Superposition of Oscillations on Steady Shear Flow as a Technique for Investigating the Structure of Associative Polymers

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ABSTRACT: The viscoelastic properties over a range of steady shear conditions of an alkali-swellable associative polymer have been determined using the technique of superposition of oscillations upon steady shear flow, thus enabling the structure of the polymer to be investigated. The associative polymer studied consists of a backbone of methacrylic acid and ethyl acrylate to which is attached macromolecules containing C_{20} hydrophobes via an ethylene oxide−isocyanate linkage. A 1 wt % solution with its pH adjusted to 9.5 was used. At high pHs, the polymer solubilizes to form a network of both intra- and intermolecular associating hydrophobic junctions. The solution shows a non-power-law shear-thinning behavior: the viscosity flow curve, when plotted against shear stress, shows two distinct regions where network rupture is prominent, at stress of 2 Pa and between 40 and 50 Pa. By superimposing small amplitude oscillations on to shear flow at constant stresses, the network structure of the polymer is unperturbed and linear viscoelastic properties of the polymer under the applied stress conditions can be obtained. At an applied stress of 2 Pa and above, both the storage and loss moduli of the polymer are greatly reduced at low frequencies, with the G' approaching second-order behavior and η' tending toward constant values. By analogy to Maxwell relaxation time, an estimate of the relaxation time of the associative polymer at different stress conditions can be made. The results show that the relaxation time is reduced by up to 4 orders of magnitude as the stress is increased from 1 to 60 Pa, while a much smaller decrease in viscosity is observed. At sufficiently high frequencies, both the storage and loss moduli show an increase above their linear viscoelastic values as the strain amplitude is increased. This behavior is believed to be dependent on the relaxation time of the polymer which is a function of the state of network disruption. Thus the technique may prove to be a powerful tool for probing the structure of network polymer in solution.

Introduction

The rheological properties of associative polymers have been the focus of attention by a number of research groups around the world. In contrast to traditional long chain polymers which form entangled networks at moderate to high concentrations, associative polymers form associative junctions through hydrophobic interactions, giving rise to network structures. The dynamics of this associative network structure confer a significant effect on the bulk solution properties. A number of techniques have been used to probe the structure in order to establish the mechanisms of the associations. These include rheological measurements,[1−5] and in conjunction with these are fluorescence spectroscopy,[6,7] pulse-gradient spin-echo nuclear magnetic resonance,[8] and computer simulation.[9,10] These polymers have been found to exhibit very interesting properties, one of which is the shear-thickening behavior of hydrophobically modified urethane−ethoxylate (HEUR) associative polymers at moderate shear rates and also marked shear-thinning at high shear rates. One technique that may prove useful for elucidating the structure of associative polymers is the superposition of oscillations on steady shear flows. It allows one to measure the linear viscoelastic properties of the polymer subjected to different amounts of shear stresses and hence under a different state of network disruption.

The technique of superposition of oscillations on steady shear flows has been used by several authors in the 1960s and 1970s to obtain rheological data for a range of polymer solutions of medium to high concentrations. These include solutions of aluminum dilaureate and ethylene−propylene copolymer in decalin,[11] polystyrene in various solvents,[12−14] and aqueous solutions of poly(ethylene oxide) at various concentrations.[14,15] Kataoka and Ueda[16] applied the same technique to polyethylene melts, and more recently, Moldenears and Mewis[17] used it to investigate the behavior of polymeric liquid crystals. These studies have mainly been carried out using a Weissenberg rheogoniometer, whereby oscillations were superimposed on steady shear flow at constant shear rates. The results generally show that with increasing shear rates, the storage and loss moduli at low frequencies of flexible polymer systems are greatly reduced, with the storage modulus showing a larger reduction. This indicates that the long time scale end of the relaxation spectrum of the polymers is truncated with shear rates.

A number of authors have used the shear-imposed oscillation results for testing the validity of constitutive equations.[13−15,18−20] Others such as Jones and Walters[21] and Powell and Schwarz[15] studied the behavior of the materials by means of a simple fluid theory. In general, the experimental data can be qualitatively predicted by the models, but no quantitative agreements have yet been found.

Using this technique, oscillation flow can be superimposed on any steady shear flow in order to probe the structure of the associative polymer network, so long

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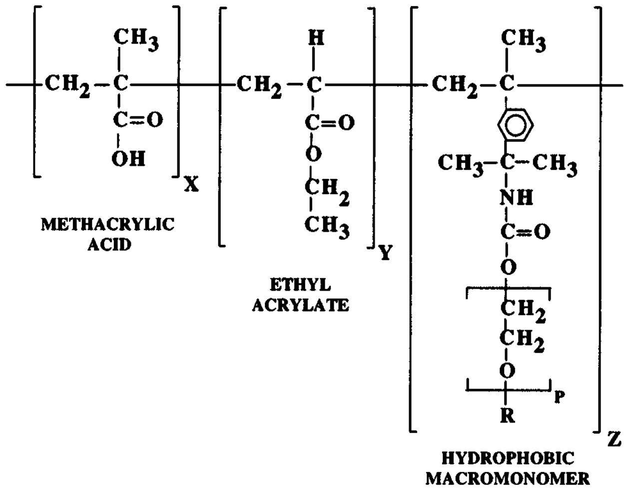

Figure 1. Chemical structure of alkali-swellable associative polymer (HASE).

Table 1. Composition of the HASE Polymer RDJY31-5 and the Unmodified Polymer RDJY31-1

polymer designation	mol ratio, MAA/EA/AM	wt ratio, MAA/EA/AM
RDJY31-1	48.75/51.25/0	45.00/55.00/0
RDJY31-5	49.05/50.05/0.90	38.14/45.25/16.61

as the strain amplitude of the oscillation is sufficiently small that the network structure is not perturbed. The viscoelastic properties of the fluid at any shear condition can be determined and hence its relaxation time. In this work, experiments involving superposition of oscillations on steady shear flows were carried out on a model alkali-swellable associative polymer, in an attempt to elucidate its network structure and to obtain an estimate of the relaxation time function of the solution under various shear conditions. In addition, the nonlinear effect of superposition of large amplitude oscillations on shear flow has been investigated, and the results are used to enhance our understanding of its structure.

