

Rheological Properties of Mixed Polysaccharides and Polysaccharide-Thickened Emulsions

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Steady flow and viscoelastic properties of mixed-polysaccharides and mixed-polysaccharide-thickened oil-in-water emulsions are investigated with a cone-and-plate system using a controlled-stress rheometer. The mixed-polysaccharide system studied is xanthan gum and guar gum. The rheological properties of the mixed-polysaccharide systems exhibit strong synergistic effects. For a total polysaccharide concentration of 0.75 wt. % investigated, the synergistic effect is maximum at a xanthan:guar ratio of 15:85. The oil-in-water emulsions, prepared from a mixed-polysaccharide system as the suspending medium, are strongly shear thinning and highly viscoelastic in nature. The rheological parameters such as apparent viscosity, storage, and loss moduli increase with an increase in the oil concentration of the emulsion.

Introduction

High molecular weight polymers are widely used as *thickeners* in many commercial emulsion formulations (McNeely and Kang, 1973; Jerome-Ganz, 1977; Kovacs and Kang, 1977; Mear, 1977; Pettitt, 1979; Glicksman, 1979; Blanshard and Mitchell, 1979; Dickinson and Stainsby, 1982; Baird, 1986; Aqualon Company, 1988; Lockhead et al., 1989; Gouldby et al., 1991; Dickinson and Galazka, 1991; Robins, 1991; Dickinson et al., 1993; Luyten et al., 1993; Pal, 1995). The addition of polymeric thickening agents to the continuous phase of the emulsion improves the stability of the emulsion, that is, the processes leading to instability in emulsions (such as creaming, sedimentation, flocculation, and coalescence) are retarded to a great extent. The polymeric agent not only increases the viscosity of the continuous phase but it often imparts yield value to that phase. In many food emulsions, there is an additional purpose for adding polysaccharide thickeners to the continuous phase than to simply extend the "shelf-life" of the product, that is, to impart the required mouth-feel properties, pleasing appearance, and texture to the food products as well as to improve moisture retention capability.

In the handling, mixing, storage, and pipeline transportation of emulsions, knowledge of the rheological properties is required for the design, selection, and operation of the equipment involved. While there exists a substantial amount of published literature on the rheology of emulsions prepared from Newtonian liquids (Sherman, 1968; Sherman, 1983; Pal and Rhodes, 1989; Pal, 1993), little rheological work has been done on emulsions in which the continuous phase is

a non-Newtonian polymeric liquid, even though such emulsions are quite important from a practical point of view, as just discussed.

In this article, we report *new* results on the steady, oscillatory, and creep behavior of mixed-polysaccharides and mixed-polysaccharide-thickened oil-in-water emulsions. The polymeric system studied is a mixture of xanthan gum and guar gum. These polysaccharides are widely used in the food industry.

Xanthan gum is a high molecular weight extracellular polysaccharide, secreted by the bacterium *Xanthomonas campestris*. The structure of xanthan gum consists of a main chain built up of β -D-glucose units linked through the 1- and 4-position, and a side chain containing two mannose units and one glucuronic acid unit found as a mixed potassium, sodium, and calcium salt (Glicksman, 1979). The molecular weight of the xanthan gum is approximately 2×10^6 as determined by light scattering (Carriere et al., 1993; Baird, 1986). Xanthan gum is of great practical interest because of its widespread use in food, pharmaceutical, oil field, agricultural, and other industrial applications (Kovacs and Kang, 1977; Baird, 1986). The unique physical and rheological properties of xanthan gum are responsible for its widespread use in various applications (Rochefort and Middleman, 1987; Carnali, 1992; Carriere et al., 1993).

Guar gum is a galactomannan with linear chains of D-mannopyranosyl units with side branching units of D-galactopyranose attached by (1 \rightarrow 6) linkages (Meer, 1977). It is de-

rived from the seed of the guar plant, *Cyanopsis tetragonolobus*. It is nonionic in nature and has a molecular weight of approximately 2.2×10^5 – 3×10^5 . Guar gum is widely used as a thickener in many food products.

Xanthan gum and guar gum display widely different rheological properties. Xanthan gum solutions display unusually strong shear-thinning behavior and high storage moduli (Pal, 1995) due to the formation of a complex network of entangled rodlike molecules (Doublier and Llamas, 1991; Carnali, 1992). It is believed that xanthan molecules in solution exist as rigid wormlike helices (either as single-stranded or multi-stranded), which interact with each other to build a complex, loosely bound network held together by intramolecular non-covalent interactions, such as hydrogen bonding (Pettitt, 1979). Guar gum solutions, on the other hand, exhibit only moderate shear-thinning behavior and much lower storage moduli. It is well known that the conformation of guar gum molecules in solution is coillike and that there exists little or no interaction between the gum molecules. The non-Newtonian behavior observed in guar gum solutions is mainly due to topological entanglements of macromolecules at high polymer concentrations (Launay et al., 1986).

When xanthan gum and guar gum are mixed together, they can display remarkable synergistic properties due to interactions between xanthan helices and unsubstituted regions of the guar gum molecules. Consequently, blends of guar gum and xanthan gum can provide a range of thickening and gelling properties that have practical significance in many emulsion formulations (particularly food emulsions).

Experimental Work

Materials

The xanthan gum used was supplied by Kelco, a division of Merck & Co., Inc. The trade name of this gum is KELZAN, and the lot number of the sample used in the experiments was 80740A. Guar gum was supplied by Sigma Chemical Co. The surfactant used was Triton X-100, a commercially available nonionic surfactant supplied by Rohm and Haas Co. This surfactant is currently manufactured by Union Carbide Co. The chemical name of Triton X-100 is isooctylphenoxy polyethoxy ethanol. The emulsions of the oil-in-water type were prepared using a Newtonian petroleum oil (trade name EDM) supplied by Monarch Oil Company, Canada. This oil is widely used as a lubricant and as a solvent. It has a mild odor and appears as an amber liquid. The viscosity of the oil batch used in this study was $5.8 \text{ mPa} \cdot \text{s}$ at 25°C .

