (XG), locust bean gum (LBG), or a 1:1 blend LBG/XG to the 20wt% sucrose solution crystallized at −7°C on storage (E', solid symbols) and loss (E'', opened symbols) modulus values. E'' values for each condition not distinguished because all were very low

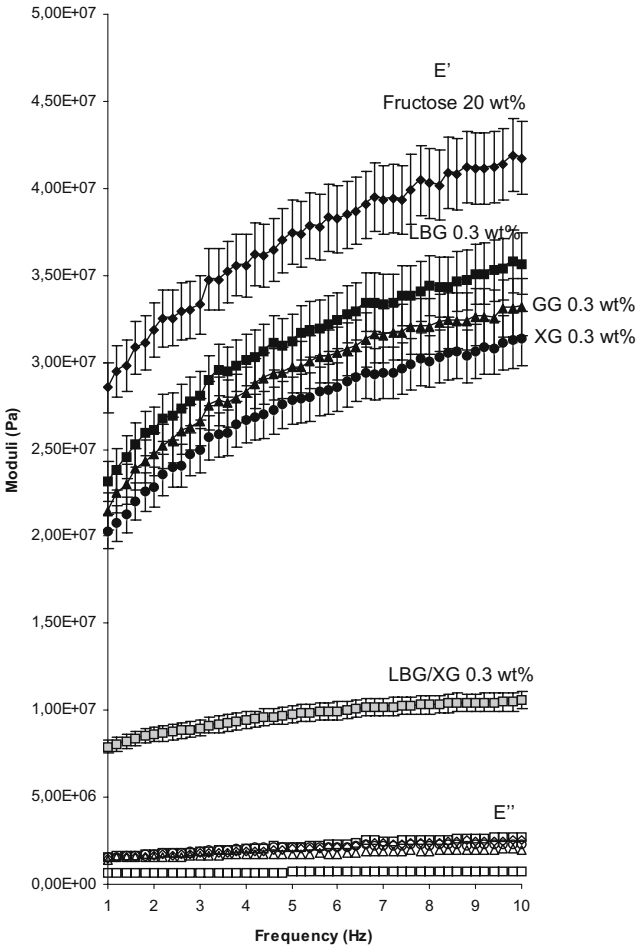

Fig. 4. Effect of the addition of 0.3wt% of guar gum (GG), xanthan gum (XG), locust bean gum (LBG), or a 1:1 blend LBG/XG to the 20wt% fructose solution crystallized at −7°C on storage (E', solid symbols) and loss (E'', opened symbols) modulus values. E'' values for each condition not distinguished because all were very low

modulus values. Although GG, LBG, and XG significantly diminished E' modulus, the 50wt% blend of LBG and XG had a much greater effect on E' modulus. It is well known that the blend of LBG and XG forms a gel at ambient temperature.[16] Under freezing conditions it produced a softening that resulted in a marked decrease in all moduli. The blend also produced a decrease in the slope of moduli vs time curves. This result was found in all conditions selected for this study (for 10 and 20wt% fructose and sucrose solutions stored at −7 or −15°C and with addition levels of gums of 0.3 and 0.5%). Figures 3 and 4 show that E' values were again more than three times higher than E''. E^* had the same behavior as E' (data not shown), showing again that elastic behavior predominated over the viscous one in these systems.

To summarize these effects, E' measured at a frequency of 1 Hz for the 10wt% sucrose and fructose solutions with and without addition of gums, kept overnight at −7 or −15°C are shown in Table 2. In agreement with the large differences in the ice content, E' values for −7°C were significantly lower than for −15°C ($P<0.05$) (Table 2). The 20wt% sucrose and fructose solutions with and without addition of gums also showed a similar behavior (data not shown). As shown in Table 2, E' values were lower ($P<0.05$) for GG, LBG, XG, and the blend of LBG and XG than for the control sugar solutions. However, there were no significant differences for gum addition levels (0.3 or 0.5wt%) ($P<0.05$) at either temperature.