Experimental Section

Materials Used. The model associative polymer used in the investigation is a hydrophobically modified alkali-swellable associative polymer (HASE), designated RDJY31-5. The chemical structure of the associative polymer is shown in Figure 1, and the mole and weight ratios of its components are listed in Table 1. The polymer consists of a backbone of methacrylic acid (MAA) and ethyl acrylate (EA), to which are attached a number of associative macromonomers (AM). Each macromonomer in the RDJY31-5 series contains an eicosanyl, C_{20}, hydrophobic group (shown as R in Figure 1) linked to the MAA−EA backbone via a dimethyl *m*-isopropenylbenzyl isocyanate/ethylene oxide (consisting of 35 mol of ethylene oxide) linkage. Also shown in Table 1 are the component ratios of the unmodified polymer which contains only the methacrylic acid and ethyl acrylate backbone with no pendant hydrophobic macromonomer attached and is designated RDJY31-1.

The alkali-swellable associative polymer was synthesized by Union Carbide Corp. via an emulsion polymerization reaction. Details of the synthesis have been described elsewhere.[5] Typically, the hydrophobe with labile hydrogens was ethoxylated to 35 mol in a pressure autoclave and the surfactant converted into macromonomers by the reaction with a stoichiometric amount of *m*-TMI. The final alkali-swellable associative polymer was prepared by the conventional semicontinuous emulsion polymerization of methacrylic acid, ethyl acrylate, and macromonomer, using the weight ratio as shown in Table 1. The polymerization product was filtered and the latex collected. The unmodified polymer RDJY31-1 was prepared using the same synthesis procedure.

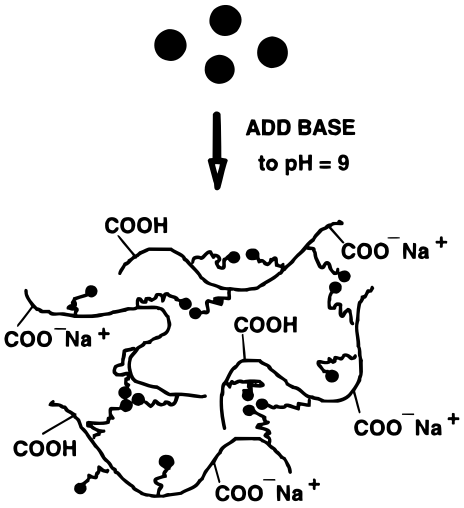

Figure 2. Schematic representation of the solubilization of HASE polymer.

The polymer latexes were dialyzed in regenerated cellulose membrane tubes with regular changing of water for approximately 4 weeks. Stock solutions containing 20 and 5 wt % of solid latex were prepared using purified water (through a Milli-Q system) and adjusted with KCl to 1×10^{-4} M. The test solutions containing 1 wt % of associative polymer were then prepared by dilution with 1×10^{-4} M KCl.

The final preparations were neutralized to pH 9.5 with 1.0 M NaOH solution. The solutions turned from a white, milky appearance to a clear solution almost immediately at pH $\approx$6. The neutralization step is best described schematically as shown in Figure 2. Upon neutralization, the methacrylic acid is ionized and the electrostatic repulsive force of the negative charges along the backbone causes the polymer chains to expand and form a network consisting of both intra- and intermolecular associations of the hydrophobic groups.

The viscosity average molecular weight of the polymers has been estimated from the intrinsic viscosity data obtained for RDJY31-1 in 0.01 and 0.1 M NaCl solution,[22] using the Mark−Houwink constants for polyacrylic acid in NaBr solutions,[23] and the value is found to be of the order of 200 000. As both the unmodified and associative polymers have been synthesized following the same procedure, it is expected that the molecular weight of the associative polymer RDJY31-5 would be of the same order of magnitude. Based on the MW of 200 000, $z = 0.9$, $p = 35$, the number of hydrophobic monomers per chain is estimated to be about 10.

At a polymer concentration of 1 wt %, the solution can be considered to be in the semidilute solution region. For the RDJY31-5 polymer, formation of hydrophobic associations with neighboring chains is facilitated by the relatively long ethylene oxide linkages of the hydrophobic groups. The effect of the ethylene oxide chain length on the association and its effect on solution viscosity are currently under investigation in our laboratory.

Experimental Technique. The rheological properties of the associative polymer solution were measured on a controlled stress rheometer, Carri-Med model CSL500, using a cone-and-plate fixture with a 40 mm diameter, 2° angle cone. The measurements were carried out at 25 ± 0.1 °C. Both steady shear and oscillatory flow measurements were conducted to obtain the steady shear viscosity and dynamic viscoelastic properties of the associative polymer. Additionally, measurements using superposition of oscillations on steady shear flows at constant shear rates or shear stresses have been carried out. In Figure 3 a schematic representation of the parallel superposition of an oscillatory stress on a steady shear flow is shown together with the corresponding strain. The equations

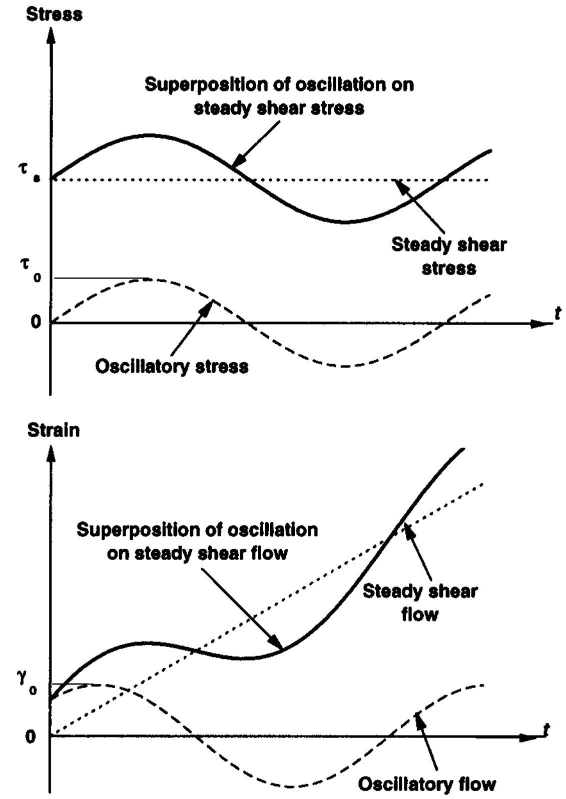

Figure 3. Curves of stress and strain functions for the superposition of an oscillation on steady shear flow.

for the shear stress, τ_{12}, and strain, γ_{12}, are as follows:

$$\tau_{12} = \tau_s + \tau_0 \sin(\omega\tau) \tag{1}$$

and

$$\gamma_{12} = \dot{\gamma}_s t + \gamma_0 \sin(\omega\tau + \delta) \tag{2}$$

where τ_s and γ_s are the steady shear stress and shear rate, respectively. τ_0 and γ_0 are the amplitudes of the oscillatory stress and strain at a frequency ω, respectively, and δ is the phase shift between the oscillatory stress and strain.

