Rheology and Microstructural Changes during Enzymatic Degradation of a Guar−Borax Hydrogel

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ABSTRACT: Hydrogels composed of borax cross-linked guar galactomannans are enzymatically degraded using *endo*-β-mannanase, an enzyme which cleaves the polymer chain backbone. Dynamic rheological measurements show the elastic (G') and viscous (G'') moduli to be sensitive to gel structure and to reduce significantly during the enzymatic hydrolysis process. The reduction in rheological properties shows three distinct regimes: an initial large decrease, a slower reduction rate at intermediate times, and an accelerated reduction at longer degradation times. In contrast, the polymer chain molecular weight, obtained from gel permeation chromatography, reduces rapidly at short times and at a slower rate subsequently. We therefore find the kinetics of moduli reduction to be dictated by the relationship between gel structure and rheological properties, rather than purely the rates of chain scission. At short times, the large decrease in moduli is analogous to changes in molecular weight and can directly be attributed to chain scission. At long times, corresponding to when the product of polymer concentration and intrinsic viscosity, $c[\eta]$, reaches a critical value ($\leq$2.5), the chains are too short to overlap and the long range network breaks down rapidly, leading to accelerated moduli reduction. Additionally, a synergistic increase in the degradation rate is observed on using a combination of backbone-cleaving β-mannanase enzyme and a side-chain-cleaving α-galactosidase enzyme, as compared to using only β-mannanase. This can be attributed to an enhancement of mannanase activity due to removal of the sterically hindering galactose side chains. Finally, a comparison of gel and solution degradation reveals very similar behavior in molecular weight changes for both but contrasting trends in rheology.

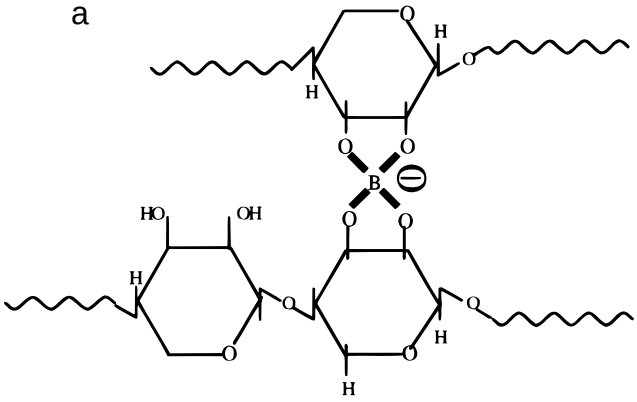
Introduction

Guar galactomannan is a plant polysaccharide with extensive applications in food, paper, textile, and petroleum industries. The main advantages for using guar are its low cost, easy availability, and capacity to form viscous solutions and gels at low concentration.[1,2] Additionally, chain architecture of guar galactomannan can be selectively modified to tailor properties of guar formulations and open up new opportunities for guar usage. For example, reducing the galactose (side chain) content of guar can be utilized to form synergistic gels with biopolymers such as xanthan and κ-carrageenan in various food applications.[3,4] In the oil and gas industry, cross-linked guar gels are used to transport sand (proppant) into artificially created fractures in oil-bearing rock in order to enhance petroleum productivity. Subsequently, the gels need to be degraded to flush out the fluid.[5] In both these applications, enzymes offer a powerful method to selectively modify the structure of guar galactomannan in a controlled fashion. Since control of rheological properties is central to use of enzymatically modified guar, it is of paramount importance to understand the structure−property relationships for guar solutions and gels.

Guar consists of a linear backbone of mannose units with galactose units as side chains. The *cis*-diol groups on the sugar units complex with borate ions (typically provided by the dissociation of borax) as shown in Scheme 1a. Two *cis*-diol pairs on different guar molecules can thus be connected by a borate ion to form an interchain cross-link. The presence of several such cross-links gives rise to gellike properties. The *nondegraded* guar−borax system has been the subject of several previous investigations. NMR spectroscopy on dilute guar−borax gels has been used to obtain information on the complexation mechanism and complexation equilibrium constants.[6−8] Rheological studies[5,9] have investigated the effect of variables such as temperature, solution pH, and guar and borax concentrations on characteristic gel moduli (e.g., G_p', plateau modulus; and

Scheme 1. (a) Schematic Representation of the Complexation Process between Guar and Borate Ions and (b) Dissociation Reaction and Equilibrium Constant of Sodium Tetraborate in Water

a



b

$$B(OH)_3 + HO^- \underset{}{\overset{K_b}{\rightleftharpoons}} B(OH)_4^-$$

$$K_b = \frac{\left|B(OH)_4^-\right|}{\left|B(OH)_3\right|\left|OH^-\right|}$$

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G_m'', maximum in the loss modulus). However, the degradation of guar borax gels has not been investigated. In an earlier study,[10] the enzymatic degradation of guar *solutions* was shown to be zeroth order in guar concentration and first order in enzyme concentration. Additionally, profiles of solution viscosity vs degradation time for different enzyme concentrations could be collapsed on to a single curve by shifts along the time axis, enabling a priori prediction of guar solution viscosity as a function of degradation time and enzyme concentration.

