# Effect of Galactomannans on the Thermal and Rheological Properties of Sago Starch

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The thermal and rheological properties of sago starch have been studied in the presence of various concentrations of locust bean gum and guar gum of various molecular masses. At the concentrations studied (<1%) the galactomannans gave rise to only a very slight increase in the gelatinization temperature (up to 0.6 °C), and the gelatinization enthalpy remained constant within experimental error. For the low molecular mass galactomannans, depending on the concentration, the storage modulus, $G'$, of the mixtures remained constant or actually decreased, and tan $\delta$ remained very low (0.01–0.03 at 0.1 Hz), indicating strong elastic gels. For the higher molecular mass samples $G'$ increased significantly; however, the loss modulus, $G''$, increased proportionally to a greater extent, and at 1% galactomannan tan $\delta$ was ~0.20 at 0.1 Hz, indicating a reduction in elastic character. The systems were shown to undergo phase separation, and the variations in rheological properties have been discussed in the context of their phase behavior and the relative rates of the phase separation and gelation processes. The presence of galactomannans significantly improved the freeze–thaw stability.

**Keywords:** *Biopolymer; galactomannans; guar gum; locust bean gum; rheological properties; sago palm; sago starch*

## INTRODUCTION

Biopolymer mixtures are widely employed to manipulate the rheological properties of food systems, and considerable work has been undertaken over recent years concerned with gaining a fundamental understanding of the interactions involved (*1*). For solutions containing two polymers intermolecular association may or may not occur. Association can result in precipitation as, for example, in the case of a mixture of an anionic polysaccharide and a protein at a pH below its isoelectric point. In some instances, however, association can lead to gel formation, as is the case in mixtures of xanthan gum with either locust bean gum (LBG) or konjac mannan (*2*). For many systems association between different polymer molecules does not occur. For such systems, above a critical total polymer concentration, polymer segregation occurs, resulting initially in the formation of so-called "water-in-water" emulsions with droplets enriched in one polymer dispersed in a continuous phase enriched in the other. Over time the droplets coalesce and eventually two liquid layers are formed, each enriched in one of the polymers. Below this critical polymer concentration the system appears visually as a single phase, although recent evidence from neutron scattering studies (*3*) and from combined image analysis and light scattering (*4*) suggests that this phase may not in fact be truly homogeneous. Phase separation is commonly described in terms of the Flory–Huggins theory (*5*, *6*), although Hoskins et al. (*7*, *8*) have recently

shown that phase separation can be considered in terms of volume exclusion effects. This is often referred to as depletion flocculation in systems consisting of particles or droplets and nonadsorbed polymer and is, therefore, particularly appropriate for these "water-in-water" emulsions.

Starch is widely used to thicken and gel food products, and the rheological properties of starch pastes and gels can be significantly influenced by the presence of other polysaccharides (*9–19*). The influence of guar gum, locust bean gum (LBG), and xanthan gum on the rheological properties of cornstarch has been attributed to phase separation (*14*). Direct observation of phase separation has been reported for wheat starch in the presence of gelatin, ι-carrageenan, xanthan gum, κ-carrageenan, and low-methoxy pectin (*20*) and in the presence of ethylhydroxyethyl cellulose (*19*). The presence of polysaccharides has been shown to have little effect on the gelatinization temperature or the gelatinization enthalpy of starch (*15*, *21*, *22*).

This paper reports results of a systematic study of the effect of the presence of galactomannans (locust bean gum and guar gum) of various molecular masses on the thermal and rheological properties of starch with a view to gaining a fundamental understanding of the mechanisms involved. The starch used in the study was from the sago palm. There are few reports in the scientific literature concerning this starch, and this is the sixth in a series of papers we have published concerned with the characterization and physicochemical properties of this material (*23–27*).

## MATERIALS AND METHODS

**Samples.** Sago starch granules are oval in shape, have a diameter in the range of 20–40 $\mu$m, and display a C-type X-ray diffraction pattern (*23*). The sample used in the study was

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**Table 1. Molecular Mass of Galactomannan Samples**

| polysaccharide | source | $[\eta]$/dL/g | molecular mass[a] |
|---|---|---|---|
| LBG 1 | Meyhall | | 220 000 |
| LBG 2 | Meyhall | | 440 000 |
| LBG 3 | Meyhall | | 830 000 |
| LBG 4 | FMC | | 840 000 |
| LBG 5 | Meyhall | | 1 000 000 |
| guar 1 | Meyhall | 4.7 | 790 000 |
| guar 2 | Meyhall | 9.0 | 1 500 000 |
| guar 3 | Meyhall | 17.0 | 2 900 000 |
| gua r4 | FMC | 4.5 | 760 000 |

[a] The molecular mass of the LBG samples was provided by the supplier. $[\eta]$ for guar gum was determined in water at 25 °C, and molecular mass was determined using $k$ and $a$ values of 0.000776 and 0.98, respectively (*34*).

obtained from N. E. Mukah, Sarawak, Malaysia. It was found to have a moisture content of 13.9% and an amylose content of 31%. Amylose and amylopectin were isolated from the starch, and their molecular masses were found to be 1 240 000 and 8 640 000, respectively, as determined by light scattering. Measurements were performed using a K 7027 Malvern Instrument equipped with a 10 mW He−Ne laser with a wavelength of 632.8 nm. The starch was dissolved in 1 M KOH, and measurements were undertaken at 25 °C. The values of the refractive index increments used were 0.146 and 0.142 mL/g for amylose and amylopectin, respectively. The molecular mass of the amylose was also determined from intrinsic viscosity measurements. The intrinsic viscosity was found to be 3.1 dL/g in 1 M NaOH at 25 °C. Using the Mark−Houwink relationship, taking values for $k$ and $a$ as 0.00118 and 0.89, respectively (*29*), a molecular mass of 1 230 000 was obtained, which was in close agreement with the light scattering data.