Experimentally, a prescribed steady shear stress τ_s or rate $\dot{\gamma}_s$ is applied to the sample until an equilibrium condition is reached. At this point an oscillatory flow at a frequency ω and a specified stress amplitude τ_0 or strain amplitude γ_0 is superimposed on the shear flow. Then by resolving the response stress or strain curve into its steady and oscillatory components, the steady shear viscosity and dynamic properties can be determined in the usual manner. The superposition experiments can be carried out over a range of frequencies, thus enabling the dynamic viscoelastic properties of the fluid at the applied shear rate/stress to be determined. That is, the storage and loss moduli at any imposed shear rate $\dot{\gamma}_s$ or stress τ_s can be defined as $G'(\dot{\gamma}_s,\omega)$ and $G''(\dot{\gamma}_s,\omega)$ or $G'(\tau_s,\omega)$ and $G''(\tau_s,\omega)$, respectively.

To check the validity of the superposition technique and the ability of the instrument software to resolve the steady shear and oscillatory components of the output stress or strain, a medium molecular weight silicone oil was tested using various imposed steady shear rates and one shear stress. The results are shown in Figure 4. The loss modulus G'' data for all the imposed shear stresses and shear rates are the same as those obtained from oscillations without the superposed steady shear flow and also the same as the steady shear stress values. The steady shear component for all the runs also agrees with the steady shear viscosity value of 12.5 Pa s at 25 °C. The storage modulus G' data all fall on the same straight line having a slope of 2 up to frequency approximately 30 rad/s, after which deviation from second-order behavior is observed.

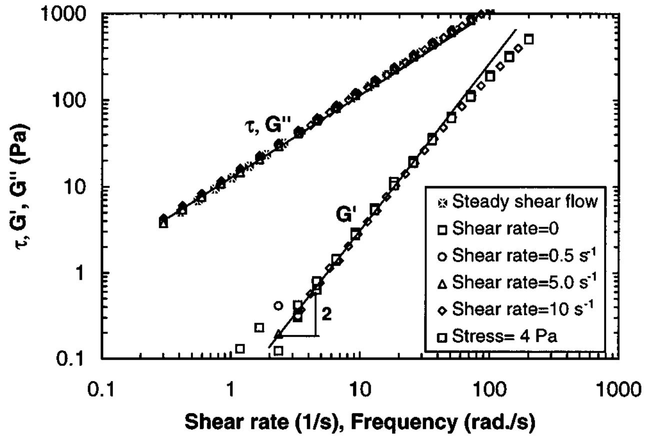

Figure 4. Storage and loss moduli of a moderate molecular weight silicone oil without steady shear and with various applied shear rates and one applied shear stress. Also shown is the steady shear stress plotted against shear rate.

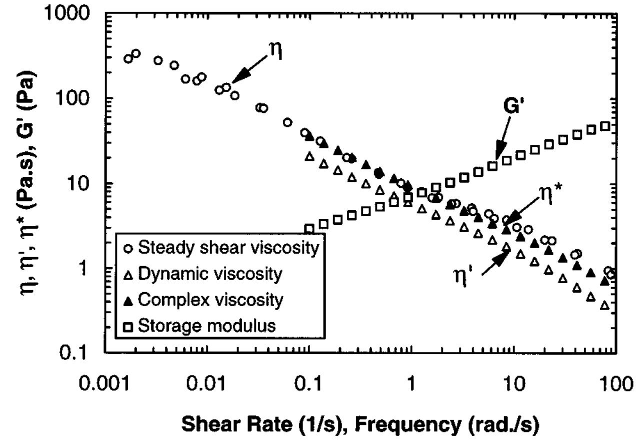

Figure 5. Steady shear and dynamic properties of the 1 wt % RDJY31-5 associative polymer.

To ensure that the associative polymer sample is subjected to the same shear history, prior to each experiment, the sample was presheared at a constant shear rate (of 10 s^{-1}) for 5 min followed by a 5 min rest period. We have carried out oscillatory tests at a frequency of 6.6 rad/s (i.e., $\approx$1 Hz) immediately after steady shearing at 10 s^{-1} and found that the storage and loss moduli increased gradually with time and reached steady values by the end of 5 min. Hence the rest time of 5 min following the preshearing would have allowed sufficient time for the polymer to restore its network structure back to the equilibrium state, prior to the commencement of any test.

Furthermore, oscillatory strain amplitude sweeps were performed at various shear stress conditions and at different frequencies to determine the linear viscoelastic regions. Subsequent oscillatory measurements were made within these linear regions. Strain values between 3% and 20%, depending on the magnitude of the shear stress and the frequency range, were used. As will be shown in a later section, thickening behavior in the storage and loss moduli has been observed under certain shear conditions as the strain amplitude is increased. Hence strain amplitude sweep at fixed frequencies has also been investigated as a means to further probe the structure of the polymer.

Results

Rheological Properties. Steady shear viscosity η and viscoelastic properties, η', η^*, and G', of the associative polymer are shown in Figure 5 as a function of shear rate or frequency, while in Figure 6 steady shear viscosity is plotted as a function of shear stress. In these figures, both the steady shear viscosity and dynamic

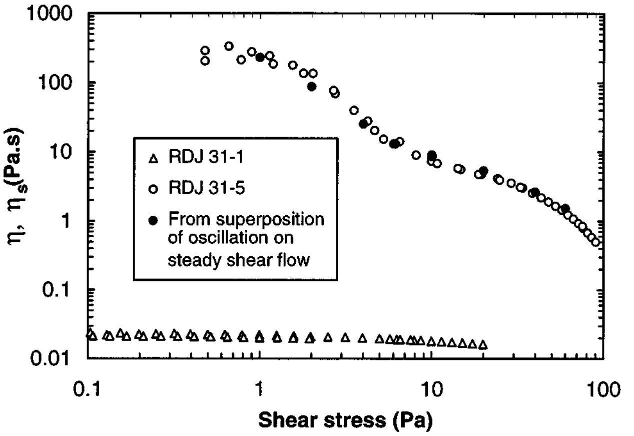

Figure 6. Steady shear viscosity against stress data for the 1 wt % RDJY31-5 associative polymer and the unmodified RDJY31-1 polymer. Also shown are the steady shear viscosities obtained from the superposition of oscillations on shear flow at various stress conditions.

