

The Effect of Particle Concentration on the Rheology of Polydimethylsiloxane Filled with Fumed Silica

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Synopsis

The effects of particle concentration on the shear-rate-dependent viscosity, stress relaxation, and stress growth function were investigated for various molecular weight polydimethylsiloxane (PDMS) fluids filled with colloidal fumed silica. Shear-rate-dependent stress relaxation was observed for all dispersions, and a significant stress growth overshoot was observed when the PDMS molecular weight was just greater than the entanglement molecular weight. The rate of stress-relaxation and the type of stress growth are primarily determined by the previous shear rate history and the PDMS molecular weight, while particle concentration only affects the quantitative details of the filled fluid's rheology. The observed effects of particle concentration are consistent with a molecular deformation process, where the silica particles interact via the entanglements of the polymer adsorbed on the surface of the fumed silica.

INTRODUCTION

The rheological behavior of a colloidal dispersion depends upon the type and the amount of dispersed particles. In this paper we will be concerned with dispersions of highly-branched, colloidal-sized particles in a polymeric continuous phase. The relative viscosity of very dilute dispersions of non-colloidal particles increases linearly with the particle volume fraction,¹ and the relative viscosity is independent of particle size for suspensions of non-colloidal monodisperse spheres.^{2,3} The rheology of simple-shaped particles dispersed in a Newtonian continuous phase has a long history and is discussed in several reviews.⁴⁻⁷ In addition to the particle concentration, the size, size distribution, and shape of the particles affect the rheology.⁸⁻¹¹

The addition of particles into Newtonian or non-Newtonian fluids often results in time- and shear-rate-dependent rheological behavior. Experimental data for spheres in polymeric media have shown the relative viscosity to be a function of both particle concentration and shear rate.¹²⁻¹⁴ A shear thinning relative viscosity has been reported for colloidal dispersions in non-Newtonian fluids,^{8,15,16} with an increased degree of shear thinning with increasing particle concentration.^{8,16} As the particle concentration is increased, the onset of shear thinning is observed at higher shear rates for polymeric dispersions.¹⁷ Generally, the relative viscosity of a filled polymer increases nonlinearly with the particle concentration, and an *apparent* yield stress is sometimes observed, when the particle concentration exceeds a

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critical value.¹⁸⁻²⁰ The primary normal stress coefficient has also been measured for several filled polymeric systems.^{8,12,16,17,21,22} At equal shear rates the primary normal stress differences usually increases with increasing particle concentration¹² and is usually more sensitive to particle concentration than the shear stress.^{8,16} Also, at equal shear stresses the primary normal stress difference usually decreases with filler concentration. Both the magnitude and the degree of shear thinning of the primary normal stress coefficients increase as particle size decreases⁸; and, although not common, negative values for the primary normal stress difference coefficient have been reported for some filled polymeric systems.^{21,22} Although many interesting properties have been reported, there is no systematic study on the effects of particle size and shape, concentration, and the continuous phase molecular weight on both the steady state and transient rheological properties of filled polymers.

This communication is the fourth in a series of experimental studies on the rheological behavior of dispersions of colloidal sized fumed silica in polydimethylsiloxanes. In the first paper²³ we reported how particle concentration influenced the viscosity and primary normal stress during hysteresis experiments. In the second paper the shear rate history dependence of the steady state viscosity, stress-relaxation, and stress growth behavior for a single PDMS/fumed silica dispersion was investigated.²⁴ In the third paper we reported how the PDMS molecular weight at a single filler concentration influenced the rheological behavior.²⁵ In this paper we will address the effects of particle concentration on the steady state and transient rheological properties. The experimental data can be rationalized via the same molecular deformation mechanism presented in earlier communications.^{24,25}

EXPERIMENTAL

Dispersions of fumed silica in PDMS were prepared by a procedure described previously.^{23,24} The fumed silica concentration in the dispersions ranged from 1.0 to 9.6% by weight. The fumed silica was Cab-O-Sil HS-5 (Cabot Corp.), which is composed of colloidal-sized branched aggregates having a specific surface area of $325 \pm 25 \text{ m}^2/\text{g}$. The individual aggregates are composed of nonporous spherical primary particles approximately 8 nm in diameter, and a typical aggregate length is a few tenths of a micron. The PDMS (Dow Corning 200 Fluids, Dow Corning Corp.) molecular weights were determined by high pressure gel permeation chromatography.²⁵ The PDMS fluids have weight average molecular weights \bar{M}_w ranging between 33,000 and 138,000 g/mol and are quite polydisperse. Steady state and transient rheological behavior of the unfilled PDMS fluids have been reported elsewhere.²⁵

The shear properties of the silica-filled PDMS fluids were tested using an Instron Model 3250 Rotary Rheometer operated in the cone and plate mode at $30.0 \pm 0.5^\circ\text{C}$. The platens were 4.0 cm in diameter, and the cone angle was 20 mrad. The shear rate history was carefully controlled and typically was as follows: (i) the specimen was presheared at $\dot{\gamma}_p$ until a constant shear stress was obtained, (ii) a step down in the shear rate (usually

to $\dot{\gamma}_r = 0$) was applied at $t = 0$ and maintained until time t_0 , and (iii) a step increase in the shear rate to $\dot{\gamma}_i$ was applied at $t = t_0$. Steady state, stress-relaxation, and stress growth material functions in shear were obtained using this deformation history. The importance of the various elements of the deformation history and the consequences of not employing a deformation history of this type were examined in an earlier publication.²⁴ The samples were tested from 3 to 15 days after preparation to minimize the effects of sample aging.^{23,25} Also, the shear rates employed in this investigation were too small to obtain measurements of the primary normal stress difference coefficient for fluids with \bar{M}_w less than 93,000 g/mol.

