

## **Dynamic rheologic measurement of the interaction between xanthan gum and colloidal magnesium aluminum silicate**

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### **Synopsis**

An oscillatory shear device was used to measure the dynamic rheology of dispersions of xanthan gum (XG), magnesium aluminum silicate (MAS), and mixtures of the two. XG exhibited linear behavior up to about 50% strain, while the linear range for MAS was much more restricted. Storage modulus ( $G'$ ) values for MAS were nearly constant over a wide range of frequencies and the loss tangent was low, indicative of rigid structure. The structure of XG depended on concentration, and no yield value was evident. XG effectiveness in reducing sedimentation is ascribed to liquid structure and high apparent viscosity at low shear. The addition of XG to MAS dispersions extended the strain at which  $G'$  remained constant. The loss modulus ( $G''$ ) increased in value as a function of XG concentration while  $G'$  was generally reduced at low frequencies but raised at high frequencies. The loss tangent was increased. These changes point to a reduction in structural rigidity and an increase in flexibility.

### **INTRODUCTION**

Xanthan gum (XG), a polysaccharide produced by the bacterium *Xanthomonas campestris*, is used industrially as a thickener and dispersion stabilizer. The material of commerce differs from most other anionic polymers in that the viscosity of water solutions is nearly insensitive to a variety of salts over a wide electrolyte concentration range.

Many of the attributes of XG relevant to its rheologic properties were summarized in a previous paper from our laboratory (1). The gum undergoes a transition from an ordered to disordered state at elevated temperatures, depending on the salt content and the ions present. Shear viscometry was used to determine the influence of concentration and several added salts on aqueous solutions of a commercial gum. Aqueous gum solutions at a concentration of 0.3% or more are very viscous at low shear; the data suggest the existence of a gel-like structure that is disrupted by shear. At moderate and high shear, the shear stress-shear rate curve exhibits no hysteresis. The power law constant, which is inversely related to the degree of pseudoplasticity, drops as the gum concentration is raised.

The effect of salts, while relatively small, depends on gum concentration in solution. At 0.3% gum there is a negligible change in viscosity in the presence of up to 0.01 M sodium or calcium chloride. At higher gum concentrations, the viscosity is raised somewhat by salts, while at lower concentrations, the opposite occurs.

Further information has been obtained from dynamic rheology measurements. Santore and Prud'homme explored the behavior of a 4.7% XG broth at shear rates as low as  $10^{-5} \text{ s}^{-1}$  (2). Both dynamic viscosity ( $\eta^*$ ) and steady shear viscosity ( $\eta$ ) followed the power law over several orders of magnitude of shear rate. In the ultra-low shear range there was no indication of either a positive deviation (which would signify the existence of a yield value) or a negative deviation that is typical of most simple polymer solutions. Values of  $\eta^*$  were higher than corresponding values of  $\eta$  (at the same shear rate), suggesting the existence of long-range order.

Rocheffort and Middleman utilized both oscillatory and steady shear measurements to assess the influence of salt and temperature on flow behavior of gum concentrations of up to 0.5% (3). The measurements confirmed the existence of an order  $\rightarrow$  disorder transition at about 55°C in water solutions containing low salt and at higher temperatures with high salt present. In the presence of salt, the "healing" of structure disrupted by shear or temperature is rapid and essentially complete.

Veegum<sup>®</sup>, a colloidal magnesium aluminum silicate (MAS), is a smectite clay whose platelets are capable of aggregating to form a "house of cards" structure in aqueous dispersions (4). The dispersions are highly thixotropic; they are disrupted by shear but then regain their structure over time. Unlike XG, the properties of these clay dispersions are highly sensitive to electrolytes.

Combinations of MAS and several polymers, including XG and carboxymethylcellulose, have been promoted as having rheologic properties superior to either of the materials alone. Mixtures of MAS and XG appear to be synergistic with respect to viscosity and yield value, based on steady shear measurements using a Brookfield viscometer (5). Thixotropy was eliminated within optimum mixtures, in which the XG:MAS ratio was 1:9 to 1:2. Furthermore, single-point viscosity of dispersions of the mixtures is affected much less by aging than are dispersions of MAS alone.

Continuous shear viscometry is widely used and the flow curves obtained by this technique contain a great deal of information about the behavior of non-Newtonian materials. However, the initial structure of the material under investigation is broken down during the course of measurement. In many cases, this structure is the most important attribute under consideration. Dynamic small strain methods have the advantage of deforming a sample without necessarily disrupting its structure. These methods provide information about elasticity as well as viscous flow.

A popular method for measuring viscoelasticity in the linear region utilizes oscillatory shear (6). The complex shear modulus,  $G^*$ , is defined by Equation 1.

$$G^*(\omega) = \frac{\sigma(t)}{\gamma(t)} \quad [1]$$

In this equation,  $\sigma(t)$  represents the time-dependent shear stress and  $\gamma(t)$  is the strain.  $G^*$  may be divided into real and imaginary parts,  $G'$  and  $G''$ , respectively.  $G'$  is called the storage modulus (or dynamic rigidity) and refers to energy stored because of elas-

ticity.  $G''$  is the loss modulus, referring to the loss of energy through viscous flow. The relationship among the moduli is given in Equation 2,

$$G^* = G' + i G'' \quad [2]$$

in which  $i = \sqrt{-1}$ . The loss tangent, a measure of the relative contributions of elasticity and viscous flow, is defined as  $G''/G'$ . Values of loss tangent below 1 indicate that elasticity dominates rheologic behavior.