In this paper, we focus on understanding the mechanism and kinetics of enzymatic degradation of guar−borax gels using dynamic rheological techniques. The dynamic elastic modulus (G'), is a sensitive probe of material microstructure[11−16] and is a useful indicator of the state of the system. In addition, we use gel permeation chromatography (GPC) to obtain information on the concomitant changes in molecular weights of the polymer chains. Thus, we can correlate the changing rheological properties of the guar−borax gels with the molecular degradation kinetics. Finally, the rates of change in the rheological and molecular properties are compared for degradation of guar solutions and guar−borax gels. The differences observed highlight the importance of understanding the relationship between molecular structure and rheological properties for effective usage of enzymatically modified guar.

Materials and Experimental Methods

Materials. Food grade guar galactomannan (Jaguar 6003, Rhone-Poulenc, NJ) was purified through Soxhlet extraction with ethanol.[17] Hydrocolloidal dispersions were prepared by dispersing purified guar powder in water containing 0.5 M sodium chloride and 0.05 M sodium thiosulfate.[18] Additionally, solutions were centrifuged at 20000*g* for 1.5 h to obtain a clarified solution. Guar−borax gels (0.5% guar and 0.06% borax) were formed by dropwise addition of stock cross-linker (sodium tetraborate decahydrate, referred to hereafter as borax) solutions to degassed guar solutions. The complexation process is extremely rapid, and gellike properties are observed immediately after addition of the borax. Homogeneity of gels was further ensured by heating the gel to 65 °C for 15−30 min and subsequent cooling to room temperature. Finally, the gels were set to mix overnight (10−12 h) on a horizontal shaker. Gels with higher borax concentration (0.5% guar, 0.2% borax) were prepared using guar solutions without salt or stabilizer using a similar protocol; the heat treatment step was eliminated to avoid thermal degradation.

Enzymatic guar degradation was performed using a purified *endo-β*-mannanase (from *Aspergillus niger*, Megazyme Corporation, Ireland) and α-galactosidase (from guar seed, Megazyme Corporation, Ireland). The degradation was performed on guar−borax gels and guar solutions at 25 °C. For GPC, eight pullulan standards were obtained from Shodex Corporation (Japan) ranging in molecular weights from 5200 to 1.6 million. Solutions were prepared in deionized water (Millipore, Bedford, MA) as prescribed by the company literature.

GPC Measurements. Molecular weight averages and molecular weight distributions (MWD) were determined by GPC on a bank of Ultrahydrogel columns (Ultrahydrogel 2000, 500 and 120, Waters Corporation, Milford, MA). A guard column was used ahead of the column bank. A Shimadzu HPLC system with RID-6A differential refractive index detector was used. The eluant was water containing 0.1 M sodium nitrate and 5×10^{-3} M sodium azide; the flow rate and temperature were maintained at 0.8 mL/min and 45 °C, respectively. All degraded guar samples were diluted to 0.05% (w/v) (to eliminate viscous spreading in the column) and filtered through a 0.45 μm filter prior to analysis. The guar gels were also treated with acid to reduce the pH to ∼6. This removes the cross-links in the system by converting all the borate ions to boric acid.[19] The bank of columns was calibrated using the pullulan standards. A Universal Calibration procedure (hydrodynamic volume correction) was applied to calculate absolute molecular weight distributions from raw chromatogram data.[10,18] The molecular weight averages were calculated by numerical integration of the MW distribution curve. The reproducibility in the MW averages was within ±2%.

Rheological Measurements. Guar−Borax Gels. After the gel had been incubated with enzyme for the required time interval, the enzymatic reaction was stopped by heating the gel to 85 °C for 10 min (at this temperature, the enzyme denatures rapidly due to the high pH of the system). Dynamic rheological measurements were then made on a Rheometrics RMS 800 (strain controlled rheometer) using a coni-cylindrical geometry with inner bob and outer cup radii of 24.0 and 25.0 mm respectively, bob length of 48 mm, and a cone angle of 0.04 rad. Samples with different preheat times and temperatures (65−98 °C) showed no change in the dynamic rheological measurements, thereby ensuring that no thermal degradation occurred during the heat treatment. Strain sweep experiments were initially performed to identify the strain range where the dynamic moduli are independent of strain (linear viscoelastic region). Subsequently, dynamic frequency sweeps were performed within the linear region, to obtain the elastic (G') and viscous (G'') moduli of the gels. Finally, Rheometrics software was used to superpose curves and calculate horizontal and vertical shift factors for master curve formation.

Dilute Solution Viscometry. Intrinsic viscosity, [η], is a measure of the inherent ability of a polymer to increase the viscosity of a particular solvent at a given temperature. It can be determined by measuring viscosity of solutions at low concentrations and extrapolating to infinite dilution. Typically, a double extrapolation can be used according to the Huggins (eq 1) and Kraemer (eq 2) relationships:[20]

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \tag{1}$$

$$\frac{\ln(\eta_r)}{c} = [\eta] + k_K[\eta]^2 c \tag{2}$$

Here, η_r is the relative viscosity ($\eta_{solution}/\eta_{solvent}$), η_{sp} is the specific viscosity ($\eta_r - 1$), c is the polymer concentration, and k_H and k_K are constants. The degraded guar−borax gels were first acidified to remove the cross-links and then diluted before being tested on a Rheometrics Dynamic Stress rheometer, DSR 200. Steady stress viscosity measurements were made using a couette geometry with inner bob and outer cup radii of 14.75 and 16.0 mm, respectively, and a bob length of 44.25 mm at 25 °C. The zero shear viscosity was measured for guar concentrations ranging from 0.12 to 0.05% and extrapolated to obtain the intrinsic viscosity.