A few general comments about rheological testing of these dispersions. It is easier to prepare a PDMS/fumed silica dispersion as the PDMS molecular weight decreases, with approximately 10–12% by weight being the maximum silica loading in the 33,000 g/mol fluid. When the particle concentration exceeds a critical value that increases with the PDMS molecular weight, cone and plate testing becomes impossible. A 7% by weight dispersion of fumed silica in 33,000 g/mol PDMS is quickly expelled from the cone and plate at shear rates of 2 s⁻¹ or larger. A 9.6% fumed silica in 76,000 g/mol PDMS dispersion was gradually expelled from the gap at a shear rate of 20.8 s⁻¹ with significant depletion of the sample before the initial preshear was completed.

RESULTS

Steady State

The steady state shear viscosities η for the fumed silica in PDMS dispersions are shown in Figures 1(A) and 1(B). The dispersions exhibit a shear thinning viscosity over the range of shear rates investigated. The degree of shear thinning is relatively independent of molecular weight for dispersions with the same particle concentration, and increased shear thinning is observed as the particle concentration increases in each of the PDMS fluids. Over the range of shear rates studied, the unfilled PDMS fluids have a constant viscosity for molecular weights of 76,000 g/mol or less, while PDMS fluids with greater molecular weights are only slightly shear thinning.²⁵ The time required to reach the steady state viscosity for the filled fluids increases as the shear rate decreases, PDMS molecular weight increases, and the particle concentration increases. Times as long as 4 days under shear were used to determine the steady state viscosities for the more concentrated, high molecular weight PDMS dispersions. For dispersions with particle concentrations of 3% or less, the rheological behavior was readily reproducible for the entire 12 days of sample testing. In the 5 and 7% dispersions, η systematically decreased over the 12 days of testing with the amount of η decrease more pronounced at lower shear rates and higher particle concentrations. However, this decrease in η with testing affected only the magnitude of η without changing the qualitative behavior and the time scales for stress relaxation and stress growth.

The primary normal stress difference coefficients ψ_1 , for the three highest molecular weight filled fluids are shown in Figure 2. Additional ψ_1 data at

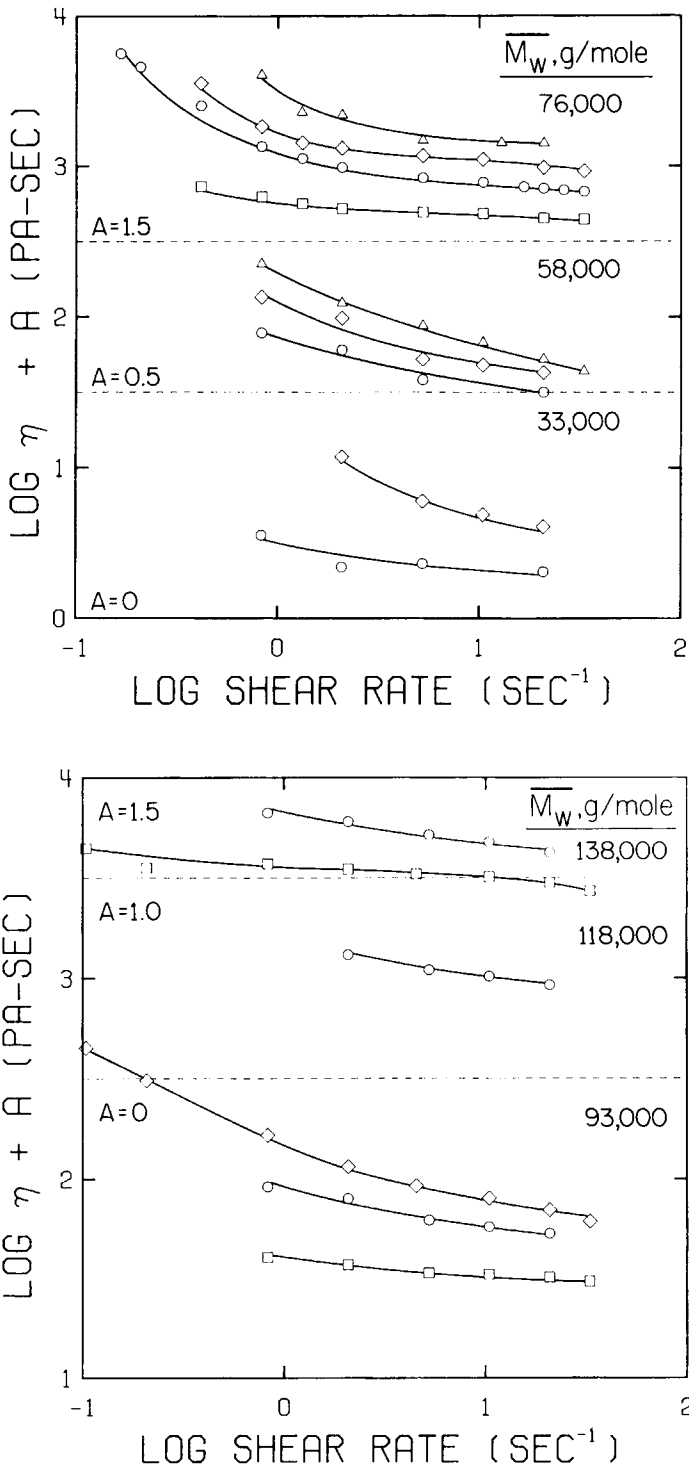


Fig. 1. Shear-rate-dependent viscosity for the filled fluids. The PDMS weight average molecular weights and vertical shifts A are indicated in the figure. The symbols refer to the following percent of silica particle weight: (□) 1%; (○) 3%; (◇) 5%; (△) 7%.