In this paper we describe rheologic measurements of MAS and XG and mixtures of the two using a dynamic technique.

## EXPERIMENTAL

XG (Keltrol T<sup>®</sup>, Kelco Division, Merck & Co., San Diego, CA), MAS (Veegum<sup>®</sup>, R. T. Vanderbilt, Norwalk, CT), and methylparaben and propylparaben (both Fisher Scientific, Springfield, NJ) were used as received. Concentrated dispersions of XG and MAS in deionized water containing 0.1% methylparaben and 0.03% propylparaben were prepared in a homomixer (30% scale). The mixing time for XG dispersions was 24 minutes; that for MAS dispersions was 50 minutes. Dispersions of either a pure component or mixtures of XG and MAS were made by appropriate dilution with water containing the preservatives and agitation for five minutes at 1000 RPM using a small propeller mixer. The concentrations indicated are the final concentrations in the dispersions. All were stored at room temperature for approximately 12 days prior to measurement. All comparisons were made on systems stored for exactly the same length of time. These mixing and storage times, though arbitrary, were chosen to ensure that the shear history of all MAS samples would be uniform so that reliable comparisons among various combinations with XG could be made. Rheologic data obtained with other preparation equipment and conditions might differ from those reported below, but we anticipate that the trends observed should be the same.

The Bohlin VOR constant strain rheometer (Bohlin Rheologi, Cranbury, NJ) was used for most measurements of viscoelastic behavior. Studies at constant stress were performed using a Bohlin CS rheometer. Concentric cylinder measuring geometry (27.5-mm diameter cup, 25-mm bob) was utilized in all cases. All measurements were made at 25°C after equilibration for 15 minutes.

## RESULTS AND DISCUSSION

The first step in measurement of viscoelasticity is performance of a "strain sweep" to evaluate the degree of strain that can be tolerated before the samples behave in a nonlinear fashion. Figure 1 contains data for two XG solutions, a 3% MAS dispersion, and combinations of 1% MAS with XG. The XG solutions can tolerate 50% strain without showing significant variation in the values of  $G'$ , the storage modulus. The  $G'$  values for MAS are approximately constant over less than 10% strain. The linear range for combinations of MAS with XG falls between the values for the component materials. To ensure that all measurements were made within the linear range, gum solutions were subjected to a strain of 20%, and 4% was used for MAS dispersions and MAS-XG combinations.

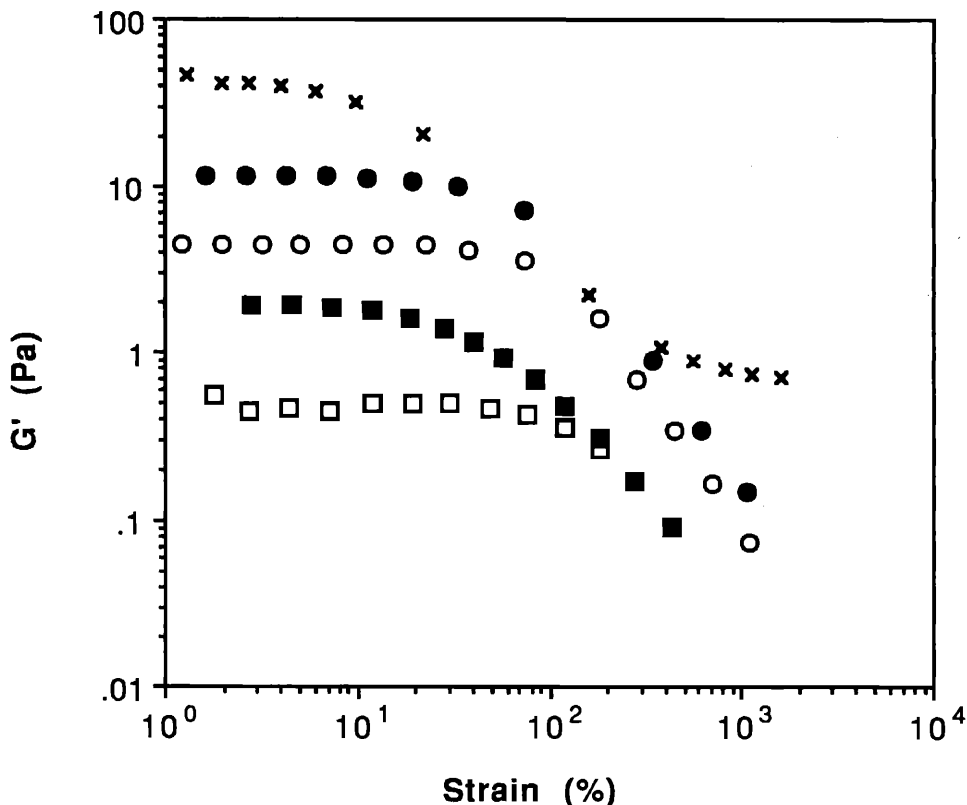


Figure 1. Linear viscoelastic region determined by strain sweep at 6.3 rad/s.  $\times$ , MAS, 3%;  $\square$ , 0.1% XG alone;  $\blacksquare$ , 0.1% XG plus 1% MAS;  $\circ$ , 0.4% XG alone;  $\bullet$ , 0.4% XG plus 1% MAS.