Procedures

A stock solution of 0.75 wt. % xanthan gum was prepared by slowly sifting a known amount of polymer powder into a known volume of gently agitated deionized water at room temperature. A variable speed homogenizer (Gifford-Wood Model 1-LV) was used to provide the necessary agitation and mixing of the fluid. The agitation was continued until the polymer was dissolved completely and the solution was lump free. A known amount of surfactant (Triton X-100) was then added to the polymer solution; the surfactant dissolved readily with gentle agitation. The resulting solution had a surfactant concentration of 0.5 wt. %. The stock solution was stored at room temperature for about two days prior to use.

The guar gum solution having a concentration of 0.75 wt. % was prepared by slowly sifting a known amount of polymer powder into a known volume of gently agitated deionized water at room temperature. The mixture was then heated at 78°C for about 25 min (while agitation was continued) in order to achieve a total solubilization. The solution was then cooled down at room temperature and a known amount of surfactant (Triton X-100) was added to the solution. The surfactant dissolved readily with gentle agitation. The resulting solution had a surfactant concentration of 0.5 wt. %. The solution was stored at room temperature for about two days prior to use.

Blends of xanthan gum and guar gum solutions, with a variable xanthan:guar ratio and a constant total polysaccharide content (0.75 wt. %), were prepared by mixing appropriate amounts of the two polysaccharide solutions at room temperature.

The emulsions of the oil-in-water type were prepared in batches of 300 g. The known amounts of aqueous polymer solution (xanthan gum, guar gum, or mixed xanthan and guar systems) and oil were sheared together in a homogenizer for about 5 min at a fixed speed. The emulsions produced were very stable with respect to creaming and coalescence. The droplet sizes were measured by taking photomicrographs of the emulsion samples using a Zeiss optical microscope equipped with a camera. The emulsion samples were diluted with 0.5 wt. % of Triton X-100 solution (same surfactant concentration as in the emulsions) before taking the photomicrographs.

All rheological experiments were carried out at 25°C using a Bohlin controlled-stress rheometer (Bohlin CS-50). A cone-and-plate measuring system was used. The cone diameter was 40 mm and the plate diameter was 60 mm. The cone angle was 4° and the gap at the cone tip was $150 \mu\text{m}$.

Results and Discussion

Rheology of polymer solutions

Figure 1 shows the plots of apparent viscosity (η) as a function of shear stress (τ) for various different xanthan:guar ratios. Note that these solutions contain 0.5% by weight Tri-

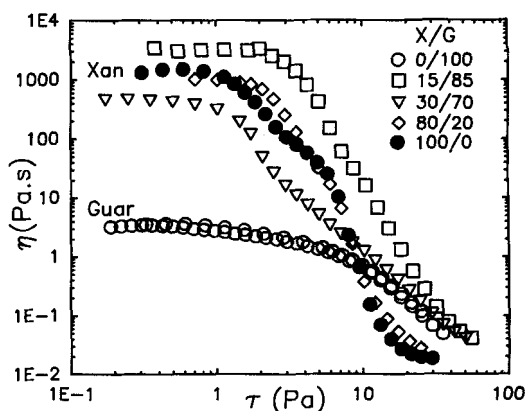


Figure 1. Apparent viscosity (η) as a function of shear stress (τ) for mixed polysaccharide solutions with various xanthan:guar ratios.

The total polysaccharide concentration is 0.75 wt. %.

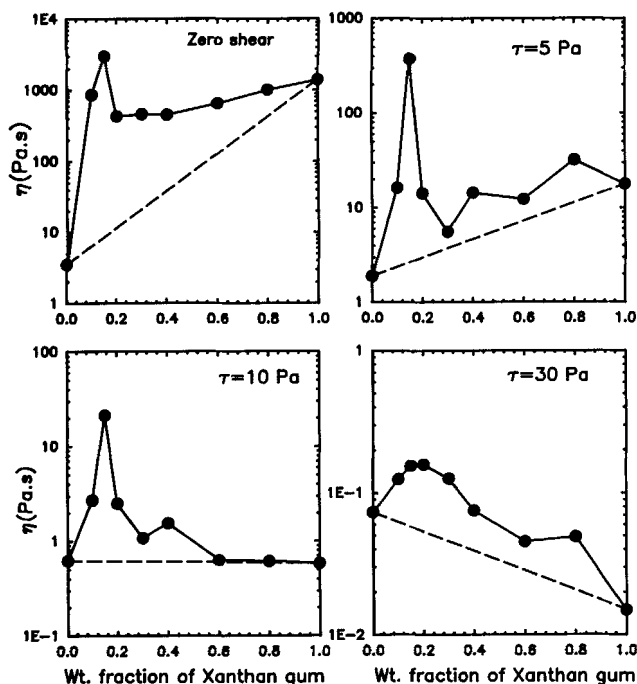


Figure 2. Apparent viscosity as a function of weight fraction of xanthan gum in the mixed polysaccharide system.

The total polysaccharide concentration is 0.75 wt. %.

ton X-100 and that the total polysaccharide content is constant, that is, 0.75 wt. %. To avoid overcrowding of data, not all the xanthan:guar ratios investigated are shown in Figure 1. The polymer solutions at various different xanthan:guar ratios are non-Newtonian in nature and they exhibit two distinct regions: the "lower Newtonian region" in the low shear stress range where the viscosity is constant, and the "shear-thinning region" where the viscosity decreases with the increase in shear stress. The guar gum solution exhibits only moderate shear-thinning, whereas the xanthan gum solution (at the same polysaccharide concentration of 0.75 wt. %) exhibits unusually strong shear-thinning behavior. It is interesting to note that a mixed polysaccharide system with xanthan:guar ratio of 15:85 exhibits viscosities higher than either gum alone.

Figure 2 shows the plots of apparent viscosity as a function of weight fraction of xanthan gum present in a mixed polysaccharide system. The total polysaccharide content is constant (0.75 wt. %). The mixed polysaccharide solutions of xanthan gum and guar gum exhibit positive deviation from log-additivity mixing rule. The viscosity of mixed polysaccharide solutions is much higher than that expected on the basis of a linear relationship drawn through the pure components. It should also be noted that the deviation from the mixing rule decreases with the increase in shear stress. Furthermore, the viscosity plots show a peak (that is, the deviation from the mixing rule is maximum) at a xanthan weight fraction of 0.15 in a mixed polysaccharide system.