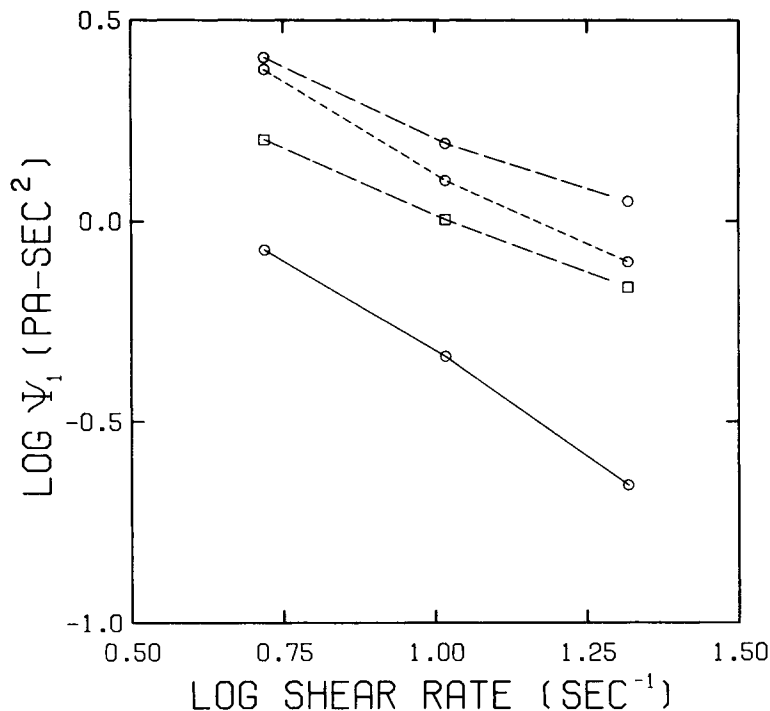


Fig. 2. Steady state primary normal stress difference coefficients. PDMS molecular weights are: (—) 93,000 g/mol; (- - -) 118,000 g/mol; (- · - ·) 138,000 g/mol. Symbols indicate the same particle concentrations as in Figure 1.

$\dot{\gamma} = 20.8 \text{ s}^{-1}$ are: 7% fumed silica, $\bar{M}_w = 76,000 \text{ g/mol}$, $\psi_1 = 0.13 \text{ Pa s}^2$; 1% fumed silica, $\bar{M}_w = 93,000 \text{ g/mol}$, $\psi_1 = 0.07 \text{ Pa s}^2$; and 5% fumed silica, $\bar{M}_w = 93,000 \text{ g/mol}$, $\psi_1 = 0.20 \text{ Pa s}^2$. The filled fluid ψ_1 increases with PDMS molecular weight and particle concentration, and the degree of shear thinning exhibited by the primary normal stress coefficients decreases with increasing PDMS molecular weight. The unfilled PDMS also exhibit shear thinning ψ_1 , when measurable.²⁵ The ratios of the filled fluid ψ_1 to the unfilled fluid ψ_1 increase with particle concentration in a given PDMS fluid and decrease with PDMS molecular weight at a given particle concentration.

Stress-Relaxation

The stress-relaxation responses of filled fluids with 76,000 g/mol PDMS and various particle concentrations are shown in Figure 3, where the stress-relaxation data are normalized by the steady state shear stress observed before the relaxation. The rate of stress relaxation from $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$ is initially independent of particle concentration and the relaxation is 99% complete within 0.7 s. The lack of complete superposition at longer times for the $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$ relaxation data is most probably a result of insufficient instrument sensitivity. The stress-relaxation curves from $\dot{\gamma}_p = 0.83 \text{ s}^{-1}$ do not superpose, and the rate of stress relaxation is much slower than from $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$. The stress-relaxation response for the other filled fluids are qualitatively similar with particle concentration influencing the

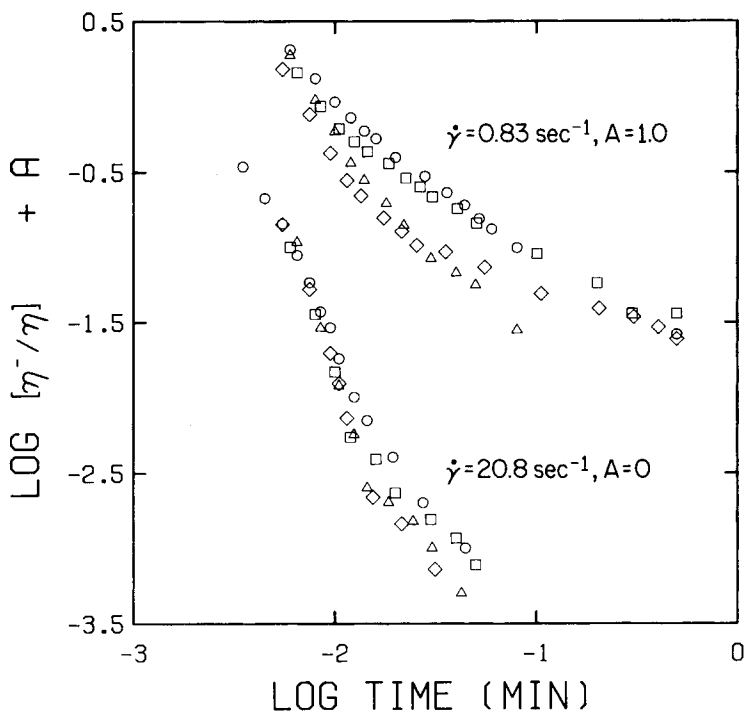


Fig. 3. The shear stress-relaxation function for 76,000 g/mol PDMS dispersions. The $\eta^-(t)$ response is normalized by the steady state viscosity at the previous shear rate. Symbols indicate the same particle concentration as in Figure 1.

stress relaxation at lower shear rates.²⁶ The stress-relaxation for all the unfilled fluids is complete within 1 s, independent of the previous shear rate.

The relaxation of the primary normal stress difference coefficient $\psi_1^-(t)$ is given in Figure 4 for both the unfilled and filled 93,000 g/mol PDMS, where the $\psi_1^-(t)$ relaxation data have been normalized by the steady state ψ_1 observed before relaxation. The $\psi_1^-(t)$ relaxation in the 1% silica dispersion is qualitatively similar to that observed with the unfilled PDMS, with just a slight increase in the normal stress. However, the 3 and 5% dispersions exhibit significantly different $\psi_1^-(t)$ relaxation, with much greater rates of $\psi_1^-(t)$ relaxation than either the unfilled fluid or the 1% fumed silica dispersion.

