Viscometric Properties of Poly(dimethylsiloxane) Filled with Spherical Silica Particles

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Synopsis

The shear viscosity and primary normal stress coefficient were measured for colloidal dispersions of monodisperse silica spheres in poly(dimethylsiloxane). The viscometric properties of the dispersions were a function of the shear rate, particle diameter, and the volume fraction of particles. Dimensional analysis of rheological properties of colloidal dispersions of spherical particles in a second-order fluid was performed, and the experimental data were analyzed in terms of the appropriate dimensionless groups. The reduced shear viscosity of the colloidal dispersions was a function of the volume fraction of particles and the reduced shear stress (or reduced shear rate). The reduced primary normal stress coefficient was a function of the volume fraction of particles, the reduced shear rate, and the Weissenberg number.

INTRODUCTION

The rheological properties of dispersions of colloidal particles in Newtonian fluids have been studied ever since the pioneering work of Einstein.[1] The theoretical predictions of Einstein on the shear viscosity of noninteracting spheres in a Newtonian fluid were verified experimentally by Cheng and Schachman.[2] Although Batchelor and Green[3] have solved the problem of two hydrodynamically interacting spheres in a Newtonian fluid, at the present time a predictive theory is not available for concentrated suspensions, where higher-order particle interactions are important. Kreiger[4] has developed a corresponding-states principle for the shear viscosity of concentrated suspensions of spherical particles in Newtonian fluids. Krieger measured the shear rate-dependent viscosity for concentrated suspensions of spherical particles while varying the volume fraction, particle diameter, and viscosity of the suspending medium. Using the appropriate dimensionless variables, a single curve of reduced shear viscosity vs. reduced shear stress was obtained for suspensions of varying particle diameters and viscosities of the continuous phase. Although dimensional analysis cannot lead to a predictive theory of suspension rheology, it is a useful procedure in analyzing experimental data. Recent theoretical and experimental advances in suspension rheology, when the continuous phase is a Newtonian fluid, have been reviewed.[5-8]

The mechanical behavior of filled polymer fluids is of considerable practical importance; however, the rheological properties are not well understood for colloidal suspensions when the continuous phase is a polymeric fluid. The steady-state shear viscosity has been measured for various polymer solutions filled with spherical particles.[9-13] The previous studies have either (a) been

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concerned with particles that are larger than the maximum colloidal size of 10 μm, or (b) have not reported on the effects of particle diameter on the rheological properties. In this communication, we report on the viscometric properties of poly(dimethylsiloxane) filled with spherical silica particles, where the particle size is monodisperse and in the colloidal size range.

EXPERIMENTAL

Spherical spheres were produced by the method of Stöber, Fink, and Bohn.[14] Briefly, a tetra-alkoxysilane is hydrolyzed to silicic acid, and the silicic acid undergoes a subsequent polycondensation reaction to form spherical silica particles. The solvent for the hydrolysis reaction was reagent-grade ethanol to which controlled amounts of water and ammonia were added. The alkoxysilane reagents were used as obtained from the manufacturer (P.C.R. Chemicals). The reaction flask was immersed in a ultrasonic bath at room temperature and the reaction was allowed to proceed to completion. Particle size was determined by electron microscopy. The particles were spherical with monodisperse particle diameters. Detailed reaction conditions used to produce the particles used in this study are given in Table I.

The silica spheres could not be added directly to the poly(dimethylsiloxane) (Dow Corning 200 Fluid, 12,500 cs viscosity), since ethanol is not a solvent for poly(dimethylsiloxane) (PDMS). In order to facilitate the transfer of the silica spheres from ethanol to the PDMS, ethyl acetate was used as an intermediate solvent. Specifically, one part by volume of PDMS was dissolved in 10 parts ethyl acetate, the dispersion of silica spheres in ethanol was also diluted with ethyl acetate, and the PDMS solution was then added to the dispersion of the spheres in ethanol and ethyl acetate. The resulting mixture was distilled under reduced pressure until all the ethanol and ethyl acetate was removed. Ethyl acetate formed minimum boiling azeotropes with the ethanol and the residual water from the hydrolysis reaction; thus, when the silica–ethanol dispersion was diluted, sufficient ethyl acetate was used so that some ethyl acetate remained after the ethanol and all the azeotropes were removed. When a sufficient amount of ethyl acetate was not present, the dispersion flocculated during the final stages of the distillation.

