Aging effects of precipitated silica in poly(dimethylsiloxane)

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Synopsis

We report the transformation from gels to viscous fluids within a time period of $10^1 - 10^3$ h in mixtures of precipitated silica in silicone oil. Scaling behavior in elastic and viscous moduli versus frequency, similar to that reported by Trappe and Weitz [Phys. Rev. Lett. **85**, 449–452 (2000)], has been observed for suspensions of different ages, silica volume fractions, and silicone oil molecular weights; this shows self-similarity in the stress-bearing silica network in these samples. The elastic plateau modulus, extracted from the scaling of the moduli for each suspension, decays exponentially with time, but the initial plateau modulus depends only on the silica volume fraction and is independent of the properties of the base fluids. The aging time constant is larger if thinner silicone oil or a higher silica volume fraction is used. The aging rate is slower for silica in methyl-terminated silicone oil than that in hydroxyl-terminated silicone oil by about an order of magnitude. We attribute the aging effects to the adsorption of poly(dimethylsiloxane) on silica and use a model based on the "poisons" model by Cohen-Addad and de Gennes [C. R. Ocad. Sci. Paris, Série II **319**, 25–30 (1994)] and on the simulation work by Tsige and co-workers [J. Chem. Phys. **118**, 5132–5142 (2003)] to explain our observations. No aging effect has been observed for silica-mineral oil mixtures. © *2007 The Society of Rheology.* [DOI: 10.1122/1.2714640]

I. INTRODUCTION

Poly(dimethylsiloxane) (PDMS) is a polymer chain with a Si–O backbone and two methyls attached to each silicon atom. The two end groups of PDMS can be functionalized, often with hydroxyl (–OH) or methyl ($-CH_3$) groups. Without cross-linking, PDMS is a liquid (silicone oil) with a wide range of viscosity values, depending on the polymer chain length.

When cross-linked, PDMS can form a silicone rubber that tends to be soft and yet fragile. Its mechanical properties can be improved significantly, however, by adding fine particle fillers such as fumed silica or carbon black [Dannenberg (1975)]. The reinforcement of rubbers by fillers is of tremendous importance for the modern rubber industry, which provides an incredibly large range of products of various mechanical properties.

Despite its important industrial applications, the knowledge of silica reinforcement of silicone rubbers has remained mostly empirical. For example, the tensile strength and elastic modulus of silica-filled silicone rubbers are affected to a large extent by filler

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concentration and silica surface chemistry, among other parameters and processing methods, but it is still not clear how silica interacts with the polymers on a molecular level [Dannenberg (1975); Cochrane and Lin (1993); Aranguren *et al.* (1994)]. It is believed that silica can reinforce silicone rubbers by forming hydrogen bonds between its surface hydroxyl groups and the polymers.

Without cross-linking, one can still obtain a gel by adding small silica particles to PDMS melts, and these gels are often used as filling compounds for optic cables to protect the fibers from water damage [Khan *et al.* (1991)]. The viscoelastic properties of silica-PDMS gels are quite complex. Hysteresis has been reported in both the viscosity and the primary normal stress when the shear rate is increased and then decreased [Ziegelbaur and Caruthers (1985)]. After an applied shear is abruptly changed from one value to another, the shear stress relaxes or grows in a complex manner that depends on the shear history [Kosinski and Caruthers (1985)]. PDMS molecular weight, silica filler concentration and surface chemistry, and sample age also seem to affect the rheological properties of these suspensions [Kosinski and Caruthers (1986); Aranguren *et al.* (1992); DeGroot and Macosko (1999)].

One of the crucial issues in understanding the viscoelastic properties of silica-filled silicone gels is the interaction between silica and PDMS. Experiments show that the interaction is strong enough that a good solvent like chloroform or toluene is not able to remove PDMS adsorbed on silica [Cohen-Addad *et al.* (1985)], although toluene under an ammonia atmosphere [Vondracek and Schatz (1979)] or a dilute solution of trimethylchlorosilane is able to do so, indicating that PDMS chains are not chemically bonded to the silica surface. Infrared spectroscopy also detects no covalent bonds between PDMS chains and silica silanol sites [Léger *et al.* (2000)]. Researchers nowadays mostly agree that PDMS is physically adsorbed on the silica surface.

When terminated with hydroxyls, the PDMS end groups can easily form hydrogen bonds with silanol groups on the silica surface; the adsorption of methyl-terminated PDMS has generally been assumed to occur through hydrogen bonding between the oxygen atoms in the PDMS backbones and the silanol groups on the silica surface [Boonstra *et al.* (1975)]. By fitting concentration profiles of the adsorbed PDMS layers on freshly cleaned plane surfaces of silicon wafers to theoretical models, Léger and coworkers (2000) have found the adsorbed PDMS layers to be "pseudobrushes" (loops of a large distribution of loop sizes and few tails), suggesting that each PDMS chain is attached to the silica surface at multiple monomer sites within the chain. The end groups of PDMS chains, however, play an important role in the adsorption; hydroxyl-terminated chains are absorbed in greater amount [Patel *et al.* (1994)].

A recent investigation on the interactions between PDMS and silicon dioxide using electronic structures calculations and molecular dynamics simulations, however, has challenged the conventional view that oxygen atoms in the PDMS backbones form hydrogen bonds with silanol groups on silica surfaces [Tsige *et al.* (2003)]. This study shows that the end groups in both methyl- and hydroxyl-terminated PDMS dominate the interactions between PDMS and the silica surface. Methyl-terminated PDMS interacts with the silica surface by a weak attraction between a hydrogen atom in the methyl group and an oxygen atom in a hydroxyl group on the silica surface; hydrogen bonding between oxygen atoms in PDMS backbones and silica hydroxyl groups cannot occur due to the steric hindrance of methyl groups on the backbones. The binding energy between a methyl end group and a silanol group is -1 to -6 kcal/mol, depending on the simulation method used; the bond between a hydroxyl end group and a silanol group is much stronger at -16 kcal/mol, which is comparable to that between a water molecule and a silanol group (-13 kcal/mol) [Tsige *et al.* (2003)].