Nuclear magnetic resonance results

Figure 5a, b shows the different relaxation curves obtained for selected systems shown as an example. The plots indicated that the spin–spin relaxation behavior of water in sucrose or fructose solutions with and without addition of hydrocolloids followed a simple exponential decay. Thus, the two-state behavior of water molecules was not observed for these systems. The possibility of detecting multi-exponential relaxation decay depends on the system being investigated. The instrument accuracy may not allow the

Table 2 Elastic modulus (E') of frozen sucrose and fructose solutions formulated with and without hydrocolloids measured at 1 Hz

	Elastic modulus ($E'\times10^{-7}$)	
	Temperature (°C)	
(a) Stabilizer concentration: 0.3wt%		
Sample	−15	−7
Sucrose 10wt%	11 ± 0.6^{a}	5.5 ± 0.2^{a}
LBG	8.4 ± 0.6^{b}	4.1 ± 0.3^{bf}
GG	7.0 ± 0.2^{c}	3.3 ± 0.1^{ch}
XG	7.0 ± 0.2^{c}	3.1 ± 0.2^{c}
1:1 XG/LBG	2.1 ± 0.2^{d}	1.1 ± 0.0^{d}
Fructose 10wt%	7.6 ± 0.3^{b}	5.0 ± 0.2^{e}
LBG	5.8 ± 0.3^{e}	3.7 ± 0.3^{g}
GG	5.2 ± 0.2^{f}	3.0 ± 0.2^{fh}
XG	2.4 ± 0.1^{d}	2.0 ± 0.1^{i}
1:1 XG/LBG	0.9 ± 0.0^{g}	0.6 ± 0.0^{j}
(b) Stabilizer concentration: 0.5wt%		
Sample	−15	−7
Sucrose 10wt%	11 ± 0.6^{a}	5.5 ± 0.2^{a}
LBG	8.2 ± 0.4^{b}	4.1 ± 0.2^{b}
GG	7.2 ± 0.2^{c}	3.5 ± 0.2^{c}
XG	6.8 ± 0.2^{d}	2.9 ± 0.1^{d}
1:1 XG/LBG	1.8 ± 0.2^{e}	1.2 ± 0.0^{e}
Fructose 10wt%	7.6 ± 0.3^{bcf}	5.0 ± 0.2^{f}
LBG	5.6 ± 0.3^{h}	3.5 ± 0.2^{cg}
GG	5.4 ± 0.2^{h}	3.1 ± 0.2^{cdg}
XG	2.3 ± 0.1^{i}	2.1 ± 0.1^{h}
1:1 XG/LBG	0.9 ± 0.1^{j}	0.5 ± 0.0^{i}

Abbreviations as in Table 1
Values without same superscript letter in the same column are significantly different ($P<0.05$).