The viscometric properties of the unfilled PDMS and the dispersions of spheres in PDMS were measured with an Instron 3250 rotary rheometer, using the cone-and-plate geometry. The diameter of the cone and plate was 4 cm, and the cone angle was 20 mrad. All measurements were carried out at 30°C. The

TABLE I
Reaction Conditions for Synthesis of Silica Spheres

Alkoxysilane reagent	Particle diameter, μm	Volume of EtOH, mL	Volume of alkoxysilane, mL	Volume of saturated NH$_4$OH in water solution, mL
Ethoxy	0.07	50	5	3
Ethoxy	0.12	50	5	4
Ethoxy	0.33	50	7	7
Butoxy	0.51	50	7	7

steady-state shear viscosity and primary normal stress difference were determined as a function of the shear rate. The shear rate was increased in discrete steps from the lowest shear rate at which meaningful torque readings could be obtained to a shear rate below the point where the fluid would begin to exude from the gap between the cone and plate. The shear rate was then decreased in discrete steps back to the initial shear rate. The torque and normal force reached their steady-state values almost as soon as the shear rate was changed. For all samples examined in this study, the viscosity and primary normal stress observed when the shear rate was increased was the same as that observed when the shear rate was decreased.

RESULTS

The effect of particle concentration on the shear-rate dependent viscosity for 0.33-μm silica spheres is shown in Figure 1. The viscosity of the unfilled PDMS fluid is essentially constant up to a shear rate of 50 s^{-1}. A very slight downturn in the log viscosity vs. log shear rate curve is observed for the pure fluid at shear rates greater than 50 s^{-1}. The shear viscosity of the dispersion increases as the volume fraction of spheres is increased. At low filler concentrations, the shear viscosity does not depend upon the shear rate. However, as the volume fraction of filler is increased, the viscosity begins to exhibit shear thinning behavior, and the degree of shear thinning increases as the concentration of spheres is increased.

The shear rate-dependent primary normal stress coefficient Ψ_1 is shown in Figure 2 for the same colloidal dispersions shown in Figure 1. The unfilled PDMS fluid exhibits a measurable primary normal stress difference, and Ψ_1 is shear thinning. Since the unfilled fluid exhibits a primary normal stress difference, the PDMS is not Newtonian even though the shear viscosity is nearly constant over the range of shear rates investigated. As the concentration of silica
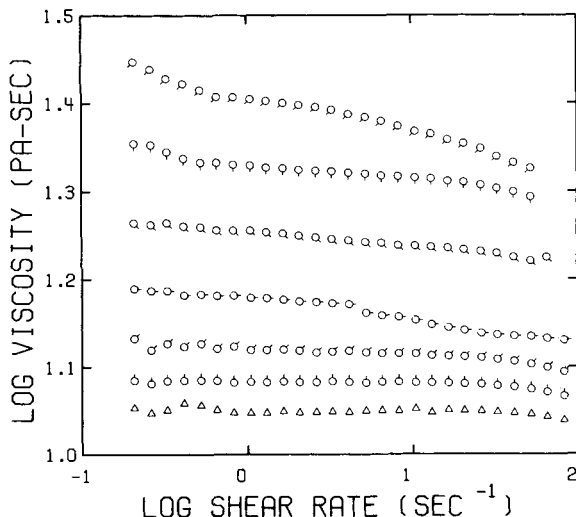

Fig. 1. Shear viscosity for dispersions of PDMS filled with 0.33-μm silica spheres. Pips, beginning upward and proceeding at 45° intervals, indicate the following volume fractions: 0.009, 0.018, 0.028, 0.047, 0.072, and 0.10; triangles indicate the unfilled fluid.
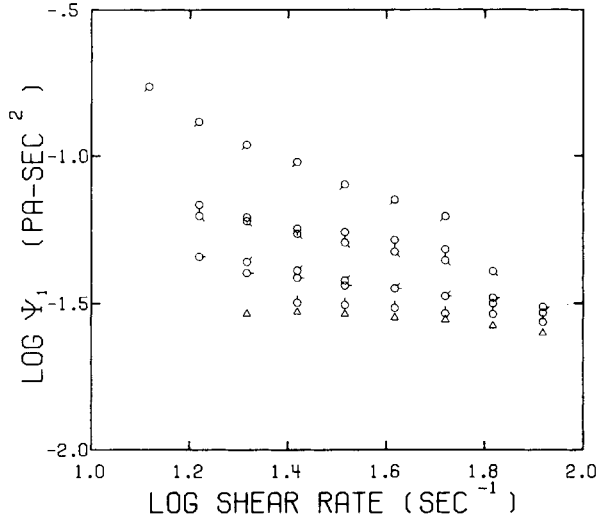
Fig. 2. Primary normal stress coefficient for dispersions of PDMS filled with 0.33-μm silica spheres. Symbols same as in Fig. 1.