The storage modulus (G') and loss modulus (G'') for various different xanthan:guar ratios in the linear viscoelastic region are plotted in Figure 3. The figure reveals the following important points: (1) the storage modulus (G') falls below the

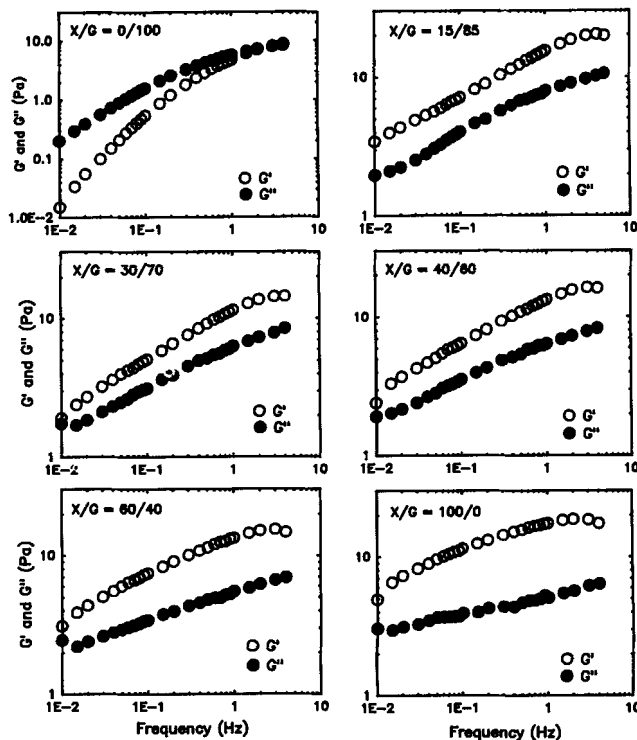


Figure 3. Storage modulus (G') and loss modulus (G''), in the linear viscoelastic region, for mixed polysaccharide solutions with various xanthan:guar ratios.

The total polysaccharide concentration is 0.75 wt. %.

loss modulus (G'') over the entire frequency range in the case of guar gum solution (0.75 wt. %), indicating that the guar gum solution (without any added xanthan gum) is predominantly viscous; (2) in the case of xanthan gum solution (0.75 wt. %), the storage modulus (G') falls above the loss modulus (G'') over the entire frequency range, indicating that the xanthan gum solution (without any added guar gum) is predominantly elastic. The high values of the storage modulus observed in the case of xanthan gum solution is clearly due to the formation of a gel-like structure between the polymer molecules (Carnali, 1992; Pal, 1995); and (3) the solutions of mixed polysaccharides at various different xanthan:guar ratios exhibit a behavior similar to that of xanthan gum alone in that the storage modulus (G') falls above the loss modulus (G'') over the entire frequency range.

Figure 4 shows the plots of storage modulus (G') as a function of weight fraction of xanthan gum present in a mixed polysaccharide system (the total polysaccharide content being constant, i.e., 0.75 wt. %). Like the viscosity plots shown in Figure 2, the storage modulus plots indicate that the mixed polysaccharide solutions of xanthan gum and guar gum exhibit positive deviation from the log-additivity mixing rule. Furthermore, the deviation from the mixing rule is maximum at a xanthan weight fraction of 0.15 in a mixed polysaccharide system.

The creep/recovery behavior for the mixed polysaccharide solutions at various different xanthan:guar ratios is shown in Figure 5. The compliance (J), defined as the ratio of strain to stress, is plotted as a function of time. The creep/recovery

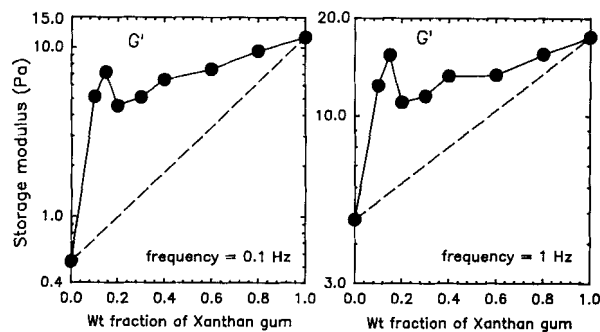


Figure 4. Storage modulus (G') as a function of weight fraction of xanthan gum in the mixed polysaccharide system.

The total polysaccharide concentration is 0.75 wt. %.

experiments were conducted as follows: a known value of shear stress (0.5 Pa in this case) was applied to the sample using cone-and-plate geometry, and the resulting strain was monitored as a function of time. The imposed stress was suddenly removed after 500 s and recovery, on the release of the stress, was monitored for another 500 s. Figure 5 indicates that all mixed-polysaccharide solutions and xanthan gum solutions exhibit a significant recovery upon removal of stress. The only exception is guar gum solution, which exhibits high values of creep compliance and little recovery upon the removal of stress.

Figure 6a shows the effect of weight fraction of xanthan gum, present in a mixed polysaccharide system, on the creep compliance (J). The compliance plot exhibits negative deviation from the mixing rule. Also, the plot shows a minimum at a xanthan weight fraction of 0.15. This is consistent with previous observations that there occurs a maximum in the viscosity and storage modulus plots at a xanthan weight fraction of 0.15.

In Figure 6b, the percent recovery in compliance is shown as a function of weight fraction of xanthan gum present in a mixed polysaccharide system. As can be seen, the percent recovery is maximum (> 70%) at a xanthan weight fraction of 0.15.

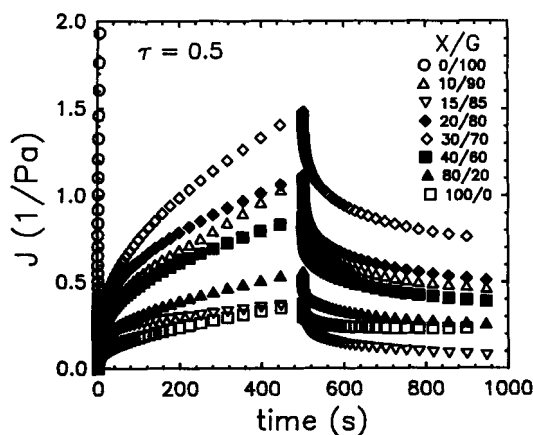


Figure 5. Creep/recovery behavior for mixed polysaccharide solution with various xanthan:guar ratios.

