

Viscous Properties of Polymer-Thickened Water-in-Oil Emulsions

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SYNOPSIS

The viscous flow properties of polymer-thickened water-in-oil emulsions were measured using a coaxial cylinder viscometer. The emulsions were prepared using deionized water and polyisobutylene in oil solutions. Three different molecular weight polyisobutylenes (Vistanex MML-140, Vistanex MML-100, and Vistanex MML-80) were studied. The effects of polymer concentration and water (droplet) concentration on the flow properties were determined. The polymer concentration varied from 0 to 3.96% by weight based on the oil phase whereas the water concentration varied from 0 to 80% by volume (based on total emulsion volume). The polymer solutions behaved like non-Newtonian Ellis model fluids. At low water concentrations, the flow curves for emulsions were similar to their suspending medium (polymer solution). At high values of water concentration, emulsions clearly exhibited a yield stress. The yield stress increased with both water and polymer concentrations. The shear stress/shear rate data for the emulsions possessing a yield stress were described adequately by a modified Herschel-Bulkley model. A comparison was also made of the relative viscosities of emulsions having different polymer concentrations. The relative viscosities for polymer-thickened emulsions were found to be significantly lower than the corresponding values for emulsions without polymer. The correlation of relative viscosity/concentration data is discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Emulsions are a class of disperse systems consisting of two immiscible liquids, one is the disperse phase and the other is the continuous phase (also referred to as external phase, dispersion medium, or suspending medium). There are two types of emulsions: oil droplets dispersed in aqueous phase, designated as O/W; and water droplets dispersed in oil phase, designated as W/O.

The applications of emulsions are numerous. Many industrial products of commercial importance are encountered or handled in the form of emulsions. Books have been written describing the applications of emulsion systems.¹⁻⁴ Some of the industries where emulsions are of considerable importance are: paint, food, polymer, petroleum, cosmetic, pharmaceutical, agriculture, textile, paper, leather, polish, and printing.

In several emulsion applications, the suspending medium of the emulsions contain a polymer. For example, polymeric thickening agents are often added to the external phase of the emulsions to increase the viscosity. An increase in the viscosity of the external phase reduces the "creaming" or sedimentation rate of dispersed droplets (oil or water depending upon the type of emulsion) and hence leads to an improved emulsion stability.

In the handling, mixing, storage, and transportation of emulsions, knowledge of the rheological properties is required for the design, selection, and operation of the equipment involved. While extensive literature is available on the flow behaviour of emulsions in Newtonian suspending media, such as dilute surfactant solutions,⁵⁻¹⁰ little work has been reported on the rheological properties of emulsions in which the suspending medium is a non-Newtonian polymeric fluid. To our knowledge, the only studies published on rheology of emulsions in non-Newtonian polymeric fluid are those of Pal¹¹⁻¹³ and Han and King.¹⁴ However, it should be pointed out

that a large body of published information is available on the rheology of suspensions of solid particles in non-Newtonian polymeric media.¹⁵⁻²³

In our earlier work, we studied the rheology of polymer-thickened oil-in-water emulsions (polymer was incorporated in the external aqueous phase). The polymers investigated were Carbopol-940, sodium carboxymethyl cellulose, and poly(ethyleneoxide) resins, respectively. Carbopol-940 caused severe flocculation of oil droplets and consequently, emulsions exhibited yield-stress and shear-thinning behaviour.¹¹ The mechanism of flocculation of oil droplets (hence yield stress) was reasoned to be the bridging of oil droplets by the polymer. Sodium carboxymethyl cellulose and poly(ethyleneoxide) resins behaved more like neutral species in that they did not cause any bridging or flocculation of oil droplets but they imparted high viscosity and shear-thinning behaviour to the emulsions. While the flow curves for these polymer-thickened emulsions were similar in shape to the flow curves of the respective suspending mediums (polymer solutions), their relative viscosities were found to be significantly lower than those of the emulsions without polymer. The lowering of relative viscosity in polymer-thickened emulsions was explained in terms of an increase in the viscosity ratio η_c/η_d where η_c is the viscosity of the polymer-thickened continuous medium and η_d is the viscosity of the dispersed oil. An increase in the viscosity ratio enhances the internal circulation effect that leads to a decrease in the relative viscosity. Based on this reasoning and the experimental results, a new equation¹³ was proposed to describe the relative viscosity versus dispersed-phase concentration behaviour of polymer-thickened emulsions. The equation is given by:

$$\ln \eta_r = \left[\frac{1 + 0.4(\eta_c/\eta_d)}{1 + (\eta_c/\eta_d)} \right] \left(\frac{2.5\phi}{1 - K\phi} \right). \quad (1)$$

Here η_r is the relative viscosity (ratio of emulsion viscosity to suspending medium viscosity, both evaluated at the same shear rate), η_c is the continuous phase viscosity (at a given shear rate), η_d is the dispersed-phase viscosity, ϕ is the volume fraction of the dispersed-phase and K is a parameter that depends on the shear rate. This equation reduces to the classical Taylor equation²⁴ in the limit of dilute concentration:

$$\eta_r = 1 + 2.5 \left[\frac{1 + 0.4(\eta_c/\eta_d)}{1 + (\eta_c/\eta_d)} \right] \phi. \quad (2)$$

For small values of (η_c/η_d) , eq. (2) reduces to the well known Einstein equation²⁵ whereas eq. (1) becomes the Mooney equation.²⁶

In the present communication, we report new results for polymer-thickened emulsions. The emulsions studied are the W/O type as opposed to the O/W type investigated earlier.¹¹⁻¹³ We believe this is the first study on the rheology of polymer-thickened W/O emulsions. The polymers studied are high molecular weight polyisobutylenes. Polyisobutylenes are elastomeric polymers used quite widely in the manufacture of adhesives, sealants, and coatings. These polymers are also used as viscosity-index modifiers for lubricants. When dissolved in organic solvents and oils, polyisobutylenes are known to impart drag reduction characteristics to the fluids.²⁷

EXPERIMENTAL

Materials

The emulsions were prepared using a petroleum oil (EDM oil) supplied by Monarch Oil Company. The oil has a viscosity of 6.4 mPa s at 23.5°C. The water used throughout the experiments was deionized. The surfactant used was Emsorb 2500 (sorbitan monooleate). Emsorb 2500 is a commercially available nonionic surfactant supplied by Henkel Corporation, Emery Group. The hydrophile-lipophile Balance (HLB) value of this surfactant is 4.6.

As mentioned earlier, the polymers used were three different molecular weight polyisobutylenes. These polymers are available commercially from Exxon chemical company under the trade name of Vistanex. We studied Vistanex MML-140, Vistanex MML-100, and Vistanex MML-80. The reported molecular weights (viscosity average) of these polymers are $(2.11 \pm 0.23) \times 10^6$, $(1.25 \pm 0.19) \times 10^6$ and $(0.90 \pm 0.15) \times 10^6$, respectively.

Procedure

The polymer solutions were prepared in the following manner: a known weight of shredded polymer was added into a known amount of agitated oil. A variable speed homogenizer (Gifford-Wood Model 1-LV) was used to provide the necessary agitation and mixing of the fluid. The agitation was continued until the polymer was dissolved completely and the solution was lump-free. The required amount of the surfactant ($\sim 1\%$ by weight Emsorb 2500) was then added to the polymer solution; the surfactant dissolved readily with gentle agitation.

Table I Dimensions of Bob and Rotor Combinations

Rotor Type	Bob Type	Rotor Inner Radius (cm)	Bob Outer Radius (cm)	Height of Bob (cm)	Gap Width (cm)
R1	B1	1.8415	1.7245	3.8	0.117
R1	B2	1.8415	1.2276	3.8	0.6139
R1	B3	1.8415	0.8622	3.8	0.9793
R1	B4	1.8415	0.8622	1.9	0.9793

The emulsions of water-in-oil type were prepared in batches of approximately 350 mL. The known amounts of deionized water and nonaqueous polymer solution (containing 1% by weight surfactant) were sheared together in a homogenizer for about 3 min at a fixed speed. The emulsions produced were quite stable with respect to coalescence.