LBG and guar gum were kindly supplied by Meyhall AG and FMC. Details of their molecular masses are given in Table 1.

**Differential Scanning Calorimetry (DSC).** DSC measurements were performed using a micro-DSC (Seteram, Lyon, France). Galactomannan solutions were prepared at various concentrations by stirring at room temperature at 500 rpm for 24 h and then heating to 80 °C and stirring vigorously for 30 min. Starch dispersions (10% w/v) were prepared by adding the appropriate weight of starch powder to the galactomannan solutions, and the pH was adjusted to 5.5. An aliquot (∼0.95 g) was added to the sample cell, the top sealed, and the weight recorded. An exactly equal weight of water was added to the reference cell. The cells were heated from 5 to 99 °C at a rate of 0.5 °C/min, and the heat flow was recorded.

**Phase Behavior.** Starch/galactomannan solutions were prepared at various concentrations by dispersing the required weight of starch in the dissolved galactomannan solution (as above) and then heating to 95 °C for 30 min with stirring at 400 rpm. It was shown by polarization microscopy that the crystalline structure of the granules (characterized by Maltese crosses) was completely destroyed by this treatment. The hot samples were transferred into glass tubes with screw caps and kept in an oven at 45 °C for 48 h. The samples were then inspected visually to see if phase separation had occurred, and the position of the binodal in the phase diagrams was estimated.

**Viscoelastic Measurements.** The storage and loss moduli ($G'$ and $G''$) were determined using a TA Instruments CSL500 controlled stress rheometer. Starch dispersions (6%) were prepared in the presence of various concentrations of galactomannan as above, and hot samples at 95 °C were placed in the rheometer measuring system (4 cm, 2° cone, and plate) equilibrated to 25 °C. $G'$ and $G''$ were determined at 1 Hz using an amplitude of 1 mrad as a function of time. At the end of the experiment $G'$ and $G''$ were determined as a function of frequency. Measurements were made in the linear viscoelastic region and were carried out in duplicate. The results were reproducible to within ±2%.

**Gel Strength.** Starch solutions (6%) containing various concentrations of galactomannan were prepared as above,

transferred to a 30 mL sample jar of diameter 3 cm, and stored at 25 °C for 6 h. The break force was determined using a Stevens texture analyzer using a 1 cm diameter probe. Measurements were performed in triplicate and agreed to within ±2%.

**Freeze−Thaw Stability.** Starch solutions (6%) containing various concentrations of galactomannan were prepared as above. The solutions were transferred to 30 mL sample jars and stored at 4 °C for 16 h. The samples were then subjected to five freeze−thaw cycles in which they were stored at −16 °C for 24 h and then at 25 °C for 6 h. The thawed samples were then centrifuged at 2200 rpm for 20 min, and the weight of exuded water was determined. The percent syneresis was defined as

$$\text{(wt of water exuded/total weight of sample)} \times 100 \quad (1)$$

Measurements were performed in triplicate and agreed to within ±2%.

## RESULTS

**DSC.** Parts A and B of Figure 1 show DSC endotherms for sago starch in the presence of LBG 4 and guar 4, respectively. $T_{gel}$ increased slightly from 70.1 °C (starch alone) to 70.7 °C (with 1% LBG and Guar). $T_0$ and $T_c$ (the temperature of the start and finish of the peak, respectively) increased slightly, but the shape of the endotherms did not change significantly. $\Delta H$ was not affected and remained almost constant at ∼16.5 J/g.

**Phase Behavior.** Figure 2 shows the phase behavior of starch/LBG 4 mixtures kept at 45 °C. In tube a, which contains 6% starch alone, phase separation was not observed. In tubes b−e, which contained various concentrations of starch/LBG, phase separation was observed. As the starch and LBG concentrations increased some of the mixtures separated into three layers as shown in tubes c and d. In the mixtures that separated into two layers, starch was found to occupy the bottom layer, whereas for the systems with three layers, the starch was concentrated in the center and bottom layers based on iodine staining experiments.

Figure 3 shows the phase behavior of starch/guar 4 mixtures at 45 °C. Tube a is 6% starch alone, which did not show phase separation. The samples in tubes b−d containing starch/guar gum mixtures at various concentrations all resulted in phase separation. For all of the mixtures the bottom layer was enriched in starch. At increased starch/guar concentration (>4% total polysaccharide) the starch was found to partition into the top layers.

Figure 4 shows the phase diagram for starch in the presence of LBG 1, LBG 4, and guar 4. The positions of the binodal are similar for each of the systems, but it is evident that for higher molecular mass LBG (LBG 4, $M = 8.4 \times 10^5$) phase separation occurred at lower total polymer concentrations than it did for the lower molecular mass sample (LBG 1, $M = 2.2 \times 10^5$). The concentration of LBG or guar required to induce phase separation is similar to that found by Annable et al. (*16*) and Closs et al. (*18*) for potato maltodextrin/LBG and amylopectin/guar gum mixtures, respectively.

