

Rheological Properties of Hydroxypropyl- and Sodium Carboxymethyl-Substituted Guar Gums in Aqueous Solution

S. VENKATAIAH and E. G. MAHADEVAN, *Research and Development Division, IDL Chemicals Ltd., Hyderabad.AP., India*

Synopsis

The aqueous solutions of guar gum and its hydroxypropyl (HP) and sodium carboxymethyl (sod CM) derivatives are pseudoplastic, and the transition from Newtonian to pseudoplastic occurs in the low-shear-rate range at the concentrations of interest to industries. The flow properties of these polysaccharide solutions were studied in the range of low to moderately high shear rates, using a very simple technique and instrument. The flow of these polysaccharide solutions can be described by equation of state based on Cross model, and the basic rheological parameters, like zero shear rate viscosity (η_0), elasticity modulus (G_0), and relaxation time (λ_0), were calculated from simple and established relations. Master viscosity curves indicate that the molecular weight distribution of native guar gum has not been changed by derivatization. The effect of concentration and temperature on rheological parameters (η_0 and λ_0) has been studied, and the relations among these were established by simple equations.

INTRODUCTION

Viscosity is one of the most important property contributed by a polysaccharide to aqueous systems, and the corresponding rheological properties are basic to any function served by the system. Pure and substituted guar gums are among the most important water-soluble polymers used mostly in the food, textile, paper, petroleum, explosives, and mining industries as protective colloids, thickeners, coating, etc. They are invariably used in the explosive industry because of their ability to efficiently thicken the nitrate salt solutions which are the basic components of slurry explosive formulations. However, the increasing use of these polysaccharides was not paralleled by a thorough rheological investigation. A literature survey reveals that flow properties of these polysaccharide solutions were either studied employing simple rheological models which are inadequate for the evaluation of true rheological parameters or confined to higher shear rate range. True correlations between the rheological parameters and other variables are lacking. Rheological properties of polymeric materials are related to and influenced by molecular parameters, like molecular weight, molecular weight distribution, etc. A better understanding of the relationships between the rheological properties and the molecular parameters is important from the standpoints of both polymer preparation (designing new polymers or modifying the existing ones) and polymer processing. Hence, evaluation of true rheological parameters and their relation with other parameters of industrial importance was sought.

The aqueous solutions of unsubstituted as well as substituted guar gum are pseudoplastic (entanglement network type) in nature. The behavior of this type of network solutions should be characterized by treating separately (a) network at rest, characterized by zero shear rate viscosity (η_0), elasticity modulus (G_0), and relaxation time (λ_0), and (b) network in streaming solutions, for which the shear dependent functions $\eta_{\dot{\gamma}}$ and $G_{\dot{\gamma}}$ apply. The behavior of any particular fluid can be partially characterized by giving the values of two parameters, η_0 and λ_0 , which locates in some systematic way the onset of non-Newtonian behavior in the viscosity-shear rate flow curves. The flow properties of polymers are altered by branching in important and unexpected ways.

The object of this work was to determine and characterize the basic rheological parameters, like η_0 , G_0 and λ_0 , for aqueous solutions of unsubstituted as well as substituted guar gums, using simple techniques and instruments, and illustrate the effect of substitution (branching) and other parameters of industrial importance, like concentration and temperature, on these rheological parameters.

MATERIALS AND METHODS

Hydroxypropyl-guar gums (HP-guar gums) of varying molar substitution (ms) and sodium carboxymethyl-guar gums (sod CM-guar gums) of varying degree of substitution (ds) along with unsubstituted guar gum were used as the materials for investigation. It has been established¹ that significant changes in properties occur when the guar molecule is substituted with various substituents, and the degree of change is not only a function of the type and amount of substitution but also the conditions of reaction. To avoid the effect of process conditions, reactions were carried out under identical conditions and under nitrogen atmosphere. High-purity, food-grade, guar flour of single lot was employed for substituted guar gums. Several experiments have been carried out and reproducibility was excellent. All the products were thoroughly characterized and the ms² or ds³ of respective samples were determined by standard methods.

Preparation of Hydroxypropyl Guar Ethers

200 g of guar flour was dispersed in 420 mL of isopropyl-alcohol (analytical reagent) in a pressure reactor equipped with stirrer, and the system was purged with nitrogen. 6 g of sodium hydroxide (analytical reagent) in 180 mL of distilled water was added slowly while stirring over a period of 20 min. Then, required amount of propylene oxide (Fluka AG, puriss.) was added and the reaction mass was heated to 65°C and maintained at that temperature for 3 h under slow stirring. The system was then cooled to room temperature, neutralized with glacial acetic acid, and filtered. The reaction mass was purified by extracting thrice with 80% aqueous methanol and finally with pure methanol. The air-dried product was ground to pass 200 B.S.S. sieve and characterized. Except for the amounts of propylene oxide used for varying ms of hydroxypropyl groups, all other parameters were kept constant.

Preparation of Sodium Carboxymethyl Guar Ethers

200 g of guar flour was slurried in 800 mL isopropyl-alcohol (analytical reagent) in a four-neck flask equipped with stirrer, thermometer, and gas-purging system. After purging the reaction vessel with nitrogen, the required amount of 50% aqueous sodium hydroxide solution (sodium hydroxide and sodium chloroacetate were used in 1:1 molar ratio) was added slowly while stirring over a period of 30 min, and then the required amount of freshly prepared saturated aqueous solution of sodium chloroacetate was added over a period of 30 min. During this time, the temperature was slowly raised to 45–48°C, and further heating was stopped. Slow stirring was continued for 2 h, during which time the temperature rose to about 60–64°C and dropped back to room temperature. The reaction product was filtered and extracted repeatedly with 80% aqueous methanol until the filtrate was free from chloride ions. After the third extraction, the pH of the mass was adjusted to 7.2 with glacial acetic acid. Finally the mass was washed with pure methanol, air-dried, ground to pass 200 B.S.S. sieve, and characterized.

