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Steady shear viscosity first normal stress difference and recoverable strain in carboxymethyl cellulose, sodium alginate and guar gum

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Steady shear viscosity, first normal stress difference and recoverable strain in carboxymethyl cellulose, sodium alginate and guar gum were studied. A master curve was obtained for the viscosity of sodium alginate and guar gum. The data for sodium carboxymethyl cellulose deviated from that of guar gum and sodium alginate. Superposition principles for the normal stress coefficient with a reduced shear rate have been attempted. Superposition was obtained for all three hydrocolloids. Additionally, the first normal stress difference appeared to be highly related to shear stress for sodium alginate and carboxymethyl cellulose at all concentrations studied. Guar gum did not follow this behavior.

INTRODUCTION

Both the first and second normal stress differences are the result of elastic behavior in fluids and the first normal stress difference significantly influences the perception of textural attributes such as thickness and slipperiness (Kokini *et al.*, 1977) by affecting the effective shear rate and thus the perception of these attributes, during the squeezing motion in the mouth. A potential, more important use of normal forces might be in their ability to complement information about structure such as MW, MWD, entanglement density, etc., that can be obtained through measurement of viscosity. Although the viscous behavior of hydrocolloid polymers has received a great deal of attention because of their obvious importance in texture design, their first and second normal stress difference have received little attention. This is due mainly to lack of understanding of how they would be significant to food-related issues. Kokini *et al.* (1984) using the Bird–Carreau model predicted the expected behavior of the primary normal stress coefficient ψ_1 of guar and carrageenan gums as well as blends of CMC/guar gums. No experimental data supported the predictions. Grizzuti (1990) studied the first normal stress difference of hydroxy-propylcellulose aqueous solutions. It was found that for 60% solutions where a liquid crystalline phase exists, N_1 initially increases with shear rate, then reaches a maximum and finally decreases at high shear rates. The samples at lower concentrations increased linearly on a log–log scale with increasing shear rate. The observed behavior was predicted by the theoretical development of the Doi model (Marucci & Maffeltone, 1989). Grizzuti's findings were consistent with earlier reports by Kiss and Porter (1978) with poly(γ-benzyl-glutamate), and by Navard (1986).

It is the objective of this paper to report viscosity and first normal stress behavior as a function of shear rate and concentration for sodium carboxymethyl cellulose, sodium alginate and guar gum and to test several superposition principles. Furthermore, the use of this data to make some preliminary structural interpretations will be illustrated.

EXPERIMENTAL

All gum dispersions were prepared by mixing in a blender with the appropriate amount of distilled, deionized water and allowing them to equilibrate at room temperature for 24 h. Occasionally, a vacuum was employed to remove air bubbles which form during blending and would cause significant experimental problems. The use of a vacuum to remove air bubbles

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was required more frequently at the more concentrated dispersions.

Dispersions of both sodium carboxymethyl cellulose and guar were prepared at 0·50%, 0·75%, 1·00% and 1·25% gum by weight in distilled deionized water. Sodium alginate dispersions included 1·25%, 1·50%, 1·75% and 2·00% sodium alginate by weight in distilled deionized water. Sodium alginate was obtained from Kelco, sodium carboxymethyl cellulose (7HOF, D.S = 0·7, Lot No. 57179) from Hercules, and guar gum (No. G-4129, Lot No. 101 F-0279) was from Sigma Chemical Company.

Shear stress and first normal stress difference data were obtained simultaneously using the cone and plate geometry of the Rheometrics Fluids Rheometer, with a cone radius of 2·5 cm, and a cone angle of 0·0196 radians. A 100 g cm transducer was used. The gap size was set at 50 μm and held constant throughout the testing. All experiments were conducted at room temperature which fluctuated between 23 and 25°C. While shear stress data could be obtained in the shear rate range of 0·1–100 s^{-1}, similar success was not obtained with reference to normal stress data, where measurements were limited by the sensitivity of the instruments. Therefore, the measurements were limited to 10–100 s^{-1}. Additionally, a significant amount of noise was also observed.