Figure 2 contains plots of  $G'$  and  $G''$  for two XG concentrations, 0.2 and 0.4%.  $G'$  dominates at high frequencies, at which there is insufficient time for significant flow to occur, while  $G''$  is more important at low frequencies. The crossover point decreases with gum concentration; the values are approximately 2 rad/s for a 0.1% solution, 0.3 rad/s for a 0.2% solution, 0.06 rad/s for a 0.3% solution, and 0.01 rad/s for a 0.4% solution. This change in the crossover point, plus the fact that the loss tangent decreases with concentration (Figure 3), shows that the contribution of elasticity becomes more significant as gum concentration is raised. These data follow the same pattern as those reported by Rochefort and Middleman (3).

The behavior of MAS dispersions is quite different from that of XG (Figure 4). There is a slight dip in the  $G''$  curve for the 3% dispersion and a more pronounced dip with the 1% dispersion at intermediate values of  $\omega$ . Curves for  $G'$  and  $G''$  do not cross. For both concentrations,  $G'$  provides the dominant contribution to  $G^*$  and is essentially constant throughout the range of frequencies shown. The loss tangent for the 3% dispersion is similar to that for the 1% dispersion at low frequencies but significantly lower at high frequencies. These data confirm that both MAS dispersions studied are highly structured.

Further differentiation between properties of XG and MAS dispersions is obtained by comparing viscosity values as a function of shear stress in the Bohlin CS rheometer

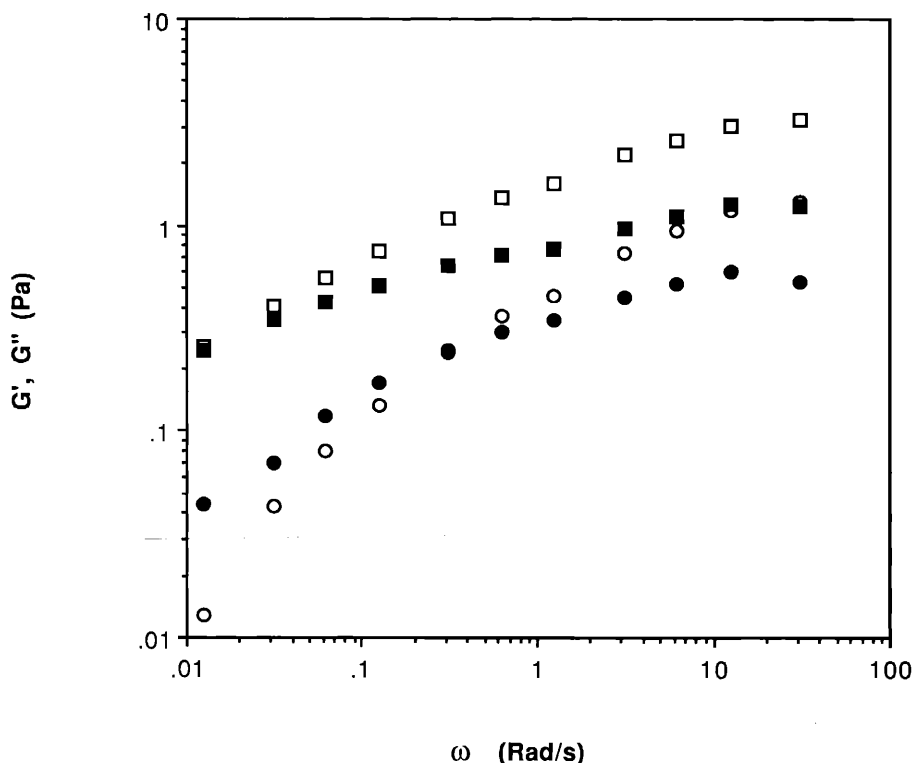


Figure 2. Effect of xanthan gum concentration on storage and loss moduli ( $G'$  and  $G''$ , respectively).  $\circ$ ,  $G'$  0.2%;  $\bullet$ ,  $G''$  0.2%;  $\square$ ,  $G'$  0.4%;  $\blacksquare$ ,  $G''$  0.4%.

(Figure 5). The data for MAS are representative of rigid structures in which viscosity increases toward infinity as the shear stress is decreased. This is the definition of yield value. XG at a concentration of 0.4%, on the other hand, behaves more like a structured fluid system; at very low shear, shear stress and shear rate are proportional so that apparent viscosity is constant. There is thus no evidence for a yield value for the XG solution, in agreement with previous work (2,7). The shear rates for the data in Figure 5 can be calculated as the ratio of shear stress to apparent viscosity; shear rate values on the high-viscosity end of the curve (left side) for XG are of the order of  $10^{-4} \text{ s}^{-1}$ . Apparently such low values are necessary to demonstrate the existence of a low-shear constant-viscosity region for this gum.

The literature contains contradictory statements regarding whether or not XG has a yield value. Part of the problem is that yield value can be estimated in a variety of ways not all of which are equivalent. It is sometimes inferred from a flow curve based on data obtained at relatively high shear rates. In such cases, extrapolation to the shear stress axis might be used to determine a "practical" yield value, which may empirically correlate with macroscopic observations of dispersion stability though it does not correspond to an actual yield value. Earlier work in this laboratory utilizing a continuous shearing procedure did not indicate the existence of a yield value, but did suggest that xanthan at moderate concentrations (0.3% and higher) was in a "gel-like" state when undisturbed (1).