HP—guar gums of *ms* of 0.26 (I), 0.53 (II), and 0.83 (III) and sod CM—guar gums of *ds* 0.57 (I), 0.93 (II), and 1.21 (III), along with pure guar gum, were taken for investigation. These materials were free of additives that are used in commercial samples.

Viscosity Measurements

Aqueous solutions were prepared by adding required amounts of powdered gums slowly to vigorously stirred water and stirring was continued for 15 min. The following concentrations (in % w/w) of solutions in distilled water were prepared: 0.5, 0.75, 1.0, 1.25, and 1.5% in case of guar gum and HP—guar gums; 0.5, 1.0, 1.5 and 2.0% in case of sod CM—guar gums. The pH of guar gum and HP—guar gum solutions was neutral, whereas that of sod CM—guar gum solutions was in the range of 7.1–7.2. The smooth solutions so obtained were stored at room temperature in air-tight bottles, and viscosities were measured after 24 h.

Wells-Brookfield cone-and-plate viscometer Model RVT equipped with 2.4-cm-diameter, 1.565°-angle cone was used for measuring the shear stress or apparent viscosity. Under rotational conditions this instrument covers the shear rate range of 1.92–384 s⁻¹ for the above cone. Employing the spring relaxation technique developed by Patton,⁴ shear rates extending into the ultralow range can be measured. The results obtained by the rotational method and spring relaxation technique are in good agreement in the overlapping region of shear rates. Thus, employing this simple, inexpensive equipment, the shear rate ranging from 384 s⁻¹ to as low as 0.001 s⁻¹ (covering a range of about six decades) could be measured. The range of temperature studied is 30–60°C, above which solvent evaporation poses a problem as the quantity of the test solution employed is small (about 1–1.5 mL), which will be in the form of a film between cone and plate.

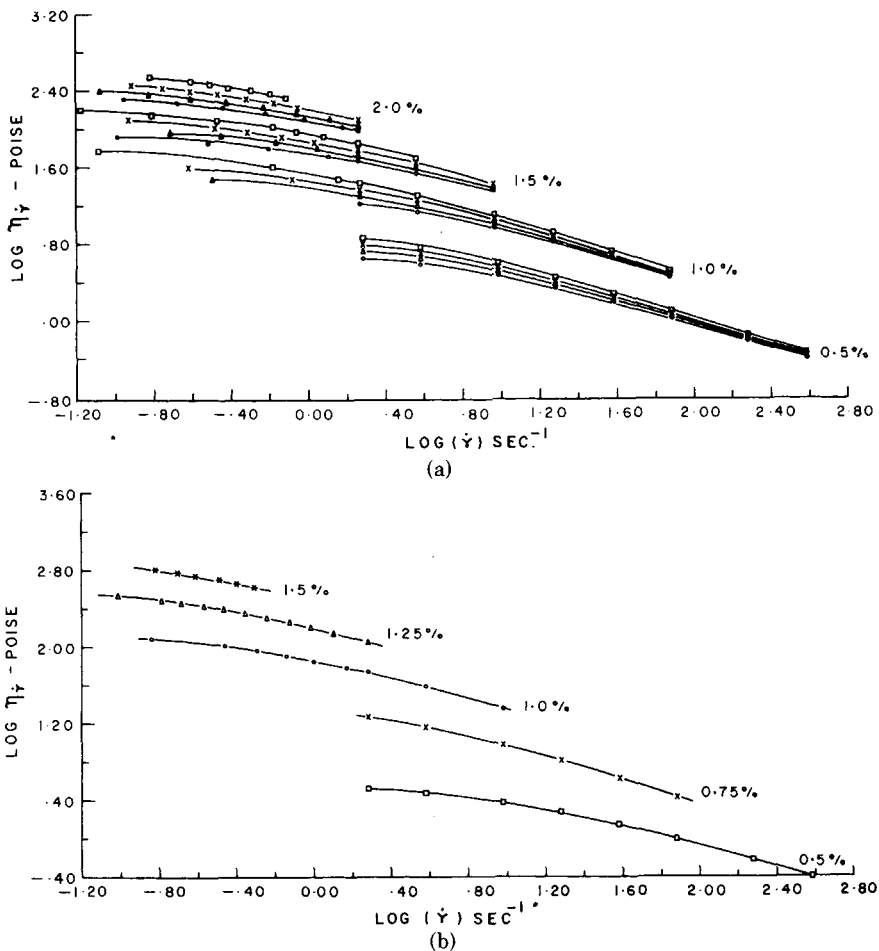


Fig. 1. (a) Sod CM—guar gum III (viscosity vs. shear rate plot) concentration and temperature variation: (\square) 30°C; (\times) 40°C; (Δ) 50°C; and (\circ) 60°C. (b) HP—guar gum I viscosity vs. shear rate (concentration variation).

RESULTS AND DISCUSSION

Viscosity vs. Shear Rate

Flow curves of log viscosity vs. log shear rate ($\log \eta_{\dot{\gamma}}$ vs. $\log \dot{\gamma}$) are pseudoplastic without any yield stress over the range of shear rate studied and show strong shear dependence of the apparent viscosity ($\eta_{\dot{\gamma}}$). According to Graessley's⁵ entanglement theory, the decrease in viscosity with shear rate is viewed as a consequence of the net decrease in entanglement density induced by flow. It is evident from the flow curves [Figs. 1(a), 1(b)] that the transition from Newtonian to pseudoplastic behavior occurs in the low shear rate range and depends on concentration and temperature for a given polymer solution. The transition shifts to higher shear rates as the concentration is decreased or temperature is increased.