The rheological measurements were made at a constant temperature of $23.5 \pm 1^\circ\text{C}$ using two coaxial cylinder viscometers having different torsion springs. In these viscometers, the outer cylinder (rotor) was rotated at a given speed and the torque on the inner stationary cylinder (bob) was measured. In order to cover a wide range of shear rates, the data were collected using different combinations of bob and rotor systems. Table I gives the relevant dimensions of the bob and rotor combinations used in the measurements. Since the fluids studied in the present work were non-Newtonian, the shear rates were calculated according to the method recommended in the literature.²⁸

RESULTS AND DISCUSSION

Flow Behaviour of Polymer Solutions

Figure 1 shows the flow curves for polyisobutylene (grade Vistanex MML-140) solutions in oil at polymer concentrations of 0, 1.98, and 3.96% by weight, respectively. In the absence of a polymer, the oil (containing 1% by weight Emsorb 2500) behaves as a Newtonian fluid. The addition of polymer to the oil phase results in an increase in the viscosity. Also, the polymer solutions are Newtonian only in the low shear-stress range; in the high shear-stress range, they exhibit shear-thinning behaviour.

The flow curves for the polymer solutions can be described adequately by the well-known Ellis model²⁹:

$$\eta = \frac{\eta_0}{1 + A\eta_0\tau^{\alpha-1}} \quad (3)$$

where η is the apparent viscosity at a given shear stress τ , η_0 is the zero shear viscosity, and A and α are constants. The solid curves shown in Figure 1 are plots of the Ellis model. The Ellis model parameters for the polymer solutions are summarized in Table II.

Figure 2 shows the plot of zero shear viscosity for Vistanex MML-140 solutions in oil as a function of polymer concentration (percent by weight). The viscosity of polymer solutions increases exponentially with an increase in the polymer concentration.

Figure 3 compares the flow curves for polymer/oil solutions prepared from different molecular weight polyisobutylenes (polymer concentration is kept constant). The data are shown for Vistanex MML-140 and Vistanex MML-80, respectively. Clearly, the viscosity of the polymer solution increases with an increase in the molecular weight of the polymer (Vistanex MML-140 has higher molecular weight). The solid curves shown in Figure 3 are plots of the Ellis model. The viscosity data for Vistanex MML-100 solution (not shown in Fig. 3), fell in between the data for Vistanex MML-140 and

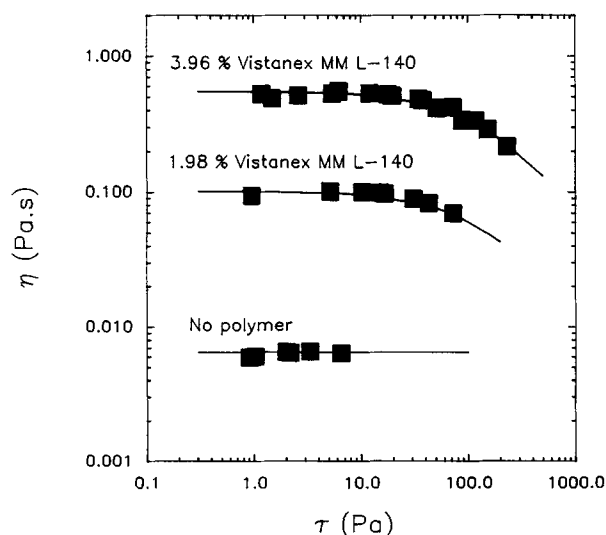

Figure 1 Flow curves for polyisobutylene solutions in oil.

Table II Ellis Model Parameters for Various Polymer Solutions

Polymer Type	Polymer Concentration (% by Weight)	η_0 (Pa s)	α	A $\text{Pa}^{-\alpha} \text{s}^{-1}$
Vistanex MML-140	1.98	0.10	2	6.81×10^{-2}
Vistanex MML-140	3.96	0.55	2	1.16×10^{-2}
Vistanex MML-100	3.96	0.46	2	1.12×10^{-2}
Vistanex MML-80	3.96	0.33	2	1.21×10^{-2}

The polymer solutions contain 1% by weight Emsorb 2500. The viscosity of oil-surfactant solution (without polymer) is 6.45 mPa s.

Vistanex MML-80 solutions. This is to be expected since the molecular weight of Vistanex MML-100 lies between the other two polymers.

Flow Behaviour of Water-In-Oil Emulsions Without Polymer

The study of the rheological behaviour of water-in-oil emulsions, without the presence of a polymer, was necessary for comparison purposes. Eight differently concentrated emulsions were prepared having water concentrations of 10, 20, 30, 40, 50, 60, 70, and 80% by volume. The continuous-phase of these emulsions consisted of 1% by weight Emsorb 2500 solution in oil. The emulsions produced were poly-disperse with respect to droplet size, as indicated by microscopic observations of the emulsion samples. The droplet size ranged from about 1 to 50 μm . At a very high water concentration of 80% by volume, few droplets as large as 120 μm were observed.

Figure 4 shows the flow curves for water-in-oil

emulsions without polymer. The emulsions are Newtonian at low water concentrations of 10, 20, and 30% by volume. At higher dispersed-phase concentrations, emulsions are non-Newtonian. The non-Newtonian emulsions follow a power-law model up to a water concentration of 70% by volume:

$$\tau = K_p \dot{\gamma}^n \quad (4a)$$

or,

$$\eta = \tau / \dot{\gamma} = K_p^{1/n} \tau^{(n-1)/n}. \quad (4b)$$

Here $\dot{\gamma}$ is the shear-rate, K_p and n are power-law parameters. According to eq. (4b), η versus τ is linear (on a log-log scale) as observed experimentally. At a very high water concentration of 80% by volume, the emulsion clearly has a yield stress; the data for this emulsion are described adequately by a Herschel-Bulkley model,³⁰ shown as the solid curve in Figure 4:

$$\tau = \tau_0 + K_h \dot{\gamma}^n \quad (5)$$

where τ_0 is yield stress and K_h is Herschel-Bulkley parameter. The power-law parameters and the Herschel-Bulkley model parameters for emulsions are summarized in Table III.

The shear-thinning behaviour observed in the present emulsions can be explained in terms of flocculation-deflocculation of dispersed water droplets. The photomicrographs of the emulsion samples (refer to Fig. 5) clearly indicated the aggregation tendency of the water droplets. The photomicrographs were taken using a Zeiss microscope equipped with a camera. The emulsion sample was diluted before taking the photomicrographs. The dilution was carried out with the dispersion medium of the emulsion. Note that even though the emulsion samples were diluted, aggregation of droplets still occurred when the droplets settled at the bottom of the sample slide. The decrease in apparent viscosity with an increase

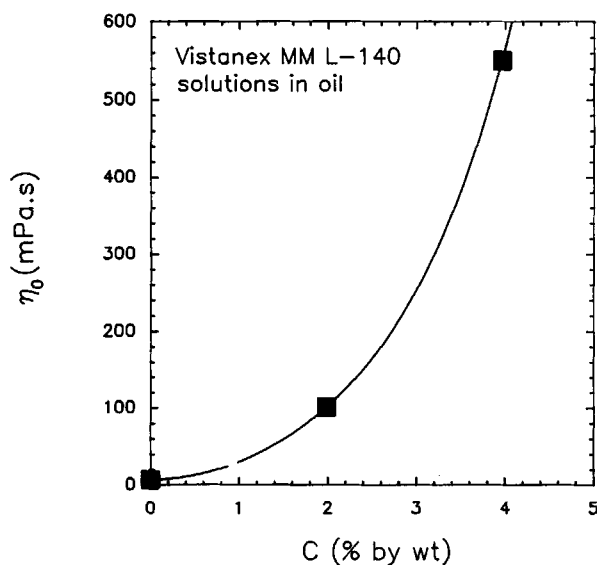


Figure 2 Zero shear viscosity of polyisobutylene solutions as a function of polymer concentration.

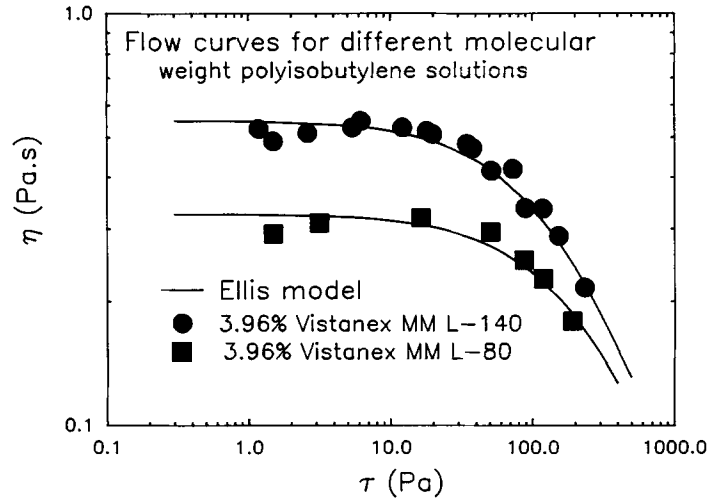


Figure 3 Flow curves for different molecular weight polyisobutylene solutions in oil (polymer concentration, 3.96% by weight).

in the shear stress is probably caused by progressive breakdown of flocs of dispersed droplets.