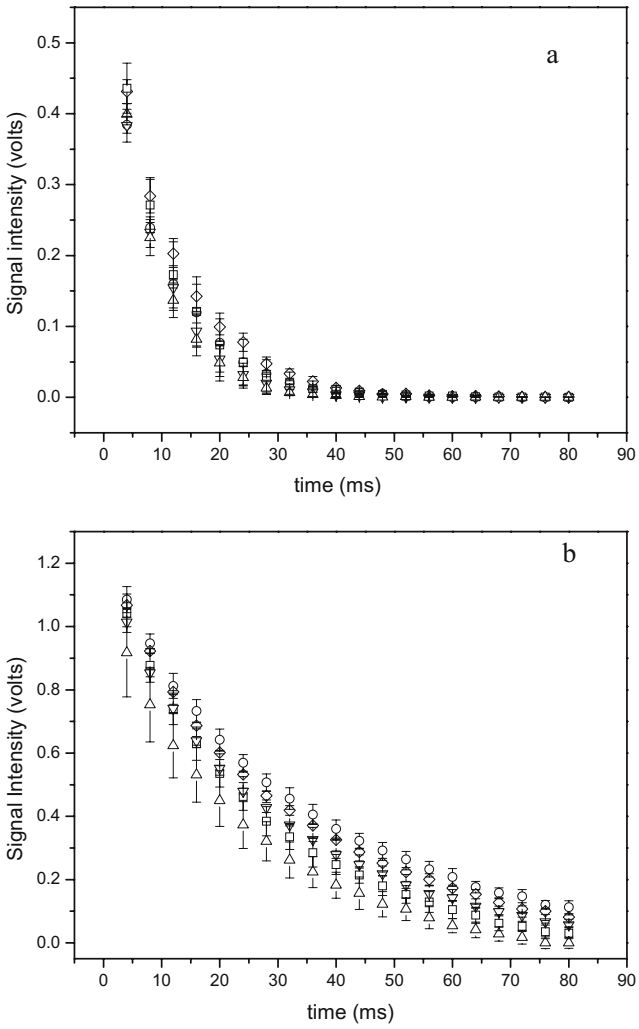

Fig. 5. **a** Signal intensity vs time output obtained by pulsed NMR for (circle) 20wt% sucrose solution, (diamond) 20wt% sucrose solution with the addition of guar gum (GG), (inverted triangle) 20wt% sucrose solution with the addition of locust bean gum (LBG) at 0.5wt%, (upright triangle) 20wt% sucrose solution with the addition of a blend of 0.25wt% locust bean gum (LBG) and 0.25wt% xanthan gum (XG), and (square) 20wt% sucrose solution with the addition of xanthan gum (XG) at 0.5wt%. **b** Signal intensity vs time output obtained by pulsed NMR for (circle) 20wt% fructose solution, (diamond) 20wt% fructose solution with the addition of guar gum (GG), (inverted triangle) 20wt% fructose solution with the addition of locust bean gum (LBG) at 0.5wt%, (upright triangle) 20wt% fructose solution with the addition of a blend of 0.25wt% locust bean gum (LBG) and 0.25wt% xanthan gum (XG), and (square) 20wt% sucrose solution with the addition of xanthan gum (XG) at 0.5wt%

observation of multistate relaxation if the exchange rate between states is fast compared with the relaxation rate, or if one state is present as a small portion, or if one of the relaxation times is very short, or if both relaxation times are similar.[12] Therefore, Eq. 1 becomes

$$I\alpha \exp\left(-t/T_2\right) \tag{2}$$

Relaxation times (T_2) were calculated with Eq. 2 and used as indicators of the molecular mobility of water in the maximally freeze-concentrated matrix. Higher T_2 values correspond to higher water mobility.

T_2 values obtained for the 20% fructose or sucrose solutions with and without addition of 0.5wt% of XG, GG, LBG, and the 1:1 blend XG/LBG frozen at −15 C° are shown in Table 3. Sucrose solutions had lower T_2 values than fructose systems ($P<0.05$). A decrease in relaxation times can be associated with a decrease in the proton mobility in the unfrozen matrix. Thus, protons in matrixes with fructose are more mobile than protons in matrixes with sucrose. A higher proton concentration in the matrix (higher A values) can be related to less ice formation in fructose systems; however, as shown previously,[10] different water diffusivities were seen for sugar solutions made with the same ice content, indicating that ice phase volume is not the only factor determining proton mobility. T_2 values were significantly lower in both sugar systems containing XG 0.25wt% and LBG 0.25wt% ($P<0.05$).

The blend of LBG and XG had a synergistic effect on molecular mobility. T_2 values obtained for this mixture were lower than those found with addition of either LBG or XG alone.

Discussion

Rheological properties of frozen solutions may be influenced by many factors. These include ice content, ice crystal morphology and size, ice crystal connectivity, and the nature of the cryo-concentrated phase. In this study, the effects of ice content and cryo-concentrated phase on rheological properties were studied.

As expected, the ice content in sucrose solutions was always higher than in fructose solutions and thus, the moduli of sucrose solutions were higher. With an increase

Table 3 Relaxation times for the different aqueous systems with sucrose or fructose and gums obtained by pulsed NMR

Sample	T_2 at −15 °C
Sucrose 20wt%	14.30 ± 0.12^{a}
With 0.5wt% GG	10.38 ± 0.23^{b}
With 0.5wt% LBG	8.03 ± 0.45^{bc}
With 0.5wt% XG	9.17 ± 0.69^{abc}
With XG 0.25 and LBG 0.25wt%	7.12 ± 0.38^{c}
Fructose 20wt%	32.35 ± 0.51^{d}
With 0.5wt% GG	29.89 ± 0.55^{e}
With 0.5wt% LBG	29.74 ± 0.64^{ef}
With 0.5wt% XG	27.00 ± 0.35^{g}
With XG 0.25 and LBG 0.25wt%	23.28 ± 0.80^{gh}