The flow of aqueous solutions can be described by equation of state based on Cross⁶ model:

$$\eta_{\dot{\gamma}} = \eta_{\infty} + (\eta_0 - \eta_{\infty}) / [1 + (\lambda \dot{\gamma})^m] \quad (1)$$

At low rates of shear $\eta_\infty \ll \eta_{\dot{\gamma}} < \eta_0$, eq. (1) can be written as

$$\eta_{\dot{\gamma}} = \eta_0/[1 + (\lambda\dot{\gamma})^m]$$

which is equivalent to

$$1/\eta_{\dot{\gamma}} = 1/\eta_0 + (\lambda\dot{\gamma})^m/\eta_0 \quad (2)$$

in its linear form.

All the viscosity-shear rate data obtained for the aqueous solutions of guar gum and substituted guar gums could be fitted satisfactorily to eq. (2), over the concentration and temperature range studied, and their flow properties could be described in terms of the constants of the relationship. The parameters of eq. (2), zero shear rate viscosity (η_0) and relaxation time (λ_0), were calculated using a computerized least-squares curve-fit method.

The relationship between the shear-thinning behavior of a liquid and its viscoelastic properties can be represented by relaxation time (λ_0), defined by the ratio of viscosity and elastic modulus constants at zero shear rate⁷:

$$\lambda_0 = \eta_0/G_0 \quad (3)$$

The above relations provide an excellent method for the evaluation of λ_0 and G_0 from viscosity-shear rate data. These rheological parameters (η_0 , G_0 , and λ_0) are very essential in characterizing the state of network at rest, which is characteristic of a system with unbroken structures. It is more important in the case of concentrated solutions where direct investigation of a highly concentrated solutions by an electron microscope encounters great experimental difficulties. Furthermore, from λ_0 it can be postulated that significant shear thinning will be experienced by any fluid when the applied shear rate approaches the reciprocal of its relaxation time. All these polysaccharide solutions have high viscosity and low elastic modulus, giving relaxation times of the order of 10^{-1} – 10 s over the temperature and concentration ranges studied. Thus, all the solutions show the transition from Newtonian to pseudoplastic at low shear rates [see Figs. 1(a), 1(b)]. Therefore, the study of these polysaccharide solutions in the range of low to moderate shear rates is far more important than the high shear rate range.

Individual flow curves for various temperatures and concentrations can be plotted in terms of reduced variables to yield one single master curve. It has been established^{5,8,9} that the viscosity versus shear rate data for entangling polydisperse polymers conform to a single master curve when log-reduced viscosity is plotted as a function of log-reduced shear rate [$\log(\eta_{\dot{\gamma}}/\eta_0)$ vs. $\log(\dot{\gamma} \cdot \lambda_0)$]. Figures 2(a) and 2(b) show such master curves for unsubstituted and substituted guar gums. Reduced viscosity (η_{red}) shows how greatly the viscosity is affected by structural changes in polymeric systems during flow. The reduced shear rate ($\dot{\gamma}_{\text{red}}$) is a measure of intensity of deformation of network at steady shear flow. The higher the value of $\dot{\gamma}_{\text{red}}$ at a given shear rate, the more intensive is the deformation action on the polymeric system in passing from a state of rest to the given state. Hence, the state of polymers in a steady shear flow regimes can be determined from these master curves. Besides, it greatly simplifies viscosity measurements over a wide range of temperature and shear rate, especially if approximate calculations are acceptable. One could use data obtained at different temperatures to predict viscosity at shear rates which may not be accessible on a particular viscometric system. The polydisperse material deviates

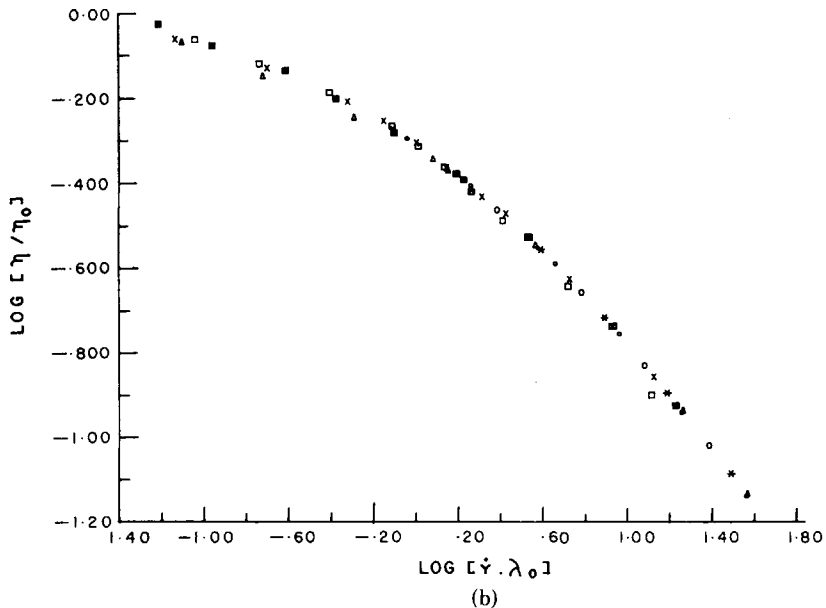
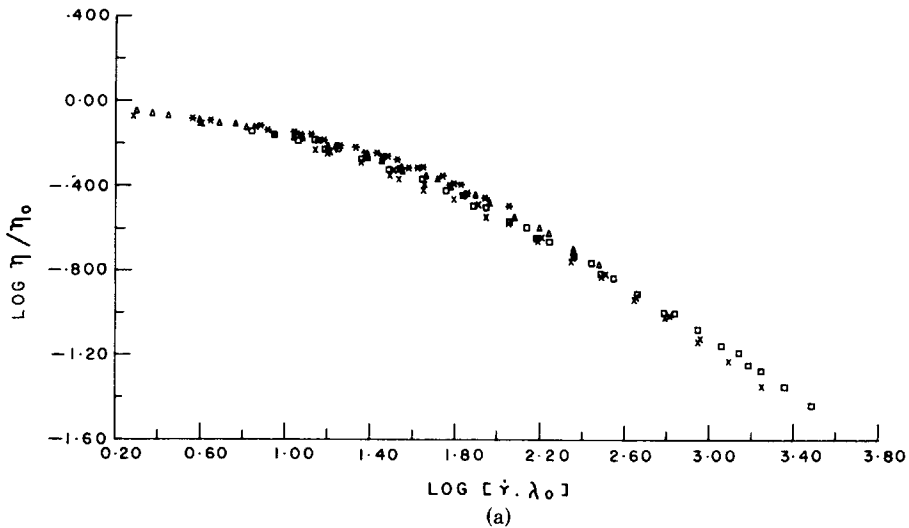