Flow Behaviour of Polymer-Thickened Water-In-Oil Emulsions

The flow curves for water-in-oil emulsions prepared from non-Newtonian polymeric suspending mediums are plotted in Figures 6 and 7. The polymeric suspending mediums are 1.98 and 3.96% by weight Vistanex MML-140 solutions in oil, respectively. For a given suspending medium, the water concentration

is varied over a wide range of 0–70% by volume. Like the previous emulsions (without polymer), the present emulsions were polydisperse with respect to droplet size, ranging from about 1 to 25 μm (see Fig. 8 for comparison of droplet-size distributions).

The flow curves for the emulsions are similar to their suspending mediums only at low values of water concentration (up to 20% by volume); the suspending mediums and the less concentrated emulsions exhibit two distinct regions: the Lower Newtonian region in the low shear-stress range where the viscosity is constant, and the shear-thinning region in the high shear-stress range where the viscosity decreases with the increase in the shear stress. At high dispersed-phase concentrations, emulsions clearly have a yield stress; the apparent viscosity/shear stress curves bend upward indicating the presence of a yield stress. The yield stress increases

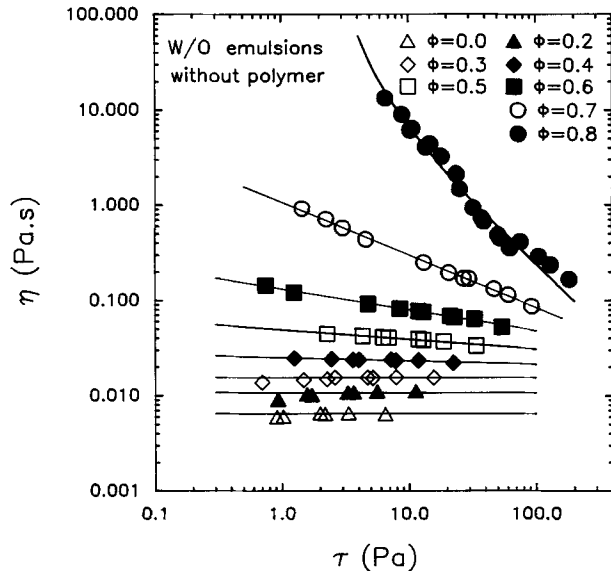


Figure 4 Flow curves for water-in-oil emulsions without polymer.

Table III Herschel–Bulkley and Power-Law Parameters for Emulsions Without Polymer

ϕ	τ_0 (Pa)	K_p or K_h (Pa s ⁿ)	n	Comments
0	0	6.45×10^{-3}	1	Newtonian
0.10	0	8.11×10^{-3}	1	Newtonian
0.20	0	10.66×10^{-3}	1	Newtonian
0.30	0	15.38×10^{-3}	1	Newtonian
0.40	0	28.06×10^{-3}	0.97	Power law
0.50	0	64.72×10^{-3}	0.91	Power law
0.60	0	189.9×10^{-3}	0.82	Power law
0.70	0	1040×10^{-3}	0.64	Power law
0.80	2	6673×10^{-3}	0.44	Yield stress

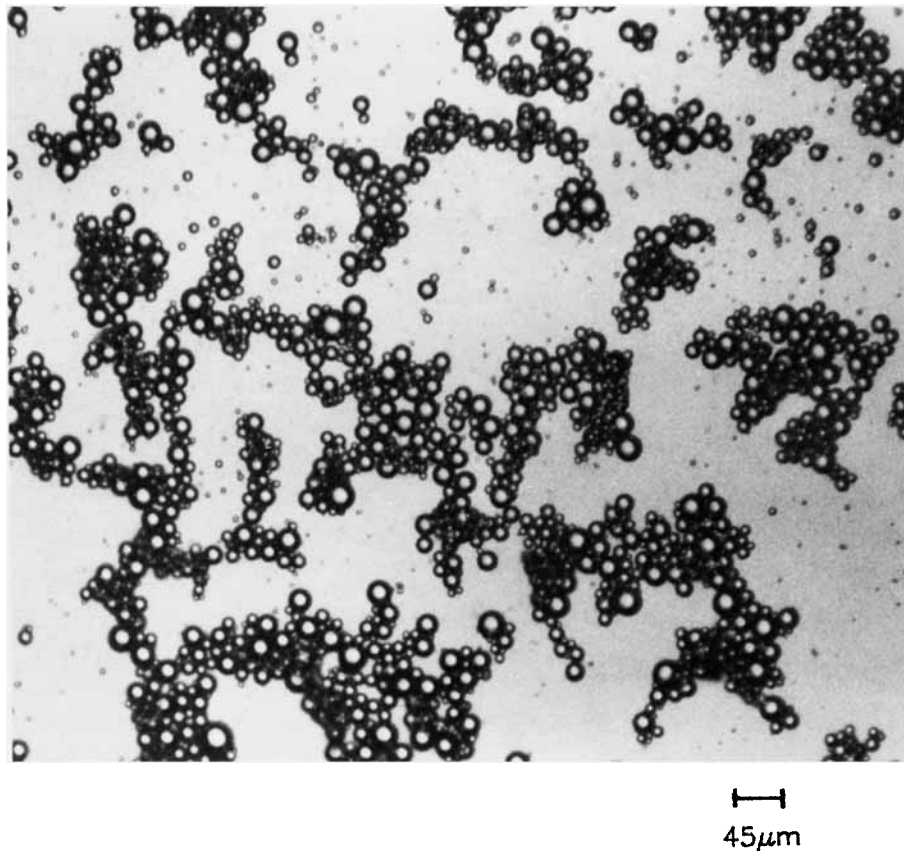


Figure 5 Photomicrograph of an emulsion sample (50% water-in-oil emulsion without polymer).

with an increase in the dispersed-phase concentration. It should be pointed out that in our earlier studies on polymer-thickened oil-in-water emulsions (thickened by sodium carboxymethyl cellulose and polyethylene-oxide resins, respectively), we did not observe any yield stress; the flow curves for the emulsions were similar to their suspending mediums over the full range of shear stress.

The presence of a yield stress in emulsions is indicative of the formation of a three-dimensional structure under no-flow conditions. As the shear stress in the fluid sample is increased, the structure responsible for the yield stress suffers breakdown and consequently, the flow curves for the emulsions become similar to the polymer solution alone at high values of shear stress. The structure in emulsions may form due to flocculation of dispersed water droplets and perhaps due to weak bridging of water droplets by the polymer molecules.

It may be appropriate to mention here that all our rheological measurements were free of any "wall-effects." The data obtained using different gap-width bob and rotor systems were in excellent agreement

indicating the absence of wall-effects; as an example, Figure 9 shows the data for 50% water-in-oil emulsions collected using different gap-width systems. Indeed, the data show excellent agreement.