The total polysaccharide concentration is 0.75 wt. %.

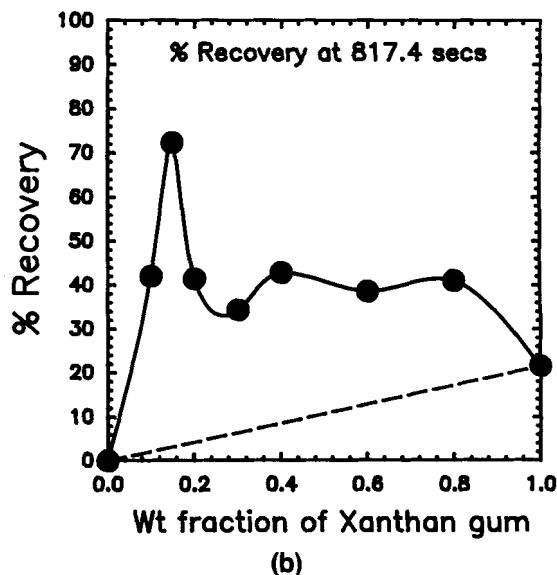
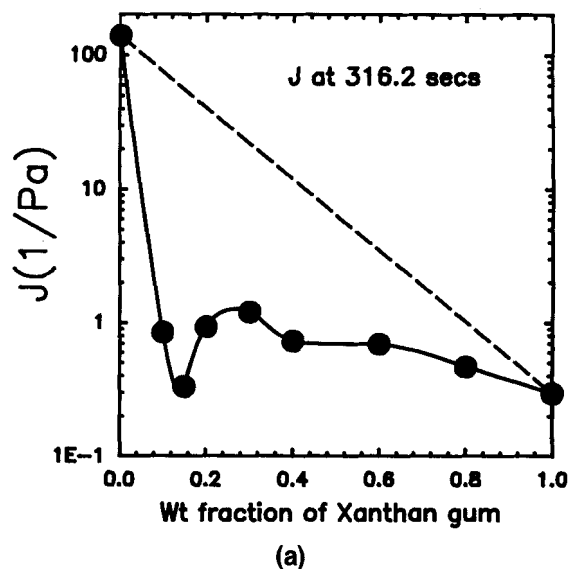


Figure 6. (a) Creep compliance (J) and (b) percent recovery in compliance as a function of weight fraction of xanthan gum in the mixed polysaccharide system.

The total polysaccharide concentration is 0.75 wt. %.

The exact molecular mechanisms underlying the observed synergistic properties in mixed polymeric systems are not clear at present. However, it is quite possible that guar gum molecules complex with xanthan gum molecules in some manner to form a three-dimensional network of polymer chains. The unsubstituted (unbranched) segments of the guar gum molecules could associate with the xanthan gum molecules to form the junction points between the chains. It is also possible that the surfactant micelles adsorbed to the polymer chains could interact to provide association points between the chains. The presence of a three-dimensional network can easily explain the observed rheological properties of xanthan/guar mixed solutions. The viscosity data for the mixed solutions discussed earlier (Figure 2) indicated that the magnitude of the synergistic effect decreases with the in-

crease in shear stress. This is likely due to the progressive breakdown in the three-dimensional network structure of polymer chains. The dynamic storage G' and loss G'' moduli data for the mixed solutions discussed earlier (refer to Figure 3) indicated that $G' > G''$ over the entire frequency range and that the moduli followed nearly a power-law behavior with respect to frequency. These observations are known to be displayed by gel-like structures (Rochefort and Middleman, 1987; Carnali, 1992).

Rheology of polymer-thickened oil-in-water emulsions

From the discussion of results in the preceding section, it is clear that the xanthan + guar mixed polysaccharide system exhibits strong synergistic properties. For a given total polysaccharide concentration (0.75 wt. %), the synergistic effect is maximum at a xanthan weight fraction of 0.15. Consequently, a mixed polysaccharide system with xanthan:guar ratio of 15:85 was used as a suspending medium to prepare oil-in-water type of emulsions. The dispersed phase (oil) concentration (ϕ) of the emulsion was varied from 0 to 79 vol. %. For comparison purposes, emulsions were also prepared with xanthan gum and guar gum alone as the suspending mediums. However, the oil concentration of these emulsions was fixed at 65 vol. %.

Figure 7 shows the apparent viscosity as a function of shear stress for emulsions prepared from a mixed polysaccharide system with xanthan:guar ratio of 15:85. The viscosity data for a given oil concentration (ϕ) emulsion is compared with that of the suspending medium alone. For oil concentrations up to 45 vol. % ($\phi \leq 0.45$), there occurs a negligible change

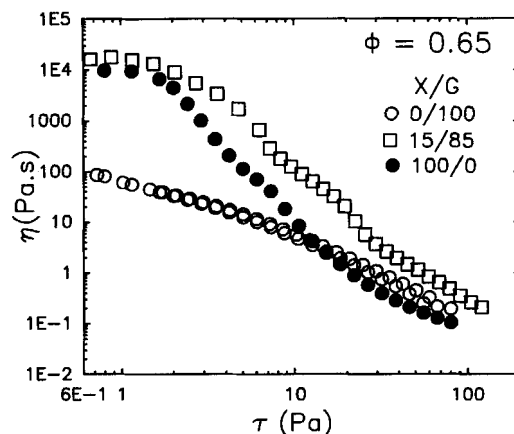


Figure 8. Apparent viscosity as a function of shear stress for a fixed oil concentration emulsion ($\phi = 0.65$) prepared from suspending mediums having different xanthan:guar ratios.

The total polysaccharide concentration of the suspending medium is 0.75 wt. %.

in the zero shear stress viscosity, although at high values of shear stress, the presence of the oil droplets clearly increases the viscosity. For oil concentrations higher than 45 vol. % ($\phi > 0.45$), the viscosity data for the emulsions fall well above that of the suspending medium alone over the entire range of the shear stress.