Fig. 2. (a) Sod CM—guar gum III (master curve: temperature and concentration variation) temperatures for each concentration at 30°C, 40°C, 50°C, and 60°C: (\square) 0.5%; (\times) 1.0%; (Δ) 1.5%; (*) 2.0%. (b) Guar gum and substituted guar gums—viscosity vs. shear rate—master curve (1% solution and 30°C temperature): (\square) guar gum; (\times) HP—guar gum I; (\boxtimes) HP—guar gum II; (\circ) HP—guar gum III; (Δ) Na—CM—guar gum I; (\circ) Na—CM—guar gum II; (*) Na—CM—guar gum III.

from Newtonian behavior at a lower shear rate than the more narrow distribution polymer, and shows a more gradual rate of change of viscosity with shear rate. Master curves are useful for comparison of polydispersity and the molecular weight of a given material using viscosity data alone. It is very interesting to note that η_{red} and $\dot{\gamma}_{red}$ data for all the gums studied is falling on single line. From

these master curves it can be concluded that unsubstituted as well as substituted guar gums are all entangling polydisperse polymers and substitution of guar molecules by HP and sod CM groups (short chain branching) under the reaction conditions specified has not affected the molecular weight distribution of the native guar gum. However, the effect of the substituent groups can be seen on the rheological parameters and other polymeric constants.

The Effect of Temperature and Concentration on η_0

The most important parameter characterizing the properties of polymers in fluid state is the zero shear Newtonian viscosity. With increase in temperature, there is a decrease in zero shear viscosity for a given concentration of these polysaccharide solutions. The temperature dependence of η_0 can be expressed by a relation of the form of the Arrhenius equation, which is very much appropriate for Newtonian viscosity:

$$\eta_0 = A \exp(E/RT) \quad (4)$$

where the two constants A and E are characteristic for the material. The preexponential constant A is the viscosity at infinite temperature if no other thermal processes were to occur at higher temperatures. E is a measure of activation energy for viscous flow. Figures 3(a) and 3(b) are based on eq. (4), and the maximum deviation in fitting the data is of the order of $\pm 1\%$ for all the polymer solutions studied. Over the range of concentration studied, first, E is increasing up to certain concentration (approximately up to 1%) and then decreasing almost to a constant value with further increase in concentration. The data are given in Table I. In long chain polymer solutions which form an entanglement network above certain concentration the unit of flow is considerably smaller than the complete independent molecule. In such systems the viscous flow is due to successive mobility of segments of polymeric network from one position to another under the influence of thermal motion. This explains the above findings that, at low concentrations or in the initial stages of network formation where polymer molecules are almost independent, E increases with concentration, and after a certain critical concentration (network solutions) the entanglement density or coupling points between polymer molecules increase with concentration, resulting in a decrease in length of polymer segments of network, and E also decreases. Therefore, in the case of network-forming solutions, E may be suitably termed as the activation energy of viscous flow per mole segment of polymer.

Zero shear viscosity (η_0) also depends on concentration (C) of the polymer in solution. As already demonstrated^{10,11} for linear and high molecular weight polymers, at moderate concentrations, zero shear rate specific viscosity increases as a power of concentration times intrinsic viscosity, $([\eta]C)^a$, beyond a certain critical value of $[\eta]C$. The relation can be expressed as

$$(\eta_0/\eta_{sol}) - 1 = (\eta_{sp})_0 = ([\eta]C)^a$$

or

$$\log (\eta_{sp})_0 = a \log [\eta] + a \log C \quad (5)$$

where $(\eta_{sp})_0$ is the zero shear rate specific viscosity of the solution at a given