When using silica—usually fumed silica—as a filler in silicone gels, a further complication is that the silica surface is generally far from clean and bare; contaminants like water are inevitable. Cohen-Addad's group has done extensive research [Cohen-Addad (2000)] on the adsorption of PDMS on fumed silica, which has an abundant amount of silanol groups on its surfaces ($\sim$ a few per nm^2). A surprising finding is that the adsorption rate is faster for PDMS with larger molecular weights [Girard and Cohen-Addad (1991)]. This shows that the chain diffusion is not the main process involved in the PDMS adsorption on silica, leading Cohen-Addad and de Gennes (1994) to develop a "poisons" model: The surface of silica particles is initially saturated with small molecules (the poisons). As the poisons slowly diffuse away from their binding sites on silica, PDMS chains replace them and form permanent bonds with silica. Studies of the kinetics of the adsorption of PDMS on fumed silica from PDMS melts have shown that the adsorption is characterized by a slow diffusion process with a $\exp(-(t/\tau)^{1/2})$ time dependence [Cohen-Addad *et al.* (1989); Girard and Cohen-Addad (1991)]. The time constant τ is on the order of 10^1-10^2 h and is shorter for hydroxyl-terminated PDMS than methyl-terminated PDMS [Cohen-Addad and Ebengou (1992)]. The amount of PDMS adsorption is proportional to the square root of the PDMS molecular weight [Cohen-Addad (1989)], although deviations from this dependence and even a linear dependence have also been found [Cohen-Addad *et al.* (1985)].

Thus, in a silica-PDMS suspension—even without knowing exactly how PDMS is attached to the silica surface—one should expect interactions between (1) silica-silica (hydrogen bonding between silanol groups on adjacent particles), (2) silica-PDMS (bonding between silica surface silanol groups and PDMS chains), and (3) PDMS-PDMS (entanglement between PDMS chains) [Cochrane and Lin (1993)].

In the following section, we report our experimental observations on a drastic change over time in the rheological properties of suspensions of precipitated silica in silicone oil (the aging effects) and the influence of PDMS molecular weights and silica particle concentrations on the aging time constant. In Sec. III, we explain our experimental observations qualitatively and self-consistently using a model based on the poisons model by Cohen-Addad and de Gennes and on the simulation work by Tsige and co-workers. When not specified, "silicone oil" refers to the methyl-terminated PDMS melt in the text below; we have also tested hydroxyl-terminated PDMS.

II. EXPERIMENTS AND RESULTS

Precipitated silica particles are comprised of solid, spherical primary particles of nanometer size fused into clusters (secondary particles), often with fractal structures [Legrand (1998)]. The precipitated silica powder used in our experiments, Zeodent 165 (J. M. Huber Corporation, Havre de Grace, MD), is highly polydisperse and has cluster diameters in the range of 10–16 μm. The Brunauer-Emmett-Teller surface area is 179 m^2/g, and the pore volume is 5.9 cm^3/g.

The silica particles were suspended in four different kinds of fluids: (1) silicone oil 100 (SO-100, methyl terminated), (2) silicone oil 350 (SO-350, methyl terminated), (3) silicone oil 2000 (SO-2000, hydroxyl terminated), and (4) mineral oil (MO). SO-100 and SO-350 were Dow Corning ® 200 fluids, purchased from the Chemical Store (Pompano Beach, FL); SO-2000 was a Dow Corning 3-0133 fluid, provided by Dow Corning Co; MO was purchased from Fisher Scientific (Fair Lawn, NJ). The molecular weight M, density ρ, and viscosity η of these fluids are listed in Table I.

Each sample was prepared by mixing the appropriate amount of silica power, untreated as received, in about 25 ml of suspending oil in a small glass jar. After 2–3 min

TABLE I. Molecular weight, density, and viscosity of suspending fluids.

	M^{a}	ρ (g/cm^3)^{a}	η (Pa s)^{b}
SO-100 (–CH$_3$ ends)	5200^{d}	0.968	0.12
SO-350 (–CH$_3$ ends)	13,650^{c}	0.975	0.36
SO-2000 (–OH ends)	~35,000^{c,e}	0.915	1.94
MO	424^{d}	0.862	0.18

[a] Information provided by the manufacturers.
[b] Measured at 25 °C in our laboratory.
[c] M_N.
[d] M_W.
[e] Calculated [Barry (1946)].

of vigorous stirring with a spatula, the mixture usually looked homogenous to the eye. The mixture was then stirred for 10 more min. For the calculation of silica volume fraction, silica density is set to 2 g/cm^3 (neglecting the moisture content). Two volume fractions were used in our experiments: 5.3% and 8.0%.

Samples were stored at room temperature, and sedimentation of silica was observed during storage. The samples, however, were manually re-suspended before each measurement. The measurement of each data point in this paper took about 15 min, and sedimentation during the measurement is negligible. The rheological measurements were carried out on a Bohlin C-VOR rheometer, using a 4-40 cone/plate tool at 25 °C. After being loaded onto the rheometer, the samples were allowed to relax for 10 min. The elastic modulus G' and the loss modulus G'' were measured using an oscillatory shear in the linear regime and as a function of angular frequency ω. These tests were conducted on each sample at various times after it was first mixed (at $t=0$).