The ability of XG to retard settling of dispersed particles is well known. Sedimentation

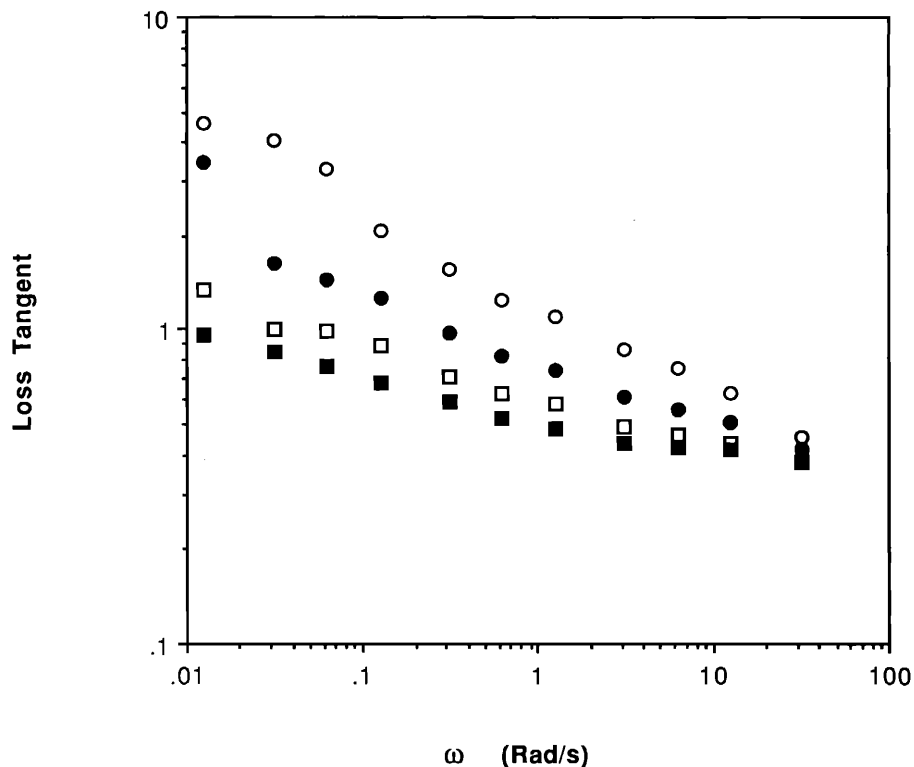


Figure 3. Effect of xanthan gum concentration on loss tangent. ○, 0.1%; ●, 0.2%; □, 0.3%; ■, 0.4%.

rates of suspensions and emulsions were highly dependent on XG concentration; in many cases, sedimentation in dispersions containing 0.4% XG was negligible during several months (8,9). Based on our results and data from previous studies, we attribute XG effectiveness in reducing sedimentation to a gel-like but not completely rigid structure and high apparent viscosity at low shear, approximately 200 Pas (or 200,000 cp) in the case of 0.4% XG.

Values of  $G'$  and  $G''$  and the loss tangent for MAS-XG combinations are compared to those for MAS alone in Figures 6 through 11. The addition of XG to MAS raises  $G''$  values (Figures 6 and 7), and the magnitude of the change is directly related to XG concentration. The straightforward conclusion is that XG raises the viscous contribution in mixtures with MAS.

The effect of XG on  $G'$  is more complex. The first thing to notice is that the  $G'$  curves for the mixtures are not horizontal, in contrast to those for MAS alone (Figures 8 and 9). This suggests a change in structural behavior that may be interpreted as a loss of rigidity. Except for the 0.4% concentration, the addition of XG to 1% MAS lowers the value of  $G'$  at low frequencies but has the opposite effect at high frequencies (Figure 8). XG at a 0.4% concentration raises  $G'$  of 1% MAS at all frequencies within the attainable measurement range. With 3% MAS, there is a lowering of  $G'$  at low frequency at all XG concentrations, and the effect is not strongly concentration-dependent (Figure 9). However, as the frequency is raised, the value of  $G'$  for the mixtures increases with XG concentration.