Results and Discussion

Figure 1 compares the dynamic rheological moduli (prior to degradation) of a guar solution with a guar−borax gel at the same guar concentration (0.5% w/v), and a borax concentration of 0.06% w/v for the gel. The loss modulus (G'') dominates the solution response over most of the frequency domain, indicating the principally viscous nature of guar solutions. Cross-linking the guar causes an increase in both moduli, with the elastic modulus (G') being affected more strongly. A distinct plateau is observed in the elastic modulus at intermediate frequencies (0.5−50 rad/s). Moreover, G' is larger than G'' in this regime. These features are characteristic of a network structure formed by the guar−borax cross-links. The cross-links break and re-form with thermal fluctuations, and as a result, the network relaxes over

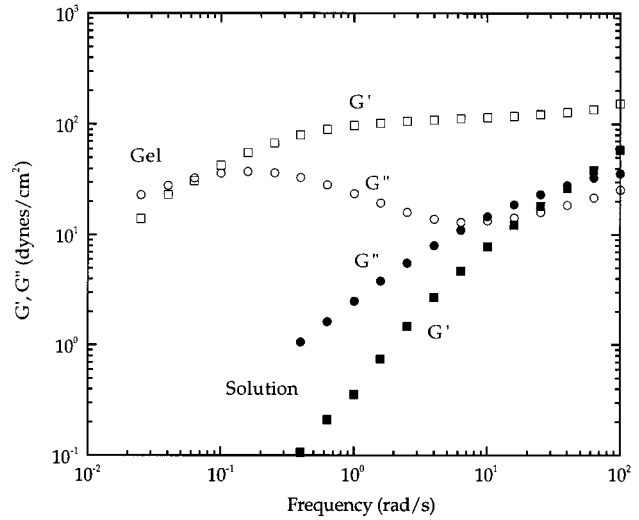

Figure 1. Comparison of the dynamic rheological moduli, G' and G'', as a function of deformation frequency, for guar solution and a guar−borate gel prior to degradation. The guar content of both systems is 0.5% w/v.

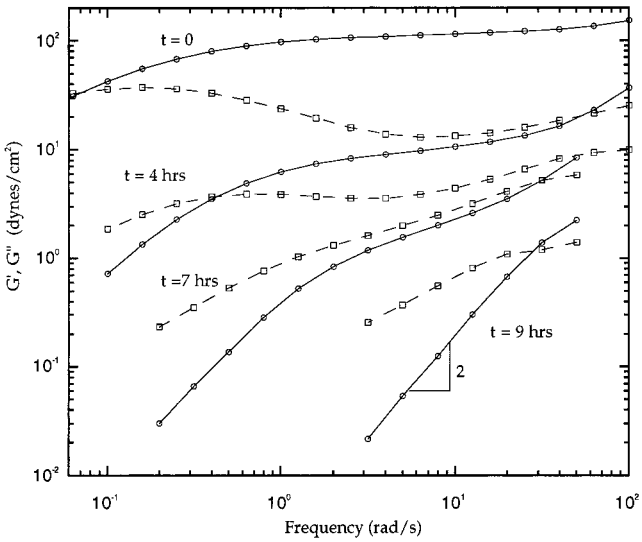

Figure 2. Reduction in the elastic (G') and viscous (G'') moduli of 0.5% guar−borax gel for different extents of enzymatic degradation. Enzyme activity was 6×10^{-4} U/mL of gel. Solid and broken curves represent G' and G'' respectively.

long time scales. Consequently, the guar−borax gels display a terminal region similar to non-cross-linked polymer solutions.[19]

The effect of enzymatic hydrolysis on the rheological properties of a 0.5% guar−0.06% borax gel is delineated in Figure 2. Upon incubation with the *endo*-β-mannanase, polymer molecules are cleaved and the moduli decrease significantly. After 4 h of degradation, a plateau in the elastic modulus is still evident, indicating that a long-range network is still existent. After 7 h of degradation, the loss modulus is slightly larger than the elastic modulus over most frequencies; a weak plateau in G' can be discerned. At longer degradation times (9 h), the plateau in G' disappears, and the loss modulus is significantly higher than the elastic modulus, indicating that the network is almost completely broken and that the system behaves as a solution (compare with trends of the *nondegraded* guar solution response in Figure 1). Thus, the dynamic moduli are very sensitive to the changes in guar−borax gel structure and indicate a continuous transition from a gellike to a solution-like