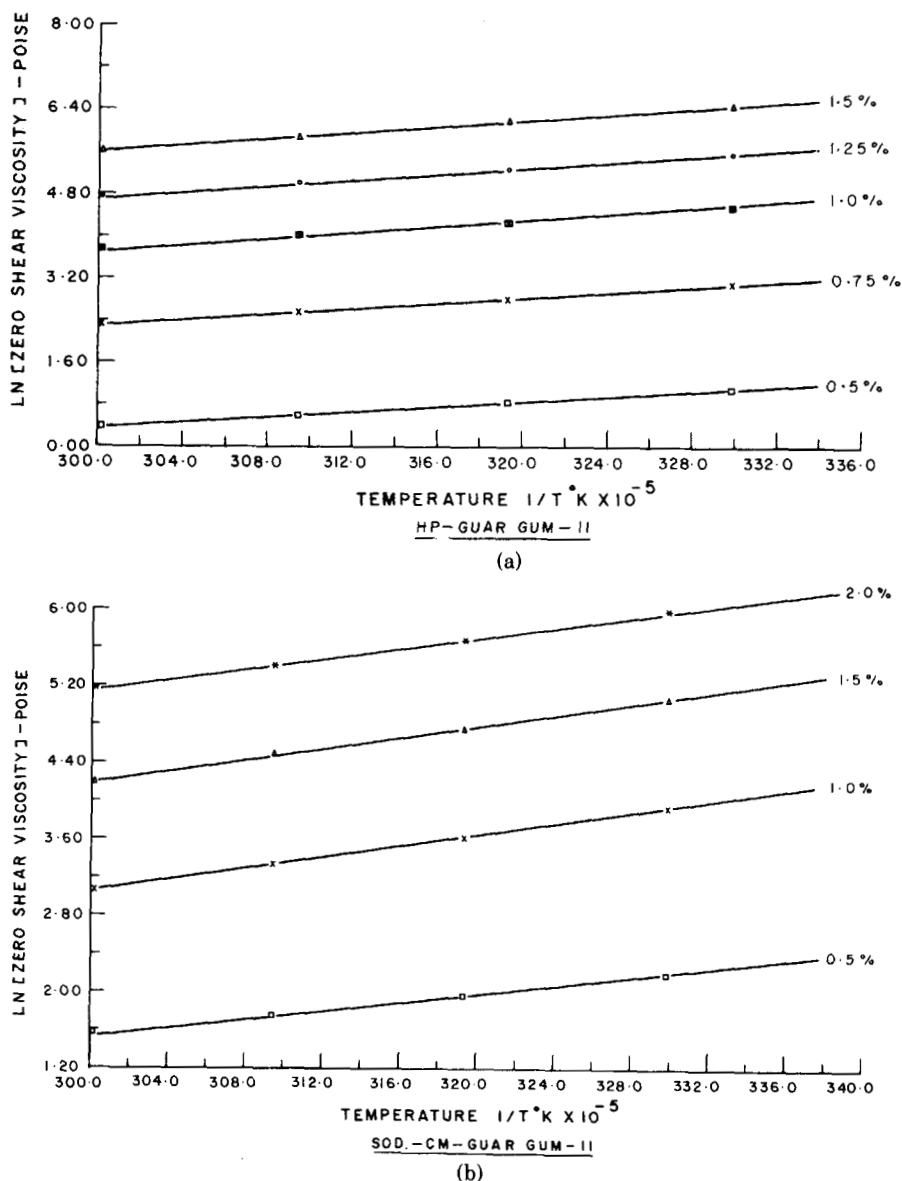


Fig. 3. (a) Effect of temperature on zero shear viscosity (η_0) (at various concentrations). (b) Effect of temperature on zero shear viscosity (η_0) (at various concentrations).

temperature, C is the concentration, $[\eta]$ is the intrinsic viscosity, and the exponent a is the characteristic constant of the given polymer-solvent system, found to be independent of temperature. The above equation (5) fits all the data very well within the limits of $\pm 1.5\%$. Figures 4(a) and 4(b) are based on this equation. The product ($[\eta]C$) is a measure of the average number of polymer molecules whose centers lie within the pervaded volume of any selected molecule in the system.¹⁰ From intrinsic viscosity values weight average degree of polymerization (\overline{DP}_w) and corresponding molecular weight (\overline{M}_w) for guar gum are calculated using the Mark-Houwink relationship¹¹:

$$[\eta] = 0.168 \overline{DP}_w^{0.98} \quad (6)$$

TABLE I
 Activation Energy of Viscous Flow for Guar Gum and Its Derivatives in Aqueous Solution. Variation with Concentration.
E Values: (kcal/mol Segment of Polymer)

Concn (g/dL)	HP—guar gums			Guar gum	Sod CM—guar gums		
	III (0.83) ^a	II (0.53)	I (0.26)		I (0.57)	II (0.93)	III (1.21)
0.50	4.773	4.816	5.137	6.558	3.934	4.232	4.631
0.75	5.403	5.459	5.858	8.063	—	—	—
1.00	5.580	5.811	6.306	9.350	5.372	5.783	6.050
1.25	5.388	5.380	5.604	6.552	—	—	—
1.50	5.380	5.315	5.644	6.342	5.260	5.670	4.674
2.00	—	—	—	—	5.512	5.470	4.611

^a Figures in parenthesis indicate ms or ds of respective samples.