Typical normal stress data, in the shear rate range of 10–100 s^{-1} is shown in Fig. 1. Each curve displayed a transient region with a considerable amount of noise. Such noise is not uncommon and has been frequently reported with reference to normal stress measurements (Kotaka *et al.*, 1959). An average of this signal was obtained and has been used for further calculations.

The first normal stress difference ($N_1(\gamma)$) is equal to

$$\sigma_{xx} - \sigma_{yy} = N_1(\gamma)$$

where σ_{xx} and σ_{yy} are diagonal components of the stress tensor. The primary normal stress coefficient ψ_1 is then defined as follows:

$$N_1 = \gamma\psi_1$$

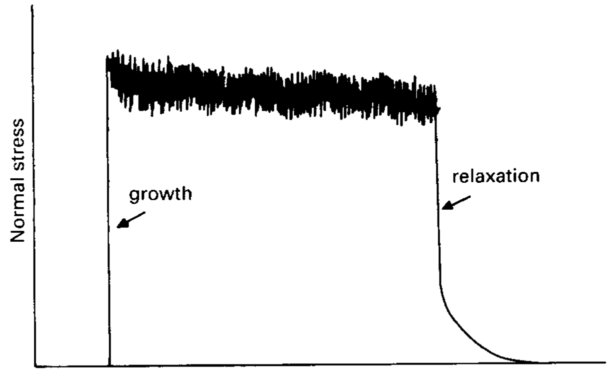

Fig. 1. Typical normal stress development.

Similarly the second normal stress difference N_2 is given by

$$N_2(\gamma) = \sigma_{yy} - \sigma_{zz}$$

The second normal stress coefficient (ψ_2) is then given by

$$N_2(\gamma) = \gamma^2\psi_2$$

First normal stress difference data was converted to a primary normal stress coefficient and plotted with respect to shear rate on log–log coordinates.

RESULTS

Viscosity *versus* shear rate behavior

The viscosity *versus* shear rate behavior of all gum dispersions showed similar behavior. That of guar gum is given in Fig. 2 as an example. At each concentration, viscosity tended to a constant zero-shear value η_0 whose magnitude depended upon the concentration of gum used. The onset of non-Newtonian behavior was also a function of gum concentration and shifted to lower shear rates as the gum concentration increased. This is due to the fact that as the concentration of gum increases, the hydrodynamic domains overlap and the relaxation time of individual hydrodynamic units is longer than the frequency of collisions caused by the increasing concentration (Graessley, 1974). For example, in the case of 0·50% guar, the onset of non-Newtonian behavior is observed at approximately 5 s^{-1} while at a concentration of 1·00% this shear rate is shifted to 0·2 s^{-1}.

A reduction of viscosities is possible using a generalized shear rate. A possible form of the reduced shear rate is that suggested by the Rouse model. In this transformation the generalized shear rate β is given by

$$\beta = \frac{\dot{\gamma}(\eta_0 - \eta_s)M}{cRT} \tag{1}$$

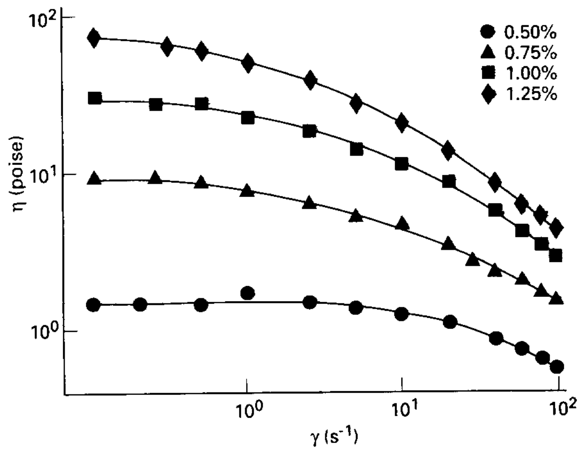

Fig. 2. Viscosity *versus* shear rate for guar gum.