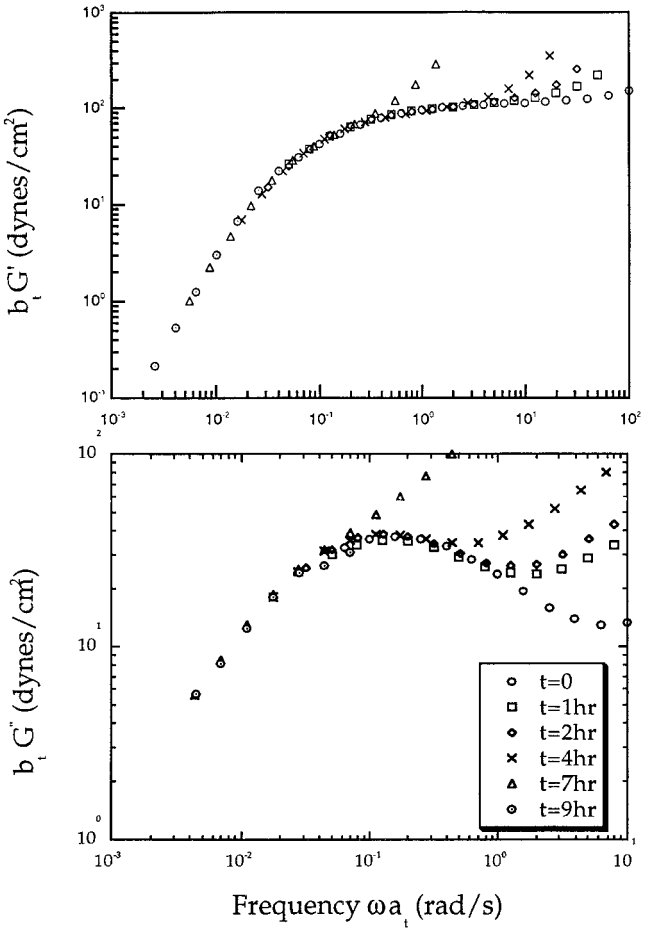

Figure 3. Master curves of the (a) elastic modulus G' and (b) viscous modulus G'', for 0.5% guar−borax gel degraded enzymatically to different extents. Enzyme activity is the same as in Figure 2.

material. It is interesting to note that the transient network structure of a guar−borax gel may lend itself to be described in terms of theories developed for associative polymers and reversible gels.[21−23] For instance, the scaling relationships between the dynamic moduli and frequency have been modeled for associative networks in the pre- and postgel states.[23] Such an approach could be taken to determine the transition from gellike to solution-like behavior of guar−borax gels as a function of enzymatic hydrolysis.

The dynamic moduli can be compared at any arbitrary frequency to quantify the rate of change of the rheological properties with degradation time. However, it is evident from the curves in Figure 2 that such a comparison will depend on the value of frequency chosen. Instead, by a technique reminiscent of time−temperature superposition, we tried to form a master curve by shifting the moduli-frequency spectra along the horizontal and vertical directions. The superposition of curves should work if all the relaxation modes of the polymer system scale with degradation in the same fashion. Figure 3 (top) shows the best-fit master curve obtained for the elastic modulus (G'). Figure 3 (bottom) shows the master curve for the viscous modulus G'' formed by using the shift factors of the G' master curve. The fact that the same shift factor can be used to obtain master curves for both the elastic and viscous moduli is an indication of the validity of the superposition. For both of these plots, the shifts were made to superimpose data in the terminal zone, that is, shifting with respect

to the longest relaxation time. Since short-time relaxation modes are unaffected by the widely spaced borate cross-links, the moduli do not superpose at high frequencies. Similar superposition behavior (overlap at low and moderate frequencies; divergence at high frequencies) has been reported[9,19] for time−temperature and time−pH superposition of *nondegraded* guar−borax gels. The modulus at any time can thus be obtained as

$$b_t G'(\omega,t) = G'(\omega a_t, t_{ref})$$
$$b_t G''(\omega,t) = G''(\omega a_t, t_{ref}) \quad (3)$$

where a_t and b_t are the horizontal and vertical shift factors respectively, t_{ref} is the reference value for the degradation time t, and corresponds to $t = 0$ for this study.

The shift factors used in the master curve can now be used to quantify the changes in rheological properties as a function of degradation time. Although it is not possible to obtain a single measure of the reduction in the "thickening efficiency" or the "viscosity enhancement", the shift factor analysis provides a framework for physically interpreting the rheological changes upon gel degradation. The vertical shift factor gives an idea of how the "mesh" size of the network changes while the horizontal shift factor provides an estimate of the longest interaction time scale in the polymer system.[19] Figure 4 (top) depicts the horizontal and vertical shift factors calculated for the data presented in Figure 3. Both shift factors diverge continuously from the value of unity, indicating a widening of the mesh size and shortening of the longest interaction time scale. These observations are consistent with the breaking down of the guar−borax network. After an initial reduction at 1 h, the horizontal shift factor appears to reduce slowly at intermediate times, followed by an accelerated reduction at longer times. Similar trends can be discerned for the vertical shift factor, though they are less pronounced. These trends become more evident in Figure 4 (bottom) which examines the vertical shift factors for gel degradation at enzyme concentrations equal to (X) and lower (X/2, X/4, and X/7) than that used for the data in Figure 4 (top). At low concentrations, the rate of change in shift factor is faster at short times and slower subsequently. At high concentrations, the accelerated rate of reduction at long times can be observed.

Mechanism of Gel Degradation. A major focus of this work has been to elucidate the reason behind the kinetics of moduli reduction as evinced, in particular, by the horizontal shift factor. We examine three factors that could possibly explain the changes in the rate of reduction of the dynamic moduli. A possible explanation of the unusual kinetics of moduli reduction could be that the effect is directly related to chain degradation kinetics; i.e., the chain degradation/scission rates themselves are rapid at short and long times and slow at intermediate times, resulting in a similar response in the moduli reduction. To examine this hypothesis, the reduction in molecular weight was followed by gel permeation chromatography (GPC). This technique provides molecular weight distributions (MWD); the MWD was integrated to yield averaged molecular weights such as the number-average molecular weight, M_n, and the weight-averaged molecular weight, M_w. The cross-linking of polymer chains is often interpreted as an increase in the effective molecular weight. However, we would like to clarify that