For results reported below, we did not preshear the samples after they have been loaded onto the rheometer, because the rheological properties of silica-PDMS suspensions were highly sensitive to the shear history [Ziegelbaur and Caruthers (1985)]. The data were taken using multiple samples, and we could see that the measurements were generally reproducible, with some scattering in the data.

It is worthwhile pointing out here that the aging effects presented in the following pages cannot be attributed to the method of sample preparation or to the measurement technique, because, as we will see, the time evolution of the rheological properties of silica-silicone oil and silica-mineral oil samples is drastically different, despite using the same mixing and testing protocol.

A. Aging effect and scaling behavior

Figure 1 shows G' and G'' as a function of ω for mixtures of silica in SO-350 at 5.3% volume fraction. We can see clearly that the freshly made suspension is an elastic gel, with G' being frequency independent and much larger than G''. The plateau value of the elastic modulus, G_0', measures the strength of the gel network.

This all changes drastically over time, however, with G' and G'' both dropping dramatically, but G' more so than G''. After approximately two weeks, G' has decreased by several orders of magnitude and has become much smaller than G'', and G'' now shows a nearly linear frequency dependence, characteristic of a viscous fluid. Figure 2 shows the time evolution of G' and G'' at a fixed frequency of 27 rad/s. Both moduli decay exponentially with time, but the time constant extracted from this figure depends on the value

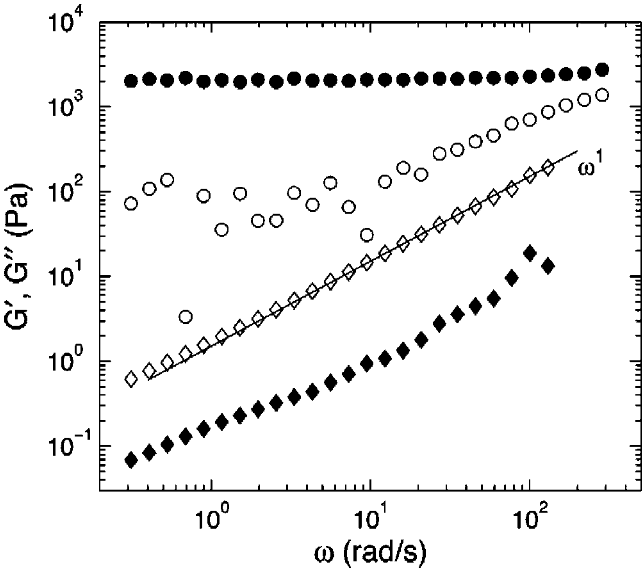

FIG. 1. The elastic modulus G' (closed symbols) and the viscous modulus G'' (open symbols) as a function of frequency for silica in SO-350 at 5.3% volume fraction. The sample ages are 0.25 h (circles) and 606.5 h (diamonds). The straight line, showing a linear relationship between the modulus and the frequency, is to guide the eye.

of the frequency and also differs for the two moduli. Curves of moduli at a fixed frequency as a function of time for other samples were published in an earlier paper [Selimovic and Hu (2004)].

A more informative picture of the time evolution of the viscoelastic properties of the suspensions emerges when we collapse different data sets for different-aged samples onto two master curves for G' and G'', following the method used by Trappe and Weitz

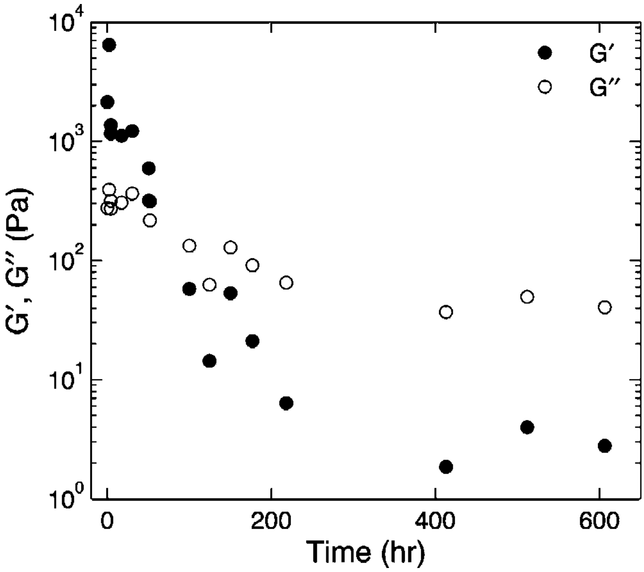

FIG. 2. The elastic modulus G' and the viscous modulus G'' as a function of sample age at a fixed frequency of 27 rad/s for silica in SO-350 at 5.3% volume fraction.

(2000). In this method, different scaling factors, a for ω and b for both G' and G'', are obtained for each individual data set, with b proportional to a/η, where η is the viscosity of the base fluid. Trappe and Weitz proposed the following model to explain this proportionality: At low frequencies, the viscoelastic properties of a particle gel are dominated by the elastic modulus of the gel network, characterized by a frequency-independent plateau modulus $G'=G'_0$. At high frequencies, the viscosity of the base fluid dominates, and the viscous modulus is $G''=\eta\omega$. The crossover of the two moduli, where G' and G'' are equal to each other, occurs at a frequency $\omega_c \approx G'_0/\eta$. For gels with differences in network strengths but with a strong similarity in structures, the crossover points can be made to coincide by normalizing the moduli by G'_0 and the frequency by ω_c. In terms of master curve scaling factors, then, $a \propto \eta/G'_0$, $b \propto 1/G'_0$, and $a \propto \eta b$.