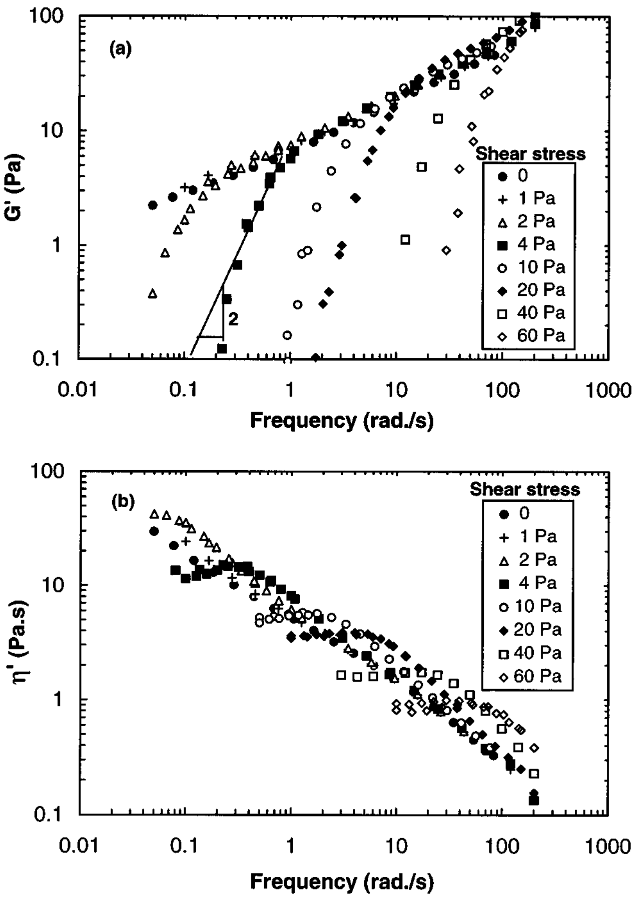

Figure 7. (a) Storage modulus and (b) dynamic viscosity of the 1 wt % RDJY31-5 associative polymer at various shear stress conditions.

results obtained from several tests after applying the same preshearing conditions show good reproducibility. Only at the very low shear rate end, i.e., below 0.01 s^{-1}, larger uncertainty is encountered and is due to the measured shear rates approaching the limit of the instrument. At shear rates below 0.005 s^{-1}, corresponding to shear stress of the order of 1 Pa, the steady shear viscosity of the associative polymer approaches a constant value of between 200 and 300 Pa s. At higher shear rates/stresses the sample becomes shear-thinning; the decrease in shear viscosity with shear rate does not obey the power law, as is usually observed for most polymeric systems. The flow curve displays an inflection point in the shear-thinning region and becomes more apparent in the viscosity–shear stress plot, see Figure 6. This result seems to indicate that the network structure of associative polymer is a function of the applied stress, and there appears to be two critical stress levels, one at approximately 2 Pa and another at higher values between 40 and 50 Pa, whereby abrupt changes in the network structure took place. This is apparent in the sudden decrease in the shear viscosity followed by a more gradual drop at higher stresses. Similar behavior has been observed by Jenkins et al.[5] for other alkali-swellable associative polymers with similar backbones of methacrylic acid and alkyl (meth)acrylate or styrene but containing different hydrophobic macromonomers. A more drastic drop in viscosity at particular stress levels has been observed by Aubry and Moan[3] and also in our laboratory for another HASE associative polymer[24] which contains different fractions of the main components from the series studied here.

As can be seen in Figure 5, the dynamic viscosity of the associative polymer is lower than the steady shear viscosity. The complex viscosity η^*, however, agrees well with the steady shear viscosity values, especially in the intermediate shear rate/frequency region. At higher shear rates/frequencies, i.e., after the inflection point in the flow curve, η^* is somewhat lower than the η value at the same frequency/shear rate. The applicability of the Cox–Merz rule found for the associative polymer may be fortuitous, as this is not always the case with other associative polymers in the series investigated in this work, having different hydrophobe chain lengths and degrees of ethoxylation. The viscoelastic properties of the associative polymer in the frequency range measured (see Figure 9a) show a typical transition region behavior of a gellike fluid, where the G' and G'' curves are both fairly flat and of the same order of magnitude.[25]

Also shown in Figure 6 is the steady shear viscosity of the control or unmodified polymer, designated RDJY31-1, which was synthesized by the same procedure as the associative polymer but without the hydrophobe-containing macromonomer. (The mole fractions of the components used in the synthesis of RDJY31-1 are also given in Table 1.) As can be seen, the shear viscosity of the unmodified polymer is several orders of magnitude lower than that of the associative polymer at the same polymer concentration, i.e., 1 wt %. The viscosity of the unmodified polymer is essentially Newtonian, except at the very high shear rate/stress region where it starts to show a slight shear-thinning behavior.