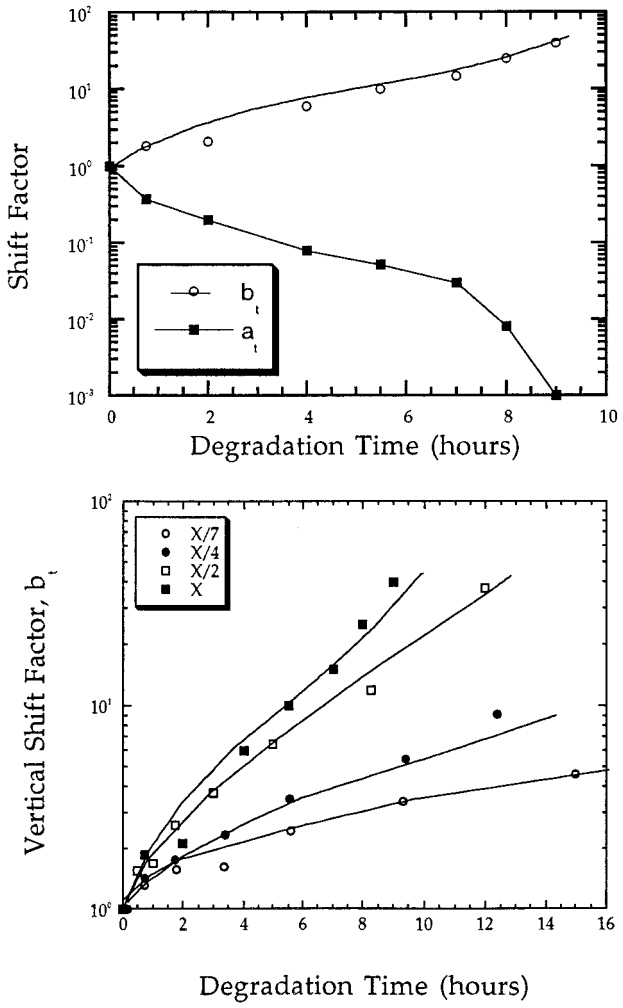

Figure 4. Variation in shift factors during enzymatic degradation of a 0.5% guar−borax gel. Top: horizontal (a_t) and vertical shift (b_t) factors obtained using data from Figure 3. Bottom: vertical shift factors for degradation using enzyme concentrations ranging from from 8.6×10^{-5} (X/7) to 6×10^{-4} (X) U/mL of gel.

for our system, the molecular weight of non-cross-linked chains was measured; the cross-links were removed by converting all the borate ions in the system to boric acid.[19] Figure 5 then shows the changes in M_w with degradation time for a 0.5% guar−0.2% borax gel. The reduction in molecular weight is observed to be rapid at first and slower at subsequent times. *This is in contrast with the kinetics of moduli reduction, where the largest decrease in modulus occurs at long degradation times*. Thus, the kinetics of moduli reduction cannot be explained purely on the basis of chain scission rates; however, the initial reduction in modulus is analogous to changes in molecular weight and can be attributed to chain scission.

Another contributing factor in the gel degradation rheology could be associated with pH changes as we observed that the pH of the gel dropped as the degradation progressed, from ~9.0 for a nondegraded gel to ~8.6 for a degraded gel. Upon enzymatic degradation, mono- and oligosaccharides are produced which bind more easily with the borate ion due to absence of the steric hindrances faced in the case of the long chain guar molecules. This displaces the equilibrium of the borax dissociation reaction toward the right (Scheme 1b), and the resultant decrease in [OH^-] reduces the pH value.

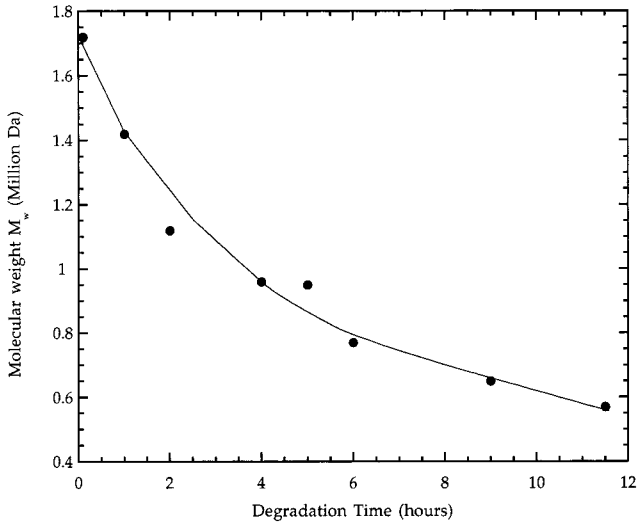

Figure 5. Weight-average molecular weight, M_w, as a function of degradation time for 0.5% guar−borax gel formed without salt. Enzyme activity was 6×10^{-4} (X) U/mL of gel.