spheres is increased, both the magnitude of the primary normal stress difference and the degree of shear thinning increase. The primary normal stress difference is much more sensitive to the concentration of particles than the shear viscosity. At a shear rate of 10 s^{-1}, the viscosity of a 10% dispersion of spheres in PDMS was twice that of the unfilled fluid; alternatively, the primary normal stress coefficient for the same dispersion at the same shear rate was more than seven times that of the pure fluid.

The effect of particle diameter on the shear viscosity is shown in Figure 3 for a series of colloidal dispersions, where the volume fraction of particles is 0.018. As the particle diameter is decreased, both the magnitude of the shear viscosity
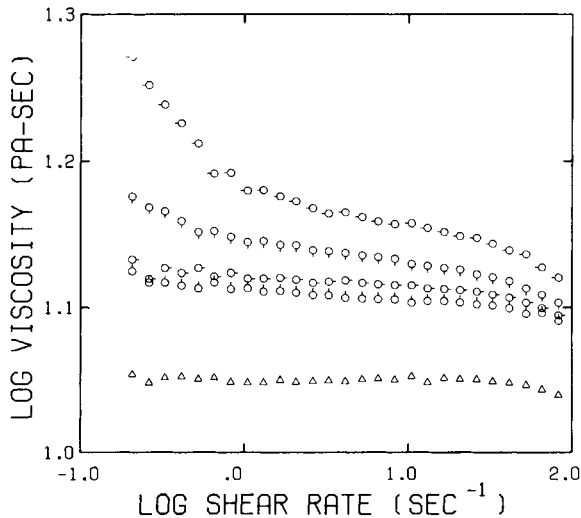

Fig. 3. Shear viscosity vs. shear rate for different diameter spheres. Volume fraction of particles equals 0.018. Pips, beginning upward and proceeding at 90° intervals, indicate the following particle diameters: 0.51, 0.33, 0.12, and 0.05 μm; triangles indicate unfilled fluid.

and the degree of shear thinning increase.   Examining the viscosity data for the dispersion of 0.05-μm particles, the degree of shear thinning is much more pronounced at low shear rates than at intermediate or high shear rates.   The primary normal stress coefficient as a function of shear rate is shown in Figure 4 for the same series of dispersions as in Figure 3.   The primary normal stress coefficient increases with decreasing particle diameter.   In addition, a slight increase in the degree of shear thinning is also observed with decreasing particle diameter; however, the effect is not as pronounced as with the shear viscosity data shown in Figure 3.

The effect of particle diameter on the shear viscosity and primary normal stress coefficient are shown respectively in Figures 5 and 6 for dispersions where the particle volume fraction is 0.028.   The effects of particle diameter on the viscometric properties for these more concentrated dispersions are qualitatively similar to those obeseved for the 0.018 volume fraction dispersions.

DISCUSSION

The viscometric properties of poly(dimethylsiloxane) filled with spherical silica particles depends upon both the concentration and size of the dispersed particles. The log viscosity vs. log shear rate curves shown in Figures 3 and 5 are similar in shape; thus, it should be possible to analyze the experimental data in terms of reduced variables.   The reduced viscosity η_r is defined as $\eta_r \equiv \eta/\eta_0$, where η is the viscosity of the filled polymer and η_0 is the viscosity of the pure fluid at the same shear rate.   A reduced shear stress τ_r is defined as $\tau_r = \tau a^3/kT$, where τ is the shear stress of the filled fluid, a is the particle diameter, k is Boltzmann's constant, and T is the absolute temperature.[4]   The reduced viscosity vs. the reduced shear stress is plotted in Figure 7 for the experimental data shown in Figures 3 and 5.   The data in Figure 7 indicate that reduced variables are applicable to these colloidal dispersions.   Excellent superposition is observed for both the 0.018 and 0.028 volume fraction dispersions.   At a given τ_r, the reduced
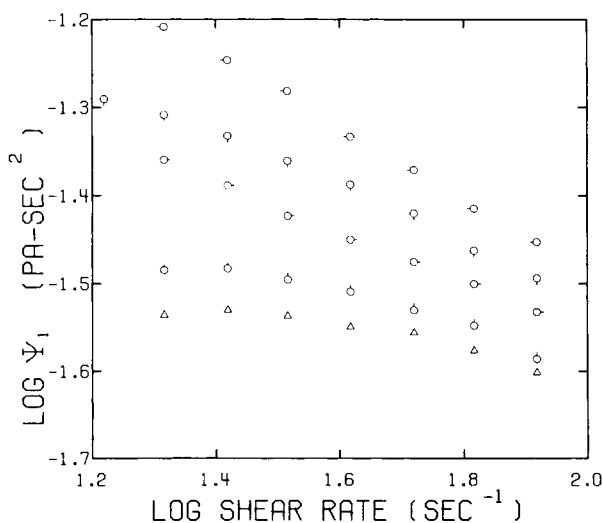