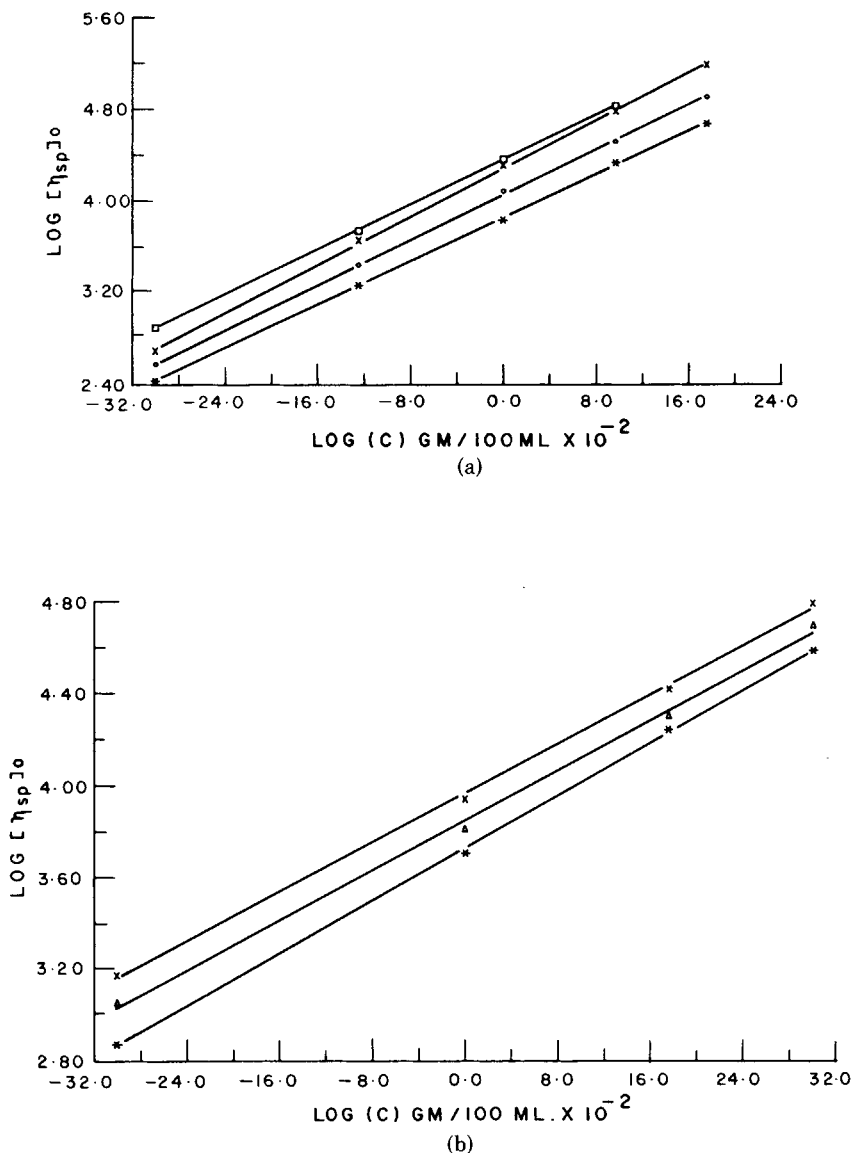


Fig. 4. (a) Guar gum and HP—guar gums: viscosity vs. concentration plot (temperature 30°C). (□) Guar gum; (X) HP—guar gum I (0.26); (O) HP—guar gum II (0.53); (*) HP—guar gum III (0.83). (b) Sod CM—guar gums: viscosity vs. concentration plot (temperature 30°C). (X) Na—CM—guar gum III (1.21); (Δ) Na—CM—guar gum II (0.93); (*) Na—CM—guar gum I (0.57).

The calculated molecular weight of unsubstituted guar gum ($\bar{M}_w = 10.001 \times 10^5$), using the above relation, is in good agreement with the reported values,¹²⁻¹⁶ giving a good support to the physical meaning of the parameters of eq. (5). The parameters of eq. (5) are listed in Table II. The exponent a is about 5 for guar gum and HP—guar gums and about 3 for sod CM—guar gums. The variations in the values of the exponent a and $[\eta]$ with degree of substitution of guar gum can be seen from the Table II.

TABLE II
 Characteristic Constants of Guar Gum and Substituted Guar Gums in Aqueous Solutions [Based on eqs. (5), (7) and (8)]: Effect of Substitution

Const	HP-guar gums		Guar gum	Sod CM-guar gums	
	III (0.83) ^a	I (0.26) II (0.53)		I (0.57)	II (0.93) III (1.21)
"a"	4.674	4.833	4.886	3.05	2.716
[η] (dL/g)	6.543	6.723	7.856	16.90	26.120
β_2	0.156	0.158	0.162	0.177	0.202
α_2	1.620	-0.911	-2.386	-4.661	-7.557
$\alpha_2 \times 10^{-2}$	3.720	3.457	3.945	4.789	5.716

^a Legend as in Table I.

Relationship between η_0 and λ_0

According to the polymer network (entanglement) theories, the zero shear rate relaxation time (λ_0) depends on zero shear rate viscosity (η_0), polymer concentration (C), molecular weight (M), and temperature (T). The relation between η_0 and λ_0 can be given by an empirical semilogarithmic equation

$$\ln (\eta_{\text{rel}})_0 = \alpha_2(\lambda_0)^{\beta_2} \quad (7)$$

where α_2 and β_2 are constants for a given polymer. It is found that β_2 is independent of temperature, while α_2 is a linear function of temperature (T), expressed as

$$\alpha_2 = \alpha'_2(T) - \alpha''_2 \quad (8)$$

Hence, one may write eq. (7) as

$$\ln (\eta_{\text{rel}})_0 = [\alpha'_2(T) - \alpha''_2](\lambda_0)^{\beta_2} \quad (9)$$

Figures 5(a), 5(b), and 6 are based on eqs. (7) and (8) respectively. The maximum error in fitting the data is of the order of $\pm 0.8\%$. Table II gives the values of constants of eq. (9) for all the polymers.

Effect of Temperature and Concentration on λ_0

As already demonstrated,^{5,8} λ_0 depends on η_0 , C , M , and T . One may expect the effect of temperature and concentration on λ_0 will be similar to the effect of these two parameters on η_0 as these two rheological parameters are related by an empirical equation (7) shown above. Relaxation time (λ_0) was found to be decreasing exponentially with increasing temperature. Concentration effects λ_0 , primarily through the concentration dependence of η_0 , which, in the concentration range usually studied, is of the order of C^3 – C^5 .

The Effect of Substitution or Branching

The effect of introduction of hydrophobic (hydroxypropyl) and hydrophilic (sodium carboxymethyl) groups onto guar molecules can be judged from the rheological parameters and other polymeric constants listed in Tables II and III. The zero shear rate viscosity (η_0) and relaxation time (λ_0) values of HP—guar gums are lower for a given concentration than the values of unsubstituted guar gum, and the decrease is more with increasing molar substitution of hydroxypropyl groups. At lower concentrations, η_0 and λ_0 values of sod CM—guar gums are higher than the unsubstituted guar gum, but, at higher concentrations, the reverse is true. This can be due to electroviscous effect of polyelectrolytes. As already stated, introduction of both types of functional groups (short-chain branching) has no effect on the molecular weight distribution of guar gum.