**Rheology.** Figure 5 shows the effect of LBG of various molecular masses on $G'$ as a function of time for 6% sago starch. The symbols represent the experimental points, and the lines have been calculated using the first-order rate equation (*29*)

$$G_{(t)} = G_{(\text{plateau})}(1 - e^{kt}) \quad (2)$$

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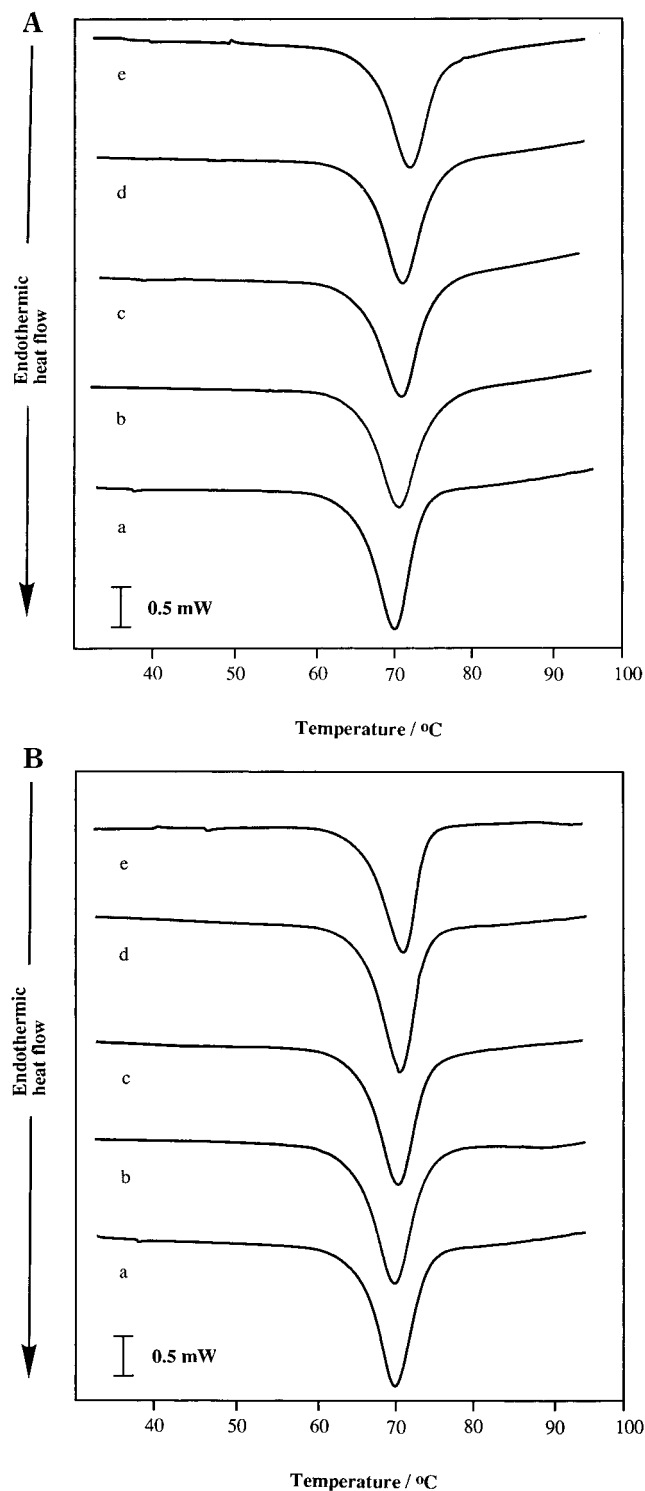Ahmad and Williams

**A**



**B**



**Figure 1.** (A) DSC heating curves for 10% sago starch (a) alone and in the presence of (b) 0.125%, (c) 0.25%, (d) 0.5%, and (e) 1% LBG 4. (B) DSC heating curves for 10% sago starch (a) alone and in the presence of (b) 0.125%, (c) 0.25%, (d) 0.5%, and (e) 1% guar 4.

where $G_{(plateau)}$ is the plateau value of $G'$, $k$ is the rate constant, and $t$ is time.

$G'$ was found to increase rapidly initially and attain a pseudoplateau value ($G'_{max}$). The figures clearly show that LBG has a significant effect on the gelation process. For mixtures containing the two lower molecular mass samples (LBG 1 and LBG 2) $G'_{max}$ was found to increase up to LBG concentrations of ~0.25% (close to the phase boundary, Figure 4) and then decrease to values close
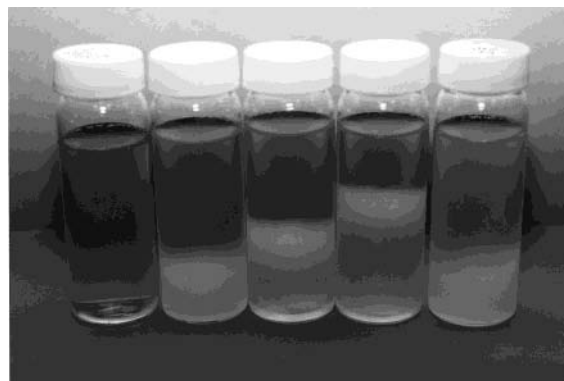


**Figure 2.** Phase behavior of starch/LBG 4 mixtures. Samples were kept at 45 °C for 48 h. The tubes, from left (a) to right (e) contain 6% starch, 1% starch/1.5% LBG, 2% starch/1% LBG, 3% starch/0.75% LBG, and 0.25% starch/1.5% LBG, respectively.
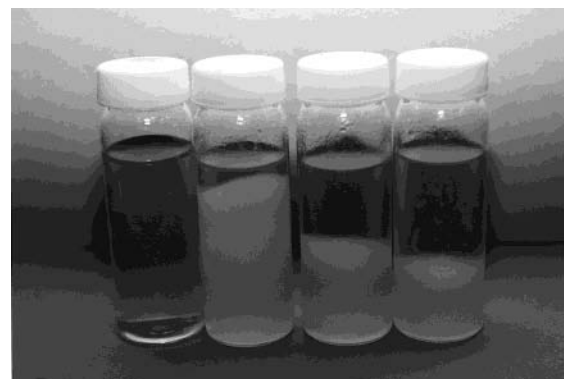