In order to further analyze the experimental data for polymer-thickened water-in-oil emulsions, we attempted to fit the data (shear stress/shear rate) using two well-known models: the Herschel-Bulkley model³⁰ and the Casson model.³¹ These models are used widely to describe the shear stress/shear rate behaviour of dispersed-systems possessing a yield stress. The Herschel-Bulkley model is given by eq. (5); the Casson model is given by:

$$\tau^{1/2} = \tau_0^{1/2} + K_c \dot{\gamma}^{1/2} \quad (6)$$

where K_c is the Casson parameter. Both these models were unsuccessful in correlating the data for the present polymer-thickened water-in-oil emulsions. However, modified form of these models, which accounted for the non-Newtonian behaviour of the suspending mediums, were successful. In particular, the modified Herschel-Bulkley model was excellent

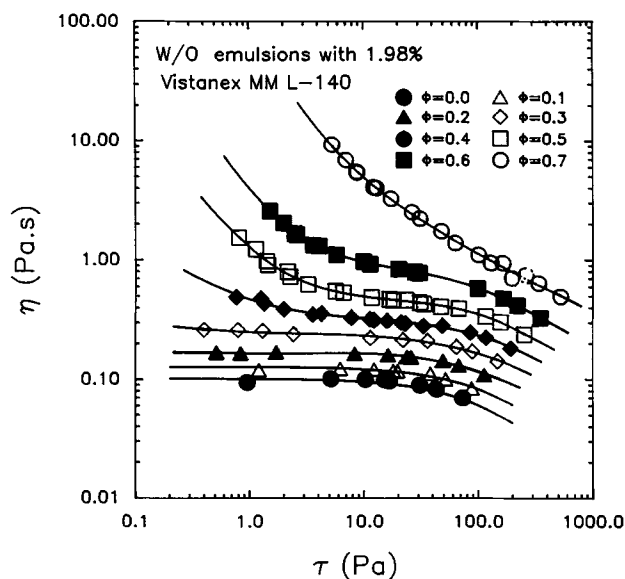


Figure 6 Flow curves for polymer-thickened W/O emulsions (polymer concentration, 1.98% by weight based on oil phase).

in describing the shear stress/shear rate behaviour of the emulsions. The modified models are given by:

$$\text{Herschel-Bulkley: } \tau = \tau_0 + K_h(\dot{\gamma}\eta/\eta_0)^n \quad (7)$$

$$\text{Casson: } \tau^{1/2} = \tau_0^{1/2} + K_c(\dot{\gamma}\eta/\eta_0)^{1/2}. \quad (8)$$

Here η is the viscosity of the suspending medium at a given shear rate and η_0 is the zero shear rate vis-

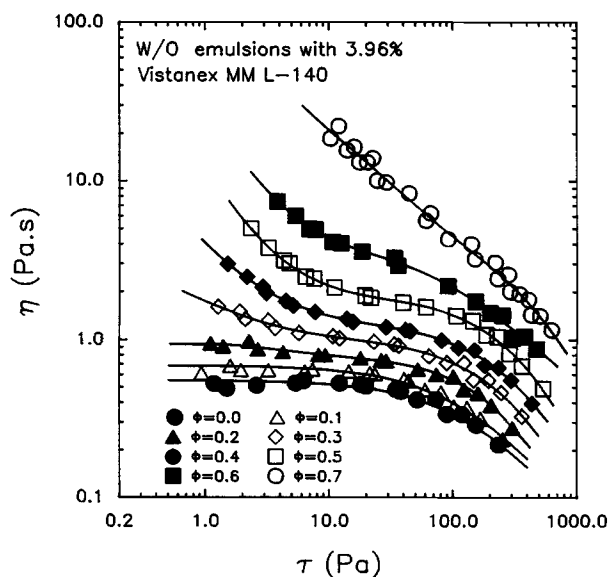


Figure 7 Flow curves for polymer-thickened W/O emulsions (polymer concentration, 3.96% by weight based on oil phase).

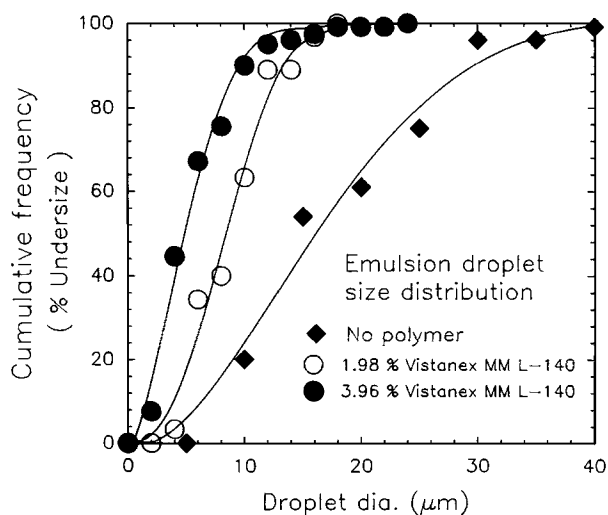


Figure 8 Comparison of droplet size distribution for 10% W/O emulsions with and without polymer.

cosity of the suspending medium. For a Newtonian suspending medium, the ratio η/η_0 is equal to unity and therefore, the above modified models become the original models. It may be mentioned that the modified Casson model has been applied before to suspensions of solid particles in non-Newtonian polymeric solutions.³²

Figures 10 and 11 show the Casson plots and the corresponding Herschel-Bulkley plots for polymer-thickened water-in-oil emulsions. In the case of Casson plots, the data are plotted as $\tau^{1/2}$ versus $(\dot{\gamma}\eta/\eta_0)^{1/2}$; according to eq. (8), such plots should be linear with a slope of K_c and an intercept of $\tau_0^{1/2}$. For Herschel-Bulkley plots, the data are plotted as $(\tau - \tau_0)$ versus $(\dot{\gamma}\eta/\eta_0)$ on a log-log scale; such plots should exhibit a linear relationship according to eq. (7). Indeed the plots are linear, as expected; however, the modified Herschel-Bulkley model appears to be superior in describing the shear stress/shear rate data of polymer-thickened emulsions (Table IV summarizes Herschel-Bulkley parameters for various emulsions).

The yield-stress data for the emulsions, obtained by fitting the modified Herschel-Bulkley model, are plotted in Figure 12. The yield stress increases with both water and polymer concentrations. Also, the log of yield stress increases linearly with the water concentration. An increase in the yield stress implies that the rigidity of the three-dimensional structure formed in the emulsions (due to droplet-droplet flocculations and possibly weak bridging of droplets by the polymer) improves with increasing water and polymer concentrations. Since water droplets and polymer molecules together form the structure, it is

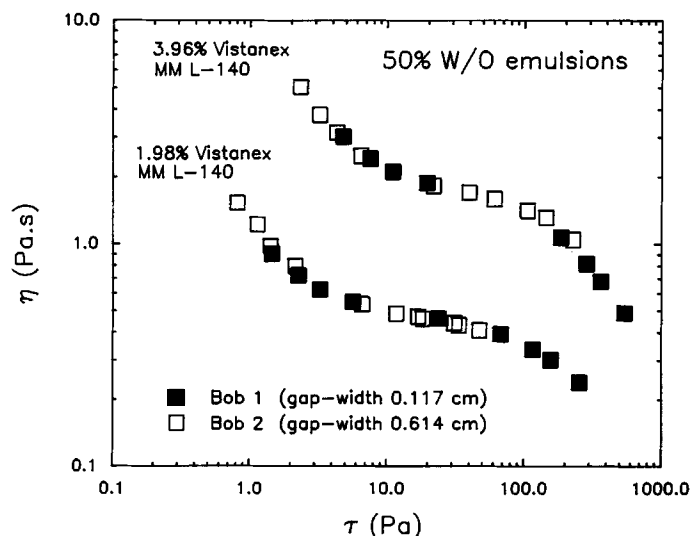


Figure 9 Rheological data for 50% W/O emulsions using different gap-width bob and rotor combinations.

expected that by increasing their concentrations the rigidity of the structure increases.

Figure 13 shows the plots of Herschel–Bulkley parameters K_h and n as a function of water concentration for the polymer-thickened emulsions. As expected, the consistency parameter, K_h , increases with the dispersed-phase (water) and polymer concentrations. The index n decreases with an increase in the water concentration. It is interesting to note that the decrease in n is rather rapid at high concentration of dispersed water droplets. Also, the dif-

ference in the n values between emulsions having 1.98 and 3.96% by weight polymer, respectively, is marginal.

Figure 14 compares the flow curves for emulsions prepared from two different molecular weight polyisobutylene solutions. The polymer concentration based on the oil phase is 3.96% by weight. The water droplets concentration in these emulsions is 50% by volume. As in the case of polymer solutions alone (refer to Fig. 3), the viscosity increases with an increase in the molecular weight of the polymer (Vis-

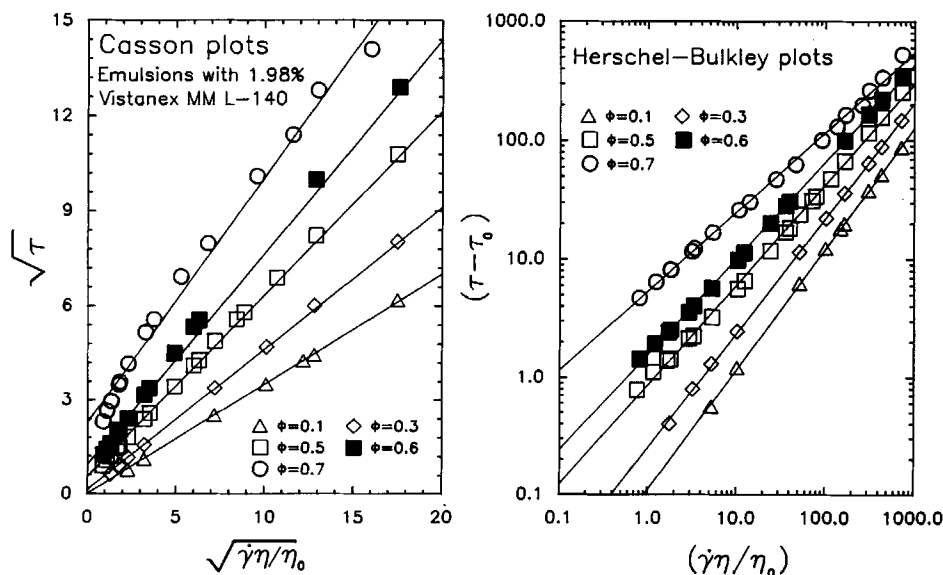


Figure 10 Casson and Herschel–Bulkley plots for polymer-thickened W/O emulsions (polymer concentration, 1.98%).