where M is the molecular weight, γ is the shear rate, η_0 is the zero shear viscosity, η_s is the solvent viscosity, R is the ideal gas constant, T is the absolute temperature and c is the concentration of the solute. The corresponding reduced viscosity is η/η_0. However, this transformation necessitates molecular weight data obtained from an independent experiment. An alternative method has been proposed by Morris and Ross-Murphy (1981) where the generalized shear rate used for superposition of the data is obtained by multiplying the inverse of the shear rate where $\eta/\eta_0 = 0{\cdot}8$ by the actual shear rate at each viscosity. Then β is given by

$$\beta = \dot{\gamma}\tau$$

where

$$\tau = \left.\frac{1}{\dot{\gamma}}\right|_{\frac{\eta}{\eta_0} = 0{\cdot}8}$$

This procedure was used in this research. The results for sodium alginate and guar are shown in Fig. 3 at all four concentrations studied. The superposition procedure does indeed generate a master curve for sodium alginate and guar as expected by Morris and Ross-Murphy (1981) and Graessley (1974). The data for sodium carboxymethyl cellulose deviated from that of guar and sodium alginate and therefore could not be superimposed on the same curve. This can be attributed to conformational differences between guar, sodium alginate and sodium carboxymethyl cellulose. On the other hand, data for sodium carboxymethyl cellulose at four different concentrations superimposed nicely using the same superposition principle (Fig. 4).

First normal stress difference

In the limited range in which first normal stress difference data could be obtained, it appeared that the primary normal stress coefficient (ψ_1) showed power-law behavior as a function of shear rate. An example is given in the case of sodium alginate in Fig. 5. The primary normal stress coefficient decreased sharply with respect to shear rate and increased with increasing concentration as expected. Similar results were obtained for both guar and sodium carboxymethyl cellulose (CMC). An initial fit of the data was obtained with a power law-type function of the form

$$\psi_1 = m'(\dot{\gamma})^{n'-2} \tag{2}$$

The values of the parameters m' and n' are shown in Table 1 along with coefficients of determination (R^2).

Primary normal stress coefficient data have also been reported to be superimposed using several transformations. In this study, a modification of the method proposed by Dewitt *et al.* (1955) has been used. In this method the reduction scheme is as follows:

$$\psi_{1r} = \psi_1 \frac{T_0}{T} \cdot \frac{C_0}{C} \tag{3}$$

where C is concentration, C_0 is a reference concentration, T_0 is a reference temperature and T is the

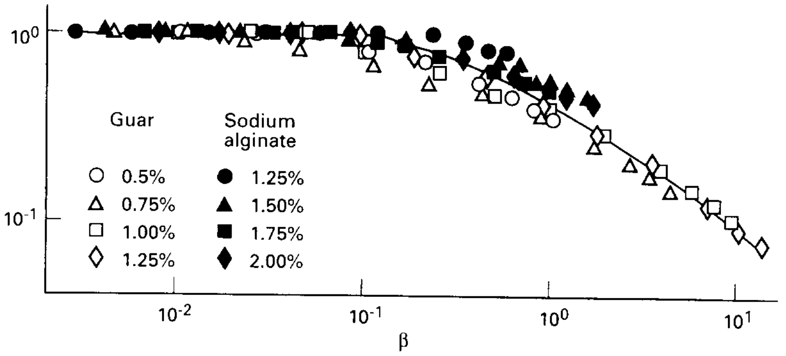

Fig. 3. Superposition of steady shear viscosity for guar gum and sodium alginate.

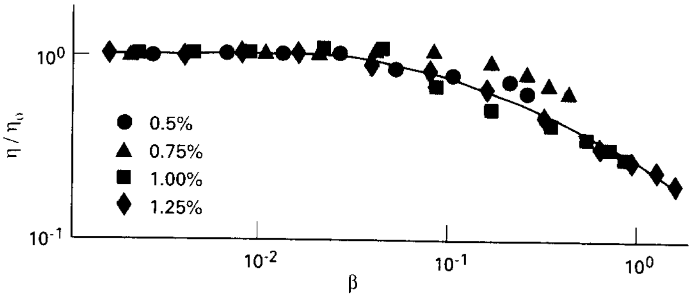

Fig. 4. Superposition of viscosity data for carboxymethyl cellulose.