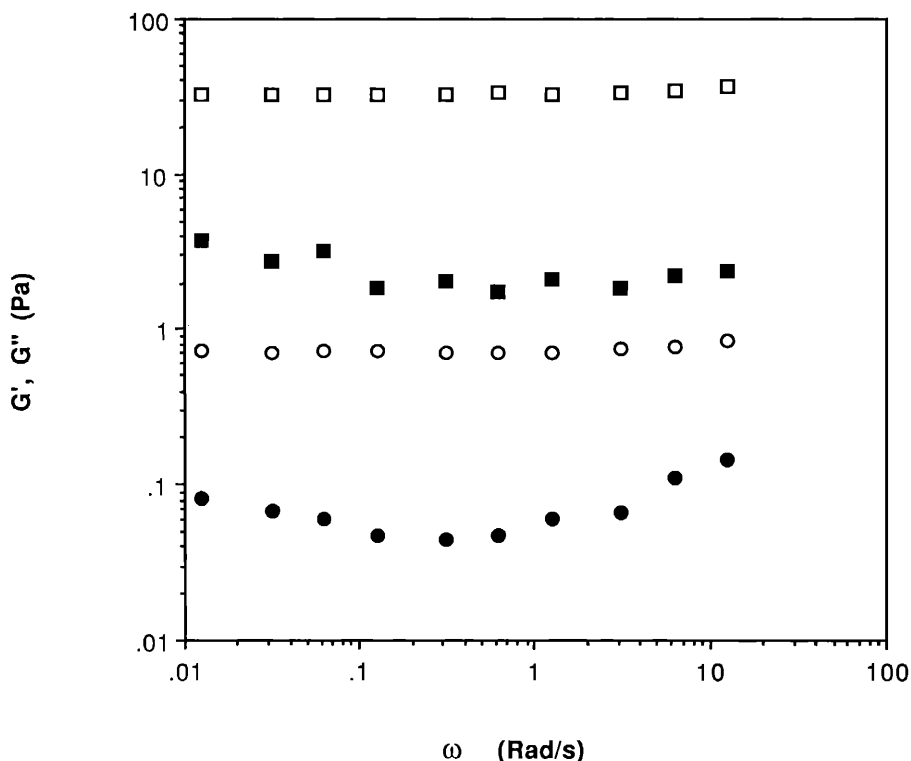


Figure 4. Storage and loss moduli of two MAS dispersions. ○,  $G'$  1%; ●,  $G''$  1%; □,  $G'$  3%; ■,  $G''$  3%.

At all concentrations and frequencies, the increase in  $G''$  attributed to the presence of XG is greater than any positive change in  $G'$ . Consequently, the mixtures have a higher value of loss tangent than for MAS alone (Figures 10 and 11). This difference, along with the  $G'$  data described above, indicates that the mixtures are less rigidly structured than the clay by itself. As might be expected, the effects of the various XG concentrations studied are more profound in the dispersions containing 1% MAS rather than in the higher concentration (compare Figures 6 and 7, 8 and 9, 10 and 11).

Based on these data, we may speculate on the nature of the interaction between XG and MAS. Structural attributes of MAS are related to the formation of particle assemblies with an open structure. At sufficient concentration, MAS units join to form a three-dimensional network that extends throughout the dispersion. Shear breaks the network, accounting for thixotropic behavior.

MAS structure persists in the presence of XG since  $G'$  values are significant, although modified from those in pure MAS dispersions (Figures 8 and 9). A picture consistent with the data is one in which assemblies of aggregated MAS units and aggregated XG units coexist. In the presence of XG, the formation of a tight single-particle network extending throughout the system that can also accommodate aggregated XG molecules is unlikely. Furthermore, the  $G'$  dependence on frequency is altered in the presence of gum. When the system is at rest, MAS aggregates are weakly connected to each other. These junctions are broken at low shear, but the separated assemblies can withstand somewhat higher shear before disruption. At high frequencies, at which there is little

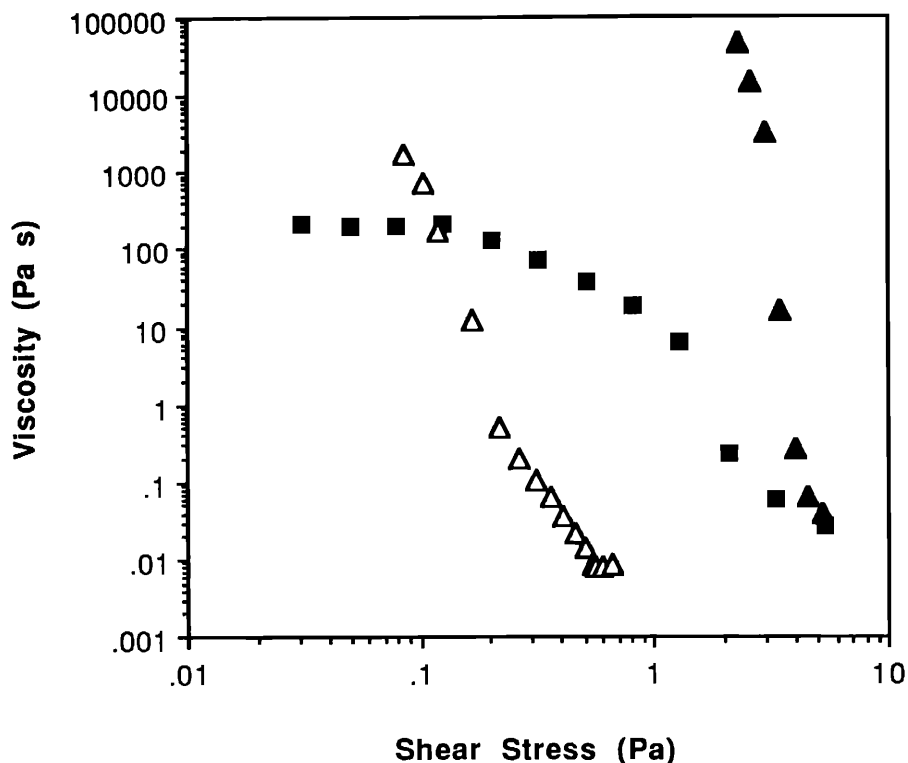


Figure 5. Apparent viscosity as a function of shear stress for two MAS dispersions and one xanthan gum solution.  $\Delta$ , 1% MAS;  $\blacktriangle$ , 3% MAS;  $\blacksquare$ , 0.4% XG.

time for structural change to occur, the elasticity provided by the two components should be additive. Indeed, at 10 rad/s and above, the  $G'$  values in Figures 8 and 9 increase with XG concentration.