Fig. 4. Primary normal stress coefficient vs. shear rate for different diameter spheres.   Volume fraction of particles equals 0.018.   Symbols same as in Fig. 3.
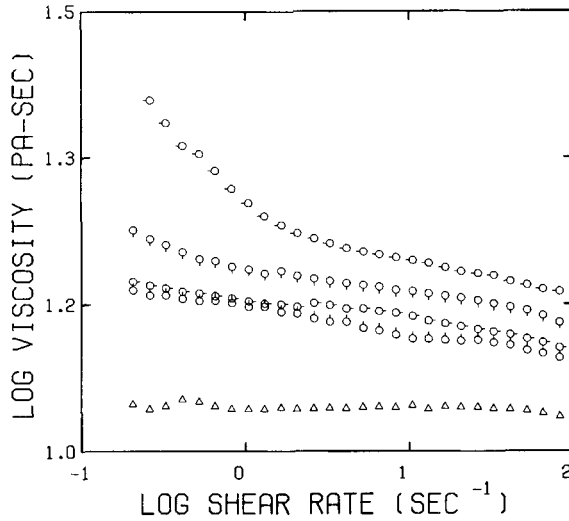
Fig. 5. Shear viscosity vs. shear rate for different diameter spheres. Volume fraction of particles equals 0.028. Symbols same as in Fig. 3.

viscosity is greater for the more concentrated suspension; however, the two curves begin to converge at higher reduced shear stresses.

Because of the success of the techniques of reduced variable in describing the shear viscosity, the primary normal stress data were analyzed in a similar manner. The ratio of the primary normal stress of the colloidal dispersion to the normal force of the unfilled fluid at the samse shear rate was plotted against both the reduced shear stress τ_r and a reduced shear rate $\dot{\gamma}_r = \tau_r/\eta_r$. The effects of particle diameter on the reduced normal force could not be correlated with either reduced shear stress or the reduced shear rate alone. This result is not unexpected, since PDMS is not Newtonian and the dimensional analysis as developed by Krieger[4] considered the viscosity of a suspension of spherical particles in a
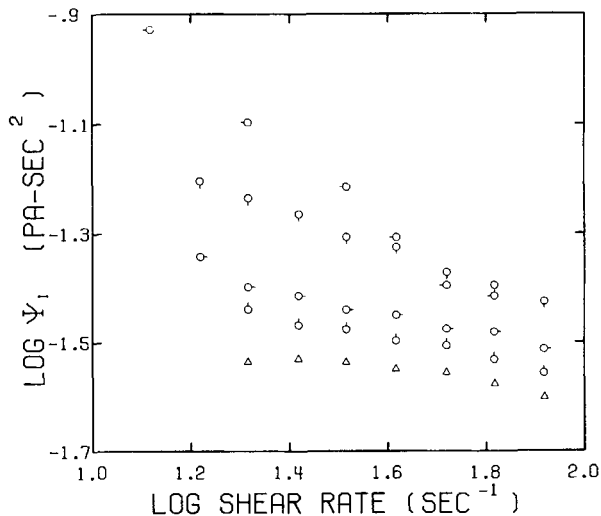