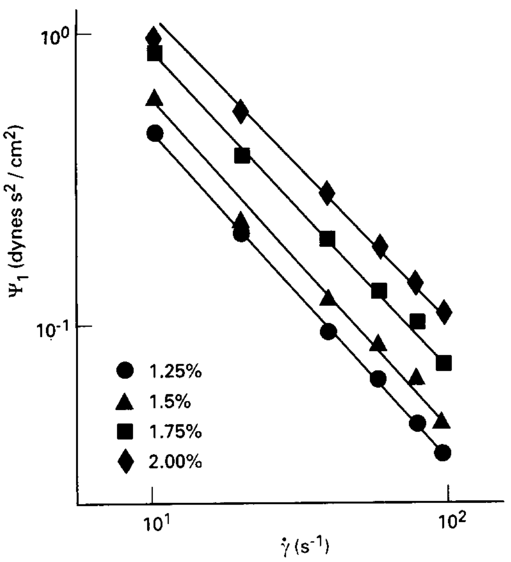

Fig. 5. Primary normal stress coefficient *versus* shear rate for sodium alginate.

temperature of the sample; ψ_{1r} is the reduced primary normal stress coefficient and ψ_1 is the measured primary normal stress coefficient. Similarly, in this transformation the shear rate is reduced as follows:

$$\dot\gamma_r = \dot\gamma\eta_0 \frac{T_0}{T}\cdot\frac{C_0}{C} \tag{4}$$

where η_0 is the zero shear viscosity obtained before. In this research, it was not possible to superimpose the data with this linear transformation. A modification involving the use of a non-linear concentration term was used in this study. This modified superposition is given as follows:

$$\psi_{1r} = \psi_1 \frac{T_0}{T}\left[\frac{C_0}{C}\right]^\alpha \tag{5}$$

$$\dot\gamma_r = \dot\gamma\eta\left[\frac{C_0}{C}\right]^\alpha \tag{6}$$

where α becomes a characteristic exponent for each system. Normal stress coefficient data *versus* reduced shear rate data are shown in Figs 6, 7, 8 for guar, carboxymethyl cellulose and sodium alginate. As can be seen from the figures, data for all concentrations superimpose nicely. The characteristic parameter α was 3·5 for guar, 2·5 for CMC and 2·75 for sodium alginate. This is typical of systems which appear to approach the entanglement plateau. Again because of the limited range of shear rates included, it is not possible to verify whether this reduction procedure would be valid for all shear rates and in particular whether it would include the zero shear primary normal stress coefficient. Further work will focus on generating normal stress data at a wider range of shear rates and to explain the structural basis for such a reduction.

Relation between shear stress and first normal stress difference

For viscoelastic fluids, according to Mooney (1953) if the fluid is subjected to continuous simple shear the elastic structure reaches a state of constant stress as a result of an equilibrium of the stressing in continuous shear and the stress relaxation of the fluid. In this constant state of shear stress there is a corresponding 'recoverable shear strain' which is due to the elastic component of the fluid and is therefore recoverable. This is called the 'recoverable strain' and is defined as

$$S = \frac{\sigma_{11} - \sigma_{22}}{\sigma_{12}} \tag{7}$$

The recoverable strains can also be regarded as an 'elastic recoil' which one would obtain if the shear stress were removed instantaneously from the fluid (Kotaka *et al.*, 1959).