According to this model, XG molecules in the mixed dispersions are joined in a manner similar to their arrangement in pure gum systems. This is in accord with the finding that dispersions containing both components remain in the linear viscoelastic region at higher strain values than dispersions containing only MAS (Figure 1). The presence of XG should also provide additional "smoothness" to the dispersions when it flows.

## CONCLUSIONS

The substances discussed in this paper (MAS and XG) utilize different mechanisms of structure formation in aqueous dispersion. Nevertheless, depending on their ratio, both materials contribute to the viscous and elastic properties of the network that exists in essentially undisturbed mixtures. MAS provides rigidity; XG augments the viscous component. The behavior of the mixtures is, in many respects, intermediate between that of the components.

Compared to MAS alone, mixtures with XG exhibit a larger linear viscoelastic range, and higher values of  $G''$  and loss tangent. These changes, along with differences in the pattern of  $G'$ , suggest a reduction in structural rigidity and an increase in flexibility.



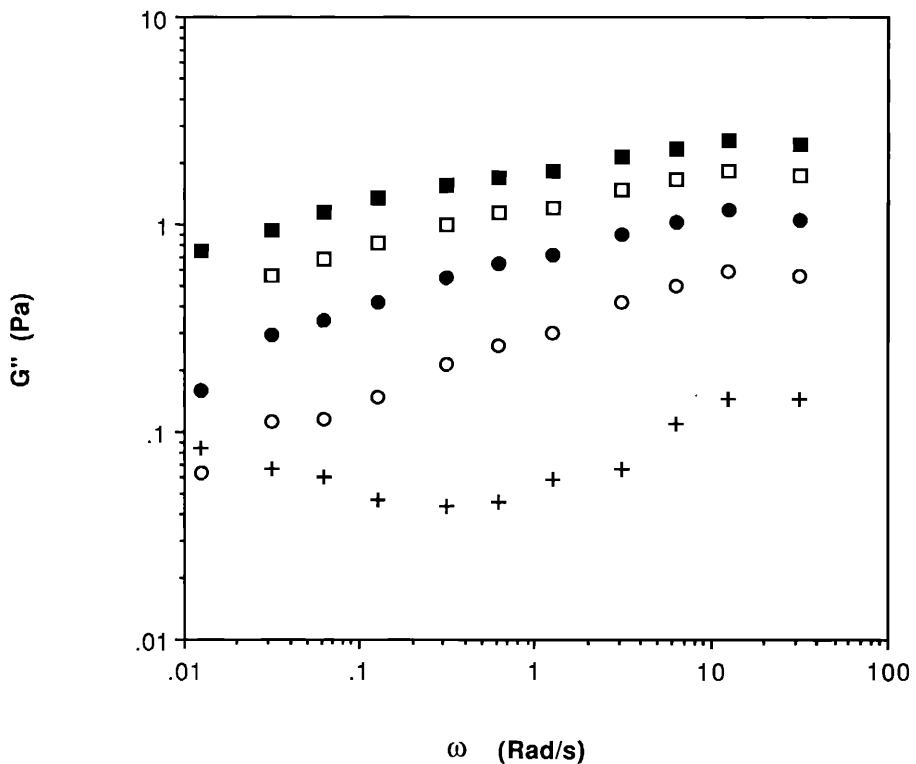


Figure 6. Effect of XG concentration on loss modulus of 1% MAS dispersions. +, 0%; ○, 0.1%; ●, 0.2%; □, 0.3%; ■, 0.4%.