Superposition of Oscillations on Shear Flow Results. As discussed previously, the associative polymer shows a critical dependence on the shear stress rather than on shear rate. Hence in order to probe its network structure in solution under various shear conditions, it is more appropriate to apply a constant shear stress on the sample and perform oscillation tests. The dynamic viscosity and storage modulus data for the associative polymer have been obtained at several shear stress conditions, ranging from 1 to 60 Pa, and the results are shown in Figure 7a,b, respectively. These results are compared with the *normal* viscoelastic properties of the associative polymer, obtained from oscillatory tests without imposed shear stress. For the experiments with superposition of oscillations on steady shear flow, steady shear viscosities at any stress condition τ_s, i.e., $\eta_s = \tau_s/\dot{\gamma}_s$, are found to be constant irrespective of the frequency of oscillation, as can be seen in

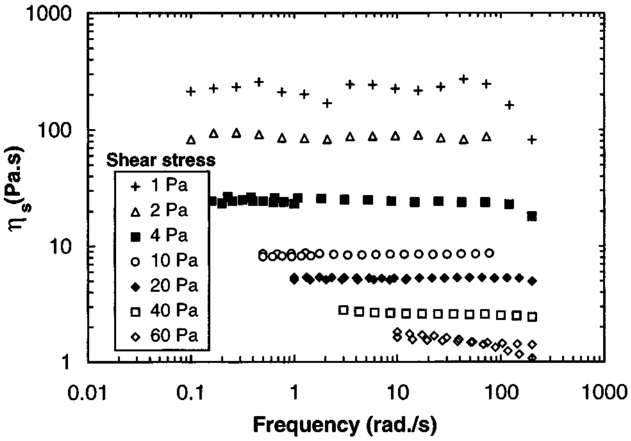

Figure 8. Steady shear viscosity obtained during superposition of oscillations on steady shear flow of the 1 wt % RDJY31-5 associative polymer at various shear stress conditions.

Figure 8. These steady shear viscosities are also in excellent agreement with the values obtained in steady shear flow (without imposed oscillation); these values are shown as solid circles in Figure 6.

At the lowest stress condition of 1 Pa, both the storage modulus and dynamic viscosity remain essentially the same as the case without an imposed stress. At this level of stress, the shear viscosity remains in the limiting zero-shear rate region, i.e., equal to η_0; hence no disruption of the polymer network occurs, and its viscoelastic property is unlikely to be different from that with no shearing.

Only at the higher stress of 2 Pa, where the first "dip" in the shear viscosity curve occurs, is the viscoelastic property expected to show a significant departure from the *normal* values. This is indeed the case as the storage moduli obtained at a stress of 2 Pa and above are greatly reduced at low frequencies, with the G' curves approaching a slope of 2 with respect to frequency. This approach to second order in the G' curves occurs at higher frequencies as the stress is increased. That is, the terminal region of the polymer is shifted to higher frequencies as the structure of the associative polymer network is increasingly being disrupted by higher shear stress. At higher frequencies in the transition region, the storage modulus curves become parallel to the *normal* G' curve, with only a slight increase in the G' values with increasing stress. At the low-frequency ends, corresponding to the second-order region in the G' curves, the dynamic viscosity at each stress condition approaches a constant value and, in some cases, shows a slight maximum followed by further decrease at very low frequencies. In the transition region, the dynamic viscosities again become shear-thinning and parallel to the *normal* dynamic viscosity curve. However, the η' values are significantly higher than the values without shear stress.

The observed slopes of greater than 2 of the G' curves at low frequencies, found for the associative polymer at stresses of 2 Pa and above, are probably due to experimental error at very low G' values. Similar results have been previously reported for polymer solutions and melt,[11,13,14,16,20] and several constitutive models that have been investigated[13,20] also predicted this phenomenon.

The storage and loss moduli curves of the associative polymer at several stress conditions are shown in Figure 9. It is apparent that with increasing shear stress, the structural changes due to the disruption of the polymer network are manifested in a shift in the terminal region toward higher frequencies. Hence at a stress of 2 Pa, the intersection of the G' and G'' curves is within the range of frequency that can be measured experimentally, i.e., at approximately 0.25 rad/s. Analogous to the determination of the Maxwell-type relaxation time of fluid at rest using the relationship $\lambda_0 = \lim_{\omega\to 0} G'/\omega^2\eta_0$, we have calculated the relaxation time function at each shear stress using the relationship:

$$\lambda(\tau_s,\omega) = \frac{G'(\tau_s,\omega)}{\omega^2\eta'(\tau_s,\omega)} \tag{3}$$

A plot of this relaxation time function against frequency is shown in Figure 10. Each of these curves goes through a maximum at frequencies which correspond approximately to the region of second order in the G' curves and the maximum in the η' data. The maximum value may be taken as an estimate of the longest or terminal relaxation time of the polymer under the prevailing stress condition. These estimates of the longest relaxation time λ are plotted as a function of the shear stress in Figure 11, together with the corresponding maximum in the η' values. Also shown in the figure, for comparison, are the steady shear viscosity values. The relaxation times agree well with those obtained from the inverse of the frequency at the intersection between the G' and G'' curves, as would be expected if the dynamic data are fitted by the Maxwell model. Hence, we have been able to obtain an estimate of the terminal relaxation time of the associative polymer under various states of network disruption caused by shear.

For the associative polymer with no shearing, i.e., in its equilibrium state, it was not possible to measure the dynamic property in the terminal region, nor could the intersection between G' and G'' curves be obtained; hence, the relaxation time could not be determined. However, one can conjecture from the G' and G'' versus frequency plot (Figure 9a) that if the G' and G'' curves intersect at a frequency of approximately 0.01 rad/s, then the relaxation time of the polymer at rest must be of the order of 100 s or higher if the intersection occurs at a lower frequency. The value obtained by extrapolation of the relaxation time versus stress curve (Figure 11) to a stress value of 1 Pa or lower gives a similar estimate. If that were the case, the relaxation time of the associative polymer is found to be reduced by 1−4 orders of magnitude as it is subjected to increasing shear stress from 2 to 60 Pa, while the shear viscosity is reduced by only 2 orders of magnitude at the extremity.

It should be pointed out that the dynamic properties reported in this section are in the linear viscoelastic region, as the amplitudes of the oscillatory strain employed are at sufficiently low values that the data are independent of the applied strain.