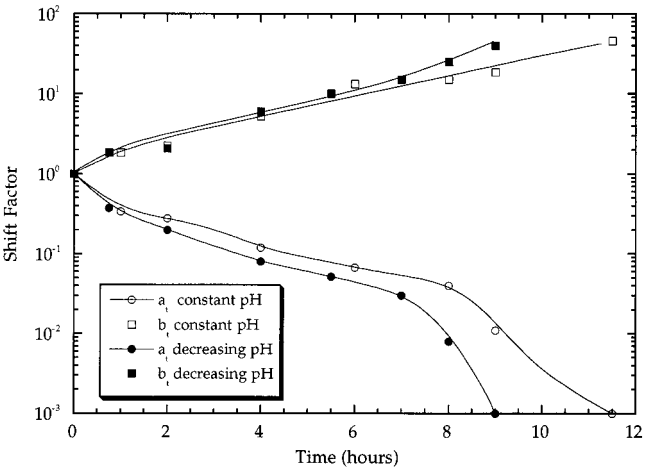

Figure 6. Effect of pH stability on the horizontal (a_t) and vertical shift (b_t) factors. Open symbols represent experiments done at a constant pH of 8.9. Filled symbols represent experiments where pH decreases from 9 to 8.6 during enzymatic degradation.

Since the optimal pH value for the enzyme is ∼4,[24−26] this reduction of pH from 9 to 8.6 could enhance enzyme activity and increase degradation rates at long times, as observed in the moduli reduction.

To test this hypothesis, we needed a system where the pH does not change upon degradation. Borax, which is used here to provide the borate ions for the cross-linking, acts as a buffering agent when used at sufficiently high concentrations. However, in the gel studied so far, salts were used to improve dispersability (NaCl) of guar and to limit thermal degradation ($Na_2S_2O_3$) of guar. The presence of salts necessitates the use of only low borax concentration (0.06% borax). This is because, at higher borax concentrations, the gel demixes into a polymer-rich phase and a solvent-rich phase.[7,8] As a result, the buffering capacity of the borax is limited in gels containing salt. However, if no salts are present, the electrostatic repulsion of charged guar−borate complexes prevents the localization of cross-links by electrostatic effects, and high borax concentrations can be used. In these systems, the pH of the gel remains constant during enzymatic hydrolysis. Figure 6 compares the shift factors for enzymatic degradation of guar−borax gels with different borax concentrations, 0.06% and 0.2%, with the higher borax concentration, maintaining a constant pH of 8.9. It is evident by the trends in the horizontal shift factor that the gel degradation is faster for the lower borax concentration, where there is a reduction in pH with degradation time. As mentioned before, this increase in moduli reduction is probably due to acceleration of chain scission rates by the pH reduction. However, the functional shapes of the curves are similar at both borax concentrations, suggesting that the pH effect alone cannot explain the kinetics of reduction of the dynamic moduli.

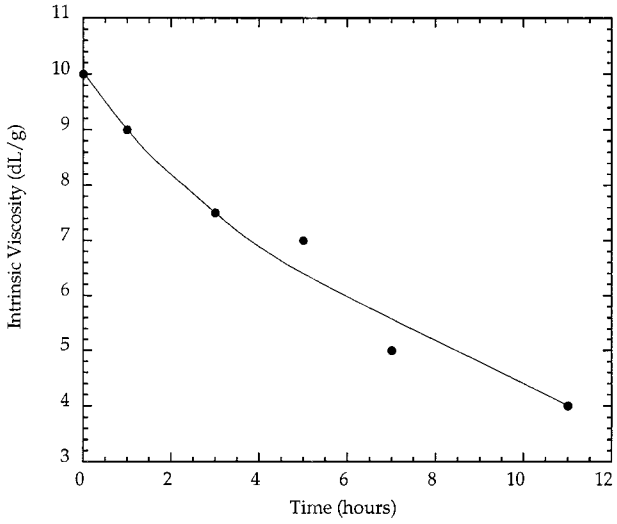

Figure 7. Intrinsic viscosity [η] of 0.5% guar−borax gel as a function of degradation time. Enzyme activity was 6×10^{-4} (X) U/mL of gel.

After discounting the two possibilities considered above, the relationship between the network structure and the rheological properties was investigated. To explain the accelerated reduction in the dynamic moduli at long degradation times, we hypothesized that after a certain degree of degradation, the guar−borax system approaches the point where the chains are not large enough to overlap with other chains. Although the borate ions may still cross-link chains on a local scale, the chains are unable to maintain any long-range connectivity. The absence of network structure significantly increases chain mobility and can explain why the horizontal shift factor, a measure of the longest relaxation time, decreases rapidly at long degradation times. For polymer solutions, the critical entanglement point below which chains can be considered as isolated coils is usually characterized by $c[\eta]$, the product of polymer concentration and intrinsic viscosity. In particular, critical overlap has been shown to occur at $c[\eta]$ of ∼2.5 for guar.[27] Figure 7 shows the changes in intrinsic viscosity of the 0.5% guar−0.2% borax system as a function of degradation time. After 8 h of degradation, the intrinsic viscosity was ∼4.8, and the product of $c[\eta]$ is ≅ 2.4. In this state, the guar−borax system is below the critical entanglement point, and the horizontal shift factor decreases rapidly (Figure 3) as a result. Thus, we infer that the kinetics of moduli reduction, particularly at long times, are a manifestation of the relation between molecular structure and rheological properties. At intermediate times, sufficient chain connectivity exists to preclude a significant drop in moduli.