Figure 8 compares the viscosity data for a fixed oil concentration ($\phi = 0.65$) emulsion prepared from three different suspending mediums, namely, xanthan gum, guar gum, and a mixed polysaccharide system with xanthan:guar ratio of 15:85. Note that the total polysaccharide concentration in any given suspending medium is 0.75 wt. % and that each suspending medium contains 0.5 wt. % surfactant (Triton X-100). The viscosity data for the emulsion having a mixed polysaccharide suspending medium falls above that of the emulsions with xanthan gum or guar gum alone as the suspending mediums. Also, at low shear stresses, emulsion with xanthan gum as the suspending medium exhibits much higher viscosities as compared with the emulsion having guar gum as the suspending medium. These observations clearly indicate that the apparent viscosity vs. shear stress flow curve for any given emulsion is highly reflective of the corresponding suspending medium flow curve shown in Figure 1.

It should be further noted that all the emulsions investigated were polydisperse with respect to droplet size. Figure 9a shows the droplet size distributions for emulsions prepared from a mixed polysaccharide system with xanthan:guar ratio of 15:85. Clearly, the droplet size increases with an increase in the oil concentration (ϕ). Figure 9b shows the effect of the suspending medium on the droplet size distribution for a 65 vol. % oil-in-water emulsion. The droplet size distribution for the emulsion having guar gum alone as the suspending medium is similar to that of the emulsion having the mixed polysaccharide system with xanthan:guar ratio of 15:85 as the suspending medium. However, the droplet sizes for the emulsion prepared from xanthan gum alone as the suspending medium are relatively large. The production of smaller droplet sizes in the presence of guar gum indicates that guar gum has some surface activity, although it is highly

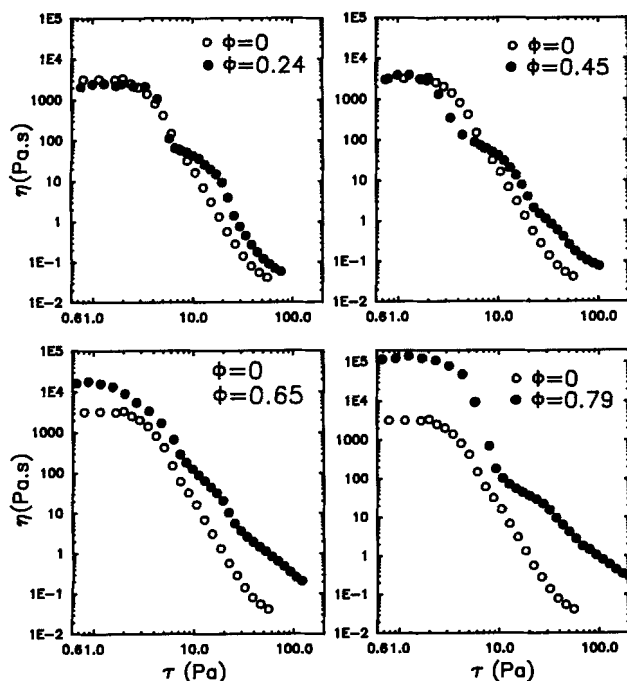


Figure 7. Apparent viscosity as a function of shear stress for emulsions prepared from the mixed polysaccharide system (with xanthan:guar ratio of 15:85) as the suspending medium.

The total polysaccharide concentration of the suspending medium is 0.75 wt. %.

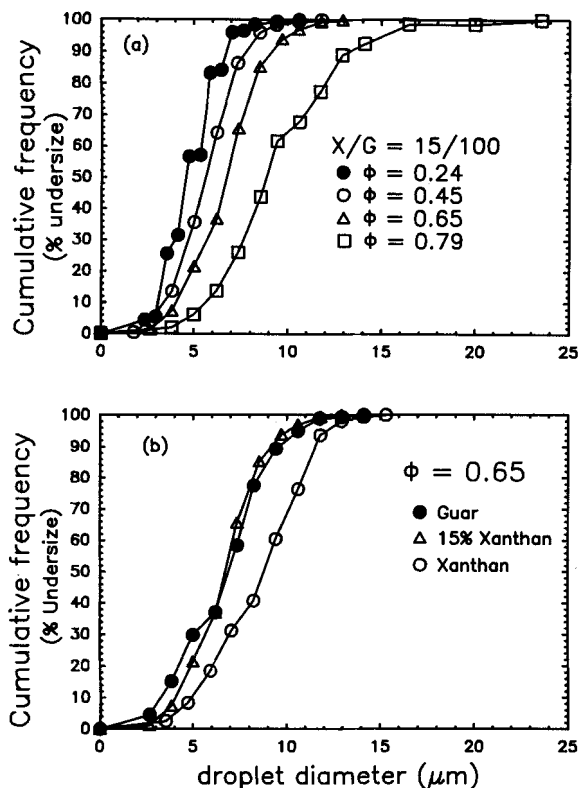


Figure 9. Droplet size distributions: (a) for emulsions prepared from a mixed polysaccharide system (with xanthan:guar ratio of 15:85) as the suspending medium; (b) for a fixed oil concentration emulsion ($\phi = 0.65$) prepared from suspending mediums with different xanthan:guar ratios.

The total polysaccharide concentration of the suspending medium is 0.75 wt. %.

hydrophilic in nature. Indeed, it has been suggested in the literature (Reichmann and Garti, 1991) that galactomannans (such as guar gum and locust bean gum) can adsorb at oil-water interfaces leading to a decrease in interfacial tension.