Stress-relaxation to a nonzero shear rate are shown in Figure 5 for various particle concentrations in 76,000 g/mol PDMS. The curves all exhibit an initial decrease followed by a slow increase to the steady state values at $\dot{\gamma}_r$. The ratios of the minimum values in shear stress to their respective steady state values are 0.91, 0.73, 0.83, and 0.71 for particle concentrations of, respectively, 1, 3, 5, and 7% by weight. Additional stress-relaxation data at nonzero $\dot{\gamma}_r$ are presented in Table I. The data indicate that the stress-relaxation response is affected by a complicated interplay of $\dot{\gamma}_p$ and $\dot{\gamma}_r$ with particle concentration, where the initial rate of recovery generally increases with particle concentration. A similar response for

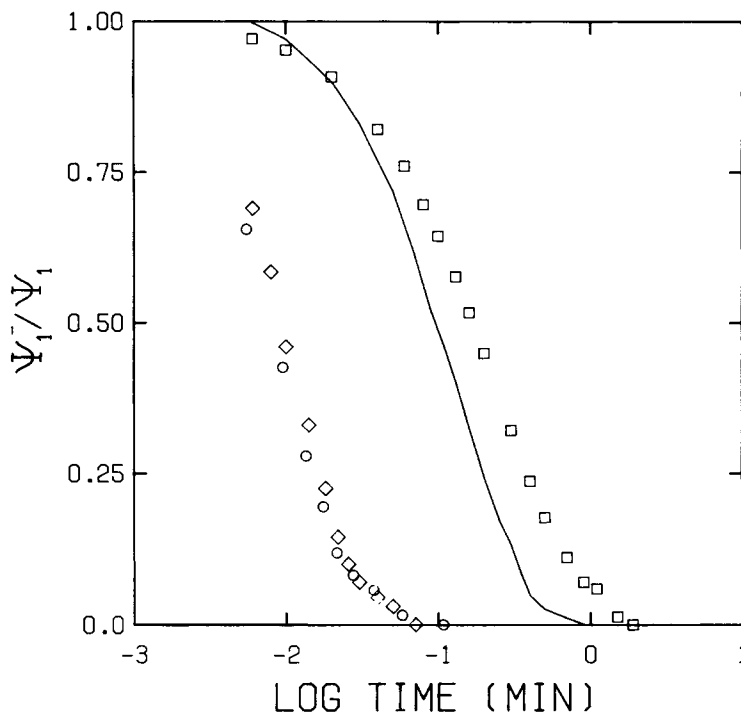


Fig. 4. Stress-relaxation of the primary normal stress coefficient for 93,000 g/mol PDMS dispersions and from a preshear rate of $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$, and $\dot{\gamma}_r = 0$. The $\Psi_1^-(t)$ responses are normalized by their respective steady state Ψ_1^- at $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$. The solid line refers to unfilled fluid $\Psi_1^-(t)$ relaxation and symbols indicate the same particle concentration as in Figure 1.

stress-relaxation to nonzero shear rates has been observed for the other molecular weight fluids, with the time required to reach steady state increasing for increased molecular weight.²⁵

Stress Growth

The qualitative features of the stress growth functions $\eta^+(t)$ for the fumed silica in PDMS dispersions are primarily determined by the PDMS molecular weight²⁵ and the previous shear rate history.²⁴ The stress growth functions for 3 and 5% by weight of fumed silica in 33,000 g/mol PDMS are shown in Figure 6. The $\eta^+(t)$ curves for the 3% dispersion with 10 min and 8 h rests superimpose and achieve 96% of the steady state viscosity after 2 s. The $\eta^+(t)$ functions for the 5% dispersion achieves 60% of the steady state viscosity after 2 s, while the 10 min rest curve exhibits a faster approach to steady state than the $\eta^+(t)$ curve for an 8 h rest. In contrast to the 33,000 g/mol PDMS fluid, the filled fluids with PDMS molecular weights of 58,000, 76,000, 93,000 g/mol exhibit $\eta^+(t)$ maxima which increase with rest time.^{24,25} Typical $\eta^+(t)$ behavior for these PDMS molecular weight filled fluids are shown in Figure 7 for a dispersion of 7% fumed silica in 76,000 g/mol PDMS. The $\eta^+(t)$ maxima increase with rest time, and the subsequent approach to steady state is via an increase for the 10 min rest, while the stress growth function decreases towards steady state

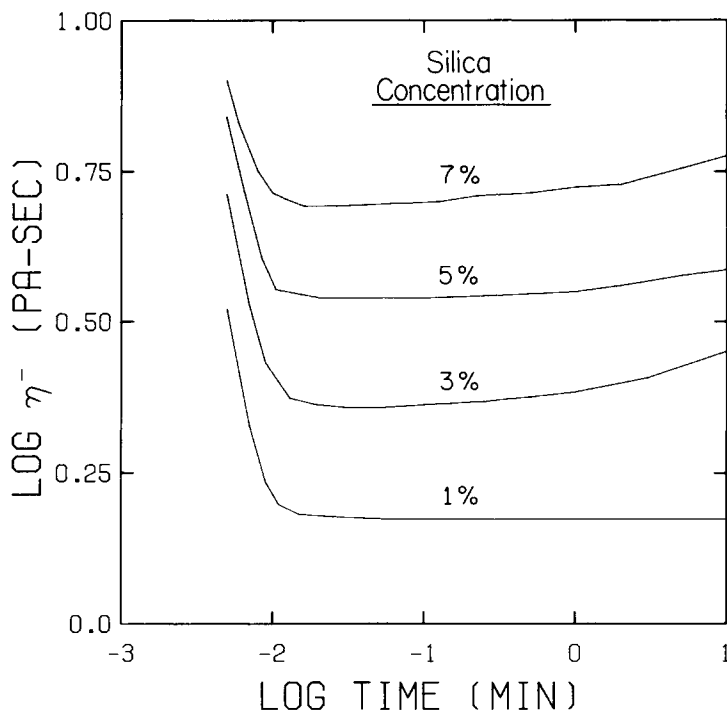


Fig. 5. The shear stress-relaxation to a nonzero shear rate for a 76,000 g/mol PDMS. Shear rate history $\dot{\gamma}_p = 2.08 \text{ s}^{-1}$. Particle concentrations are indicated in the figure.