Synergistic Effects of Enzymes. The guar molecule can be modified by two main enzymes, the backbone-

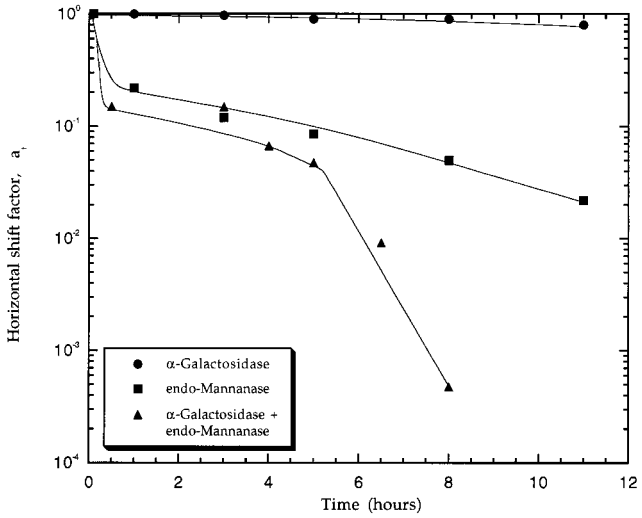

Figure 8. Horizontal shift factor as a function of time for gel degradation using different enzyme systems: 6×10^{-4} U endo-β-mannanase, 6×10^{-3} U α-galactosidase, and a mixture of 6×10^{-4} U *endo*-β-mannanase and 6×10^{-3} U α-galactosidase.

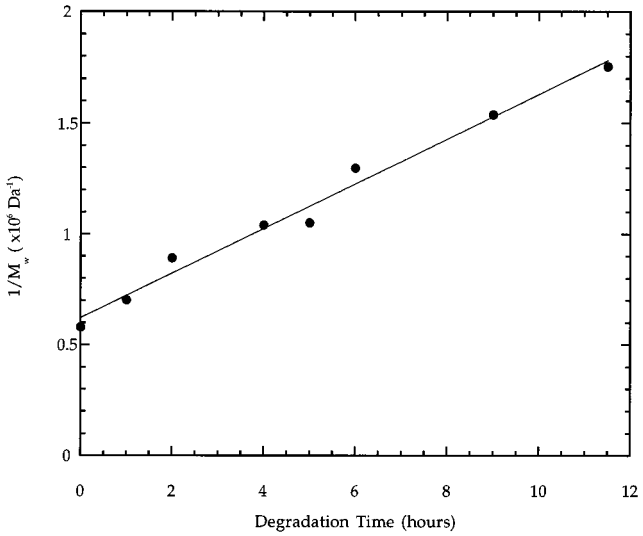

Figure 9. Reciprocal of weight-average molecular weight, M_w, for a guar−borax gel as a function of degradation time.

cleaving *endo*-β-mannanase and side-chain-removing α-galactosidase. So far, our attention has focused on the mannanase because it causes the largest reduction in molecular weight and the gel moduli. However, we were also interested in understanding the effect of degradation by galactosidase on gel moduli and the possibility of synergistic effects by using a mixture of the two enzymes. Figure 8 compares the shift factors for degradation of a 0.5% guar−0.2% borax gel by α-galactosidase, *endo*-β-mannanase, and a combination of the two enzymes. It is seen that the α-galactosidase shows a minimal decrease in gel moduli even after prolonged enzymatic hydrolysis. The combination of *endo*-β-mannanase and α-galactosidase, on the other hand, degrades the gel considerably faster than what would be expected on a simple addition of the two enzymes rates. It is interesting to note that the three-step reduction in gel modulus is clearly evident in this case.

Two possible reasons can be attributed to the synergistic effects of enzymes on gel degradation. First, the activity of *endo*-β-mannanase may be affected by the presence of α-galactosidase. An earlier study performed on a series of guar galactomannan solutions with varying degrees of galactose content has revealed that the *endo*-mannanase activity increases with reduction in the galactose content.[28] This is evidently due to the steric hindrance offered by the galactose substituents to the attack by *endo*-mannanase. Since the α-galactosidase will continuously reduce the galactose content of the guar chains, the *endo*-mannanase activity will correspondingly increase with degradation time, as is observed in the shift factor in our case. Second, it has been suggested[7,8] that the galactose sugars are more likely the cross-linking sites on the guar molecule. Thus, at low galactose content, the cross-linking capability of guar can be expected to decrease resulting in a corresponding reduction in the gel moduli. A combination of these two effects is consistent with the observed synergistic decrease in gel properties on degradation. This synergy can potentially be exploited to controllably enhance rates of gel degradation.

Gels vs Solutions. Finally, we compare the degradation of guar solutions and gels. It was shown earlier that the reduction in the average molecular weights of guar−borax gels is rapid initially and slower subsequently. If the data are plotted as reciprocal of the weight-average molecular weight, M_w, a straight line fit is observed (Figure 9), so that