The values of some of the constants listed in Table II show a definite trend, either decreasing or increasing, with the type and amount of these functional groups introduced on to the guar molecules.

Equations (4), (5), and (9), though empirical, give key relationships. Once the constants of these equations are established for a given type of polysaccharide of known substitution, using the constants and respective equations and with the help of master curves, the flow properties as well as the effect of parameters, like temperature and concentration, in aqueous solutions can be determined.

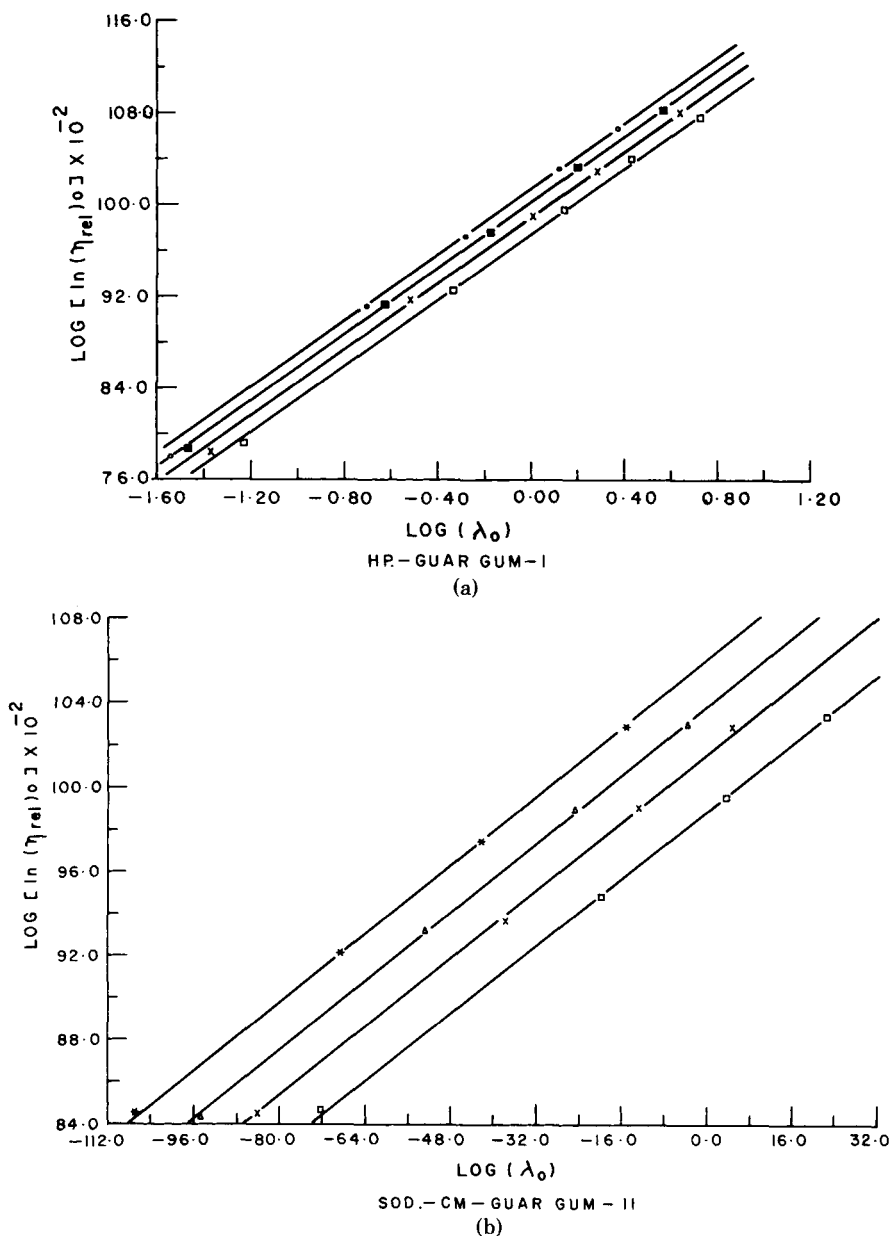


Fig. 5. (a) Relation between zero shear relative viscosity $(\eta_{\text{rel}})_0$ and relaxation time (λ_0) (temperature variation): (\square) 30°C; (\times) 40°C; (\blacksquare) 50°C; (\circ) 60°C. (b) Relation between zero shear relative viscosity $(\eta_{\text{rel}})_0$ and relaxation time (λ_0) (temperature variation): (\square) 30°C; (\times) 40°C; (Δ) 50°C; ($*$) 60°C.

CONCLUSIONS

The study confirms that aqueous solutions of hydroxypropyl- and sodium carboxymethyl-guar gums, like unsubstituted guar gum, show a high degree of pseudoplasticity. Even at low concentrations all these polysaccharides form

TABLE III
Rheological Parameters of Guar Gum and Substituted Guar Gums in Aqueous Solutions (Temperature 30°C): Effect of Substitution

Rheological parameter	Concn (gm/dL)	HP—guar gums			Guar gum	Sod CM—guar gums		
		III (0.83) ^a	II (0.53)	I (0.26)		I (0.57)	II (0.93)	III (1.21)
η_0 (poise)	0.50	2.164	2.971	3.897	6.284	9.053	12.03	
	0.75	14.700	22.040	36.350	43.876	—	—	—
	1.00	44.150	95.120	160.900	183.570	36.940	51.580	70.18
	1.25	170.990	261.300	471.100	538.010	—	—	—
	1.50	375.980	643.700	1219.000	—	139.600	160.300	187.20
	2.00	—	—	—	—	433.200	403.100	493.34
λ_0 (s)	0.50	0.035	0.044	0.059	0.159	0.190	0.29	
	0.75	0.214	0.292	0.464	0.525	—	—	—
	1.00	0.476	0.892	1.390	1.365	0.405	0.635	0.964
	1.25	1.309	1.603	2.692	2.415	—	—	—
	1.50	2.011	3.248	5.280	—	0.859	1.086	1.207
	2.00	—	—	—	—	1.863	1.685	2.058

^a Legend as in Table I.