Fig. 6. Primary normal stress coefficient vs. shear rate for different diameter spheres. Volume fraction of particles equals 0.028. Symbols same as in Fig. 3.
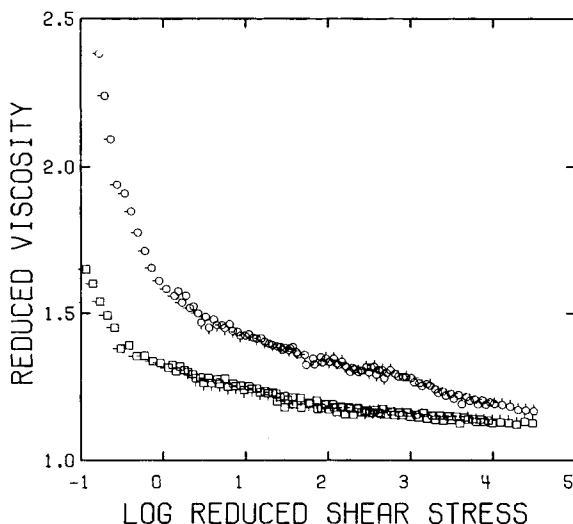
Fig. 7. Reduced shear viscosity vs. reduced shear rate. Pips same as in Fig. 3. Circles denote $\phi = 0.018$; squares denote $\phi = 0.028$.

Newtonian fluid. The dimensional analysis for poly(dimethylsiloxane) filled with spherical particles must acknowledge the primary normal stress of the unfilled PDMS as shown in Figure 4.

The rheological properties of a colloidal dispersion of hard spheres will depend upon the following variables: particle diameter a, particle density ρ_p, the number density of particles n, shear rate $\dot{\gamma}$, the time t, thermal energy kT, the density of the fluid ρ_0, and the rheological properties of unfilled fluid. The suspending fluid will be described by a shear viscosity η_0 and a primary normal stress coefficient ψ_{10}. Furthermore, it will be assumed that both η_0 and ψ_{10} are independent of the shear rate. The data shown in Figure 1 indicates that η_0 is essentially independent of $\dot{\gamma}$ over the range of shear rates investigated. The shear rate dependence of the primary normal stress for the pure fluid as shown in Figure 4 indicates that as a first approximation of the primary normal stress coefficient is independent of shear rate. A fluid with constant η_0 and ψ_{10} is the well-known second-order fluid.[15]

The functional dependence of the shear viscosity of the colloidal dispersion, η, is given as

$$\eta = f_1(\dot{\gamma}, t, \eta_0, \psi_{10}, \rho_0, a, n, \rho_p, kT) \tag{1}$$

Application of the Buckingham Pi Theorem indicates that the functional relationship can be formulated in terms of seven dimensionless groups.[16] One such set of dimensionless groups is the reduced shear viscosity $\eta_r = \eta/\eta_0$, the volume fraction of particles $\phi = \pi n a^3/6$, a reduced shear rate $\dot{\gamma}_r = a^3 \eta_0 \dot{\gamma}/kT$, a reduced time $t_r = tkT/\eta_0 a^3$, a relative density $\rho_r = \rho_p/\rho_0$, a particle Reynolds number $Re = a^2 \dot{\gamma} \rho_0/\eta_0$, and the Weissenberg number $We = \psi_{10}\dot{\gamma}/\eta_0$. This set of dimensionless groups is the same as that previously determined by Krieger,[4] with the addition of the Weissenberg number. The reduced form of eq. (1) is

$$\eta_r = f_2(\phi, \dot{\gamma}_r, We, t_r, \rho_r, Re) \tag{2}$$

For steady flow ($t_r \rightarrow \infty$) of neutrally buoyant spheres ($\rho_r = 1$) in the limit of creeping flow ($Re \rightarrow 0$), the rheological equation of state becomes
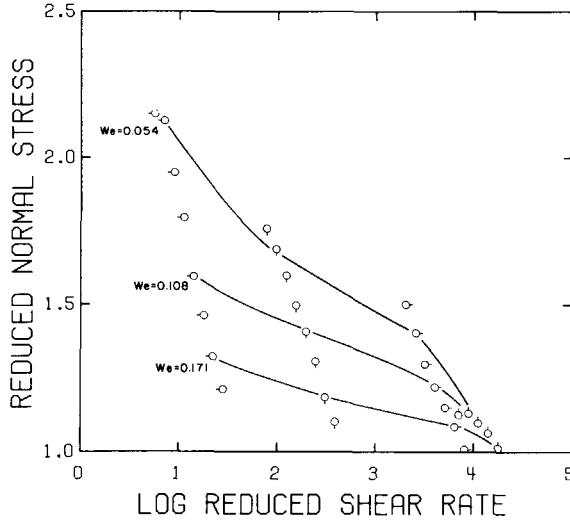
Fig. 8. Reduced primary normal stress coefficient vs. reduced shear rate. Volume fraction of particles equals 0.018. Pips same as in Fig. 3. $We \equiv \psi_{10}\dot{\gamma}/\eta_0$ was computed using $\psi_{10} = 2.91 \times 10^{-2}$ PA-S^2 and $\eta_0 = 11.2$ PA-S.