In Fig. 3(a), we graph G' and G'' master curves obtained from 12 different data sets for different-aged samples of silica in SO-350 at 5.3% volume fraction. In this figure, we plot scaled modulus values versus scaled frequency. To identify scaling factors a and b for each individual data set, we first found crossover points for data sets where the G' and G'' curves actually intersected and extrapolated crossover points for nonintersecting data sets. We then determined a and b factors for each data set that would make all of the actual and extrapolated crossover points to coincide. Finally, we fine tuned the values of a and b until we had produced continuous and visually smooth master curves. We did not use data for which the extrapolated crossovers had large uncertainties.

The master curves in Fig. 3(a) closely resemble those obtained by Trappe and Weitz (2000): At low frequencies, bG' reaches a constant value and is much larger than bG''; at high frequencies, the relationship between bG'' and $a\omega$ is close to linear, and bG'' is much larger than bG'. The inset in Fig. 3(a) shows that the scaling parameters are related by a power law, $b \sim a^z$, with $z=0.91$, which is very close to the value of 1 in the Trappe-Weitz model.

One of the benefits of scaling G' and G'' to master curves is that one can extract the elastic plateau modulus G'_0 ($G'_0 \propto 1/b$) for very weak gels, even when the direct measurement of G'_0 is impossible because of instrument limitations. Figure 3(b) shows G'_0 as a function of sample age t, fitted to an exponential function

$$G'_0(t) = G'_{0\infty} + (G'_0(0) - G'_{0\infty})e^{-t/\tau}, \tag{1}$$

where $G'_0(0)$ is the plateau modulus of freshly made samples at time $t=0$, $G'_{0\infty}$ is the plateau modulus of the aged samples, and τ is the aging time constant. For silica in SO-350 at 5.3% volume fraction, $\tau=22$ h.

Trappe and Weitz's master curves contained viscoelasticity data of samples of carbon black suspended in oil with various volume fractions and particle-particle interaction strengths (controlled by adding surfactants). They observed a shallow minimum in G'' at low frequencies and attributed the minimum to the flow of suspensions at low frequencies. For our aged samples, we notice plateaus in both G' and G'' at (unscaled) low frequencies that do not fit well onto the master curves in Fig. 3(a). The flow of suspensions is a possible explanation for the plateaus in G'', but not for G', because G' should fall, not rise, in magnitude as the gel network is strained beyond its elastic linear regime, as seen in our amplitude sweeps. A possible explanation for these plateaus is the limitation of the self-similarity argument used in the Trappe-Weitz model, because self-similarity cannot extend indefinitely to higher and higher volume fractions due to the finite particle size; this limitation is probably more pronounced at low frequencies when the suspensions are strained more in our frequency sweeps at constant stress.

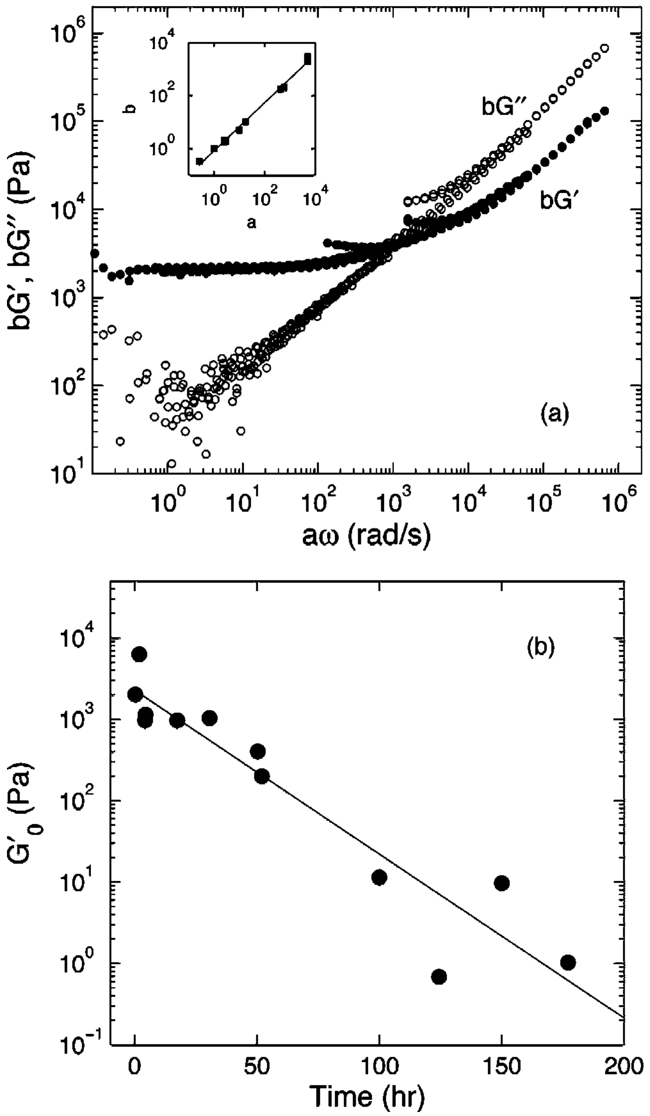

FIG. 3. (a) The scaling of the elastic modulus G' and the viscous modulus G'' as a function of frequency for silica in SO-350 at 5.3% volume fraction. Twelve sets of data, for samples of ages ranging from 0.25 to 177 h, are used. The inset is the relationship between fitting parameters b and a, showing a power law relationship with an exponent of 0.91. (b) The plateau modulus G_0' as a function of sample age. The solid line is a fit to an exponential function given by Eq. (1) with a time constant $\tau=22$ h.

