Aging Effects in Suspensions of Silica Particles

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ABSTRACT

In our study of the aging phenomena in silica suspensions we immersed precipitated silica particles in methyl-terminated PDMS (silicone oil), mineral oil, and glycerol/water and measured their viscoelastic properties as a function of time. We found that the samples based on silicone oil, initially of a pasty consistence, became fluid-like after a period of about three weeks. Aqueous samples aged much faster than the oily samples. Samples containing mineral oil did not exhibit any changes in viscosity and elasticity. In this paper we discuss a possible mechanism for these aging behaviors.

INTRODUCTION

Fumed silica forms a viscoelastic gel when suspended in silicone oil and in mineral oil, and these suspensions are widely used as filling compounds for fiber-optic cables [1]. Because these filling compounds provide mechanical support for the optic fibers, their viscoelastic properties are of great interest to researchers.

The viscoelastic properties of a gel are determined largely by the interactions between the particles that form the gel, and the chemical environment of these particles plays an important role in these interactions. The surface of native silica particles has a large amount of silanol groups (Si-OH), which are hydrophilic. When immersed in a hydrophobic base fluid, silica particles form a gel network because it is energetically favorable for them to form hydrogen bonds with each other. When immersed in a polar medium, however, molecules from the base fluid form a solvation layer around the silica particles due to hydrogen bonding, preventing silica particles to bond with each other, and the suspension is a viscous fluid [2].

For obvious reasons, the stability of the viscoelastic properties of a fiber-optic cable filling compound over time is also of great importance. Reports on the aging behavior of fumed silica in silicone oil have been mixed. Some suspensions showed no significant aging behavior [1,3], while others softened with time [4,5].

In our study of silica gels, we discovered that suspensions of precipitated silica in silicone oil showed drastic aging behavior, turning from a gel to a fluid in a few weeks. In this paper, we report our preliminary observations of this aging behavior and suggest a possible mechanism for it. For comparison, we also used mineral oil and a glycerol/water mixture as base fluids.

EXPERIMENTAL DETAILS

The precipitated silica particles Zeodent 165, provided by Huber Engineered Materials, are highly polydisperse and amorphous, with a particle diameter ranging from 10-16 μm . The

Table I. Overview of Samples.

Sample	*Base fluid*	*Viscosity of base fluid (in Pa s)*	*Average molecular weight of base fluid*	*Relaxation Time τ** (in hr)*
1	Silicone oil	0.36	13650†	68
2	Silicone oil	0.12	5200‡	67
3	Mineral oil	0.18	424‡	-
4	Glycerol and water	0.30	92*	14

† M_N; ‡ M_W; * Glycerol
** These values are obtained by fitting the measured viscosity to Eq. (1).

moisture content ranges between 3% and 7%. The silica powder, untreated as received, was suspended in three different kinds of base fluids: silicone oil, mineral oil, and glycerol/water mixture.

The samples were mixed manually in small glass jars. Usually, after a vigorous mixing of two to three minutes, the silica powder was homogeneously distributed in the fluid, as suggested by a visual inspection. To ensure a high level of homogeneity, each sample was mixed for 10 minutes.

To observe the aging behavior of the oily samples we used mineral oil and two silicone oils with different molecular weights. The aqueous sample contains glycerol and water ($m_{\mathrm{Glycerol}} : m_{\mathrm{Water}} = 19 : 1$). This glycerol-water ratio ensures that the viscosity of this sample's base fluid is of the same order of magnitude as the silicone oil viscosities. In all cases a volume fraction of 5.3% was used. The samples are listed in Table I.

All tests were conducted on a commercial Bohlin C-VOR stress-controlled rheometer, using a cone-and-plate tool (∅ = 40 mm, ∠ = 4°) at 25°C. The samples were manually stirred before being loaded onto the rheometer and left to relax for 10 minutes. The elastic modulus G' and loss modulus G'' were measured using dynamic shear in the linear regime and as a function of frequency ω from 0.05 to 100 Hz.

The (apparent) viscosity of the suspensions was measured using a steady shear at a rate of 1 s^{-1} immediately after the dynamic measurement. Data were collected over a time period of 5 minutes. Some samples showed a slight initial rise or fall in viscosity; the viscosity data were obtained by averaging the steady-state values. All these tests were conducted for several weeks and on multiple samples of each type.