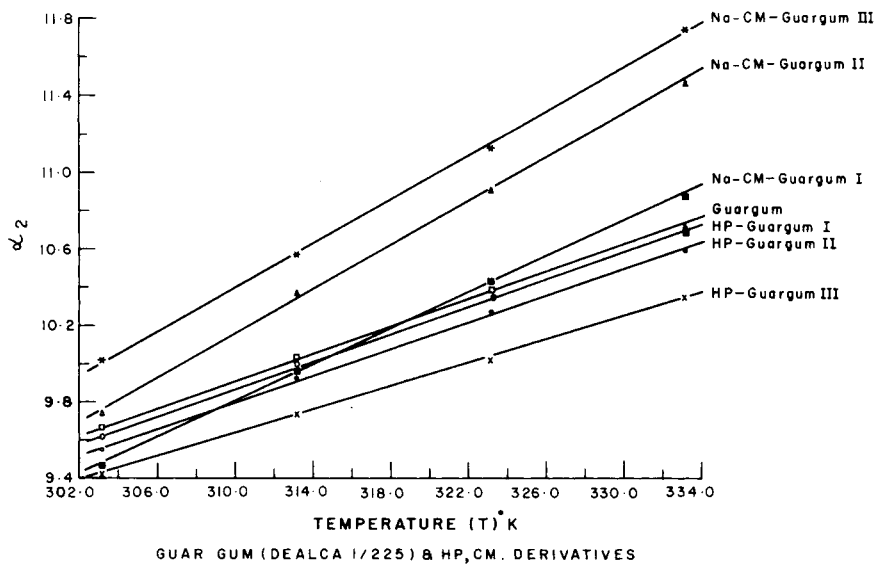


Fig. 6. Variation of α_2 with temperature (effect of substituent).

entanglement network type solutions. Master curves along with the Cross equation give a rather good method of deducing the rheological properties of a given polymer using viscosity data alone.

The activation energy of viscous flow corresponds to activation energy of viscous flow per mole segment of polymer rather than per mole polymer.

The effect of temperature and concentration on rheological parameters is in agreement with the behavior of typical network type solutions.

For a given narrow range of m s or d s of any type of polysaccharide, using empirical equations and polymer constants, the flow curves and the effect on these of parameters like temperature and concentration can be determined to a fairly good approximation.

Introduction of short-chain branches like hydroxypropyl and sodium carboxymethyl groups onto guar molecules has no effect on molecular weight distribution, but rheological parameters (η_0 , λ_0) and polymeric constants are altered, depending on the nature and extent of substituent.

The authors are grateful to the Management of IDL Chemicals Ltd. for granting them permission to publish this paper. One of the authors (S.V.) wishes to thank the Management for sponsoring him in the Ph.D. program. Also, the authors are thankful to Professor T. Navaneetha Rao for useful discussions.

References

1. James K. Seaman, "Guar Gum," in *Handbook of Water Soluble Gums and Resins*, Robert L. Davidson, Ed., McGraw-Hill, New York, 1980.
2. (a) *Methods in Carbohydrate Chemistry*, R. L. Whistler, Ed., Academic, New York, 1963, Vol. III, pp. 309. (b) Schwarz Guenther W. G., *Z. Analyt. Chem.*, **271**(1), 31 (1974).
3. (a) *Methods in Carbohydrate Chemistry*, R. L. Whistler, Ed., Academic, New York, 1963, Vol. III, pp. 325; (b) *Standard Methods of Chemical Analysis—III, B*, F. J. Welcher, Ed., Van Nostrand, New York, 1966, pp. 1815.
4. T. C. Patton, *J. Paint Technol.*, **38**(502), 656 (1966).

5. W. W. Graessley, *J. Chem. Phys.*, **43**(8), 2696 (1965); **47**(6), 1942(1967).
6. M. M. Cross, *J. Colloid Sci.*, **20**, 417 (1965); *Eur. Polym. J.*, **2**, 299 (1966).
7. M. M. Cross, *Rheol. Acta*, **18**, 609 (1979).
8. F. Bueche, *J. Appl. Phys.*, **30**, 1114 (1959).
9. S. Middleman, *The Flow of High Polymers*, Wiley-Interscience, New York, 1968.
10. W. W. Graessley, *Macromolecules*, **9**(1), 127 (1976).
11. J. L. Doublier and B. Launay, *Proceedings of the Seventh International Congress on Rheology*, C. Klason and J. Kubat, Eds., 1976, pp. 532.
12. S. K. Deb and S. N. Mukherjee, *Ind. J. Chem.*, **1**(10), 413 (1963).
13. D. A. Hui and H. Neukom, *Tappi*, **47**, 39 (1963).
14. I. C. M. Dea and A. Morrison, *Advan. Carbohyd. Chem.*, **31**, 241 (1975).
15. W. R. Sharman, E. L. Richards, and G. N. Malcom, *Bipolymers*, **17**, 2817 (1978).
16. H. G. Barth and D. A. Smith, *J. Chromatogr.*, **206**(2), 410 (1981).

Received June 26, 1981

Accepted September 30, 1981