Figure 10 gives the plots of storage modulus (G') and loss modulus (G''), in the linear viscoelastic region, for oil-in-water emulsions prepared from a mixed polysaccharide system with xanthan:guar ratio of 15:85. For comparison purposes, the values of the moduli predicted from the following Palierne model (Palierne, 1990) are also shown:

$$G^*(w) = G_c^*(w) \frac{1 + 3\sum_i \phi_i H_i(w)}{1 - 2\sum_i \phi_i H_i(w)}, \quad (1)$$

where

$$H_i(w) = \frac{4(\sigma/R_i)[2G_c^*(w) + 5G_d^*(w)] + [G_d^*(w) - G_c^*(w)][16G_c^*(w) + 19G_d^*(w)]}{40(\sigma/R_i)[G_c^*(w) + G_d^*(w)] + [2G_d^*(w) + 3G_c^*(w)][16G_c^*(w) + 19G_d^*(w)]}, \quad (2)$$

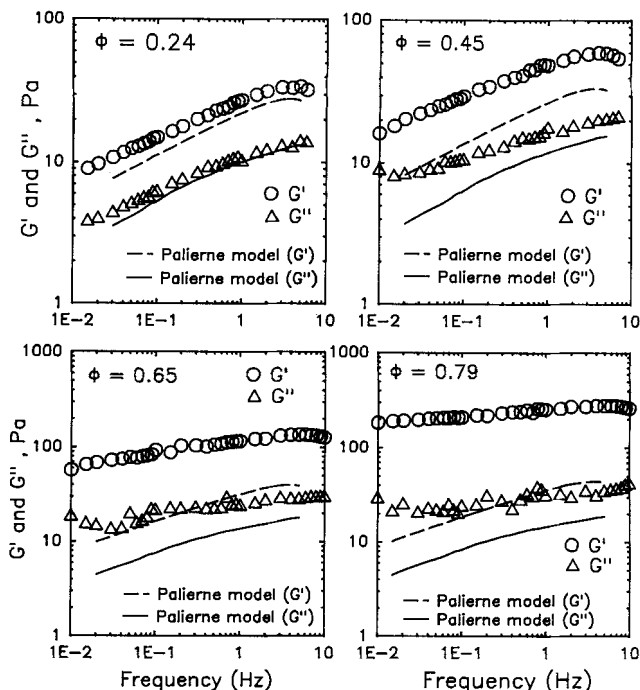


Figure 10. Storage and loss moduli (in the linear viscoelastic region) for the emulsions prepared from a mixed polysaccharide system (with xanthan:guar ratio of 15:85) as the suspending medium.

The total polysaccharide concentration of the suspending medium is 0.75 wt. %.

G^* is complex modulus of emulsion, w is frequency, G_c^* is a complex modulus of continuous phase, G_d^* is a complex modulus of dispersed phase, σ is interfacial tension, and ϕ_i is the volume fraction of particles of radius R_i . The summation in Eq. 1 is carried out over the distribution of particle sizes. For emulsions with monodisperse particle-size distribution, Eq. 1 reduces to the following equation:

$$G^* = G_c^* \left[\frac{1 + 3\phi H}{1 - 2\phi H} \right], \quad (3)$$

where

$$H = \frac{(4\sigma/R)(2G_c^* + 5G_d^*) + (G_d^* - G_c^*)(16G_c^* + 19G_d^*)}{(40\sigma/R)(G_c^* + G_d^*) + (2G_d^* + 3G_c^*)(16G_c^* + 19G_d^*)} \quad (4)$$

and ϕ is the total volume fraction of particles. Since the present emulsions were polydisperse in nature, the volume-average radius was used in applying the model just given (Eq. 3). The value of the interfacial tension used in the calcula-

tions was 2.5 mN/m. This is the measured value of the interfacial tension between oil and 0.5 wt. % Triton X-100 solution, obtained by the drop-volume (drop-weight) method. An attempt was made to measure the interfacial tension between oil and the mixed polymeric system (xanthan:guar ratio of 15:85 and Triton X-100 concentration of 0.5 wt. %) with the drop-volume method. However, we could not produce drops of well-defined shape because of the extremely high viscosity and elasticity of the polymeric solution.

Figure 10 reveals the following important points: (1) the storage modulus for various differently concentrated emulsions falls above the loss modulus over the entire frequency range, indicating that these emulsions are predominantly elastic in nature; (2) the values of G' and G'' increase with an increase in the concentration of the dispersed phase (oil droplets); and (3) the Palierne model gives reasonable prediction of G' and G'' only when the dispersed-phase concentration of the emulsion is low ($\phi \leq 0.24$). At higher values of ϕ , the Palierne model predicts the values of G' and G'' to be lower than the experimental values. The deviation increases with an increase in ϕ .

The high values of the storage modulus exhibited by the emulsions in Figure 10 is due to two reasons: first, the continuous phase of the emulsions itself is predominantly elastic,

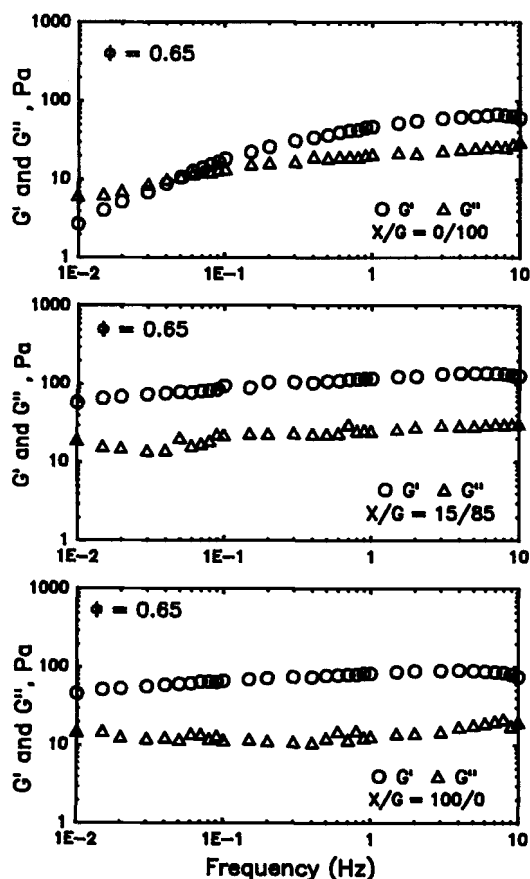


Figure 11. Storage and loss moduli for a fixed oil concentration emulsion ($\phi = 0.65$) prepared from suspending mediums having different xanthan:guar ratios.

The total polysaccharide concentration of the suspending medium is 0.75 wt. %.