for the 2 and 8 h rests. A small shear rate during the 8 h rest reduces the height of the $\eta^+(t)$ maximum and retards the approach to steady state relative to recovery at $\dot{\gamma}_r = 0$. Similar rest time and $\dot{\gamma}_r$ effects were observed for all the concentrations studied in the filled fluids and PDMS molecular weights of 58,000, 76,000, and 93,000 g/mol and these results are reported elsewhere.²⁶

The effect of silica concentrations on $\eta^+(t)$ is shown in Figure 8. The magnitude of $\eta^+(t)$ increases with particle concentration; the time of the

TABLE I
Stress-Relaxation at Nonzero Shear Rates for Fumed Silica Filled 76,000 g/mol PDMS

Particle concentration	$\dot{\gamma}_p$ (s^{-1})	$\dot{\gamma}_r$ (s^{-1})	Minimum in $\eta^-(t; \dot{\gamma}_p, \dot{\gamma}_r)^a$
			$\eta^-(t = \infty; \dot{\gamma}_p, \dot{\gamma}_r)$
1%	20.8	0.83	0.75
	20.8	2.08	0.91
	5.24	0.83	0.99
3%	20.8	0.83	0.56
	20.8	2.08	0.73
	5.24	0.83	0.61
5%	20.8	0.83	0.61
	20.8	2.08	0.83
	5.24	0.83	0.68
7%	20.8	2.08	0.71

^a The quantity $\eta^-(t; \dot{\gamma}_p, \dot{\gamma}_r)$ equals the negative of the value at time t of the shear stress divided by $\dot{\gamma}_p$ for stress-relaxation at $\dot{\gamma}_r$.

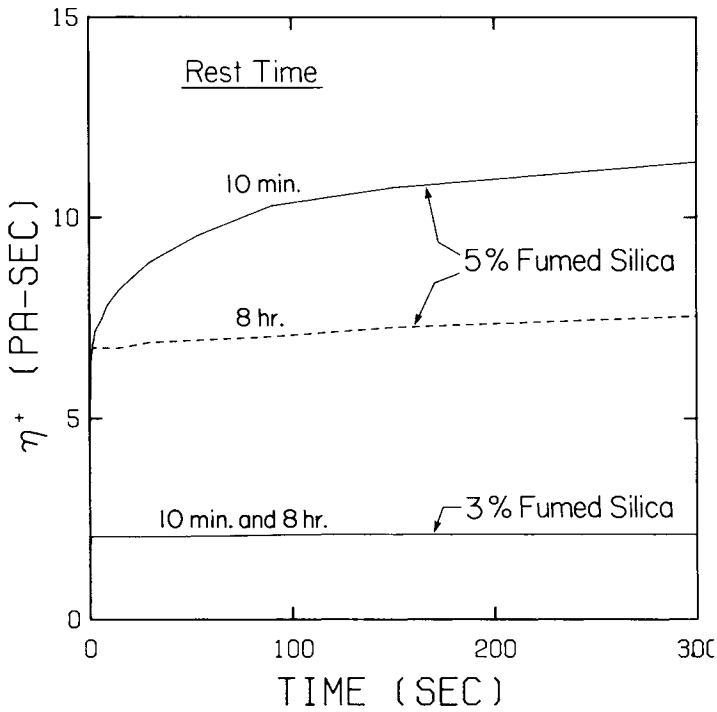


Fig. 6. The stress growth function for filled fluids with 33,000 g/mol PDMS. Shear rate history $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$, $\dot{\gamma}_r = 0.0 \text{ s}^{-1}$, and $\dot{\gamma}_t = 2.08 \text{ s}^{-1}$.

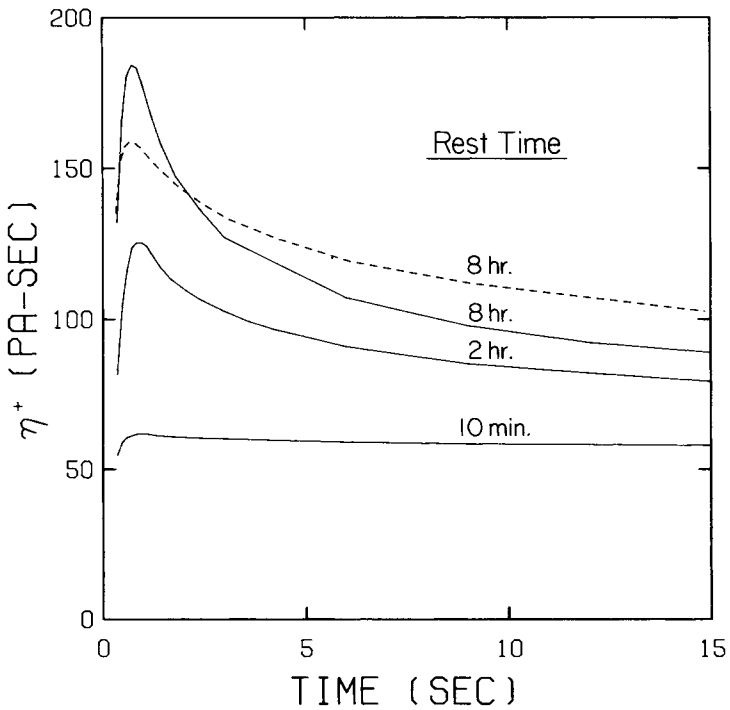


Fig. 7. Rest time dependence of the stress growth function for a 7% fumed silica in 76,000 g/mol PDMS. Shear rate history $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$ and $\dot{\gamma}_t = 2.08 \text{ s}^{-1}$. (—) rest in undeformed state; (---) $\dot{\gamma}_r = 0.104 \text{ s}^{-1}$.