What is interesting is to investigate whether for a viscoelastic material $\sigma_{11} - \sigma_{22}$ and σ_{12} are related. In this particular study it was observed that the first normal

Table 1. Power-law parameters for primary normal stress coefficient *versus* shear rate

		m' [dimensionless]	n' [dynes s^2/cm^2]	R^2
Guar	0·50%	3·70	1·26	0·99
	0·75%	6·83	1·19	0·99
	1·00%	15·37	1·25	0·99
	1·25%	21·40	1·30	0·99
CMC	0·50%	0·86	0·97	0·98
	0·75%	4·17	1·13	0·99
	1·00%	5·97	1·18	0·99
	1·25%	14·27	1·31	0·99
Sodium Alginate	1·25%	4·96	1·07	0·99
	1·50%	5·82	1·04	0·99
	1·75%	8·64	1·02	0·99
	2·00%	10·69	0·93	0·99

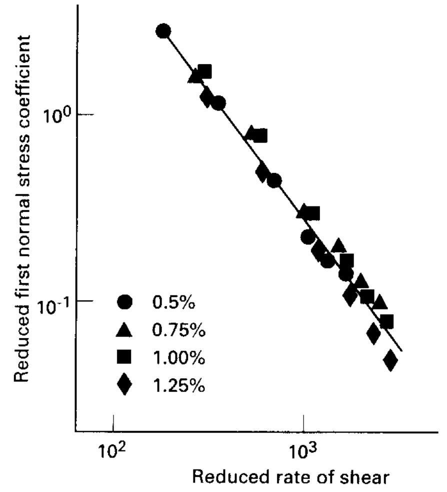

Fig. 6. Reduced primary normal stress coefficient *versus* reduced shear rate for guar gum.

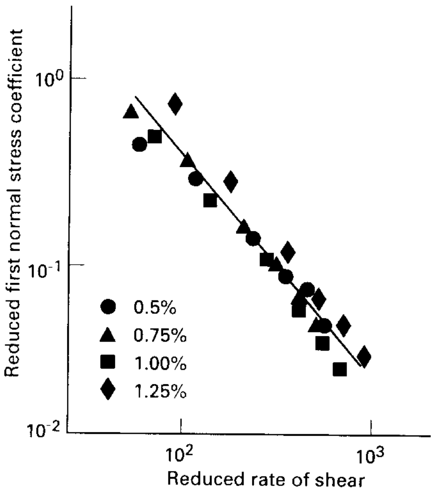

Fig. 7. Reduced primary normal stress coefficient *versus* reduced shear rate for carboxymethyl cellulose.

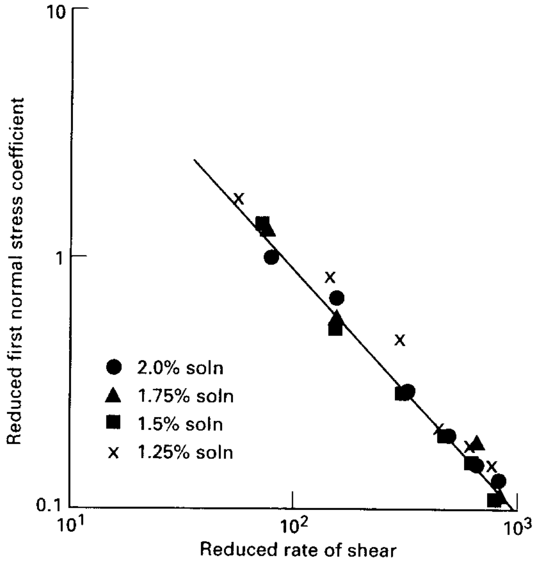

Fig. 8. Reduced primary normal stress coefficient *versus* reduced shear rate for sodium alginate.

stress difference data and shear stress data superimposed on logarithmic coordinates for sodium alginate as shown in Fig. 9 and for sodium carboxymethyl cellulose in Fig. 10. The remarkable aspect of this correlation is the fact that for these two gums the gradients of the lines are nearly 45° or equal to 1. This would suggest that the recoverable strain is nearly equal at all concentrations and shear rates. This result is consistent with the results obtained by Kotaka *et al.* (1959) using also commercial-type Na–CMC. Their experiments showed a small increase in recoverable strain with shear rate, but data at several concentrations of sodium carboxymethylcellulose also superimposed.