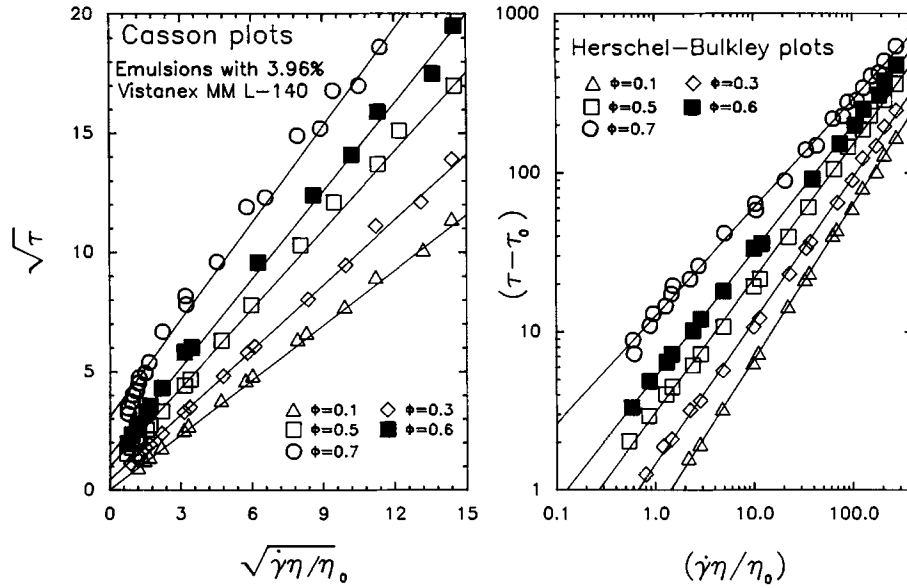


Figure 11 Casson and Herschel-Bulkley plots for polymer-thickened W/O emulsions (polymer concentration, 3.96%).

tanex MML-140 has a higher molecular weight than Vistanex MML-80). It may further be mentioned that the data for a 50% W/O emulsion, prepared using 3.96% by weight Vistanex MML-100 solution, fell in between the data for the two polymeric systems shown in Figure 14. (Note that the molecular weight of Vistanex MML-100 lies in between the other two polymers.)

Table IV Herschel-Bulkley Parameters for Polymer-Thickened Water-in-Oil Emulsions

Vistanex MML-140 Concentration (% by Weight)	Water Concentration (% by Volume)	τ_0 (Pa)	K_p or K_h (Pa s ⁿ)	n
1.98	10	0	0.11	1.02
	20	0	0.17	0.99
	30	0	0.25	0.97
	40	0.01	0.44	0.91
	50	0.03	0.86	0.85
	60	0.08	1.55	0.81
3.96	70	0.60	5.35	0.67
	10	0	0.70	0.97
	20	0	0.98	0.95
	30	0.01	1.50	0.90
	40	0.08	2.09	0.87
	50	0.30	3.06	0.85
	60	0.50	5.17	0.79
70	3.0	12.49	0.68	

Relative Viscosity of Emulsions Without Polymer

The relative viscosity data for emulsions are analyzed in terms of eq. (1), which can be re-written as:

$$\frac{\ln \eta_r}{\phi} = K \ln \eta_r + 2.5K_I \tag{9}$$

where K_I is equal to $[1 + 0.4(\eta_c/\eta_d)]/[1 + (\eta_c/\eta_d)]$. According to this equation, we should observe a lin-

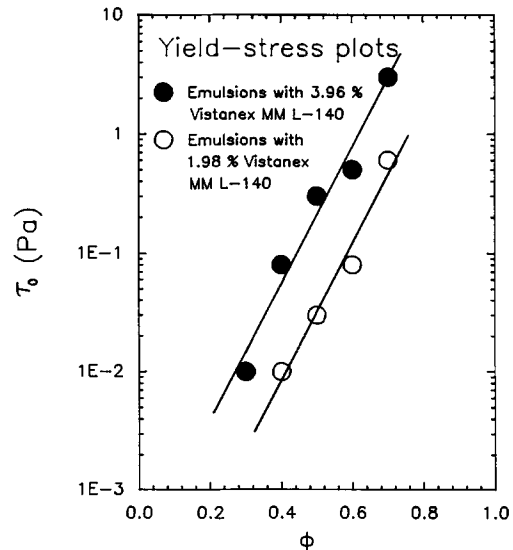


Figure 12 Variation of yield stress with water concentration for polymer-thickened emulsions.

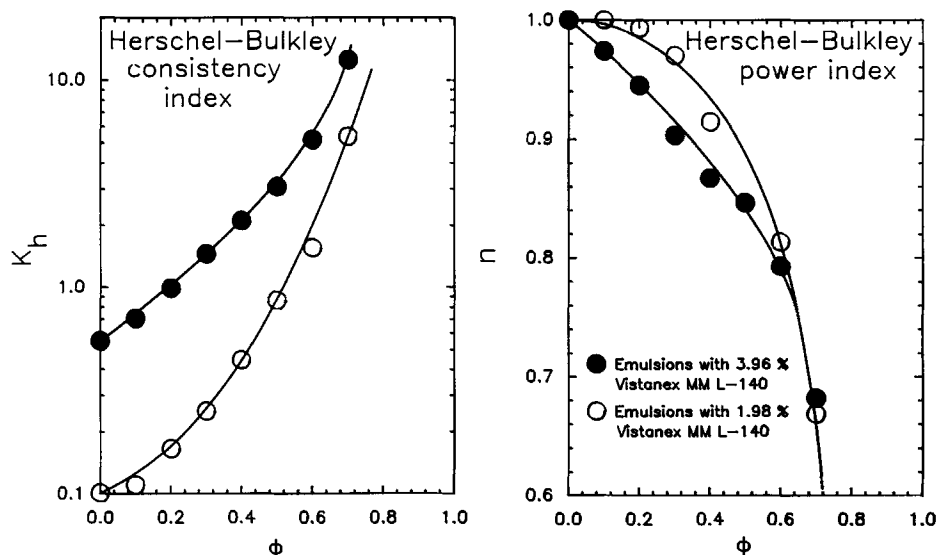


Figure 13 Variation of Herschel-Bulkley parameters with water concentration for polymer-thickened emulsions.

ear relationship between $[(\ln \eta_r)/\phi]$ versus $[\ln \eta_r]$ with an intercept of $2.5 K_I$ and a slope of K (for emulsions without polymer K_I is 0.475 so that the intercept is expected to be about 1.19).

Figure 15 shows the plots of $[(\ln \eta_r)/\phi]$ versus $[\ln \eta_r]$ for water-in-oil emulsions without polymer. The plots are shown for four different values of shear rates. Indeed, the data exhibit a linear relationship as expected from eq. (9). The slope of the line decreases with an increase in the shear rate [meaning K in eq. (9) decreases with the shear rate]. However, the data does not give an intercept of 1.19 as expected from eq. (9). The intercept is significantly

higher (the average value of the intercept for the four plots in Fig. 15 is 2.2). We believe that this deviation is mainly caused by inhibition of internal circulation; it is now well known that adsorption of an emulsifier at the surface of the emulsion droplets can significantly inhibit internal circulation leading to higher emulsion viscosities. Neither the Taylor equation, eq. (2), nor our equation, eq. (9), takes into consideration this effect of emulsifier adsorption.