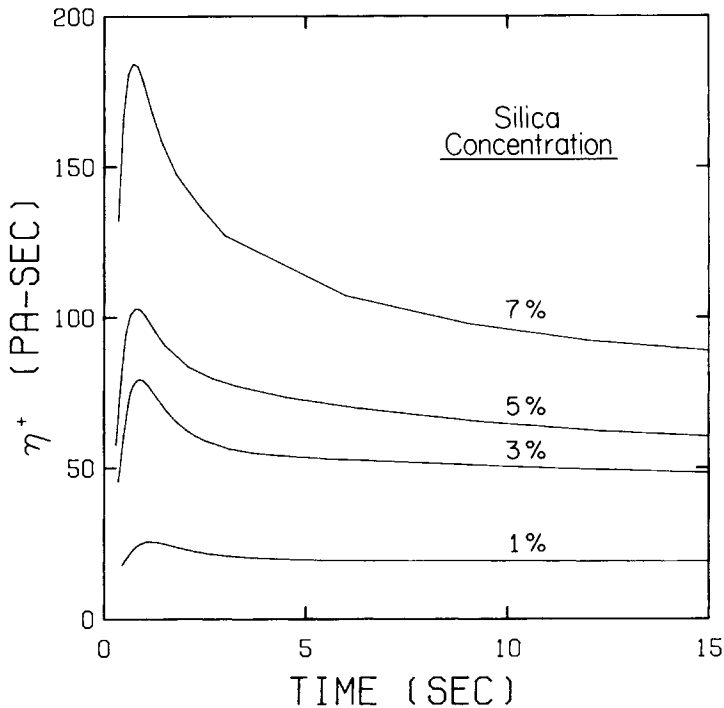


Fig. 8. Effect of particle concentration on the stress growth function for dispersions in 76,000 g/mol PDMS. Shear rate history $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$, rest time 8 h at $\dot{\gamma}_r = 0$, and $\dot{\gamma}_r = 2.08 \text{ s}^{-1}$.

$\eta^+(t)$ maxima decreases slightly with particle concentration; and the time of the maximum in $\eta^+(t)$ decreases slightly when a small $\dot{\gamma}_r$ is applied during the rest. Stress growth results for 1 and 3% fumed silica in 138,000 g/mol PDMS are shown in Figure 9. The dispersions with 138,000 g/mol PDMS do not exhibit $\eta^+(t)$ maxima after resting in the undeformed states for 10 min and 8 h in the undeformed state. The 1% dispersion $\eta^+(t)$ curves virtually superimpose, while the 3% dispersion exhibits a slow approach towards steady state, but no overshoot in the stress growth function. Maxima in the 1 and 3% $\eta^+(t)$ curves occur for the 8 h rest at $\dot{\gamma}_r = 0.104 \text{ s}^{-1}$. The $\eta^+(t)$ results in Figure 9 are representative of both the 118,000 and 138,000 g/mol PDMS dispersions as $\eta^+(t)$ maxima are not observed for rests in the undeformed state but slight $\eta^+(t)$ maxima are induced by a small shear during the rest period.²⁵

The effect of rest time on the $\eta^+(t)$ maxima [or $\eta^+(t)$ at 2.0 s when maxima absent] is summarized in Figures 10(A) and 10(B) for dispersions of various molecular weights and particle concentrations. The results for the 33,000 g/mol PDMS dispersions have been omitted, since there is no effect of rest time. The stress growth maxima increase with particle concentration in a given molecular weight PDMS for all rest times considered. Figure 10(B) illustrates the dramatic change in $\eta^+(t)$ as a dispersion's PDMS molecular weight increases above 93,000 g/mol. The 118,000 and 138,000 g/mol filled fluids exhibit only slight changes in the initial $\eta^+(t)$ values with rest time, while the $\bar{M}_w = 93,000 \text{ g/mol}$ PDMS dispersions

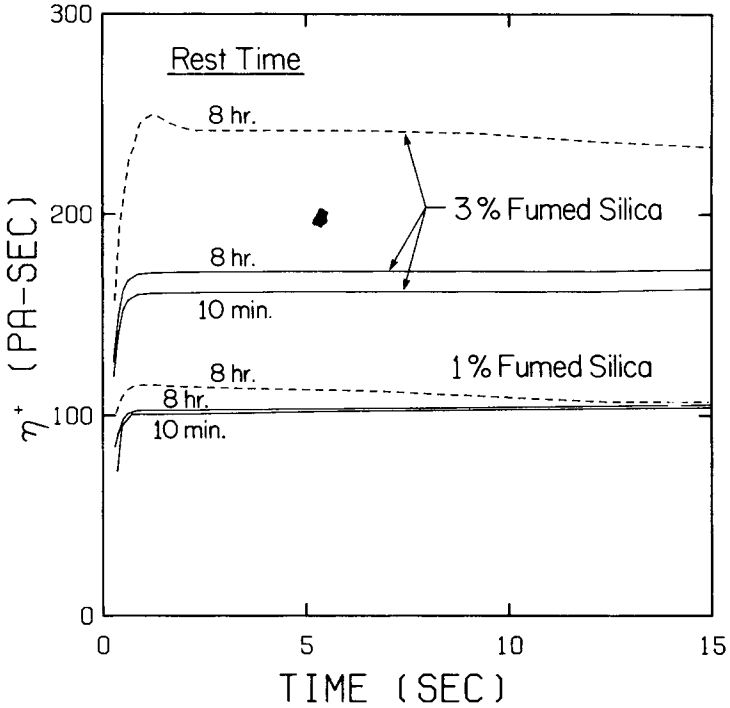


Fig. 9. Stress growth function for fumed silica dispersions with 138,000 g/mol PDMS. Shear rate history $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$ and $\dot{\gamma}_t = 2.08 \text{ s}^{-1}$: (—) $\dot{\gamma}_r = 0.0 \text{ s}^{-1}$; (- - -) $\dot{\gamma}_r = 0.014 \text{ s}^{-1}$.