**Figure 3.** Phase behavior of starch/guar 4 mixtures. Samples were kept at 45 °C for 48 h. The tubes, referred to from left (a) to right (e) contain 6% starch, 0.5% starch/2% guar, 1% starch/1.5% guar, and 0.5% starch/1.5% guar, respectively.
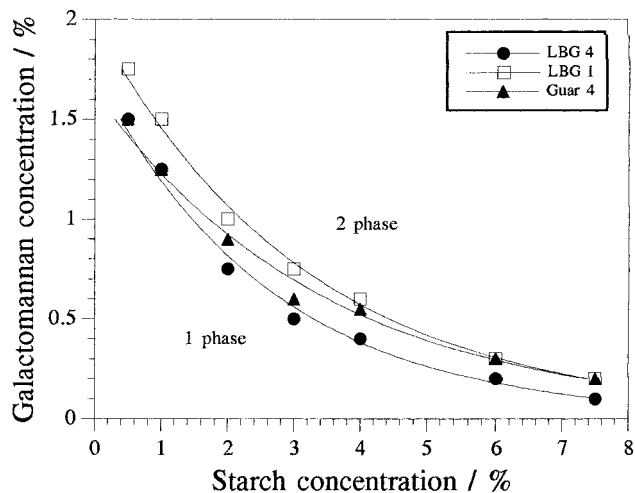


**Figure 4.** Phase diagram for sago starch/galactomannan mixtures obtained at 45 °C.

to that of the starch alone. For mixtures containing the higher molecular mass samples (LBG 3, LBG 4, and LBG 5) $G'_{max}$ increased continuously with increasing LBG concentration as illustrated in Figure 6. The presence of LBG also significantly reduced the time required to reach $G'_{max}$. For example, in the presence of 1% LBG 5 the time required to reach $G'_{max}$ was ~1.5 h, for 0.5% LBG it was 2.5 h, whereas for sago starch alone it was ~3.5 h. For lower molecular mass samples a longer time was required to achieve $G'_{max}$. The rate
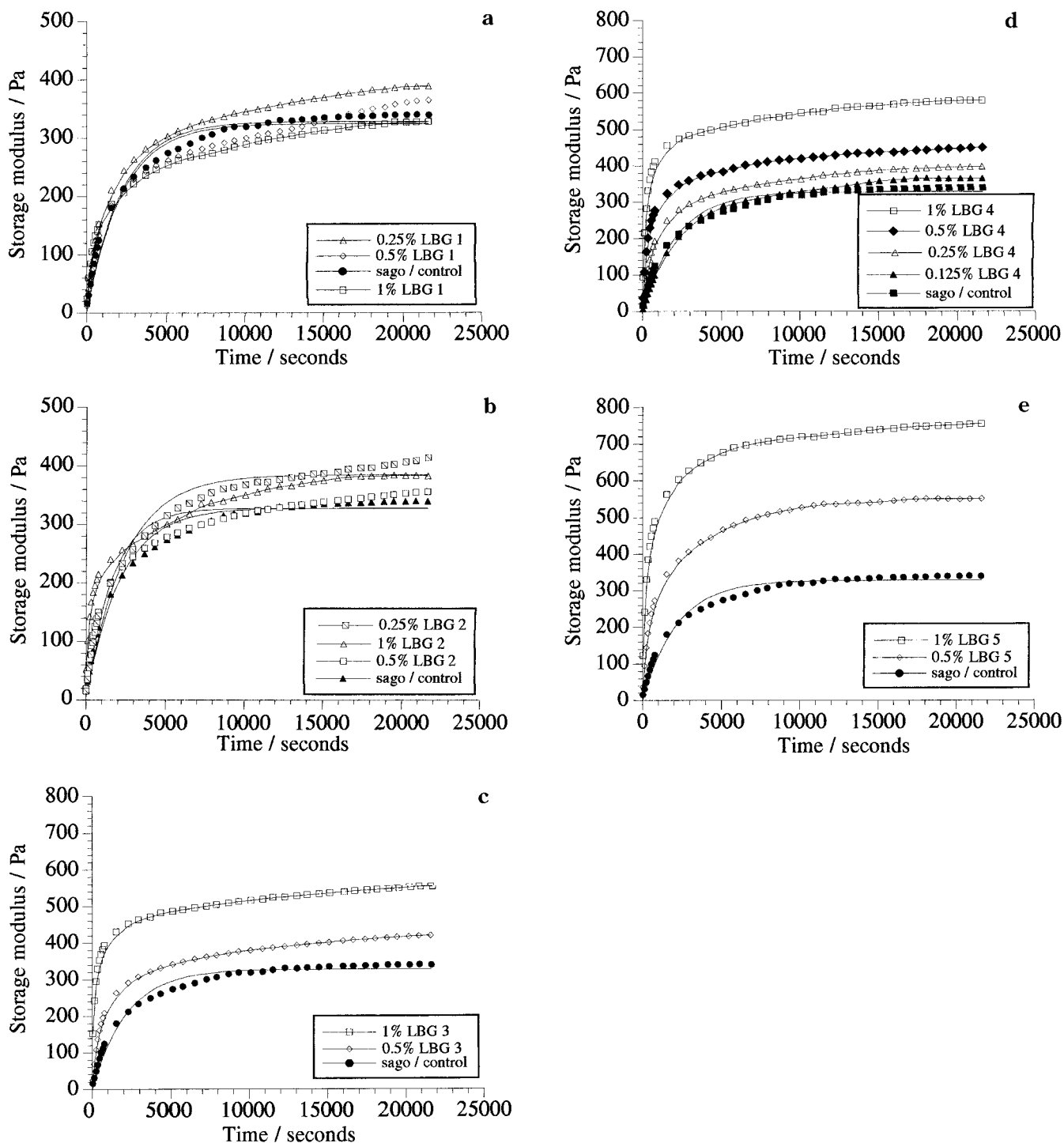
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**Figure 5.** Storage modulus for 6% sago starch as a function of time with various amounts of (a) LBG1, (b) LBG 2, (c) LBG 3, (d) LBG 4, and (e) LBG 5.

constants of gelation are shown in Figure 7 as a function of LBG concentration. In the presence of LBG the gelation rate increased with increasing concentration of LBG, but the effect was far more pronounced for the higher molecular mass samples (LBG 3, LBG 4, and LBG 5).