From a molecular standpoint it is already well established that elastic behavior is a function of the number of effective chains that temporarily participate in the formation of a network structure through entanglements and the interchain relaxation process due to temporary junction (entanglement) breakage and formation as well as rearrangements of distorted chains. Because sodium carboxymethyl cellulose and sodium alginate are charged molecules, relatively strong junctions (entanglements) could exist and the interchain relaxation processes, which are concentration-dependent, might play a secondary role. The presence of a significant charge density is known to contribute to the expansion of the molecule, making the formation and maintenance of entanglements more likely.

Guar gum on the other hand is a neutral polysaccharide consisting of mannose and galactose. Here, interchain relaxation processes are not affected by the presence of 'charge' and therefore would play a dominant role since junctions caused by electrostatic interactions would not control the behavior of the network.

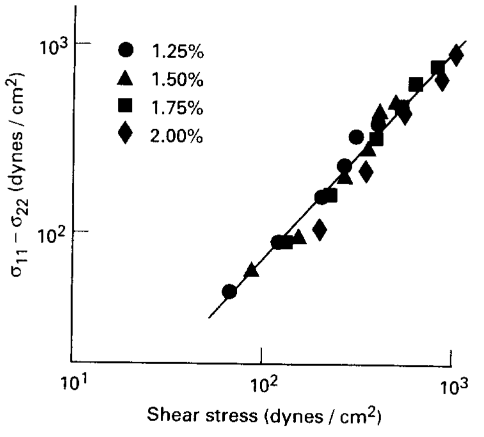

Fig. 9. First normal stress difference *versus* shear stress for sodium alginate.

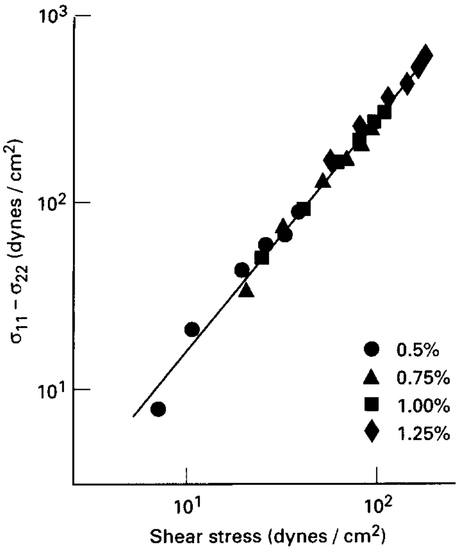

Fig. 10. Reduced first normal stress difference *versus* shear stress for carboxymethyl cellulose.

Clearly interchain relaxation processes are a function of collision frequency between the molecules, which in turn is a function of concentration. This argument is substantiated in Fig. 11 for guar where all the data at a constant concentration superimpose but those at different concentrations fall on different curves.

Additionally, a creep compliance $J(\gamma)$ can be obtained by appropriate treatment of the first normal stress difference and shear stress data. The relation which holds in this case is (Graessley, 1974)

$$\sigma_{11} - \sigma_{22} = 2J(\dot\gamma)\tau^2 \qquad (8)$$

at low shear rates

$$J_e^\circ = \frac{1}{2\eta_0^2} \lim_{\gamma \to 0} \psi_1(\dot\gamma) \qquad (9)$$

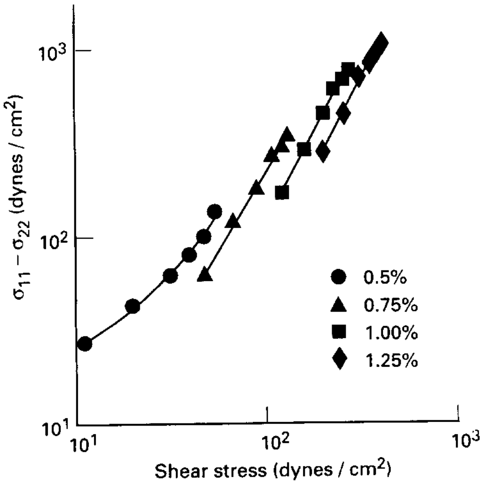

Fig. 11. Reduced first normal stress difference *versus* shear stress for guar gum.