B. Effect of silica volume fractions

Figure 4(a) shows a set of master curves for moduli versus frequency for four different kinds of samples: (i) silica in SO-350 at 5.3% volume fraction, 12 sets of data, sample age 0.25–177 h; (ii) silica in SO-350 at 8.0% volume fraction, 31 sets of data, sample age 0.3–595 h; (iii) silica in SO-100 at 5.3% volume fraction, 13 sets of data, sample age 0.25–248 h; and (iv) silica in SO-2000 at 5.3% volume fraction, 17 sets of data, sample age 0.12–11.3 h. Figure 4(b) shows b vs a/η in a log-log plot with a slope of 0.91, again very close to the exponent of 1 predicted by the Trappe-Weitz model (2000).

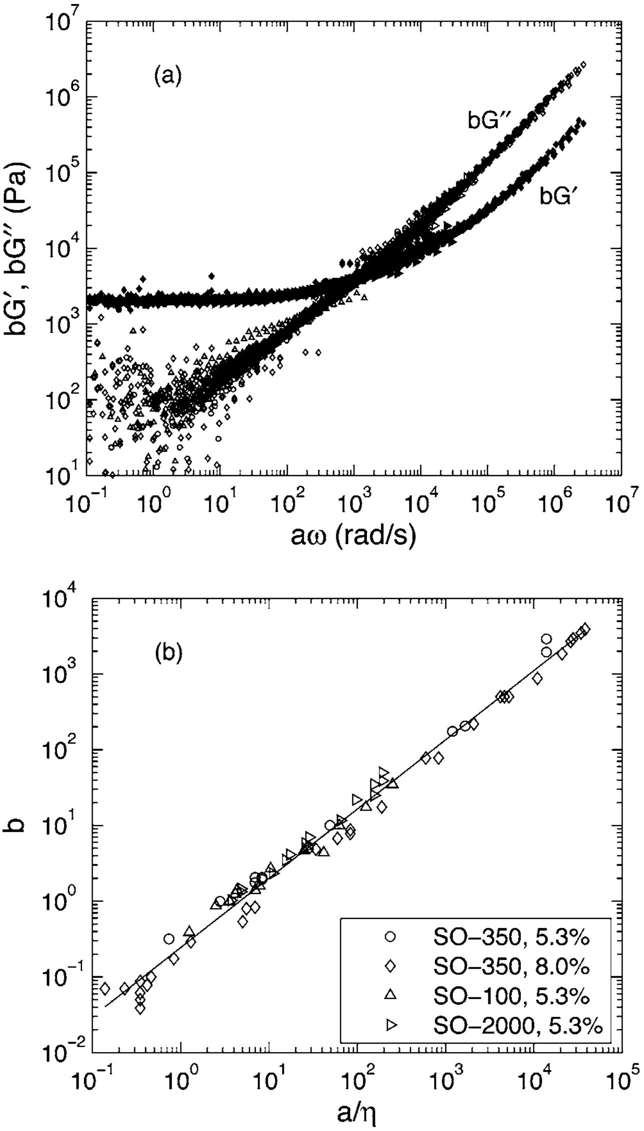

FIG. 4. (a) The scaling of the elastic modulus G' and the viscous modulus G'' as a function of frequency for four sets of samples: silica in SO-350 at 5.3% and 8.0% volume fractions, silica in SO-100 and in SO-2000, both at 5.3% volume fraction. (b) The fitting parameter b as a function of the fitting parameter a divided by the base fluid viscosity η. The power law relationship has an exponent of 0.91.

The effect of silica volume fractions is shown by comparing the plateau modulus G_0' as a function of sample age for silica in SO-350 at 5.3% and at 8.0% volume fractions (Fig. 5). Two features show up clearly in this plot: The initial plateau modulus $G_0'(0)$ at 8.0% volume fraction is about an order of magnitude higher than that at 5.3%, reflecting a stronger silica gel network at a higher volume fraction; the aging time constant is longer for the higher silica volume fraction ($\tau=48$ h for 8.0%, and $\tau=22$ h for 5.3%).

C. Effect of PDMS molecular weights

Figure 6 shows the effect of PDMS molecular weights by plotting the plateau modulus G_0' as a function of sample age for silica in SO-350 and in SO-100, both at 5.3% volume

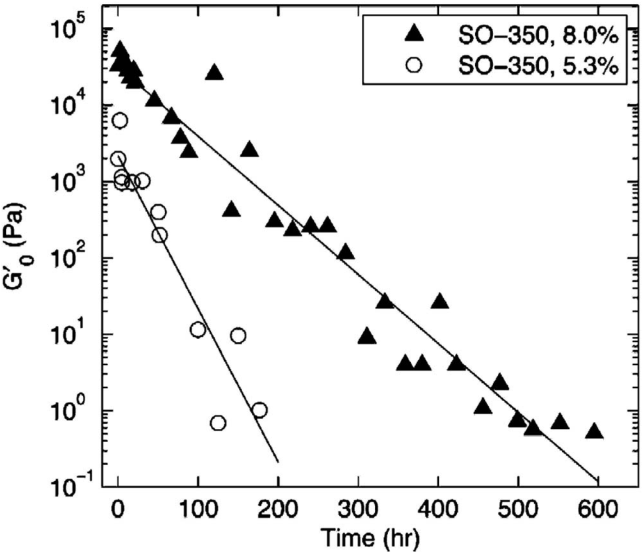

FIG. 5. The plateau modulus G_0' as a function of sample age for silica in SO-350 at 8.0% (closed triangles) and at 5.3% (open circles) volume fractions. The solid lines are fits to an exponential function given by Eq. (1). Samples with a higher silica volume fraction have a larger initial plateau modulus and a longer aging time constant τ (48 and 22 h, respectively).

fraction. We notice again two features: The initial plateau modulus $G_0'(0)$ is about the same for the two base fluids, indicating that the silica networks are similar in strength for these two base fluids; a smaller PDMS molecular weight results in a slower aging process ($\tau=76$ h for SO-100, and $\tau=22$ h for SO-350).