Figure 8 shows $G'$ as a function of time for 6% sago starch in the presence of guar with various molecular masses. $G'$ was found to increase sharply initially and attain a pseudoplateau value, $G'_{max}$. The figures clearly show that generally whereas guar 1 has little influence on $G'_{max}$, increasing the molecular mass of guar resulted in much higher $G'_{max}$ values, particularly at higher

concentrations. At 0.25% concentrations guar 1 actually resulted in a decrease in $G'_{max}$ (Figure 9). The rate constants of gelation in the presence of guar increased significantly with increasing guar molecular mass and concentrations (Figure 10) apart from mixtures containing 0.25% guar 1, for which a decrease was observed.

Figure 11 shows the mechanical spectra of sago starch alone and in the presence of LBG with various molecular masses. For the pure starch, $G'$ did not vary significantly with frequency, but $G''$ showed some frequency dependence. $G'$ was found to be over a decade higher than $G''$. The addition of LBG clearly altered the mechanical spectra. In the presence of LBG 4 and
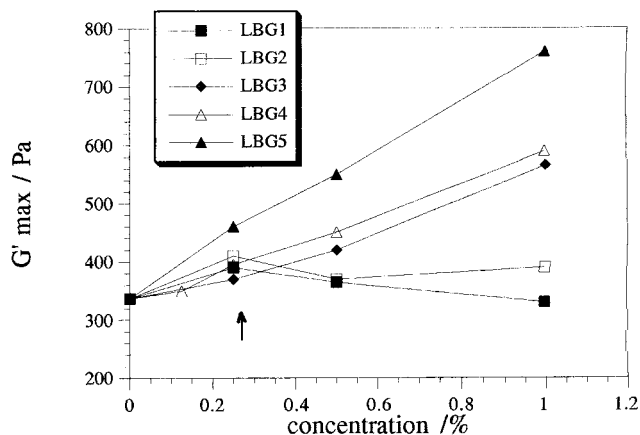
**Figure 6.** $G_{max}$ for 6% sago starch containing various concentrations of the various LBG samples. The arrow indicates the position of the binodal for LBG 1 and LBG 4.
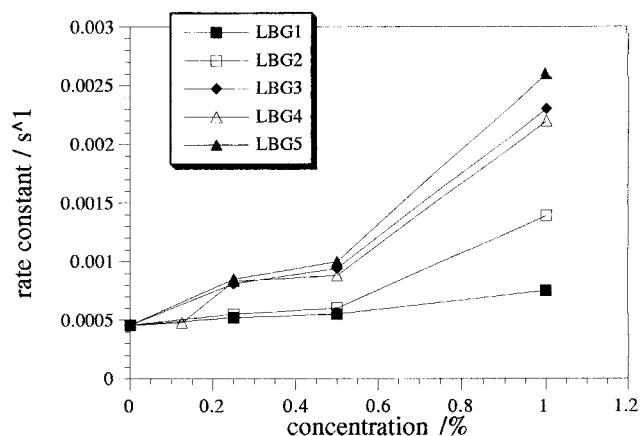


**Figure 7.** Effect of LBG on the rate constant of gelation of 6% sago starch.

LBG 5 $G'$ increased but $G''$ increased to an even greater extent. Also, $G'$ became slightly frequency dependent, whereas $G''$ became less frequency dependent. The effect became more significant at higher concentrations of LBG. For LBG 1 $G'$ actually decreased slightly, whereas $G''$ showed only a marginal increase at higher LBG concentrations. The difference in the viscoelastic behaviors of the various systems is illustrated in Figure 12, which gives tan $\delta$, that is, $G''/G'$, as a function of frequency for 6% starch/LBG mixtures. Values for tan $\delta$ <1 and >1 indicate predominantly elastic and viscous behavior, respectively. The figure clearly shows that in the presence of LBG 1 tan $\delta$ showed only a slight increase compared to the starch alone (0.03 compared to 0.01 at 0.1 Hz), indicative of a strong highly elastic gel. For LBG 4 and LBG 5, on the other hand, tan $\delta$ increased significantly (0.2 at 0.1 Hz), indicating a reduction in the overall elasticity. Similar trends were observed for starch/guar mixtures (data not shown).