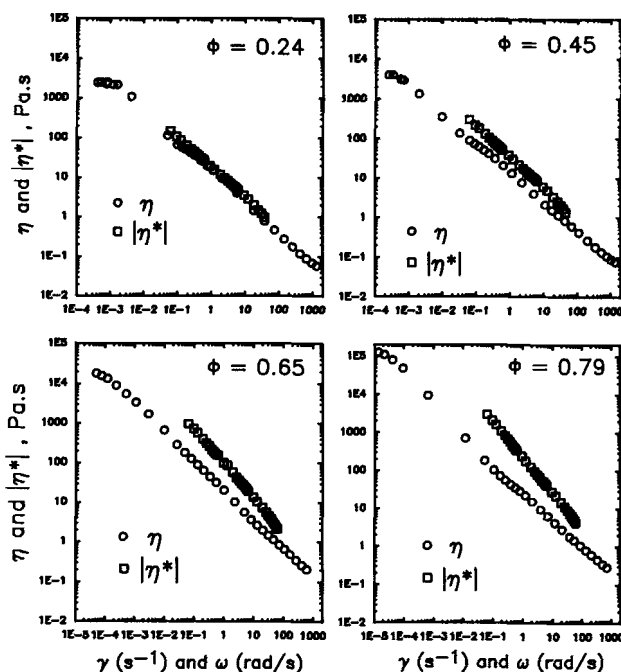


Figure 12. Complex viscosity data vs. steady shear viscosity data for the emulsions prepared from a mixed polysaccharide system (with xanthan:guar ratio of 15:85) as the suspending medium.

The total polysaccharide concentration of the suspending medium is 0.75 wt. %.

and second, an additional mechanism for elasticity is present in emulsions, that is, the elasticity of shape of droplets.

Figure 11 shows the storage and loss moduli data for a fixed oil concentration ($\phi = 0.65$) emulsion prepared from three different suspending mediums: guar gum, xanthan gum, and a mixed polysaccharide system having xanthan:guar ratio of 15:85. This figure reveals that the emulsion having guar gum as the suspending medium has the lowest elasticity, whereas the emulsion with a mixed polysaccharide system as the suspending medium has the highest degree of elasticity.

The complex viscosities of emulsions, prepared from a mixed polysaccharide system with xanthan:guar ratio of 15:85, are compared with the corresponding steady shear viscosities in Figure 12. At low values of oil concentration ($\phi \leq 0.24$), there is a reasonable agreement between the complex viscosity and steady shear viscosity. However, at higher oil concentrations ($\phi \geq 0.45$) the complex viscosities fall well above the steady shear viscosities. Thus, the Cox-Merz rule (Cox and Merz, 1958) is obeyed by the emulsions only at low values of ϕ .

Figure 13 shows the creep/recovery behavior for emulsions, prepared from a mixed polysaccharide system with a xanthan:guar ratio of 15:85, at various different oil concentrations (ϕ). They all exhibit an instantaneous elastic compliance and a recoverable compliance. The emulsions become more elastic with an increase in the oil concentration. In fact, the highly concentrated emulsion containing 79 vol. % oil droplets exhibits elastic solidlike behavior; the recovery in compliance is nearly complete for this emulsion.

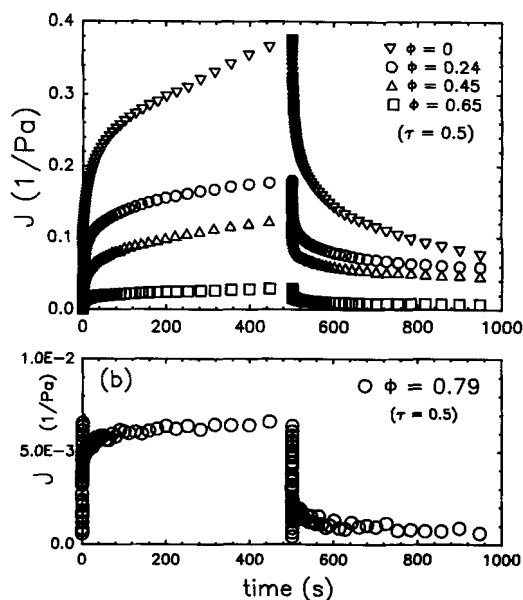


Figure 13. Creep/recovery behavior for emulsions prepared from a mixed polysaccharide system (with xanthan:guar ratio of 15:85) as the suspending medium.

The total polysaccharide concentration of the suspending medium is 0.75 wt. %.

The creep/recovery data were also measured for a fixed oil concentration emulsion ($\phi = 0.65$) with three different suspending mediums: guar gum, xanthan gum, and a mixed polysaccharide system having xanthan/guar ratio of 15:85. The plots revealed that (1) the emulsion having guar gum as the suspending medium behaves like a viscous liquid in that the creep compliance increases proportionally with time and that the recovery in compliance is negligible after removal of stress; and (2) emulsions with xanthan gum and mixed polysaccharide system (xanthan:guar ratio of 15:85) as the suspending mediums give viscoelastic responses—they both exhibit a significant recovery in compliance upon removal of stress.

Conclusions

Based on the results of this study, the following conclusions can be made:

- The rheological properties of mixed xanthan gum + guar gum systems exhibit strong synergistic effects. The apparent viscosity, the storage modulus, and the percent recovery in compliance (upon removal of stress), and so forth, all exhibit positive deviations from log-additive mixing rule. For a total polysaccharide concentration of 0.75 wt. % investigated in the present work, the synergistic effect (and, hence, deviation from the mixing rule) is maximum at a xanthan:guar ratio of 15:85.

- Oil-in-water emulsions prepared from a mixed polysaccharide system having xanthan:guar ratio of 15:85 are strongly shear-thinning and viscoelastic in nature. The apparent viscosity of emulsions increases with the increase in dispersed-phase (oil) concentration, particularly at high values of shear stress. The storage modulus for the emulsions, at various dif-

ferent oil concentrations, falls above the loss modulus over the entire frequency range. Also, the storage and loss moduli increase with the increase in oil concentration, and the emulsions do not follow the Cox–Merz rule. The creep/recovery experiments confirm that the emulsions are highly viscoelastic in nature and that the degree of elasticity increases with the increase in oil concentration.