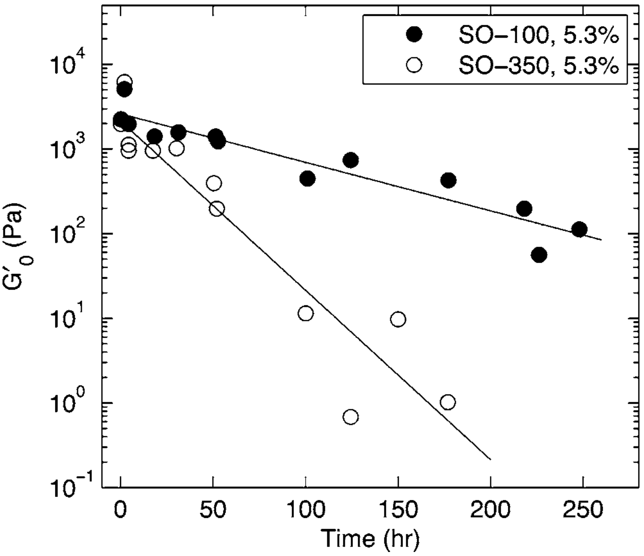

FIG. 6. The plateau modulus G_0' as a function of sample age for silica in SO-100 (closed circles) and in SO-350 (open circles), both at 5.3% volume fraction. The solid lines are fits to an exponential function given by Eq. (1). Both suspensions have about the same initial plateau modulus. Suspensions of silica in silicone oil of a smaller molecular weight have a longer aging time constant τ (76 and 22 h, respectively).

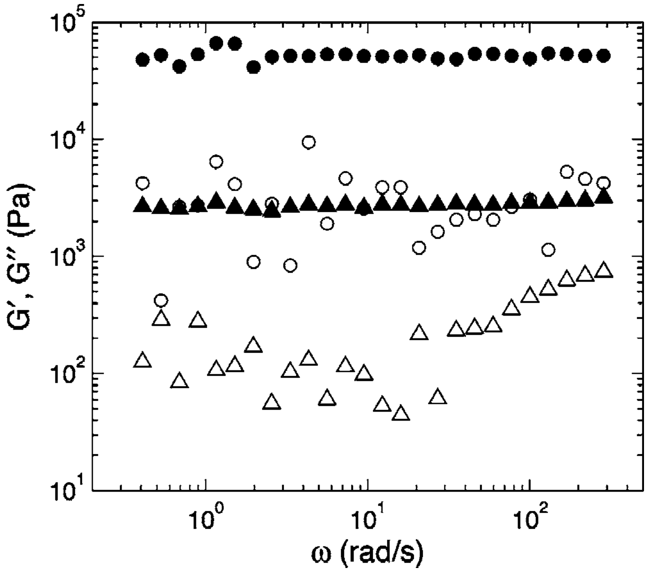

FIG. 7. The elastic modulus G' (closed symbols) and the viscous modulus G'' (open symbols) as a function of frequency for silica in mineral oil at 8.0% (circles) and at 5.3% (triangles) volume fractions.

We should mention that the moduli versus frequency curves for silica in SO-100 do not fit onto the master curves after G'' becomes larger than G' and are not included in Fig. 4. This could be due to the loss in self-similarity in the stress-bearing silica network during the aging process, or it could be due to the loss of space-spanning silica network altogether.

D. Silica in mineral oil

Figure 7 plots G' and G'' as a function of ω for suspensions of silica in mineral oil at 5.3% and 8.0% volume fractions. For each volume fraction, G' is independent of ω and is much larger than G'', indicating that the elastic properties of the gel network dominate in this frequency regime for both volume fractions. Furthermore, the plateau modulus G_0' is very close in magnitude to the initial plateau modulus $G_0'(0)$ for silica in silicone oil at the same volume fractions (Figs. 5 and 6), suggesting that the silica gel network formed in mineral oil is similar to the initial network in silicone oil.

A major difference between silica suspended in silicone oil and in mineral oil, however, is that the mineral oil suspensions do *not* age. Figure 8 shows that the plateau modulus G_0' for silica in mineral oil at 8.0% volume fraction does not change with time; the plateau modulus for silica in SO-350, also at 8.0%, is plotted in the same graph for comparison.

E. Hydroxyl-terminated silicone oil

Figure 9 plots the plateau modulus G_0' as a function of sample age for silica suspended in hydroxyl-terminated SO-2000 at 5.3% volume fraction. We can see that with a time constant $\tau=2.0$ h, the aging process for silica suspended in hydroxyl-terminated silicone oil is much faster than that for silica in methyl-terminated silicone oil. The initial plateau

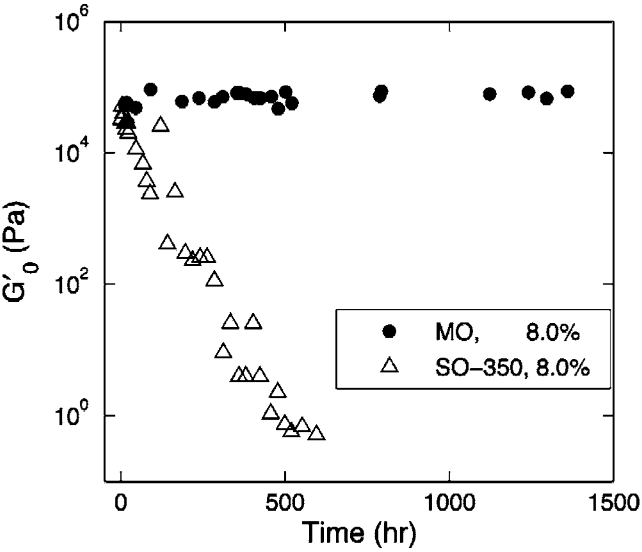

FIG. 8. The plateau modulus G_0' as a function of sample age for silica in mineral oil (closed circles), in comparison to that for silica in SO-350 (open triangles), both at 8.0% volume fraction. Mineral oil suspensions show no aging behavior.

modulus, $G_0'(0)$, however, is about the same for silica in silicone oils of both end groups (at the same volume fraction), reflecting again that both suspensions have similar initial gel network strength.