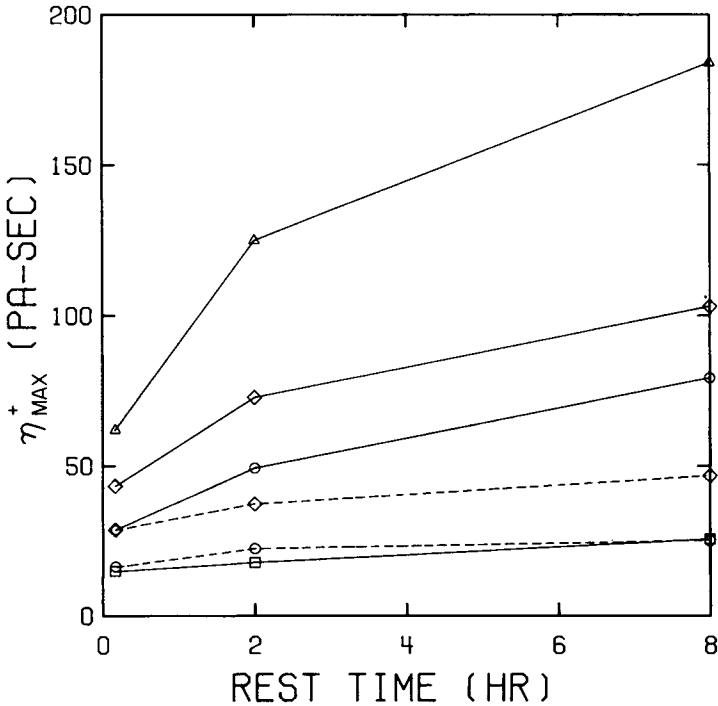


Fig. 10(A). Stress growth maxima as a function of rest time: (- - -) 58,000 g/mol PDMS; (—) 76,000 g/mol PDMS; symbols indicate the same particle concentrations as in Figure 1. Shear rate history $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$, $\dot{\gamma}_r = 0.0 \text{ s}^{-1}$, and $\dot{\gamma}_t = 2.08 \text{ s}^{-1}$.

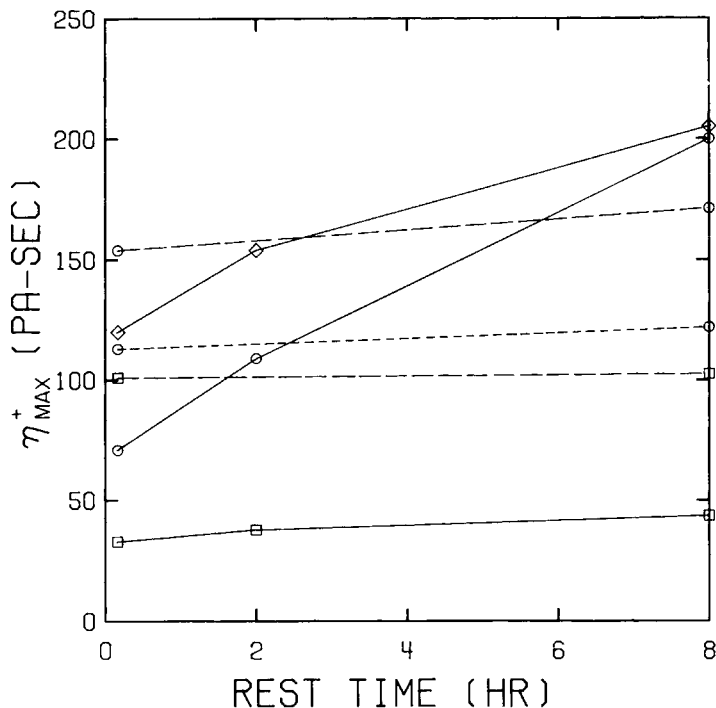


Fig. 10(B). Stress growth maxima as a function of rest time: (—) 93,000 g/mol PDMS, (- - -) 118,000 g/mol PDMS; (· · ·) 138,000 g/mol PDMS; symbols indicate the same particle concentrations as in Figure 1. Shear rate history $\dot{\gamma}_p = 20.8 \text{ s}^{-1}$, $\dot{\gamma}_r = 0.0 \text{ s}^{-1}$, and $\dot{\gamma}_t = 2.08 \text{ s}^{-1}$.

show a significant effect on the rest time. The complete stress growth transients for all the dispersions discussed in this paper are reported elsewhere.²⁶

DISCUSSION

The rheological properties of the dispersions of fumed silica in PDMS are affected quantitatively, but not qualitatively, by the filler concentration. The qualitative features of the dispersions' rheological behavior are primarily determined by the PDMS molecular weight and the previous shear rate history. The stress growth results are particularly sensitive to PDMS molecular weight with no stress growth maxima observed for dispersions with both low (33,000 g/mol) and high (118,000 and 138,000 g/mol) molecular weight fluids, while intermediate (58,000, 76,000, and 93,000 g/mol) molecular weight dispersions exhibit substantial stress growth overshoot with maxima that markedly increase the rest time. The effects of particle concentration on the rheology are less dramatic, where increasing concentration (i) increases the magnitude of the rheological properties, (ii) increases the time required to reach steady state, (iii) changes the rate of stress relaxation, and (iv) decreases slightly the time of the stress growth maxima.

The effect of the viscosity of the continuous phase and/or filler concentration on the rheological properties of dispersions can often be described by reduced material properties, where the dispersion's steady state viscosity,

stress-relaxation, etc., are scaled by some characteristic viscosity.^{8,27,28} The rheological properties reported in this communication cannot be successfully described by reduced variables. The shear rate dependence of the steady state viscosity cannot be reduced to a single curve by either of the following procedures: (i) normalizing all the different molecular weight fluids for a given particle concentration by the viscosity of the unfilled PDMS or (ii) scaling the viscosity for dispersions with the same continuous phase molecular weight, but with different particle concentration, by the dispersion's viscosity at high shear rates. Reduced variables are also unsuccessful in unifying the stress-relaxation and stress growth data. This is particularly obvious for the stress growth data, where there are substantial qualitative differences between the $\eta^+(t)$ response for dispersions of low, intermediate, and high molecular PDMS fluids. The failure of reduced variables to describe the rheological data is a strong indication that the fundamental deformation process must change as the viscosity, and thus the molecular weight, of the continuous phase increases.