Figure 13 shows the effect of LBG and guar concentrations on the gel strength of sago starch. Generally, increasing LBG and guar molecular mass and concentration increased the gel strength. In the presence of 0.25% low molecular mass LBG (LBG 1 and LBG 2) the gel strength was higher compared to 1% LBG, which is in good agreement with small deformation oscillation measurements. For LBG and guar with similar molecular masses (LBG 3, LBG 4, and guar 1, $M \sim 8 \times 10^5$) the gel strength for the starch/LBG was higher com-
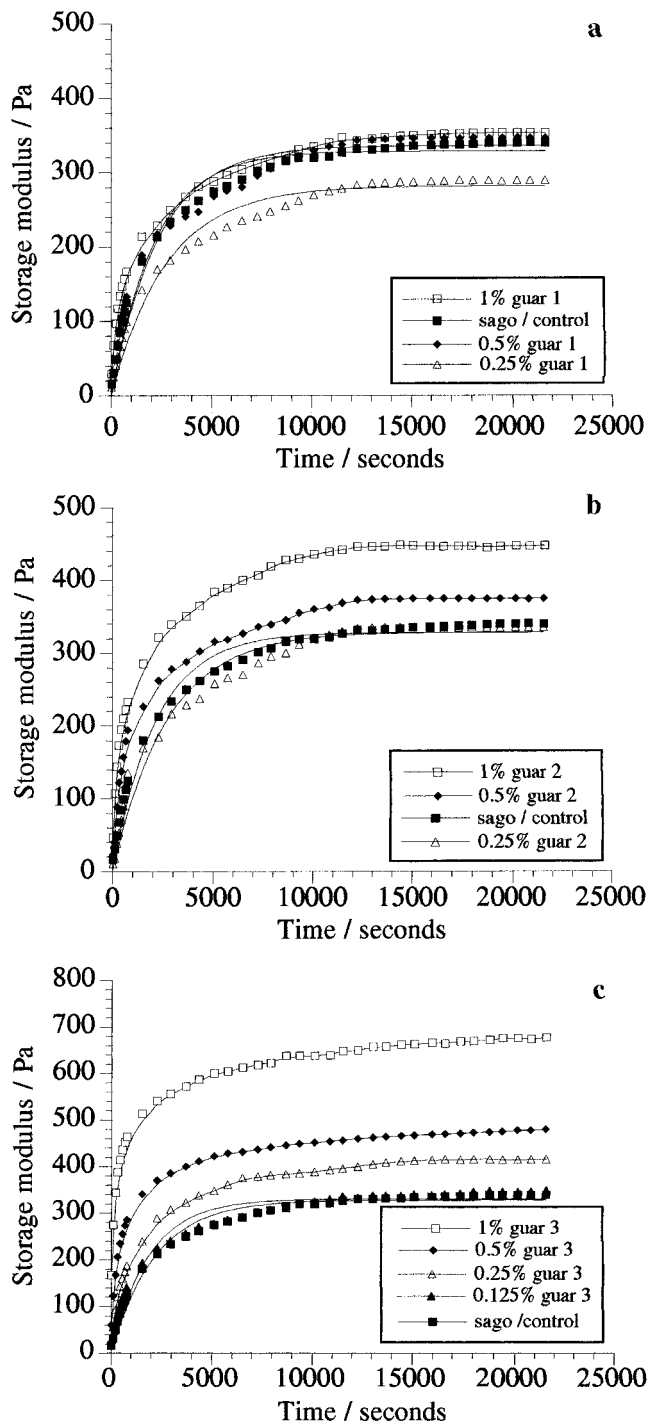


**Figure 8.** Storage modulus for 6% sago starch as a function of time with various amounts of (a) guar 1, (b) guar 2, and (c) guar 3.

pared to starch/guar. For guar 1 at a concentration of 0.25% the gel strength was lower compared to that of starch alone. Similarly, the gel strength in the presence of >0.25% LBG 1 and LBG 2 was reduced compared to that of starch alone.

**Freeze—Thaw Stability.** The effect of galactomannans on the syneresis of starch gels is shown in Table 2. Both LBG and guar reduced the amount of water leakage, and the high molecular mass guar gum sample (guar 3) was the most effective. For starch alone after one freeze—thaw cycle the gels became spongy, but for starch/galactomannan mixtures, even after several freeze—thaw cycles, the gels remained smooth.
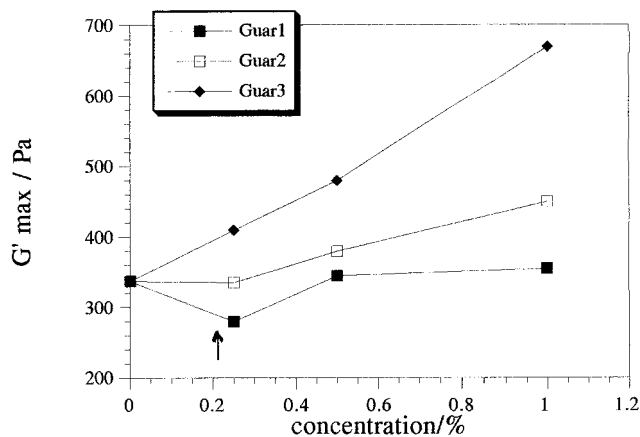
**Figure 9.** $G_{max}$ for 6% sago starch containing different concentrations of the various guar gum samples. The arrow indicates the position of the binodal for guar 4.
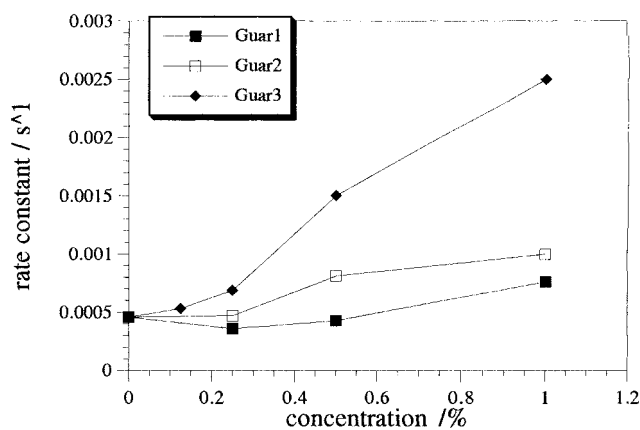


**Figure 10.** Effect of guar gum on the rate constant of gelation of 6% sago starch.

## DISCUSSION

On heating starch dispersions up to and above a critical temperature, commonly referred to as the gelatinization temperature, granule swelling occurs, the crystalline structure arising from the association of amylopectin chains is lost, and amylose leaches into the solution. The loss in crystalline structure is an endothermic process. For the mixed systems studied, both $T_{gel}$ and $\Delta H$ were found to remain almost constant, indicating that the presence of LBG or guar did not significantly influence the gelatinization process. The results are consistent with studies on other starch/polysaccharide mixtures (*15, 21, 22*). Peak broadening has been shown to occur for some mixed systems but only when the polysaccharide added is at much higher concentrations. For example, for sago starch in the presence of dextran, $\Delta T$ (i.e., $T_c - T_0$) was found to have values of 17.7, 21.3, and 32.9, respectively, for starch alone, starch plus 1% dextran, and starch plus 20% dextran (*27*). For all three systems $\Delta H$ remained constant. Ferrero et al. (*22*) have attributed such broadening to the reduced availability of water for crystalline melting, and this is analagous to the situation observed for the gelatinization of starch at low water content (*30*).