$$\frac{1}{M(t)} = \frac{1}{M_0} + kt \tag{4}$$

In our earlier work,[10] an identical relation between molecular weight and time was observed for the degradation of guar solutions. Additionally, it was found that the rate constants obtained from the slope of $1/M_w$ vs time plot were the same (data not shown) for degradation of guar solutions and gels within experimental error. Thus, the rates of molecular weight reduction are very similar for the two systems. The polymer chain dynamics are very different for the two systems with the mobility of guar molecules being much lower in the gel state than in the solution state. However, the rates of chain scission are very similar for solution and gel degradation, suggesting that the reaction rate is not affected by diffusion rates of the enzyme or guar molecules. In contrast, the rates of change in the rheological properties of the guar−borax gels and guar solutions show significant differences when the complex viscosity, η^*, is compared for solution and gel degradation. Figure 10 exhibits the changes in complex viscosity upon degradation of a 0.5% guar−0.2% borax gel as a function of frequency. Since the complex viscosity is not independent of frequency, using complex viscosity as a measure of degradation extent of the gel is somewhat arbitrary. However, at a frequency of 0.1 rad/s, the complex viscosity approaches a plateau value for most extents of degradation, allowing one to determine the trend in the kinetics of viscosity reduction. Figure 11 plots the complex viscosity for guar solutions and gels at a frequency of 0.1 rad/s. It should be noted that the complex viscosity of guar solution reached a constant, "zero-frequency" value at 0.1 rad/s for all extents of degradation (data not shown). Three distinct kinetic regimes can be discerned in gel viscosity, a trend similar to that for the horizontal shift factor reduction. In contrast, most of the reduction in guar solution viscosity takes place at short times with slower reduction thereafter. For polymer solutions at concen-

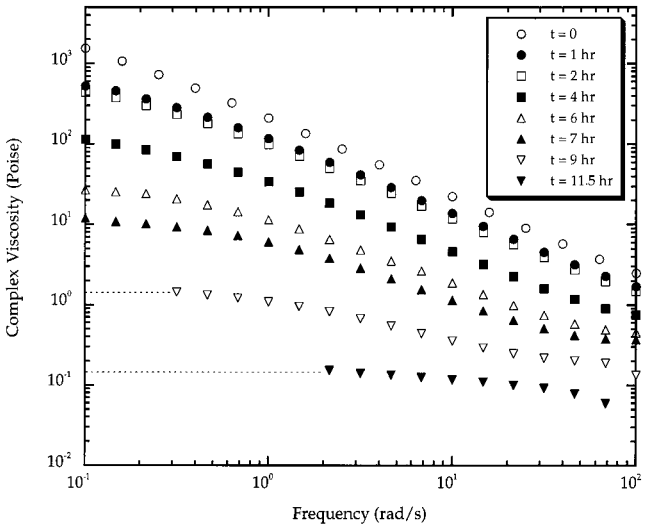

Figure 10. Reduction in the complex viscosity of a guar−borax gel as a function of frequency of deformation for different time periods of enzymatic hydrolysis.

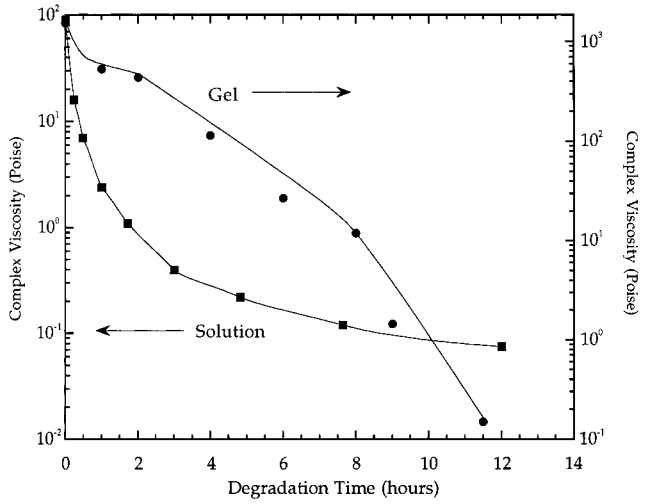

Figure 11. Comparison of the changes in complex viscosity, η^*, of a 1% guar solution and a 0.5% guar−borax gel upon enzymatic degradation. Viscosity values were obtained at 0.1 rad/s.

trations well above the entanglement limit, viscosity scales as a power law function of molecular weight, with an exponent of ∼3.4.[29] Thus, viscosity reduction follows the same trend as the molecular weight reduction, i.e., rapid decrease at short times and slower reduction thereafter. Consequently, gel and solution degradation, two processes very similar at a molecular level, exhibit very different trends in the macroscopic properties. This sensitivity of the rheological kinetics presents an interesting caveat to tailoring guar properties in applications where solutions and gels are used interchangeably.

Conclusions

Dynamic rheological measurements (elastic and viscous moduli, G' and G'' respectively) are extremely sensitive to molecular level changes in polymer solutions and gels. Upon hydrolysis by *endo-β*-mannanase, a backbone cleaving enzyme, aqueous formulations of guar galactomannan and borax display a continuous transition from a gellike to a solution-like system. The dynamic moduli measured at different extents of degradation can be superposed to form a master curve by shifting data along the horizontal and vertical axes. The shift factors can be used to quantify the rate of change in the rheological properties upon degradation. The horizontal shift factor displays three distinct regimes of moduli reduction: initial and terminal rapid regimes, with an intermediate slower regime. These results can be explained by combining knowledge of the chain scission rates with an understanding of the relation between the rheological properties and the molecular structure. Thus, the initial rapid reduction can be attributed to the large rates of molecular weight reduction while the long-time moduli reduction is due to the critical breakdown of the gel structure. The effect of a side-chain-removing enzyme, α-galactosidase, on the moduli reduction was also investigated. While the α-galactosidase had a minimal effect on gel moduli when used by itself, it provides for a synergistic rate of moduli reduction when used in tandem with the *endo-β*-mannanase. It is postulated that the removal of the galactose units reduces the cross-linking sites and the steric hindrance to backbone cleavage, thereby enhancing moduli reduction. Finally, a comparison of gel and solution degradation reveals that though the rates of molecular weight reduction are very similar, the changes in the rheological properties display contrasting trends.

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