Once again, after G'' becomes larger than G', G' and G'' for silica in hydroxyl-terminated SO-2000 can no longer be scaled onto the master curves in Fig. 4(a); after

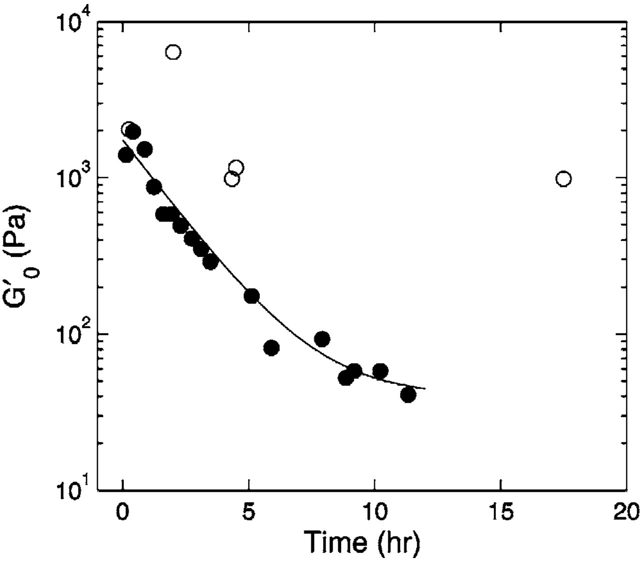

FIG. 9. The plateau modulus G_0' as a function of sample age for silica in hydroxyl-terminated SO-2000 (closed circles), in comparison to that for silica in methyl-terminated SO-350 (open circles), both at 5.3% volume fraction. The solid line is a fit to an exponential function given by Eq. (1) with a time constant $\tau=2.0$ h. Both suspensions have similar initial plateau modulus, but suspensions of silica in hydroxyl-terminated silicone oil age much faster.

24 h, the suspension is Newtonian with shear stress proportional to shear rate. In contrast, the scaling behavior for silica in methyl-terminated SO-350 extends into the range of $G'' > G'$.

We have also tested a suspension of silica in a thinner hydroxyl-terminated silicone oil (Dow Corning Q1-3563 fluid). This suspension showed similar aging behavior compared to silica in SO-2000 and became a free-flowing Newtonian fluid within 24 h.

III. MODEL AND DISCUSSION

Since the initial elastic plateau modulus of all suspensions in our experiments depends only on the silica volume fraction and is independent of the properties of the base fluids, there is little doubt that the silica gel network is responsible for the initial elastic properties of our suspensions. The formation of a gel by suspending hydrophilic silica particles in silicone oil and in mineral oil (both hydrophobic) does not come as a surprise, because silica particles prefer to bind with each other in order to lower free energy. The silica network thus formed can sustain small deformation and is responsible for the elastic properties of the gel. The aging of the silica-silicone oil suspensions indicates a gradual deterioration of the silica network over time. The silica-mineral oil suspensions, however, remain stable with time.

What causes the gradual breakdown of the silica network in silicone oil? Why is the aging time constant longer when the PDMS molecular weight is smaller and when the silica volume fraction is larger? Why is the aging time constant for silica in hydroxyl-terminated silicone oil much smaller than that in methyl-terminated silicone oil?

To answer these questions, it is helpful to correlate the aging behavior we have observed with the dynamics of PDMS adsorption on silica [Cohen-Addad (2000)]. As mentioned in the Introduction, PDMS is physically adsorbed on silica with a time constant on the order of $10^1 - 10^2$ h, and the adsorption rate is faster for PDMS with larger molecular weights. In addition, the adsorption of hydroxyl-terminated PDMS is faster than that of methyl-terminated PDMS. In comparison, the aging time constant we have observed for silica in silicone oil is also on the order of $10^1 - 10^2$ h, and the aging process is faster for PDMS of larger molecular weights. Furthermore, the aging time constant for silica suspended in hydroxyl-terminated PDMS is about an order of magnitude shorter than that in methyl-terminated PDMS. These comparisons strongly suggest that the PDMS adsorption on silica plays a key role in the aging process of concern here.

Let us then consider the following scenario: When first suspended in PDMS, hydrophilic silica particles are attracted to each other in a hydrophobic medium and form a gel network. As PDMS slowly adsorbs onto the surface of silica, silica particles gradually lose direct contact with each other. To maintain a gel network under these circumstances, PDMS would have to be the intermediate connecting agent between silica particles. This could be accomplished by the adsorption of a single polymer on two adjacent particles (bridging) or by the entanglement between polymers adsorbed on adjacent particles. Both of these two situations, however, require PDMS of sufficient molecular weights (the entanglement limit for PDMS is 47 000 g/mol) [Fox and Allen (1964); Cohen-Addad (2000)]. Since the silicone oils we used have relatively small molecular weights, it is unlikely that silica particles can maintain a gel network with PDMS as connecting agents in our experiments. Without PDMS connecting silica particles, the attractions between silica particles become weaker and weaker as more and more PDMS are adsorbed on the silica surface, resulting in the suspensions' gradual transition to a viscous fluid.