Starch gels are commonly envisaged as composite systems consisting of swollen particles embedded in a three-dimensional network of aggregated amylose chains. The rheological behavior will depend on the volume fraction and viscoelastic properties of the dispersed
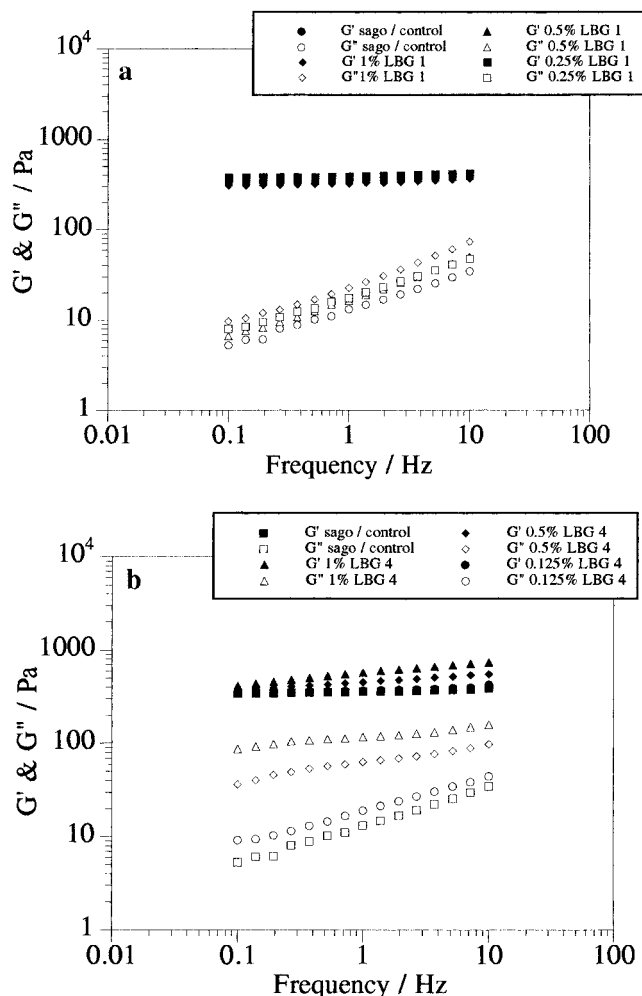


**Figure 11.** Mechanical spectra of 6% sago starch in the presence of various concentrations of (a) LBG 1 and (b) LBG 4.

phase, the rheological properties of the continuous phase, and interactions between the dispersed and continuous phases (*31*). In our studies on sago starch alone the values of $G'$ and $G''$ at zero time can be considered to be a consequence of both the dispersed and continuous phases. The rapid rise observed in $G'$ with time and the formation of a pseudoplateau region are attributed to the aggregation of amylose chains. Because $G'_{max}$ is more than an order of magnitude greater than $G'$ at zero time it can be concluded that amylose aggregation plays the dominant role. Alloncle and Doublier (*14*) studied the rheological properties of 4% cornstarch gels in the presence of LBG and guar. They pointed out for their systems that the rheological properties were governed primarily by the dispersed phase with $G'_{max}$ having a value only 2−3 times $G'$ at zero time. This can be explained by the fact that they used a lower concentration of starch and hence the total amylose content was less and probably below the minimum concentration required to produce a gel. Alloncle and Doublier (*14*) reported that $G'$ and $G''$ varied in a complicated way with the galactomannan concentration and suggested that the effect may be due to phase separation. Our studies support this view. It is apparent from our work that for 6% starch dispersions containing galactomannan at concentrations $> \sim 0.25\%$ that phase separation will occur. Although the phase separation studies were carried out at 45 °C to acceler-
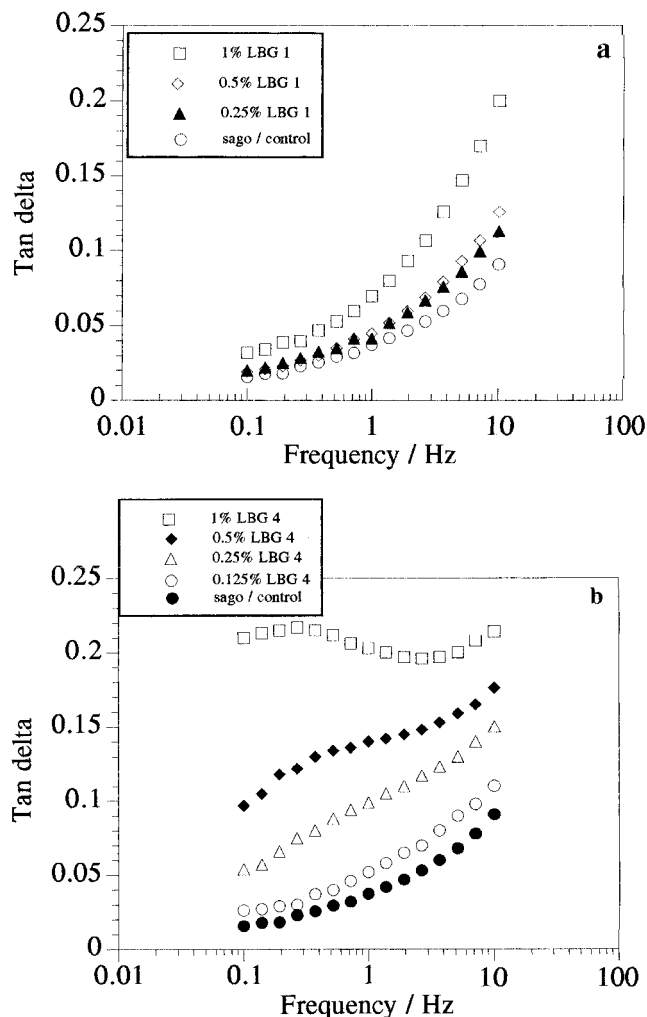
**Figure 12.** Tan $\delta$ as a function of frequency for 6% sago starch in the presence of various concentrations of (a) LBG 1 and (b) LBG 4.
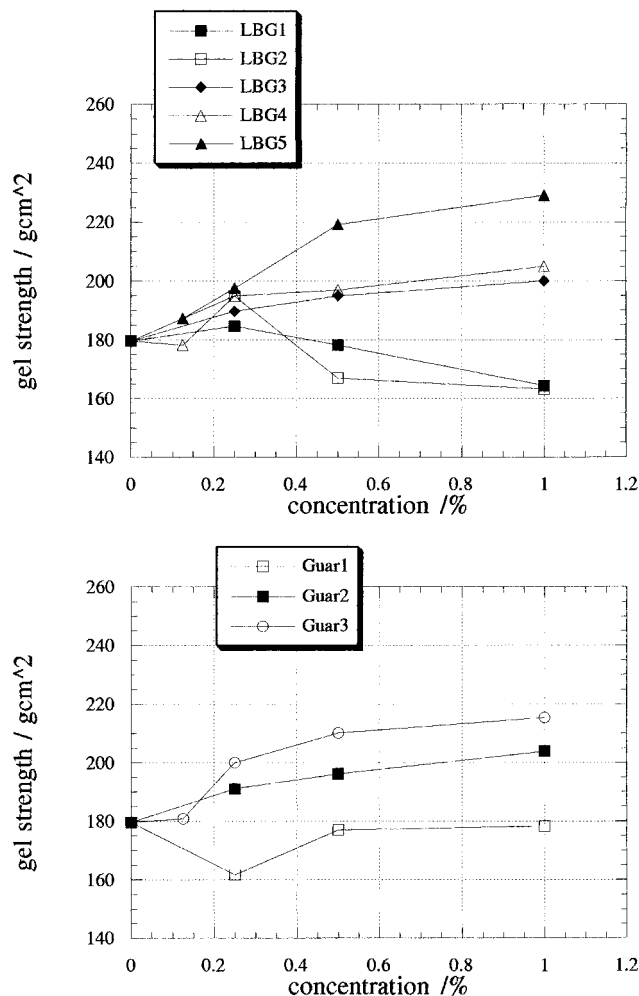