Strain Amplitude Sweep Results. In most polymeric systems, the linear viscoelastic properties are limited to low strains and generally show a decrease with increasing strain amplitude beyond the linear region. By contrast, the alkali-swellable associative polymer may show an increase in the elastic and/or viscous components when subjected to increasing strain amplitude. These thickening effects become more prominent at higher frequencies. The storage and loss moduli, normalized with respect to the corresponding

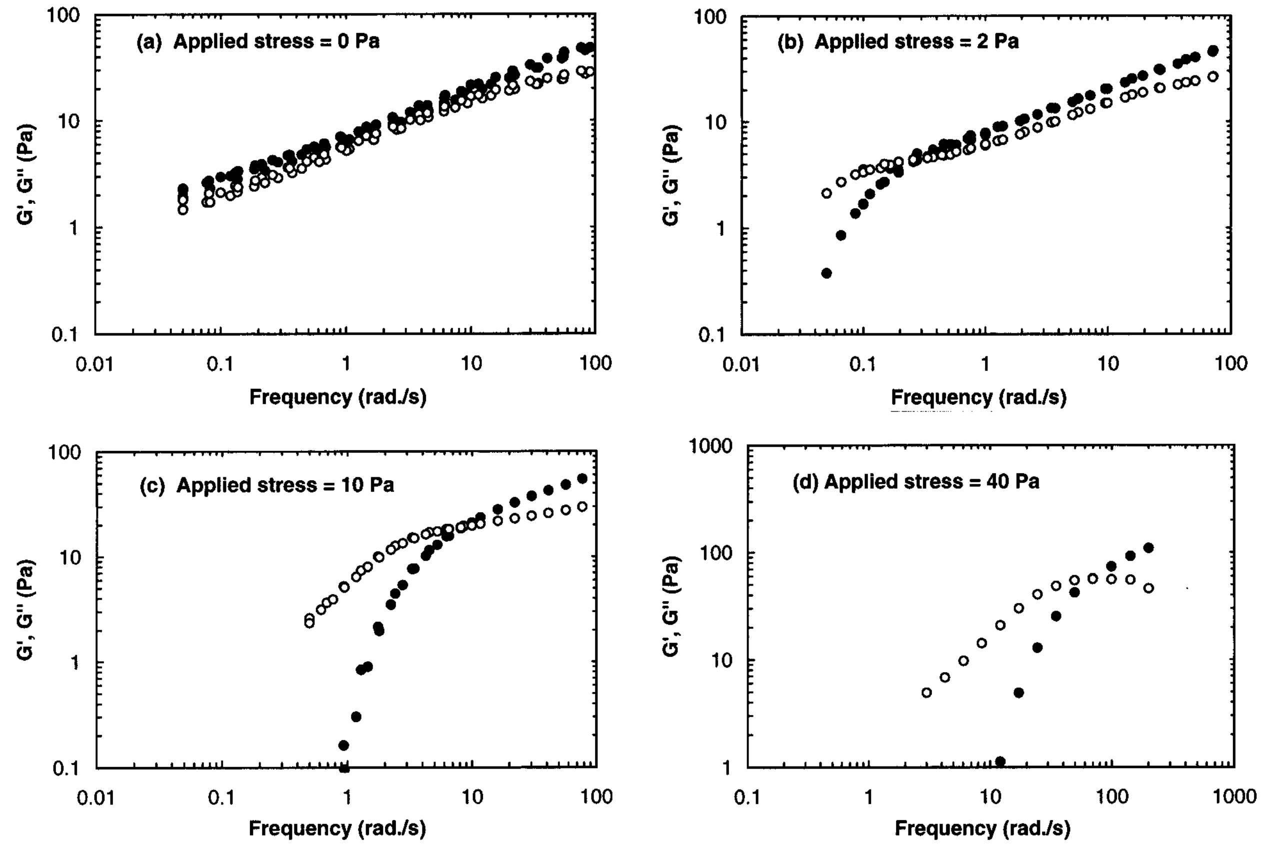

Figure 9. Storage and loss moduli plots of the 1 wt % RDJY31-5 associative polymer at stress conditions of (a) 0, (b) 2, (c) 10, and (d) 40 Pa.

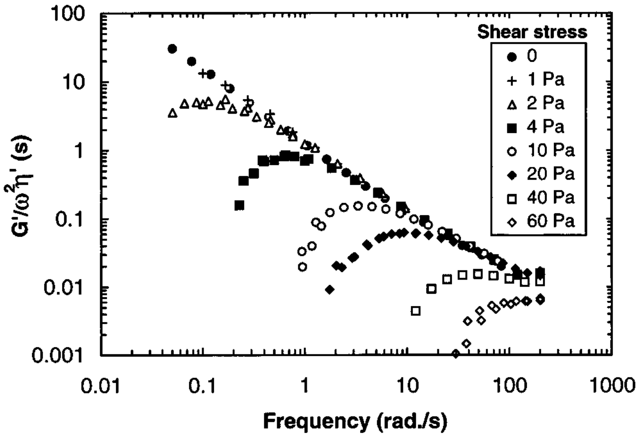

Figure 10. $G'(\tau_s,\omega)/\omega^2\eta'(\tau_s,\omega)$ function of the 1 wt % RDJY31-5 associative polymer at various shear stress conditions.

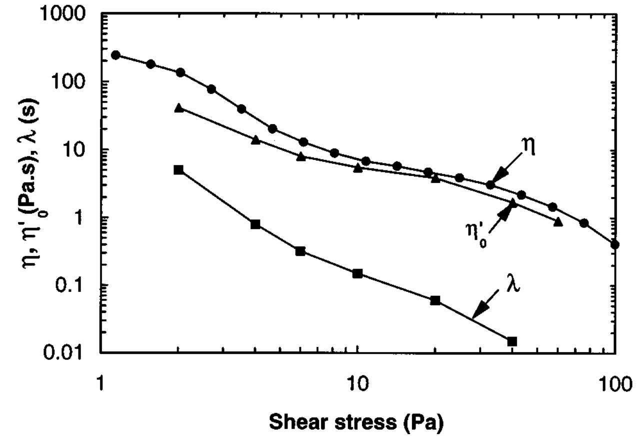

Figure 11. Longest relaxation time, η'_0 and η, of the 1 wt % RDJY31-5 associative polymer plotted against shear stress.

linear viscoelastic value, for normal oscillation at two frequencies are shown in Figure 12. At the high frequency of 100 rad/s, both the storage and loss components of the dynamic shear modulus show a significant increase above its linear viscoelastic value as the strain is increased beyond a certain value, reaching a maximum before decreasing with further increase in strain. In this instance the normalized G'' value, i.e., the viscous component, rises to 1.7 at its peak and is somewhat higher than that found in the normalized G' values. At lower frequencies the increase is less, and in fact at 1 rad/s the G' values show no increase beyond their linear viscoelastic value while there is only a very slight increase in the viscous component. With increasing stress, causing greater degree of disruption to the polymer network, the nonlinear behavior found in oscillation flows at large strain is different from the normal oscillation case. One such case is shown in Figure 13, where the normalized G' and G'' values at a frequency of 10 rad/s and shear stress of 10 Pa are shown. The increase in the viscous component is much reduced compared to the case with no shear stress at the same frequency, and furthermore, no increase in the elastic component is observed. In general, the nonlinear behavior of the associative polymer is found to be dependent on the structure of the network under the prevailing shear stress conditions and is thus a function of the relaxation times of the polymer.