To account for partial (complete) inhibition of internal circulation, Oldroyd³³ derived the following modified Taylor equation:

$$\eta_r = 1 + 2.5 \left[\frac{1 + 0.4(\eta_c/\eta_d) + (0.4/r\eta_d)(2\eta_s + 3\eta_\beta)}{1 + (\eta_c/\eta_d) + (0.4/r\eta_d)(2\eta_s + 3\eta_\beta)} \right] \phi \quad (10)$$

in which η_s is the shear viscosity of emulsifier film, η_β is the area viscosity of the film and r is the droplet radius. The quantity $(2\eta_s + 3\eta_\beta)$ is known to vary from 10^{-9} to 10^{-7} kg/s for many emulsion systems.⁵

Like the Taylor equation, the above equation is valid only for the dilute systems. For concentrated emulsions, eq. (1) is modified as follows:

$$\ln \eta_r = \left[\frac{1 + 0.4(\eta_c/\eta_d) + (0.4/r\eta_d)(2\eta_s + 3\eta_\beta)}{1 + (\eta_c/\eta_d) + (0.4/r\eta_d)(2\eta_s + 3\eta_\beta)} \right] \times \left(\frac{2.5\phi}{1 - K\phi} \right). \quad (11)$$

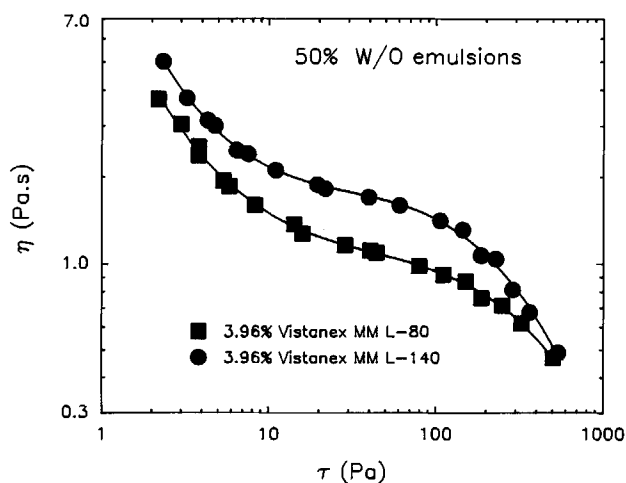


Figure 14 Flow curves for 50% W/O emulsions prepared from different molecular weight polyisobutylenes.

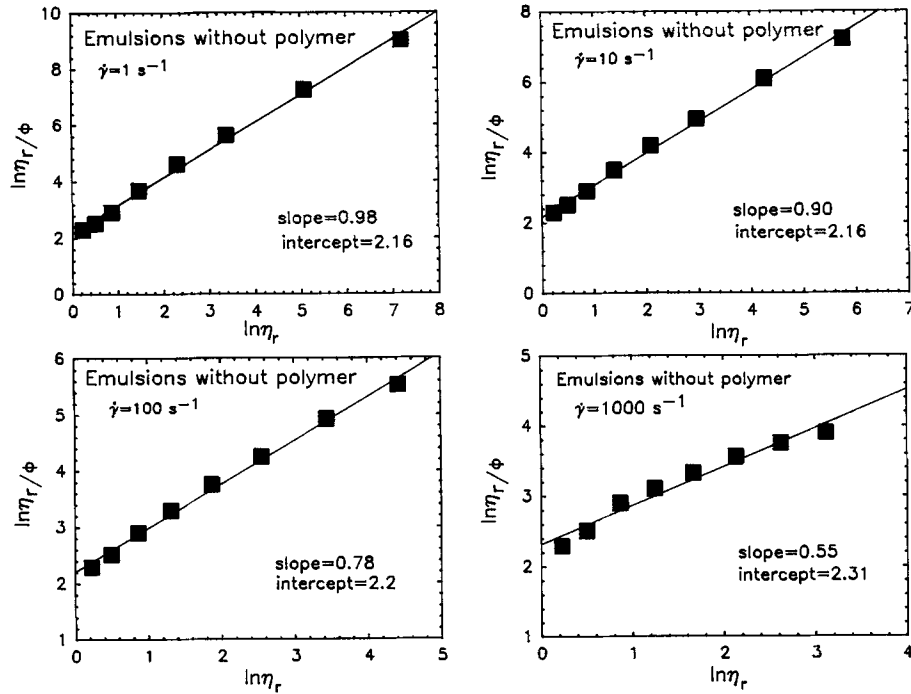


Figure 15 Relative viscosity data for W/O emulsions without polymer.

Clearly, this equation does take into account the effect of emulsifier adsorption (inhibition of internal circulation). In addition, it reduces to Oldroyd equation, eq. (10), in the limit of dilute concentration.

Although in the present work we did not directly measure the properties of the adsorbed emulsifier film (such as η_s and η_β), we can easily test the validity of eq. (11). Furthermore, we can determine the values of $(2\eta_s + 3\eta_\beta)$ from our experimental data (droplet size and rheological data).

One can rewrite eq. (11) as follows:

$$\frac{\ln \eta_r}{\phi} = K \ln \eta_r + 2.5K'_I \quad (12)$$

where K'_I is $[1 + 0.4(\eta_c/\eta_d) + (0.4/r\eta_d)(2\eta_s + 3\eta_\beta)] / [1 + (\eta_c/\eta_d) + (0.4/r\eta_d)(2\eta_s + 3\eta_\beta)]$. Thus, the experimental data of $(\ln \eta_r/\phi)$ versus $\ln \eta_r$ should exhibit a linear relationship. This is what we found experimentally (refer to Fig. 15). From the intercept values ($2.5K'_I$) one can evaluate the unknown quantity $(2\eta_s + 3\eta_\beta)$. For the present emulsions without polymer, the average value of the intercept in Figure 15 is 2.2 so that K'_I is 0.88, η_c/η_d for this system is 7 and the mean droplet diameter (d_{50}) is 16 μm . Using these data, the value of $(2\eta_s + 3\eta_\beta)$ is found to be 5×10^{-7} kg/s which is within the reported range.

To show the goodness of fit of the proposed eq. (11), the data of Figure 15 are replotted in Figure 16 as η_r versus ϕ . As can be seen, eq. (11) describes the viscosity/concentration behaviour of the emulsions quite well.

Relative Viscosity of Emulsion with Polymer

The relative viscosity of emulsions in which the suspending medium is a non-Newtonian fluid can be defined in two ways: In one case the relative viscosity is defined as the ratio of emulsion viscosity to suspending medium viscosity, both evaluated at the same shear stress. In the second case the relative viscosity is defined as the ratio of emulsion viscosity to suspending medium viscosity, both evaluated at the same shear rate. Both these definitions of relative viscosity are widely used in the literature for solids suspension in non-Newtonian polymeric liquids.¹²⁻²³

Figures 17 and 18 give the relative viscosities for polymer-thickened water-in-oil emulsions (1.98 and 3.96% polymer concentrations, respectively). The constant-stress relative viscosity, denoted by $(\eta_r)_\tau$, initially decreases with an increase in the shear stress and then tends to increase with further increase in the shear stress. Similar trends were observed in our earlier studies on oil-in-water emulsions.¹² However, the constant shear-rate relative

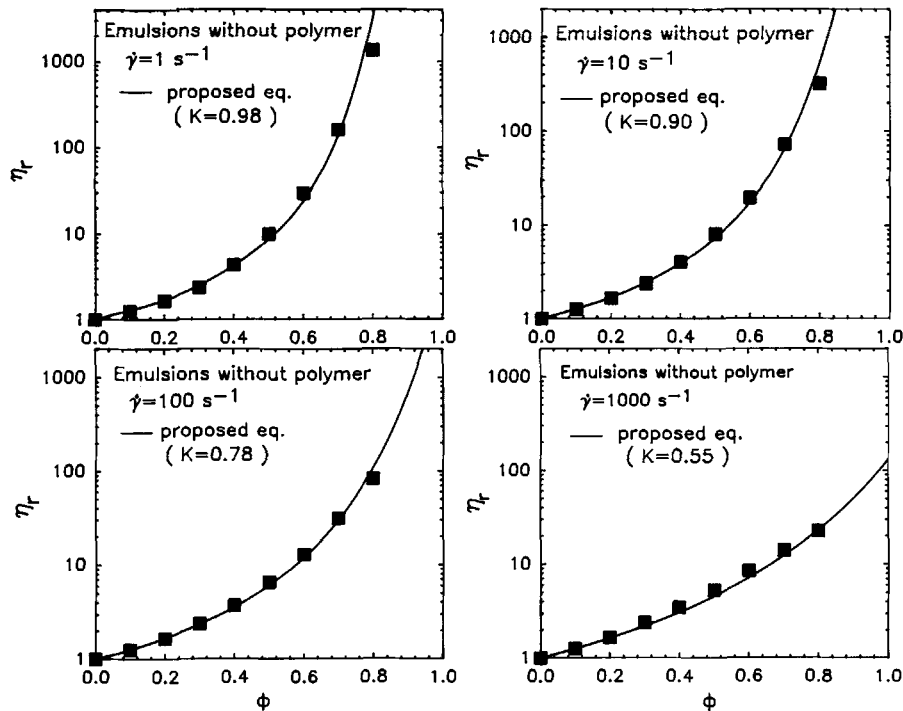


Figure 16 Correlation of relative viscosity data for water-in-oil emulsions without polymer.