RESULTS

a) Oily samples

The viscoelastic properties of all three kinds of oily samples are about the same immediately after the samples are made. The elastic modulus G' (~ 10^3 Pa) is an order of magnitude larger than the loss modulus G' (~ 10^2 Pa), suggesting that these specimens are viscoelastic gels. They do not flow under the influence of gravity. The viscosity is about 150 $\mathrm{Pa} \cdot \mathrm{s}$, which is much

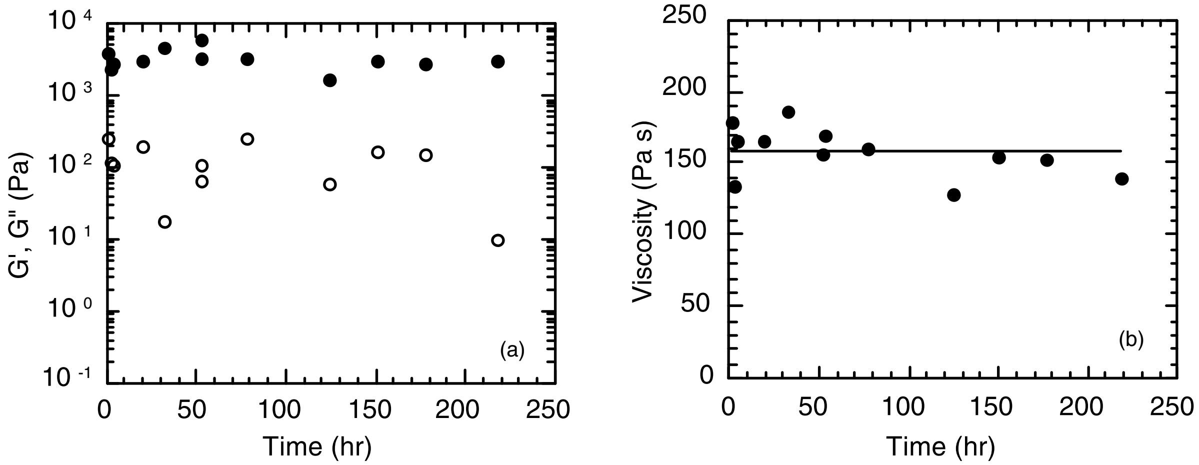

Fig. 1 Viscoelastic properties of silica particles in mineral oil as a function of time.
(a) G' (closed circles) and G'' (open circles) at 1.14 Hz; (b) viscosity at a shear rate of 1 s^{-1}.

larger than that of the base fluids. These results suggest that right after the samples are mixed, the silica gel network is very similar in all three oily base fluids.

Samples containing silica particles immersed in mineral oil do not show any aging behavior (Fig. 1). Over the ten-day testing period it remains a gel of constant G' and G'. The viscosity also shows no appreciable change.

Suspensions of silica in silicone oil, on the other hand, show drastic decrease in G' and G'' over time (Figs. 2a and 3a). Initially, the samples are gels with G' larger than G'' at the dynamic shear frequency of 1.14 Hz. After several days, however, G'' becomes larger than G', showing that the samples have become more fluid-like. This crossover occurs earlier at high frequencies than at low frequencies. Moreover, at a given frequency, it occurs earlier in samples with a higher molecular weight PDMS than in those with a lower molecular weight. The trend in both samples is a rapid decrease in G' by close to four orders of magnitude and a decrease in G'' by one order of magnitude. From the semi-log plots of G' and G'' versus time, we can see that the decrease is nearly exponential. Samples with higher molecular weight PDMS are fully aged after three weeks (Fig. 2a), while the aging time for samples with lower molecular weight PDMS is four weeks (Fig. 3a).

Viscometry tests also quantify our visual observation that the samples flow better with time (Figs. 2b and 3b). The viscosity of samples with both PDMS molecular weights, initially on the order of 10^2 $\mathrm{Pa \cdot s}$, decreases exponentially by an order of magnitude in 10 days. The measured viscosity η as a function of time t can be fitted to the following equation

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)e^{-t/\tau}, \tag{1}$$

where τ is a relaxation time constant, η_0 the viscosity right after a sample is made, and η_∞ the viscosity of the aged sample. The relaxation time constant τ extracted from the fit is recorded in Table I.

The viscosity of samples with both PDMS molecular weights seems to decrease with nearly identical time constants (Table I), but the measurements of G' and G'' seem to indicate that samples with the higher PDMS molecular weight age faster. This discrepancy can be attributed