$$\eta_r = f_3(\phi, \dot{\gamma}_r, We) \tag{3}$$

or equivalently

$$\eta_r = f_4(\phi, \tau_r, We) \tag{4}$$

The data in Figure 7 indicate that the reduced viscosity is a function of both the volume fraction and reduced shear stress, as suggested by eq. (4). However, the reduced viscosity is not a function of the Weissenberg number, even though the Weissenberg number changes by more than two orders of magnitude for the data shown in Figure 7. Thus, the reduced viscosity is an extremely weak function
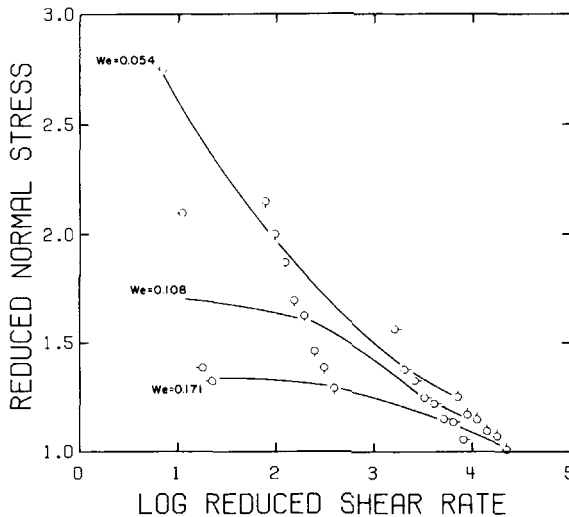

Fig. 9. Reduced primary normal stress coefficient vs. reduced shear rate. Volume fraction of particles equals 0.028. Pips same as in Fig. 3. $We \equiv \psi_{10}\dot{\gamma}/\eta_0$ was computed using $\psi_{10} = 2.91 \times 10^{-2}$ PA-S^2 and $\eta_0 = 11.2$ PA-S.

of the Weissenberg number over the range of shear rates and particle concentrations investigated in this study.

The functional dependence of the primary normal stress coefficient of the colloidal dispersion, ψ_1, is given by

$$\psi_1 = g_1(\dot{\gamma}, t, \eta_0, \psi_{10}, \rho_0, a, n, \rho_p, kT) \tag{5}$$

Proceeding in a similar manner as in the previous development, the relevant dimensionless groups are $\phi, \dot{\gamma}_r, We, t_r \rho_r, Re$, and the reduced primary normal stress coefficient $\psi_{1r} = \psi_1/\psi_{10}$. The reduced form of eq. (5) is

$$\psi_{1r} = g_2(\phi, \dot{\gamma}_r, We, t_r, \rho_r, Re) \tag{6}$$

For steady, creeping flow of neutrally buoyant spheres, the rheological equation of state becomes

$$\psi_{1r} = g_s(\phi, \dot{\gamma}_r, We) \tag{7}$$

Equation (7) states that the reduced primary normal stress coefficient for a dispersion of spherical particles in a second-order fluid depends upon the volume fraction of particles, the dimensionless shear rate, and the Weissenberg number.

The reduced primary normal stress coefficient is plotted as a function of the reduced shear rate in Figures 8 and 9 for the colloidal dispersions, where the volume fraction of spheres equals 0.018 and 0.028, respectively. The reduced primary normal stress coefficient is slightly less than unity for the 0.5-μm-sphere dispersions at high shear rates. This difficulty is a direct consequence of the assumption that the rheological properties of the pure fluid could be described by a second-order fluid model. If ψ_{10} is allowed to be a function of $\dot{\gamma}$, then ψ_{1r} would not be less than 1; however, this generalization would require the addition of another dimensionless group. The reduced primary normal stress coefficient is a strong function of the Weissenberg number, in contrast to the reduced shear viscosity, which is essentially independent of We. The sensitivity of ψ_{1r} to We is not surprising, since the parameter describing the normal stress of the pure fluid is contained in We. The experimental data shown in Figures 8 and 9 indicate that We must be included in a dimensional analysis of the primary normal stress data for colloidal dispersions. However, from the experimental data presented in this report, it is not possible to conclude that ϕ, $\dot{\gamma}_r$, and We are a sufficient set of dimensionless parameters to describe ψ_{1r}. In order to assess the validity of eq. (7), additional normal stress data must be obtained for colloidal dispersions where the primary normal stress coefficient of the continuous phase has been varied.

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