Discussion

The alkali-swellable associating polymer (HASE) investigated in this work has a distinctly different network structure to the HEUR type polymer with the hydrophobic units end-capped on the chain backbone,

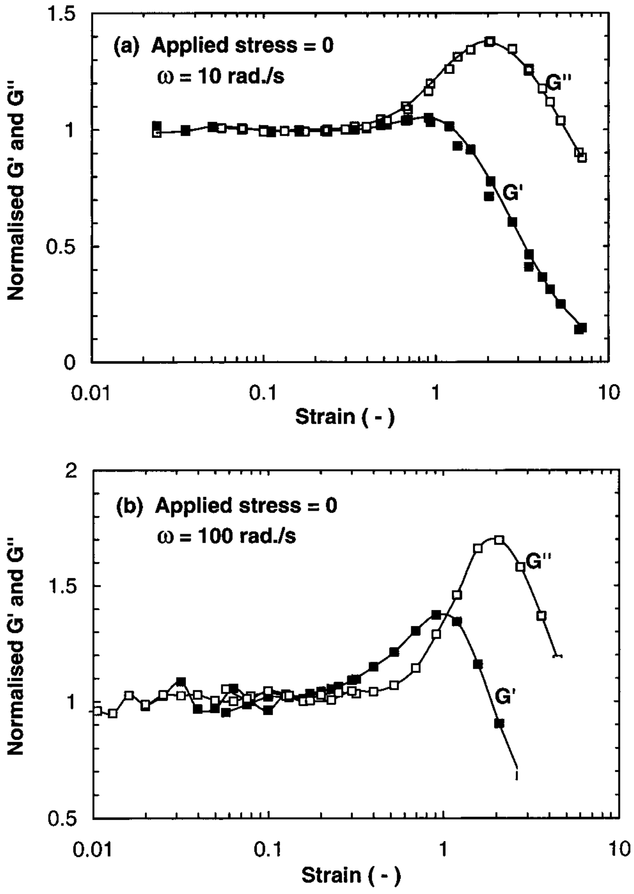

Figure 12. Normalized storage and loss moduli of the 1 wt % RDJY31-5 associative polymer as a function of strain for normal oscillation at frequencies of (a) 10 and (b) 100 rad/s.

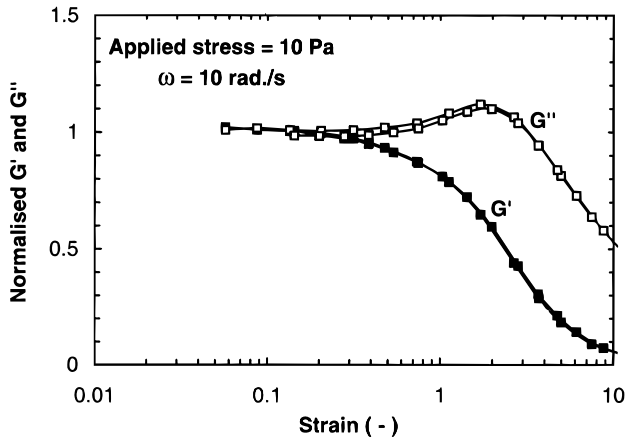

Figure 13. Normalized storage and loss moduli of the 1 wt % RDJY31-5 associative polymer as a function of strain at a stress of 10 Pa and a frequency of 10 rad/s.

a system which has been studied by a number of authors.[1,2,4,6] It is now widely accepted that the HEUR system forms micelles of constant functional number above its critical micelle concentration, and it is the secondary association of these micelles which forms the three-dimensional network in solution.[6] Our associating polymer system resembles more closely the one studied by Aubry and Moan,[2] which is a hydrophobically modified (hydropropyl) guar, consisting of a number of hydrophobic macromolecular groups attached to the main backbone. The HASE system investigated also consists of a number of macromolecules, each end-capped with a hydrophobic group, attached to the MAA−EA backbone. These hydrophobic end-capped macromolecules are thought to be distributed evenly along the backbone.

At high pHs, the polymer molecules are ionized and the polymer chains expand due to the repulsive force of the negative charges on the chain backbone. This provides opportunity for the association of hydrophobic groups between neighboring chains, as well as within the same polymer chain, and hence the formation of a network structure of associating junctions which, at sufficiently high concentration, may span the whole network domain. The formation of a network structure in the 1 wt % solution of RDJY31-5 at the pH of 9.5 is evident from the fact that its shear viscosity is several orders of magnitude higher than that of the unmodified polymer at the same concentration. At 1 wt % concentration hydrophobic associations between neighboring chains of the HASE polymer are probable because of the relatively long and flexible ethylene oxide linkage that exists between the hydrophobic group and the chain backbone.

The formation of intermolecular associations of the HASE polymer is further supported by the viscosity results at lower concentrations obtained in our laboratory.[6] At values below a critical concentration, the viscosity of the associative polymer is slightly lower than that of the unmodified polymer at the same concentration and is possibly due to intramolecular associations of the hydrophobic groups, forcing the associative polymer chains to become more compact compared to the polymer without hydrophobes. This result is similar to that found by Aubry and Moan[2] for the hydrophobically modified (hydropropyl) guar. The network junctions formed by the intermolecular hydrophobic associations are temporary junctions which are continually being destroyed and reformed. Its lifetime is expected to be of the order of 0.1 s or less. As the network is subjected to increasing shear stress, the hydrophobically associating intermolecular junctions are destroyed at a faster rate than their rate of formation, resulting in a decrease in the junction density and hence a drop in the steady shear viscosity. Consequently, as shown in Figure 11, the terminal relaxation time of the polymer network is also greatly reduced. The relaxation time of the solution is decreased by almost 4 orders of magnitude, while the viscosity function is only reduced by approximately 2 as the shear stress is increased to 60 Pa.