viscosity, denoted by $(\eta_r)_{\dot{\gamma}}$ behaves in a more regular way. At low values of dispersed-phase (water) concentration, $(\eta_r)_{\dot{\gamma}}$ is nearly constant with respect to shear-rate variation. At higher values of water concentration, $(\eta_r)_{\dot{\gamma}}$ initially decreases with an increase in the shear rate and then tends to level off with further increase in the shear rate.

A comparison is made of the constant shear-rate relative viscosities for polymer-thickened water-in-oil emulsions with the same emulsions without polymer, as shown in Figure 19. Clearly, the relative viscosities for polymer-thickened emulsions are lower than those without polymer. This observation is consistent with our earlier studies on oil-in-water

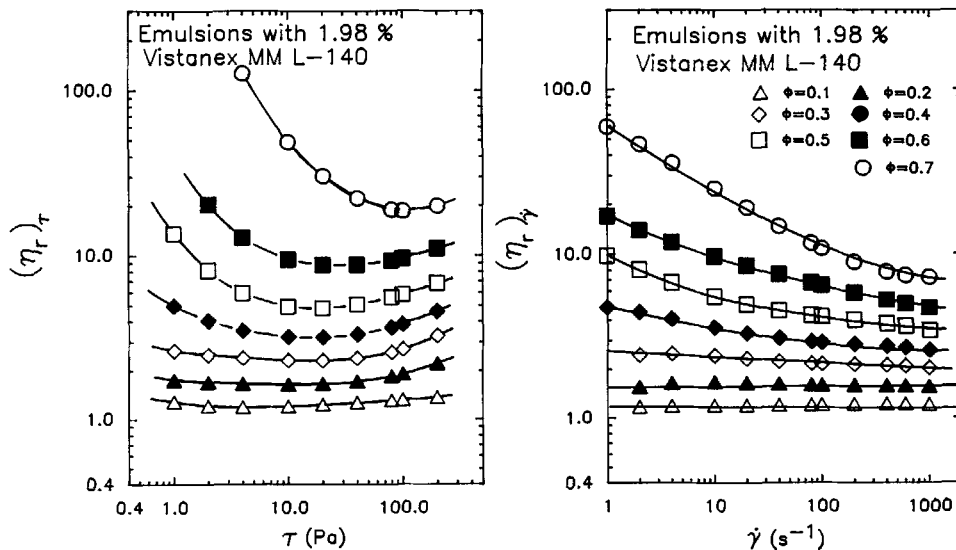


Figure 17 The relative viscosities for polymer-thickened W/O emulsions (polymer concentration, 1.98%).

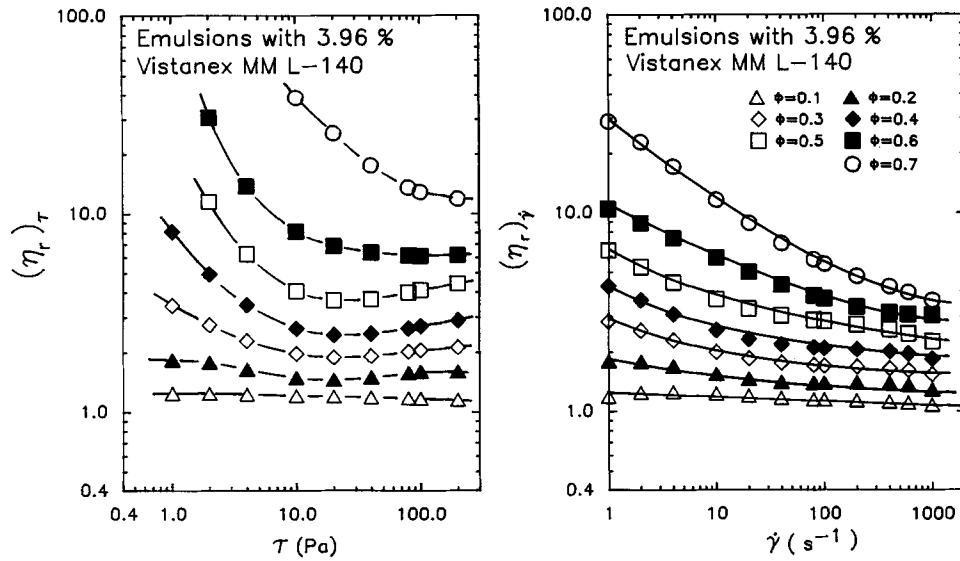


Figure 18 The relative viscosities for polymer-thickened W/O emulsions (polymer concentration, 3.96%).

emulsions. We believe that the lowering of relative viscosities is mainly caused by an increase in the viscosity ratio η_c/η_d (the suspending medium viscosity, η_c , is large for polymer-thickened emulsions); the internal circulation effect becomes more important for large values of η_c/η_d .

Equation (11) is employed to correlate the relative viscosity (constant shear-rate) data for polymer-thickened emulsions. Figures 20 and 21 show the goodness of fit of eq. (11) for these emulsions. Clearly, the equation describes the data very well. The quantities K and $(2\eta_s + 3\eta_p)$ for the plots (solid

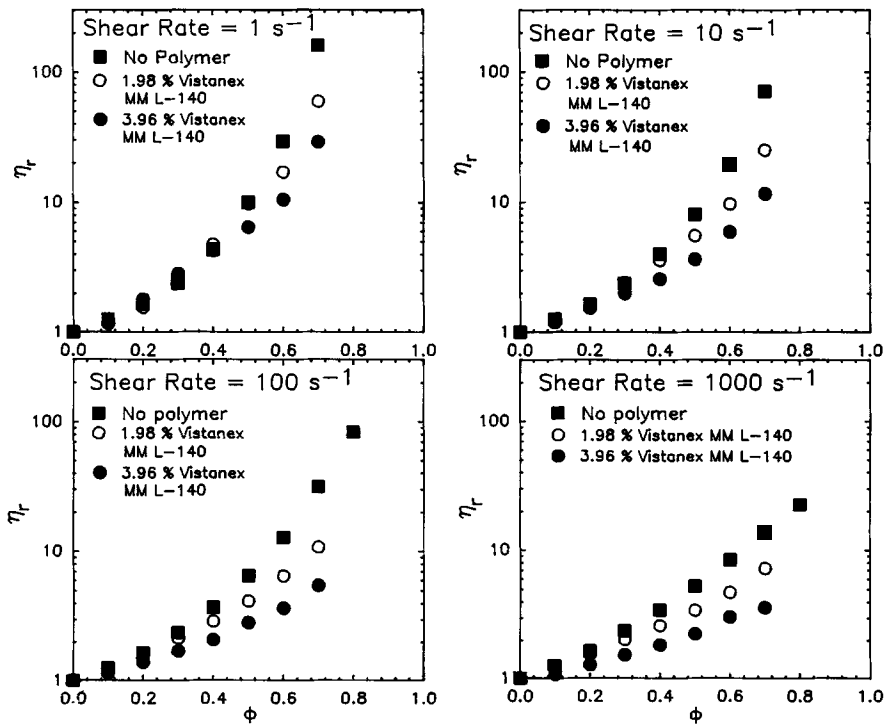


Figure 19 Comparison of constant-shear relative viscosities for polymer-thickened W/O emulsions with the same emulsions without polymer.