**Figure 13.** Gel strengths for 6% sago starch in the presence of various concentrations of (a) LBG and (b) guar gum.

**Table 2. Effect of Galactomannans on the Syneresis of Sago Starch Gels after Freezing**

| % syneresis | cycle 1 | cycle 2 | cycle 3 | cycle 4 | cycle 5 |
|---|---|---|---|---|---|
| control | 12 | 16 | 20 | 23 | 29 |
| guar 2 | 5 | 8 | 13 | 14 | 16 |
| guar 3 | 0 | 0 | 3 | 7 | 11 |
| LBG 4 | 4 | 7 | 10 | 12 | 13 |

ate the separation process, it is expected that phase separation will also occur at 25 °C and, furthermore, it is probable that the binodal shifts to lower total polysaccharide concentrations (see, for example, ref *18*). As described in the Introduction such phase separating systems are envisaged as "water-in-water" emulsions (*6*). Initially droplets enriched in one polysaccharide are formed in a continuous phase enriched in the other polysaccharide. Over time, the droplets coalesce to form larger and larger domains eventually leading to the formation of two separate layers. The rheological properties of the gels produced, therefore, will depend on the relative rates of the phase separation and gelation processes. For the starch/galactomannan systems studied here, segregation of the amylose, the swollen starch granules, and the galactomannan will be inhibited by the aggregation of amylose chains, which gives rise to gel formation. The rate of amylose chain aggregation does not appear to be affected appreciably for the low molecular mass galactomannans at low concentrations (i.e., where molecular entanglement and volume exclusion effects are least) but are significantly increased for the higher molecular mass galactomannans at higher concentrations (i.e., where entanglement and volume exclusion are greatest). All systems can be considered to be in the "semidilute" regime because the coil overlap concentrations, $C^*$, for the galactomannans are likely to be of the order of 0.2−1.0% (for the highest to lowest

molecular mass samples, respectively) and for amylose ~1.3% (assuming $C^* = 4/[\eta]$; *32*). The reason that high molecular mass galactomannans at high concentrations are more effective at promoting amylose aggregation (i.e., gelation) is not certain, but a clearer understanding may be achieved by analysis of the compositions of the various phases in the water-in-water emulsions and applying depletion theory (*7*). In its simplest form the theory requires knowledge also of the hydrodynamic radius of the droplets and of the radius of gyration of the polymer molecules ($R_g$) in the continuous phase. The attractive force due to exclusion of polymer segments from the layers adjacent to the droplet surface increases with increasing $R_g$.

In the presence of galactomannans the freeze−thaw stability of starch gels was improved significantly. Syneresis of starch gels after freezing and thawing is due to increased association of the amylose and amylopectin, which results in expulsion of water. The galactomannans may inhibit the aggregation process by acting as a physical barrier preventing amylose/amylopectin self-association or by associating with

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amylose (and also perhaps amylopectin) aggregated chains. LBG is known to associate with other polysaccharides, for example, xanthan gum and $\kappa$-carrageenan, but this is not the case for guar gum (*2*). In addition, LBG alone is known to form thermally irreversible gels due to association of galactose-deficient regions along the mannan chain (*33*), and hence it is possible that a bicontinuous gel network of separate amylose and LBG aggregated chains is formed. Further work is required to elucidate the precise mechanism.

## ACKNOWLEDGMENT

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