Abbreviations as in Table 1
Values without same superscript letter in the same column are significantly different ($P<0.05$).

in temperature, less ice was formed in the systems and values of moduli decreased. The addition of GG, XG, or LBG to either sucrose or fructose solutions caused a decrease in elastic moduli; however, only relatively small changes (if changes were seen at all) in ice content were measured with the addition of most hydrocolloids studied. Considering that rheological behavior was significantly affected by the presence of gums, this would indicate that these macromolecules induce changes in the properties of the cryo-concentrated phase rather than by their effect on ice content. However, the effects of hydrocolloids on ice crystal morphology or interconnectivity cannot be ruled out as a possible mechanism for their rheological effects.

When the 50wt% blend of XG and LBG was added to sugar solutions, rheological moduli markedly decreased, indicating that both ice content and physical interactions among the components of the systems were important. Locust bean gum is composed of long, rather rigid linear chains with single-unit branches and behaves as a linear polymer. Xanthan gum is a rod-like polysaccharide with trisaccharide unit branches on every other main chain unit. Its very high molecular weight (up to 2.5×10^6) makes it able to render high viscosity solutions.[17] Because of the difference in structures, LBG and XG have different physical properties. Particularly, concentrated aqueous systems of these gums display quite different rheological properties: the former shows the behavior typical of hyperentangled macromolecular solutions, whereas the flow and viscoelastic properties of XG systems correspond to those of weak gel networks. Interestingly, when mixed together these macromolecules interact to form a firm, thermoreversible gel with synergistic effect, with the maximum effect at the XG to LBG ratio of 1:1.[16] The addition of the 50wt% blend decreased moduli in higher degree than either XG or LBG individually added, giving a more viscous behavior to the system. The lower E' moduli found in systems with XG/LBG mixture could be related to a mechanical interference established between ice crystal phase and cryo-concentrated phase. According to Muhr and Blanshard,[18] the presence of stabilizers that form a gel network affect ice crystals morphology and growth rate. Gel fibers would cause the ice interface to develop a radius of curvature comparable in size to the mesh size of the network. Thus, the gel fibers will be subjected to a tension, which may result in a lower resistance to mechanical deformation. Again, the effects of hydrocolloids on ice crystal morphology and interconnectivity cannot be ruled out as possible factors affecting rheological properties.

With reference to the relaxation times measured by pulsed NMR, the lower molecular mobility found in sucrose-containing systems, as revealed by NMR time relaxation assays (T_2), can be attributed to a higher quantity of frozen water, resulting in less water in the unfrozen matrix. The cryo-concentrated phase showed a higher restriction on molecular mobility. On the contrary, fructose-containing systems showed a higher mobility in agreement with a lower quantity of frozen water and more water present in the unfrozen matrix. The synergistic effect of 50wt% XG/LBG blend was also evident in these measurements because the formation of a gel changed relaxation properties of the frozen sugar solutions to a greater extent than in GG, XG, or LBG systems.

Conclusions

The addition of polysaccharides (GG, XG, or LBG) to sugar aqueous solutions (sucrose and fructose) did not significantly affect ice content in systems. Ice content was mainly dependent on the type of sugar added.

The addition of hydrocolloids led to lower values of the rheological moduli; this decrease was more pronounced for the LBG/XG gel-forming blends. A more restricted molecular mobility, as measured by NMR (lower relaxation times), was also observed in these systems. These results indicate that, contrary to expectations, a more rigid, less mobile structure of the cryo-concentrated phase is related to a weaker structure of the total system (frozen phase + cryo-concentrated phase). Mechanical interactions between both phases, leading to disruptions of the gum-containing phase could explain this behavior. These results indicate that the effects of hydrocolloid addition observed in frozen systems such as ice creams cannot be related to one particular factor but to several interaction effects. Textural properties are influenced by ice content, the characteristics of the cryo-concentrated phase and the interactions between both phases. The stabilizing effect attributed to hydrocolloids may be related al least in part with their effect on molecular mobility and the consequent control of diffusional-dependent processes such as crystallization.

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