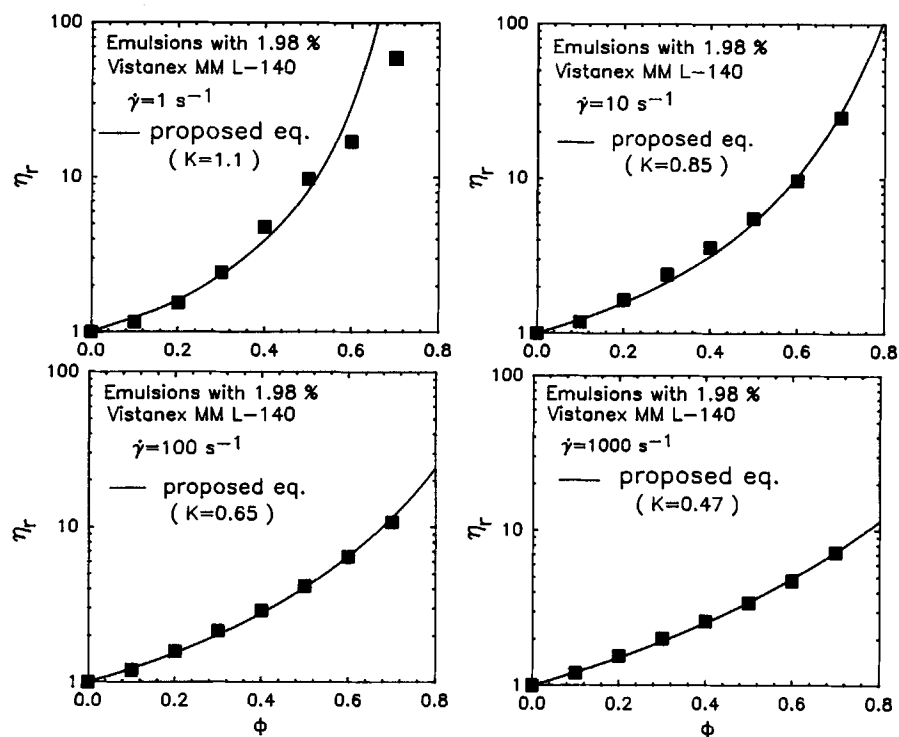


Figure 20 Correlation of relative viscosity versus dispersed-phase (water) concentration data for polymer-thickened W/O emulsions (polymer concentration, 1.98%).

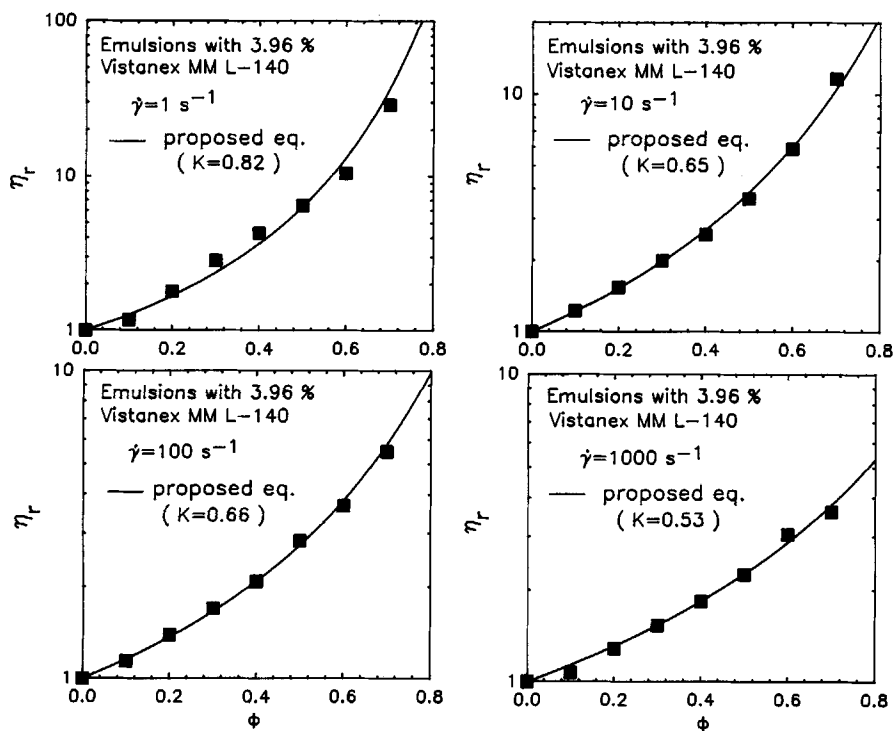


Figure 21 Correlation of relative viscosity versus dispersed-phase (water) concentration data for polymer-thickened W/O emulsions (polymer concentration, 3.96%).

Table V Values for Various Parameters in Eq. (11)

Emulsion System	Shear Rate (s ⁻¹)	η_c/η_d	d_{50} (μm)	$(2\eta_s + 3\eta_\beta)$ (kg/s)	K
1.98% Vistanex MML-140	1	109.2	8	1.51×10^{-6}	1.1
	10	109.2	8	1.51×10^{-6}	0.85
	100	108.4	8	1.49×10^{-6}	0.65
	1000	76.4	8	1.05×10^{-6}	0.47
3.96% Vistanex MML-140	1	595	5	12.42×10^{-6}	0.82
	10	572	5	4.03×10^{-6}	0.65
	100	489	5	0.85×10^{-6}	0.66
	1000	243	5	0.21×10^{-6}	0.53

curves) shown in Figures 20 and 21 are summarized in Table V. The value of K decreases with an increase in the shear rate. This was also found in the case of emulsions without polymer. The values of $(2\eta_s + 3\eta_\beta)$ are generally larger than what we found for emulsions without polymer. This is perhaps due to adsorption of polymer at the surface of the droplets.

CONCLUSIONS

Based on the experimental results, the following conclusions can be drawn:

1. Emulsions of water droplets in a Newtonian oil behave as Newtonian fluids at low values of water concentration. At high concentrations, emulsions exhibit shear-thinning (power-law) behaviour. Emulsions also develop a yield stress at a very high concentration of dispersed phase (water concentration $\geq 80\%$ by volume).
2. The viscous flow behaviour of emulsions of water droplets in non-Newtonian polyisobutylene/oil solutions is similar to the polymer/oil solution alone when the water concentration is low (polymer/oil solutions behave as Ellis model fluids).
3. At high water concentrations, polyisobutylene-thickened water-in-oil emulsions exhibit a yield stress. The yield stress increases with both polymer and water concentrations.
4. The flow behaviour of polymer-thickened emulsions possessing a yield stress can be described adequately by a modified Herschel-Bulkley model. The modified model accounts for the non-Newtonian behaviour of the suspending medium of the emulsions.

5. The relative viscosities of polymer-thickened emulsions are significantly lower than the corresponding values for the unthickened emulsions. The cause of this behaviour is reasoned to be internal circulation in emulsion droplets. The relative viscosity/dispersed-phase concentration data are described adequately by a modified form of the equation proposed earlier in our work on oil-in-water emulsions. The equation takes into account the effect of internal circulation on the emulsion viscosity. The equation also accounts for inhibition of internal circulation caused by adsorption of surfactant at the droplet surface.

Financial support from Natural Sciences and Engineering Research Council (NSERC) of Canada is gratefully appreciated.

NOMENCLATURE

- A Constant in Ellis model, eq. (3)
 d_{50} Mean droplet diameter (50% of the total number of droplets counted are below this diameter)
 K Constant in eq. (1)
 K_c Constant in Casson model, eq. (6)
 K_h Constant in Herschel-Bulkley model, eq. (5)
 K_I Factor that takes internal circulation into account, eq. (9)
 K_I' Parameter in eq. (12)
 K_P Constant in power-law model, eq. (4)
 n Exponent in power-law and Herschel-Bulkley models
 r Droplet radius

Greek Symbols

α	Parameter in Ellis model, eq. (3)
$\dot{\gamma}$	Shear rate, s^{-1}
η	Viscosity, Pa s
η_0	Zero shear viscosity, Pa s
η_c	Continuous-phase viscosity, Pa s
η_d	Dispersed-phase viscosity, Pa s
η_r	Relative viscosity
η_s	Shear viscosity of emulsifier film, kg/s
η_β	Area viscosity of emulsifier film, kg/s
$(\eta_r)_\dot{\gamma}$	Constant shear-rate relative viscosity
$(\eta_r)_\tau$	Constant shear-stress relative viscosity
τ	Shear stress, Pa
τ_0	Yield stress, Pa
ϕ	Dispersed-phase concentration (volume fraction)

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Received September 21, 1992

Accepted October 20, 1992