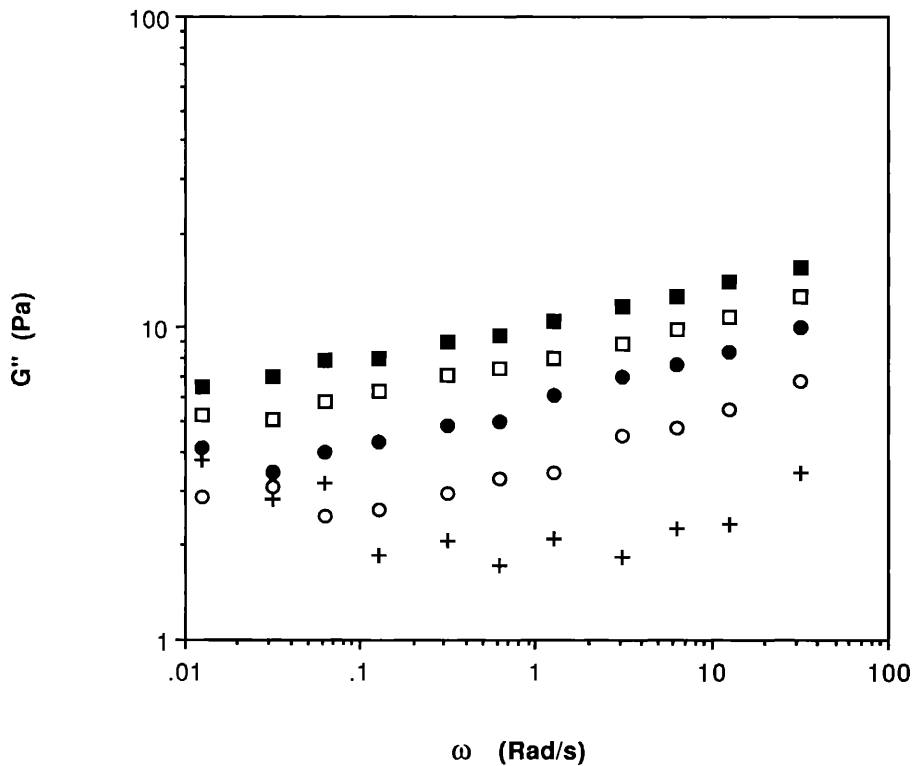


Figure 7. Effect of XG concentration on loss modulus of 3% MAS dispersions. Symbols are the same as in Figure 6.  
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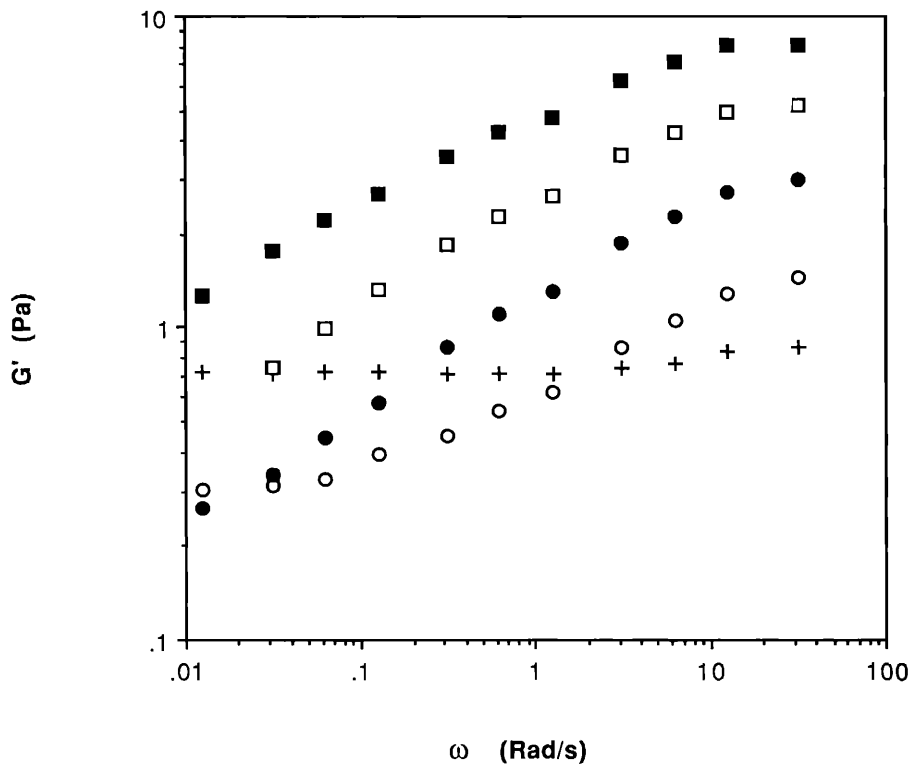


Figure 8. Effect of XG concentration on storage modulus of 1% MAS dispersions. Symbols are the same as for Figure 6.