The experimental data are consistent with the following microscopic picture.²⁵ The colloidal particles do not directly interact, but rather associate via entanglements of the polymer adsorbed on the particle surface. A similar molecular viewpoint has been suggested for dispersions of spherical particles sterically stabilized by adsorbed polymers in Newtonian solvents.^{29,30} When the continuous phase molecular weight is below the molecular weight of entanglement \bar{M}_{en} , significant interactions between the various particles/adsorbed-polymer entities are not possible. The molecular weight of entanglement for PDMS is approximately $\bar{M}_{en} = 47,000$ g/mol.³¹ Entanglements between adsorbed polymer on different silica particles will yield a flocculated microstructure, where the size of the flocculate depends upon the applied shear rate. At high shear rates the size of the flocculates are reduced; and a three-dimensional network forms via interparticle entanglements, when the dispersion is allowed to rest in the undeformed state. The entanglement/disentanglement process and its shear rate dependence controls the transient rheological properties. Finally, once the continuous phase molecular weight becomes much greater than \bar{M}_{en} , the particle diffusivity is reduced such that significant microstructural recovery, and consequently stress growth maxima, do not occur. A more complete discussion of the transient rheological properties in terms of this molecular deformation mechanism is given elsewhere.^{25,26}

As the filler concentration is increased, the underlying deformation processes described above will not be substantially altered. The effects of filler concentration on the experimentally observed rheological behavior can also be rationalized via this microscopic picture. An increased particle concentration will result in dispersions with less PDMS, a greater proportion of adsorbed polymer, and shorter average particle-particle distances. Since there is less unadsorbed polymer as the particle concentration increases, the resulting flocculates should be larger. The experimentally observed increases in viscosity and the degree of shear thinning with filler concentration for these dispersions is due to these larger flocculates, which exhibit a larger change in size over the same range of shear rates. Short range interactions and small size scale reorganization occur more quickly as particle concentration increases, which is consistent with the stress relaxation

data in Figure 3; however, the time required to reach steady state increases with increased particle concentration due to the larger flocculate size.

APPENDIX: NOMENCLATURE

η	steady shear viscosity
$\eta^+(t)$	shear stress growth function
$\eta^-(t)$	shear stress relaxation after steady shear
ψ_1	steady primary normal stress difference
$\psi_1^+(t)$	primary normal coefficient for stress growth experiment
$\psi_1^-(t)$	primary normal stress coefficient for stress relaxation after steady shear
$\dot{\gamma}_p$	preshear shear rate
$\dot{\gamma}_r$	rest shear rate
$\dot{\gamma}_t$	test shear rate

We would like to thank Exxon for a graduate student fellowship for L. E. K.

References

1. P. Y. Cheng and H. K. Schachman, *J. Fluid Mech.*, **56**, 401 (1955).
2. I. R. Rutgers, *Rheol. Acta*, **2**, 305 (1962).
3. T. B. Lewis and L. E. Nielson, *Trans. Soc. Rheol.*, **12**, 421 (1968).
4. G. K. Batchelor, *Ann. Rev. Fluid Mech.*, **6**, 227 (1974).
5. D. J. Jeffrey and A. Acrivos, *AIChE J.*, **22**, 417 (1976).
6. J. Mewis, *8th Int. Cong. Rheol.*, **1**, 149 (1980).
7. W. B. Russel, *Ann. Rev. Fluid Mech.*, **13**, 425 (1981).
8. T. S. Cantu and J. M. Caruthers, *J. Appl. Polym. Sci.*, **27**, 3079 (1982).
9. J. S. Chong, E. B. Christensen, and A. D. Baer, *J. Appl. Polym. Sci.*, **15**, 2007 (1971).
10. E. A. Bullins, D. J. Hoffman, and P. L. Soni, *J. Colloid Interface Sci.*, **71**, 21 (1979).
11. L. G. Leal and E. J. Hinch, *Rheol. Acta*, **12**, 127 (1973).
12. D. J. Highgate and R. W. Whorlow, *Rheol. Acta*, **9**, 569 (1970).
13. T. Kataoka, T. Kitano, M. Sasahara, and K. Nishijima, *Rheol. Acta*, **17**, 149 (1978).
14. T. Kataoka, T. Kitano, Y. Oyanagi and M. Sasahara, *Rheol. Acta*, **18**, 635 (1979).
15. L. Nicodemo, L. Nicolais, and R. F. Landel, *Chem. Eng. Sci.*, **29**, 729 (1974).
16. N. Minagawa and J. L. White, *J. Appl. Polym. Sci.*, **20**, 501 (1976).
17. J. Mewis and R. de Bleyser, *Rheol. Acta*, **14**, 721 (1975).
18. L. A. Utracki, *Rubber Chem. Technol.*, **57**, 507 (1984).
19. T. S. Chow, *J. Mater. Sci.*, **15**, 1873 (1980).
20. H. S.-Y. Hsich, *J. Mater. Sci.*, **17**, 438 (1974).
21. K. Lem and C. D. Han, *J. Rheol.*, **27**, 263 (1983).
22. J. F. Hutton, *Rheol. Acta*, **14**, 979 (1975).
23. R. S. Ziegelbauer and J. M. Caruthers, *J. Non-Newt. Fluid Mech.*, **17**, 45 (1985).
24. L. E. Kosinski and J. M. Caruthers, *J. Non-Newt. Fluid Mech.*, **17**, 69 (1985).
25. L. E. Kosinski and J. M. Caruthers, *Rheol. Acta*, to appear.
26. L. E. Kosinski, Ph.D. thesis, Purdue University, West Lafayette, IN, 1985.
27. I. M. Krieger, *Adv. Colloid Interfac. Sci.*, **3**, 111 (1972).
28. V. V. Jinescu, *Int. Chem. Eng.*, **14**, 397 (1974).
29. T. Van Vliet, J. Lyklema, and M. Van Den Tempel, *J. Colloid Interface Sci.*, **65**, 505 (1978).
30. M. D. Croucher and T. H. Milkie, in *The Effect of Polymers on Dispersion Properties*, Th. F. Tadros, Ed., Academic, New York, 1981, p. 101.
31. T. Fox and V. Allen, *J. Chem. Phys.*, **41**, 344 (1964).

Received July 10, 1985

Accepted January 27, 1986