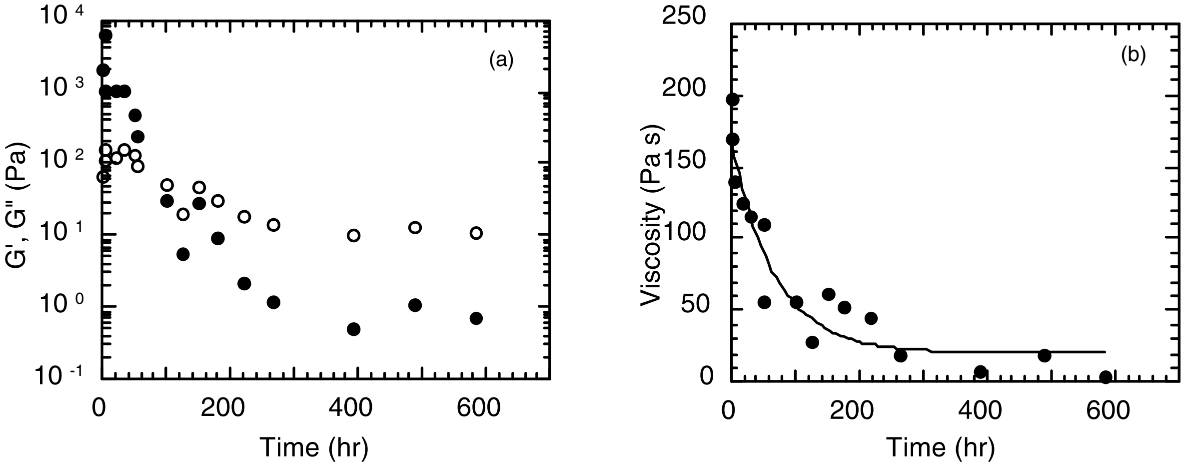

Fig. 2 Viscoelastic properties of silica particles in heavy silicone oil as a function of time. (a) G' (closed circles) and G'' (open circles) at 1.14 Hz; (b) viscosity at $1 s^{-1}$.

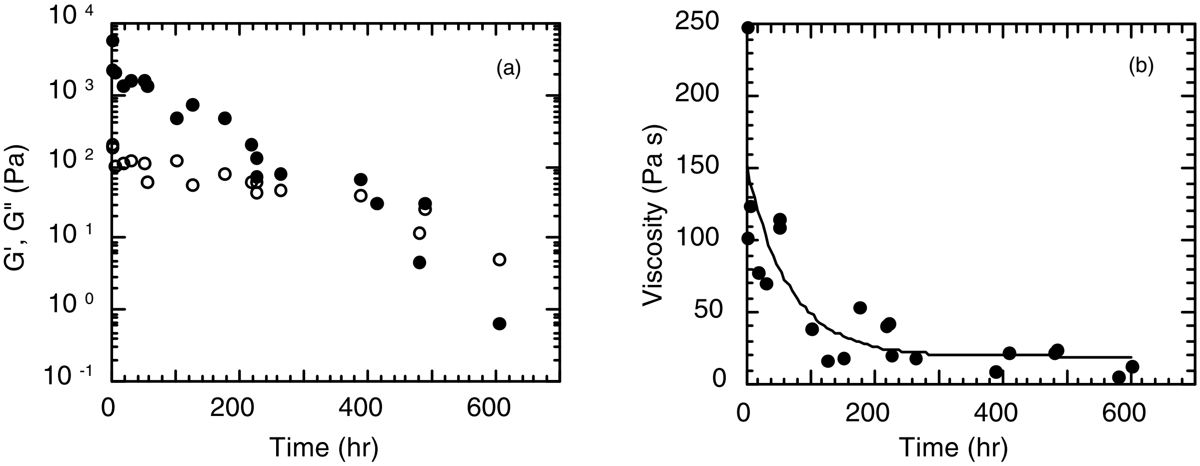

Fig. 3 Viscoelastic properties of silica particles in thin silicone oil as a function of time. (a) G' (closed circles) and G'' (open circles) at 1.14 Hz; (b) viscosity at a shear rate of $1 s^{-1}$.

to the different system properties probed by these two tests. The dynamic measurements of G' and G'' are conducted under a quasi-static condition in which the samples are disturbed minimally and the gel network remains intact. The viscometry measurements, on the other hand, are conducted under a flow condition, where the gel network can be destroyed by the flow.

b) Aqueous samples

Like samples with silicone oil, the aqueous samples also exhibit aging, although the changes in G' and G'' are not as drastic (Fig. 4a). G'' decreases slightly with time, and G', always much smaller than G'', decreases by an order of magnitude. The samples never form gels and are viscous fluids. The fact that the samples flow better with time is also reflected in our viscosity measurements. The viscosity decreases by an order of magnitude and reaches a steady