- For a given oil concentration, the values of the rheological parameters (viscosity, storage, and loss moduli) for the emulsion having a mixed polysaccharide suspending medium (xanthan:guar ratio of 15:85) are higher than those for the emulsions having xanthan gum or guar gum as the suspending mediums. Also, emulsion with guar gum as the suspending medium exhibits the lowest degree of viscoelasticity.

Acknowledgment

Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully appreciated.

Literature Cited

- Aqualon Company, "Aqualon Cellulose Gum," Bulletin No. 250-10C Rev. 1-88 10M 1P, Aqualon Co., Wilmington, DE (1988).
- Baird, J. K., "Xanthan," *Encyclopedia of Polymer Science and Engineering*, J. L. Kroschwitz, ed., Wiley, New York (1986).
- Blanshard, J. M. V., and J. R. Mitchell, *Polysaccharides in Food*, Butterworths, London (1979).
- Carnali, J. O., "Gelation in Physically Associating Biopolymer Systems," *Rheol. Acta*, **31**, 339 (1992).
- Carriere, C. J., E. J. Amis, J. L. Schrag, and J. D. Ferry, "Dilute Solution Dynamic Viscoelastic Properties of Xanthan Polysaccharide," *J. Rheol.*, **37**(3), 469 (1993).
- Cox, W. P., and E. H. Merz, "Correlation of Dynamic and Steady Flow Viscosities," *J. Poly. Sci.*, **28**, 619 (1958).
- Dickinson, E., and V. B. Galazka, "Bridging Flocculation in Emulsions Made with a Mixture of Protein and Polysaccharide," *Food Polymers, Gels, and Colloids*, E. Dickinson, ed., Roy. Soc. of Chemistry, Cambridge, U.K. (1991).
- Dickinson, E., and G. Stainsby, *Colloids in Food*, Applied Science Publishers, London (1982).
- Dickinson, E., M. I. Goller, and D. J. Wedlock, "Creaming and Rheology of Emulsions Containing Polysaccharide and Non-Ionic or Anionic Surfactant," *Colloids Surf. A*, **75**, 194 (1993).
- Doublier, J. L., and G. Llamas, "Flow and Viscoelastic Properties of Mixed Xanthan Gum + Galactomannan Systems," *Food Polymers, Gels, and Colloids*, E. Dickinson, ed., Roy. Soc. of Chemistry, Cambridge, U.K. (1991).
- Glicksman, M., "Gelling Hydrocolloids in Food Product Applications," *Polysaccharides in Food*, J. M. V. Blanchard and J. R. Mitchell, eds., Butterworths, London (1979).
- Gouldby, S. J., P. A. Gunning, D. J. Hibberd, and M. M. Robins, "Creaming in Flocculated Oil-in-Water Emulsions," *Food Polymers, Gels and Colloids*, E. Dickinson, ed., Roy. Soc. of Chemistry, Cambridge, U.K. (1991).
- Jerome Ganz, A., "Cellulose Hydrocolloids," *Food Colloids*, M. D. Graham, ed., AVI, Westport, CT (1977).
- Kovacs, P., and K. S. Kang, "Xanthan Gum," *Food Colloids*, M. D. Graham, ed., AVI, Westport, CT (1977).
- Launay, B., J. L. Doublier, and G. Cuvelier, *Functional Properties of Food Macromolecules*, J. R. Mitchell and D. A. Ledward, eds., Elsevier, London (1986).
- Lockhead, R. Y., J. A. Davidson, G. M. Thomas, "Poly(acrylic acid) Thickeners," *Polymers in Aqueous Media*, J. E. Glass, ed., Adv. in Chemistry Ser. 223 (1989).
- Luyten, H., M. Jonkman, W. Klok, and T. van Vliet, "Creaming Behavior of Dispersed Particles in Dilute Xanthan Solutions," *Food Colloids and Polymers: Stability and Mechanical Properties*, E. Dickinson and P. Walstra, eds., Roy. Soc. of Chemistry, Cambridge, U.K. (1993).

- McNealy, W. H. and K. S. Kang, "Xanthan and Some Other Biosynthetic Gums," *Industrial Gums*, R. L. Whistler and J. N. BeMiller, eds., Academic Press, New York (1973).
- Meer, W. A., "Plant Hydrocolloids," *Food Colloids*, H. D. Graham, ed., AVI, Westport, CT (1977).
- Pal, R., "Pipeline Flow of Unstable and Surfactant-Stabilized Emulsions," *AIChE J.*, **39**(11), 1754 (1993).
- Pal, R., "Oscillatory, Creep and Steady Flow Behaviour of Xanthan-Thickened Oil-in-Water Emulsions," *AIChE J.*, **41**(4), 783 (1995).
- Pal, R., and E. Rhodes, "Viscosity/Concentration Relationships for Emulsions," *J. Rheol.*, **33**, 1021 (1989).
- Palierne, J. F., "Linear Rheology of Viscoelastic Emulsions with Interfacial Tension," *Rheol. Acta*, **29**, 204 (1990).
- Pettitt, D. J., "Xanthan Gum," *Polysaccharides in Food*, J. M. V. Blanchard and J. R. Mitchell, eds., Butterworths, London (1979).
- Reichman, D., and N. Garti, "Galactomannans as Emulsifiers," *Food Polymers, Gels, and Colloids*, E. Dickinson, ed., Roy. Soc. of Chemistry, Cambridge, U.K. (1991).
- Robins, M. M., "Effect of Polysaccharide on Flocculation and Creaming in Oil-in-Water Emulsion," *Microemulsions and Emulsions in Foods*, M. El-Nokaly and D. Cornell, eds., ACS Symp. Ser. 448 (1991).
- Rochefort, W. E., and S. Middleman, "Rheology of Xanthan Gum," *J. Rheol.*, **31**(4), 337 (1987).
- Sherman, P., *Industrial Rheology*, Academic Press, London (1968).
- Sherman, P., "Rheological Properties of Emulsions," *Encyclopedia of Emulsion Technology*, P. Becher, ed., Vol. 1 (1983).

Manuscript received May 12, 1995, and revision received Nov. 3, 1995.