The associative polymer investigated here does not show a discontinuity or sudden drop in the viscosity flow curve as found by Moan and Aubry.[2] The reason for the difference is unknown at this stage, and studies using different hydrophobic chain lengths as well as associative polymers containing different proportions of the hydrophobic macromolecules are underway in our laboratory. It is hoped that the results for these studies will provide us with a better understanding of the structure of these molecules in solutions.

Contrary to the end-capped hydrophobic polymer, i.e., HEUR, studied by Jenkins,[1] Annable et al.,[2] Hulden [4] and Yekta et al.,[6] our HASE system does not show shear-thickening behavior in the viscosity curve with increasing shear rates. However, the thickening behavior found in the storage and loss moduli with increasing strain amplitude in oscillatory flows at certain frequencies is rather unique and has not been reported previously. In general, it is assumed that the storage modulus reflects the density of association junctions and the loss modulus reflects the effective volume occupied by the association network. In the linear viscoelastic region, the amplitude of the applied strain is sufficiently small as not to cause disruption to the polymer network. At higher strain the thickening in the loss modulus may result from the extension of the polymer coils and of the polymer backbones which would result in an increase in the volume occupied by the network. This view of an increase in the volume occupied by the associated polymer molecules causing an increase in the viscous component is similar to that proposed by the Winnik group[6] for the rosette-forming HEUR system. As the polymer network is expanded, some of the intramolecular associations may be forced to disengage, providing more hydrophobic groups to be available for intermolecular associations with neighboring polymer chains. Consequently, the number of intermolecular associations and hence the storage modulus may increase. As the strain is increased further, these intermolecular network junctions are eventually disrupted, resulting in a drop in the G' values. When a sufficiently large number of junctions are broken, the network collapses and the viscous component then starts to decrease.

The effect of increasing strain on the behavior of the G' and G'' values relative to their linear viscoelastic values is clearly a function of the structure of the polymer under various stress conditions. It is believed that this response is dependent on the relaxation time of the polymer relative to the characteristic process time. The interpretation of this phenomenon in terms of the structure of the polymer network in solution will be the subject of a separate publication.

Concluding Remarks

The superposition of oscillations on shear flows at constant shear rates or constant shear stresses has been shown to be a useful technique for studying the structure of the associative polymer in solution under different shear conditions. The 1 wt % solution of the alkali-swellable associative polymer investigated forms a network consisting of temporary junctions of the hydrophobic units. As these associated junctions are being disrupted by a constant stress, the terminal regions in the linear viscoelastic flow curve are shifted toward higher frequencies. By applying the technique of superposition of oscillations on shear flow, we are able to obtain an estimate of the longest relaxation times of the polymer at shear stress conditions ranging from 2 to 60 Pa. The estimated longest relaxation times are reduced by several orders of magnitude as the intermolecular associations between the hydrophobic units in the network are disrupted by the increase in the shear stress. Furthermore, when subjected to increasing strain amplitude in oscillation flow, the viscous and elastic responses of the polymer show an increase above its linear viscoelastic values at high frequencies, a behavior which is believed to be a function of the relaxation time of the network at the particular stress condition.

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References and Notes

(1) Jenkins, R. D. Ph.D. Thesis, Lehigh University, Bethlehem, PA, 1990.
(2) Annable, T.; Buscall, R.; Ettelaie, R.; Whittlestone, D. *J. Rheol.* **1993**, *37* (4), 695.
(3) Aubry, T.; Moan, M. *J. Rheol.* **1994**, *38* (6), 1681.
(4) Hulden, M. *Colloids Surfaces A* **1994**, *84*, 263.
(5) Jenkins, R. D.; DeLong, L. M.; Bassett, D. R. In *Hydrophilic Polymers: Performance with Environmental Acceptability*; Glass, J. E., Ed.; ACS Symposium Series American Chemical Society: Washington, DC, 248; 1995; p 425.
(6) Yekta, A.; Xu, B.; Duhamel, J.; Adiwidjaja, H.; Winnik, M. *Macromolecules* **1995**, *28*, 956.
(7) Kumacheva, E.; Rharbi, Y.; Winnik, A. M.; Guo, L.; Tam, K. C.; Jenkins, R. D. *Langmuir*, submitted for publication.
(8) Rao, B.; Uemura, Y.; Dyke, L.; Macdonald, P. M. *Macromolecules* **1995**, *28*, 531.
(9) Leibler, L.; Rubinstein, M.; Colby, R. H. *Macromolecules* **1991**, *24*, 4701.
(10) Groot, R. D.; Agterof, W. G. M. *J. Chem. Phys.* **1994**, *100* (2), 1657.
(11) Booij, H. C. *Rheol. Acta* **1966**, *5*, 215.
(12) Kotaka, T.; Osaki K. *J. Polym. Sci. Part C* **1966**, *15*, 453.
(13) Macdonald, I. F. *Trans. Soc. Rheol.* **1973**, *17* (3), 537.
(14) Laufer, Z.; Jalink, H. L.; Staverman, A. J. *Rheol. Acta* **1975**, *14*, 641.
(15) Powell, R. L.; Schwarz, W. H. *Trans. Soc. Rheol.* **1975**, *19* (4), 617.
(16) Kataoka, T.; Ueda, S. *J. Polym. Sci. Part A-2* **1969**, *7*, 475.
(17) Moldenears, P.; Mewis J. *J. Rheol.* **1992**, *37* (2), 367.
(18) Booij, H. C. *Rheol. Acta* **1966**, *5*, 222.
(19) De Cleyn, G.; Mewis J. *J. Non-Newtonian Fluid Mech.* **1981**, *9*, 91.
(20) Isayev, A. I.; Wong, C. M. *J. Polym. Sci. Part B* **1988**, *26*, 2303.
(21) Jones, T. E. R.; Walters, K. *J. Phys. Part A* **1971**, *4*, 85.
(22) Guo, L. M.Sc. First Year Report, Nanyang Technological University, Singapore, 1996.
(23) Brandrup, J.; Imergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley: New York, 1989.
(24) Tan, C. B. B.Eng. Thesis, Nanyang Technological University, Singapore, 1995.
(25) Ferry, J. D. *Viscoelastic Properties of Polymers*; John Wiley and Sons: New York, 1980.

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