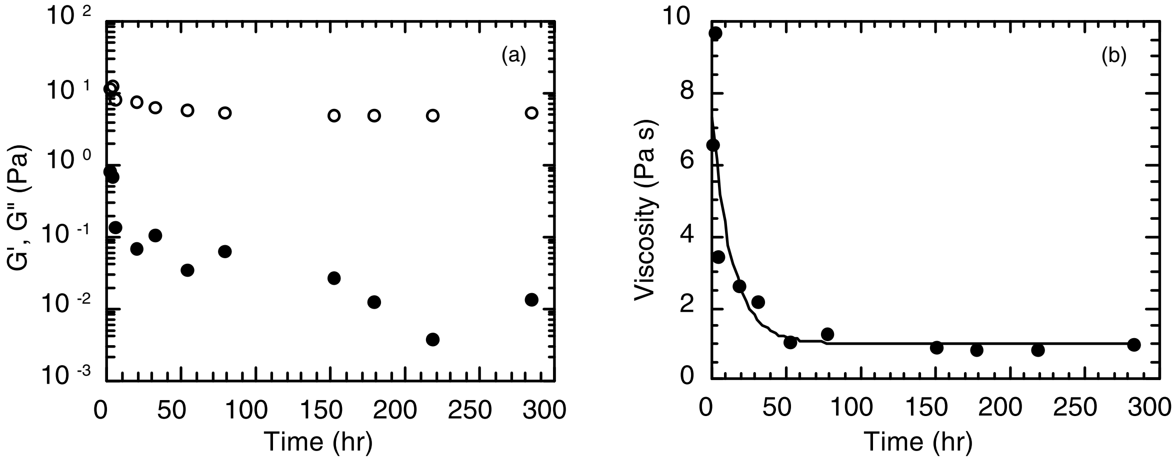

Fig. 4 Viscoelastic properties of silica particles in glycerol/water as a function of time. (a) G' (closed circles) and G'' (open circles) at 1.14 Hz; (b) viscosity at a shear rate of 1 s^{-1}.

level within 4 days (Fig. 4b). This is a much shorter aging period than the aging times of samples with silicone oil.

DISCUSSION

It is not surprising that suspensions of silica particles in mineral oil do not age. Because mineral oil (C_2H_{2n}) is non-polar, it cannot attach to the silanol groups on the silica surface to form a solvation layer. Therefore, the mineral oil allows silica particles to remain organized in a stable gel structure.

Glycerol ($C_2H_8O_3$), on the other hand, contains three hydroxyl groups, which make the molecule hydrophilic and enable it to attach to the silanol sites on the silica particle surface, forming a solvation layer. We thus expect aqueous suspensions of silica particles to be viscous fluids, and this is indeed what we have observed. We do not, however, fully understand why the aqueous samples flow better with time. Additional tests will be necessary to determine the cause of this aging behavior.

The aging process of suspensions of silica in silicone oil has been attributed to the formation of hydrogen bonds between PDMS and silica [5]. The oxygen atom in the backbone of the PDMS molecule $(\text{-Si(CH}_3)_2\text{O-})_n$ has two lone pairs, which enable PDMS to create hydrogen bonds with the silanol groups on the silica surface. The ability of PDMS to form hydrogen bonds, however, is probably very weak, given the fact that silicone oil is highly hydrophobic. We suspect that the aging process happens as follows:

Before mixing, the silanol groups on the silica surface are bonded to water due to the moisture content in the powder. Immediately after the silicone oil is added to the silica powder, the hydrophilic silica particles form a gel network in the hydrophobic silicone oil. Eventually, PDMS molecules can replace the water molecules on the silica surface by forming hydrogen bonds with silanol groups. This process continues until the silica particles are completely surrounded by the oil. As a result, the gel network breaks down, and the samples behave more fluid-like. The exact mechanism that allows for increased bonding of PDMS molecules onto silanol sites, however, is not yet fully understood.

In their study of the aging process of fumed silica in silicone oil, DeGroot and Macosko saw no aging behavior when the molecular weight of PDMS was less than 20,000; the elastic modulus remained large and did not change with time. Aging behavior was observed for suspensions with larger PDMS molecular weights, and a larger PDMS molecular weight correlated to a larger decrease in the elastic modulus over time [5]. DeGroot and Macosko proposed a model in which larger PDMS molecules formed stronger bridges between silica particles, causing them to re-agglomerate and resulting in more destruction of the gel network. The volume fraction of our samples (5.3%) is less than DeGroot and Macosko's (16%), and precipitated silica is less porous than fumed silica. In our samples, aging occurs even though the molecular weights of our silicone oils are both under 20,000. Thus more investigation is needed to understand the aging process of silica particles in silicone oil.

CONCLUSIONS

The aging behavior of suspensions of silica particles in silicone oils, mineral oil, and glycerol/water is analyzed by observing their viscosity, the elastic modulus, and the loss modulus over time. The hydrophilic silica particles form a gel network in hydrophobic mineral oil. The mineral oil samples do not age, because mineral oil cannot interact with silica particles. In the aqueous medium the silanol groups on the silica surface readily bond with water and glycerol because of the hydrophilic character of all three substances. As a result, no gel network is formed, and the aqueous samples are viscous fluids from the beginning. The viscosity of aqueous samples decreases with time. Silica-silicone oil suspensions exhibit drastic aging behavior, turning from gels to fluids in a few weeks. We believe this is due to the formation of a solvation layer on the silica surface that results from the hydrogen bonding capability of the silicone oil with the silanol groups. However, further tests will be necessary to strengthen this hypothesis.

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