The Rouse model predicts that $J(\dot\gamma)$ is constant, while the entanglement theory of Graessley (1974) suggests that

$$J(\dot\gamma) \approx \dot\gamma^{2/11} \qquad (10)$$

In both cases a weak dependence of $J(\dot\gamma)$ on shear rate is expected. Experimentally it is observed that $J(\dot\gamma)$ is a decreasing function of shear rate for all concentrations of sodium carboxymethyl cellulose and sodium alginate, as shown in Fig. (12). Graessley (1974) and Graessley and Segal (1969) found that $J(\gamma)$ increased with shear rate in concentrated solutions of polystyrene with narrow molecular weight distribution, while decreasing with shear rate in broad-distribution samples. Tanaka *et al.* (1966) also came to similar conclusions.

Based on the experimental data obtained here for CMC and sodium alginate, it is possible to suggest that the range of molecular weight distribution, while decreasing with shear rate in broad-distribution samples. Tanaka *et al.* (1966) also came to similar conclusions.

Based on the experimental data obtained here for CMC and sodium alginate, it is possible to suggest that the range of molecular weights for each sample is quite broad, as would be expected from biological polymers. The approximate constancy of $J(\dot\gamma)$ in the case of three concentrations of guar is predicted by the Rouse model. It must be noted that a thorough understanding of molecular weight and molecular weight distribution of each sample would support the qualitative arguments presented. No molecular weight data were available to directly substantiate these arguments.

In conclusion, first we have shown that the primary normal stress coefficient *versus* shear rate showed power-law behavior. Second it is possible to reduce the primary normal stress coefficient *versus* shear rate data at all concentrations studied when a gum characteristic reduction method is used. In addition, shear stress and first normal stress difference appear to be related for the charged systems sodium carboxymethyl cellulose and sodium alginate, while this was not so for the neutral polysaccharide guar gum. Finally, creep compliance $J(\dot\gamma)$ data followed the predictions of the Rouse model for three concentrations of guar, and for all cases $J(\dot\gamma)$ data was typical of broad molecular weight distribution polymers.

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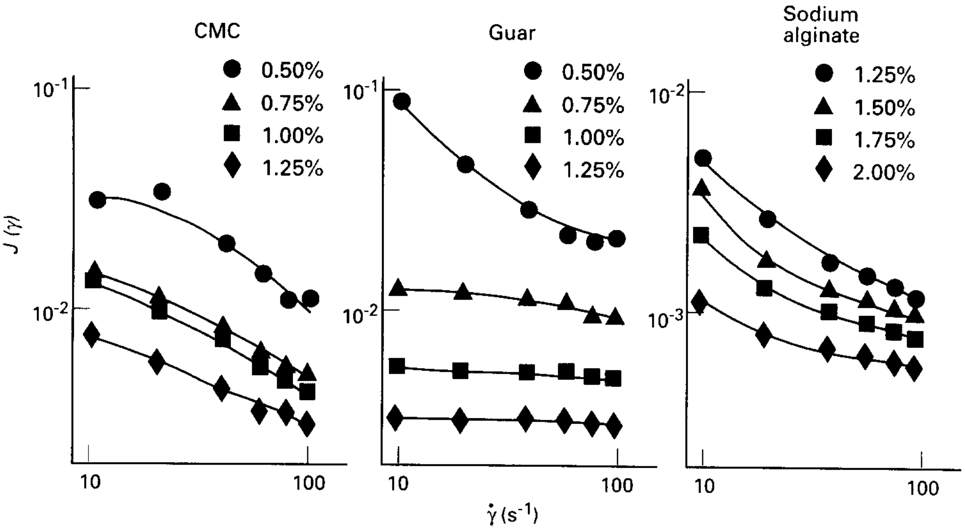

Fig. 12. Steady shear creep compliance *versus* shear rate for carboxymethyl cellulose, guar and sodium alginate gums.

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