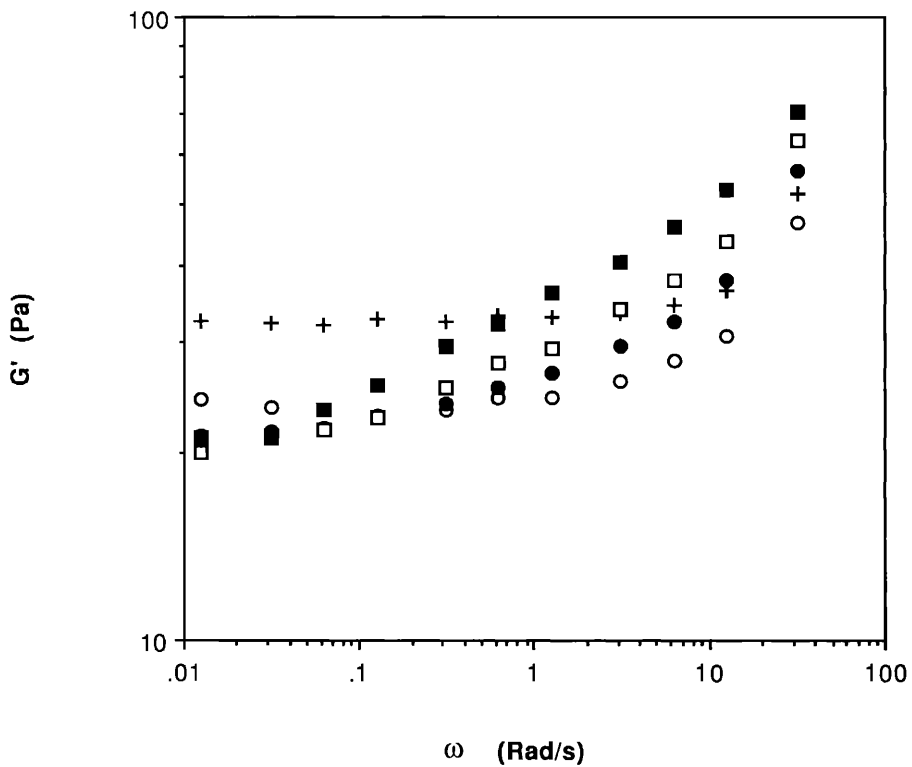


Figure 9. Effect of XG concentration on storage modulus of 3% MAS dispersions. Symbols are same as for Figure 6.  
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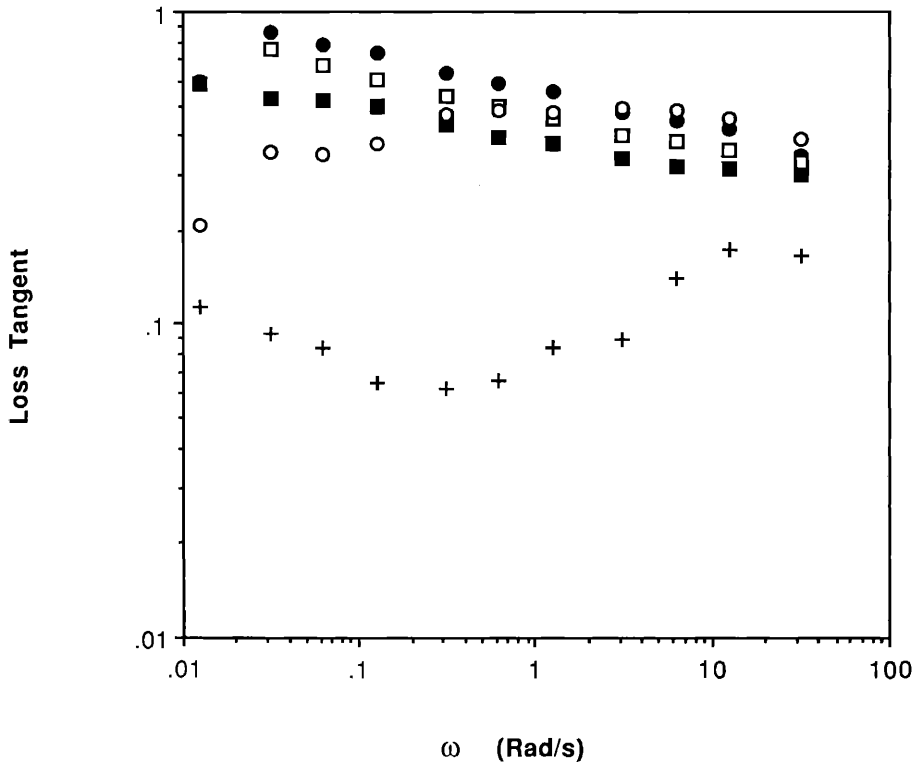


Figure 10. Effect of XG concentration on loss tangent of 1% MAS dispersions. Symbols are the same as for Figure 6.

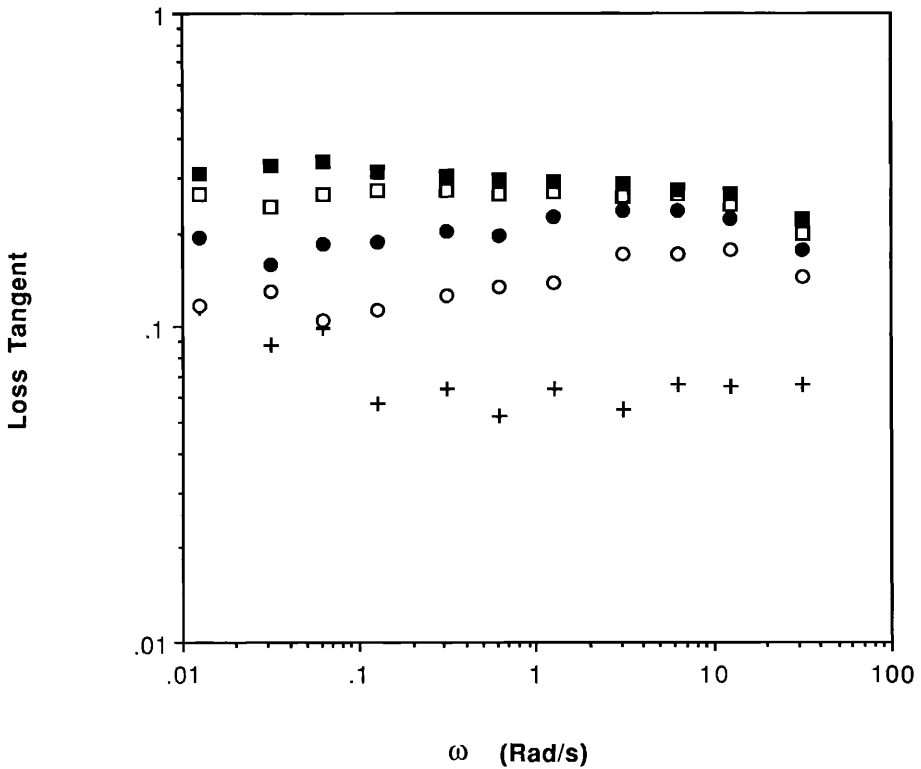


Figure 11. Effect of XG concentration on loss tangent of 3% MAS dispersions. Symbols are the same as for Figure 6.  
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