The poisons model proposed by Cohen-Addad and de Gennes (1994), on the other hand, provides a possible explanation. In this model, small poison molecules, which are initially adsorbed on the silica surface, slowly diffuse away from their binding sites and are replaced by PDMS. If silica particles coated with PDMS cannot bind with each other, the gel network then falls apart. The poisons in our samples are water molecules, because we used untreated silica powders.

Water molecules bind strongly with silica hydroxyl groups, and it is very difficult to remove all residual water molecules from silica surface, even with oven heating at moderate temperatures. The bond between methyl-terminated PDMS and silica silanol groups, on the other hand, is weaker, as shown by the fact that silicone oil is hydrophobic and is immiscible with water. Why should PDMS replace water on silica surface? A possible explanation is provided by the recent simulation work by Tsige and co-workers (2003), which predicts that a PDMS polymer binds with a silanol group on the silica surface primarily through the end groups and not through the PDMS backbone. Since it prefers to lie with its backbone parallel to the silica surface, a PDMS polymer can "cover up" a large silica surface area without actually forming bonds with all silanol groups underneath and thus sterically hinder the formation of silica network. In other words, only a fraction of the silanol groups on the silica surface need to bind with PDMS for the silica network to be significantly weakened. This also explains qualitatively why the aging time constant is larger for smaller PDMS molecular weights and why suspensions with high silica volume fractions age more slowly.

To sterically cover up a given area of the silica surface with smaller PDMS polymers, more polymers are needed. If the binding is made primarily with PDMS end groups, a larger percentage of hydroxyl sites on the silica surface would need to be occupied by PDMS instead of water, and this will take a longer time. When the volume fraction is high, each silica particle has more neighbors on average. To break down the silica network, more PDMS polymers need to bind to silica surface, and this also takes longer time.

If, on the other hand, we assume that the adsorption of PDMS on silica is through the PDMS backbone, we then would have a more difficult time justifying the PDMS molecular weight dependence of the aging process, because the silica particles are immersed in a polymer melt and the number of monomers in the polymer backbones that are available to form bonds with the silica surface should not be sensitive to the polymer molecular weight. In fact, the original poisons model by Cohen-Addad and de Gennes (1994), which assumes that PDMS makes multiple bonds with silica along the polymer chain, cannot explain the molecular weight dependence of the PDMS adsorption dynamics.

We want to emphasize here that we do not have direct experimental evidence to show how PDMS is attached to the silica surface. Even though our results can be explained more easily using the end-adsorption model, we do not know for sure whether this is indeed the case. The mechanism responsible for the PDMS adsorption on silica thus remains an open question.

Finally, we compare our experimental results with the earlier work on the aging effect of silica in PDMS by DeGroot and Macosko (1999). These authors reported a reduction of G' (at a fixed frequency) by several orders of magnitude in suspensions of fumed silica in PDMS of molecular weights higher than 36 000 g/mol; no aging effects were found if the PDMS molecular weight was less than 20 000 g/mol. They also observed filler re-agglomeration in the samples that aged and attributed it to the bridging of PDMS between silica particles when PDMS is adsorbed asymmetrically on different regions of a particle. We, on the other hand, used PDMS of molecular weights smaller than 20 000 g/mol and still saw drastic aging effects. Since bridging is insignificant for these short polymer chains, the bridging mechanism cannot explain our experimental observations. Since

DeGroot and Macosko did not report how G'' changed with time or how the moduli depended on frequency, it is difficult to compare our findings directly with theirs. The discrepancies between our work and theirs could arise from using different kinds of silica fillers (we used precipitated silica while they used fumed silica).

IV. CONCLUSIONS

Precipitated silica particles suspended in silicone oil initially form a gel, because the hydrophilic silica particles prefer to bind with each other in the hydrophobic silicone oil to form a space-spanning network. This network breaks down, however, on a time scale of around 10^1-10^2 h for silica in methyl-terminated silicone oil; the breakdown rate for suspensions in hydroxyl-terminated silicone oil is about ten times faster. This aging process can be slowed down by increasing the silica volume fraction or by decreasing the PDMS molecular weight.

The suspensions of silica in mineral oil, however, show no aging effects. The initial elastic modulus of all the suspensions tested in our experiments depends only on the silica volume fraction and is insensitive to variations in base fluid properties (methyl- or hydroxyl-terminated silicone oil, mineral oil, different silicone oil molecular weights, etc.). This strongly indicates that the silica network is responsible for the initial mechanical properties of all the samples we tested, and that this initial silica network depends only on the silica volume fraction.

Furthermore, the curves of elastic modulus and viscous modulus versus frequency for silica-silicone oil suspensions can be scaled to a set of master curves for samples of different age using the method and model by Trappe and Weitz (2000). This scaling behavior shows that the stress-bearing silica network is self-similar in structure during the aging process (at least up the crossover of G' and G''; the scaling does not work for suspensions of silica in SO-100 and in SO-2000 after G'' becomes larger than G'). The scaling of the moduli also allows us to extract the low-frequency elastic plateau modulus, even when the direct measurement of this quantity is beyond the instrument limitations in our experiments. We have found that the elastic plateau modulus, which measures the strength of the silica network, decays exponentially with time.

The eventual breakdown of the silica network in silicone oil can be explained qualitatively by the poisons model by Cohen-Addad and de Gennes (1994). In this model, PDMS polymers bind to the silica surface by gradually replacing some of the water molecules (poisons) that are originally bound to silica silanol groups; silica particles coated with PDMS cannot bind with each other in our experiments, causing the gels to eventually transform to viscous fluids.

More experimental and theoretical work is required, however, to fully understand the aging process of the silica-silicone oil system. In particular, direct experimental evidence on how PDMS is adsorbed on silica will be helpful to developing a model that can predict the PDMS molecular weight and the silica volume fraction dependence of the aging time constant. We hope to address some of these issues in our future research.

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