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Role of Surfactants in Suppressing Aging of Silica−Poly(dimethylsiloxane) Gels

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ABSTRACT: Gels formed by mixing fine silica powders and poly(dimethylsiloxane) (PDMS) transform into viscous fluids over a period of a few days. By adding small amounts (a few weight percent) of surfactant-like block copolymers to the gel, we are able to slow down the aging process significantly, increasing the aging time constant by more than 700-fold in some samples. This aging process is closely associated with the adsorption of PDMS onto silica surfaces. We propose a model in which surfactant and PDMS polymers compete for adsorption sites on silica after "poison" molecules desorb from these sites. This model predicts that the coating of silica by surfactants and PDMS grows with a characteristic time constant, and that this time constant depends on surfactant concentration with an equation that is similar to the Langmuir isotherm. This model gives an excellent fit for our experimental data. Our analysis indicates that the "poisons" are water molecules physically adsorbed on surface silanol groups on silica.

Introduction

Fine powders of silica and carbon black are the two main types of fillers used to improve the mechanical properties of rubbers.[1] The reinforcement capability of these powders is attributed to filler−elastomer and filler−filler interactions. Although the study of surface chemistry of filler particles, in an effort to alter the interactions between filler particles and their surrounding materials, has been a major research and development effort for achieving optimal mechanical properties of rubbers, the understanding of filler−elastomer and filler−filler interactions on a molecular level is still a work in progress.[2,3]

For example, silanol groups (SiOH), abundant on silica particle surfaces, can form hydrogen bonds with elastomers and are considered particularly important for silica as a reinforcement agent in rubbers. Thus, one might expect the removal of silanol groups from silica surfaces to reduce the reinforcement capability of silica greatly. Only a modest effect from this effort, however, was seen in a silicone rubber reinforced with silica.[4] In contrast, graphitization of carbon black, which renders carbon black inactive as a filler, produces a much more dramatic reduction in the strength of a hydrocarbon rubber reinforced with carbon black.[4] Naturally, one would ask, how does silica interact with elastomers?

In this paper, we try to illuminate this issue by reporting a study on a system of precipitated silica particles mixed in silicone oil. Silicone oil is a polymer melt of poly(dimethylsiloxane) (PDMS, a linear polymer) with a wide range of viscocity that depends on the molecular weight of PDMS. When silicone oil is mixed with silica powder, a gel forms. Similar to the PDMS-fumed silica system,[5,6] the gel formed by precipitated silica and PDMS is highly viscoelastic, showing complex rheological behavior that depends on shear history. After a period of a few days, however, this gel transforms into a viscous, nearly Newtonian fluid. Our initial findings on this intriguing aging behavior have been published elsewhere,[7] and we will give a brief summary here.

We have found that the following factors affect the aging rate of silica-PDMS mixtures: (i) PDMS molecular weight (samples with longer PDMS polymers age faster), (ii) end-groups of PDMS (hydroxyl end-groups cause faster aging than methyl end-groups), and (iii) silica concentration (samples with larger silica volume fraction age more slowly).

Since the elastic modulus of freshly made samples depends only on silica concentration and not on PDMS viscosity, we conclude that the initial gel network is formed by silica particles, which are hydrophilic and attract each other when immersed in a hydrophobic oil. Extensive experimental work conducted by Cohen-Addad's group[8] has shown that PDMS can be physically adsorbed onto silica over a time period of about 10^2 hours, and that the adsorption time constant is shorter for PDMS with larger molecular weight. This strongly suggests that the breakdown of the gel network in our system occurs when silica particles slowly adsorb PDMS onto their surfaces and lose their attraction to each other as a result.

The slowness of the adsorption of PDMS on silica is explained by a "poison" model developed by Cohen-Addad and de Gennes:[9] Initially the surface of silica is covered by small poison molecules (water in this case). When poisons slowly diffuse away from their binding sites, PDMS chains replace them and adsorb onto the silica surface.

What is not clear, however, is how PDMS adsorbs onto silica. Researchers have generally believed that oxygen atoms in the PDMS backbone can form hydrogen bonds with silanol groups on silica surfaces.[4] But this theory does not explain why the adsorption rate has such a strong dependence on the PDMS molecular weight, because the availability of oxygen atoms in the backbones should not depend strongly on the PDMS molecular weight in a polymer melt.

In the following sections, we will report our new experimental results on the drastic slowing of the aging process when small amounts of surfactants are added to the silica−PDMS system. We will also explain our findings using a lattice model inspired by Cohen-Addad and de Gennes's "poison" model.

Experimental Section

Materials. The surfactants we used were block copolymers: (1) CMS-222, poly(dimethylsiloxane-*b*-hydroxyethyleneoxy-propylmethylsiloxane), 20% nonsiloxane, by Gelest, Inc.; (2) EO-600, poly(dimethylsiloxane-*b*-ethylene oxide), 75% nonsiloxane, by

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Polysciences, Inc.; (3) EO-3000, poly(dimethylsiloxane-*b*-ethylene oxide), 80% nonsiloxane, by Polysciences, Inc.

Precipitated silica consists of nanometer size primary particles fused into secondary clusters. The J. M. Huber Corporation (Havre de Grace, MD) provided us with Zeodent 165, which is highly polydisperse with a cluster size 10−16 μm. The Brunauer−Emmett−Teller surface area[10] is 179 m^2/g, and the pore volume is 5.9 cm^3/g.

We used two kinds of silicone oil purchased from Sigma-Aldrich. One is methyl-terminated (SO-1000, Dow Corning 200 fluid) and the other hydroxyl-terminated (SO-2000, Dow Corning 3−0133 fluid). The molecular weight M, density ρ, and viscosity η of the silicone oil and surfactants are listed in Table 1.

Sample Preparation and Measurements. Samples were prepared by manually mixing appropriate amounts of silica powder, silicone oil, and surfactant in small glass jars. The mixtures were stirred vigorously with a spatula for about 10 min until reaching a homogeneous consistency by visual inspection. All sample components were used as received. Silica volume fraction for all samples was 5%, calculated using a silica density of 2 g/cm^3.

Rheological measurements were conducted at 25 °C using Bohlin C-VOR (Malvern Instruments) and AR-G2 (TA Instruments) rheometers in a strain-controlled mode. Parallel plate tools of 20−60 mm diameters were used and the gap size was set at 0.4 mm for the 60 mm tool and 0.5 mm for the smaller tools. After being loaded onto the rheometer, samples were allowed to relax for 10 min before taking a set of stress-vs-strain measurements at several frequencies to ensure that experiments were conducted in the linear regime. Elastic and viscous moduli of the samples were measured as a function of frequency from 0.05 to 100 Hz, with strain typically under 10^{-3}. Samples were allowed to age in glass jars at room temperature, and the data at each sample age were collected after remixing the sample in the jar. Remixing was necessary due to sample sedimentation, and samples were allowed to relax for 10 min after remixing. To investigate whether the aging rate was affected by remixing, we stirred some samples more frequently than others between meansurements; no difference in aging rate was detected between these samples as long as they were of the same composition. These measurement protocols were the same ones used in our previous experiments.[7]

Table 1. Molecular Weight M, Density ρ, and Viscosity η of PDMS and Surfactants

	M (g/mol)	ρ (g/cm^3)	η (pa·s)
CMS-222	6500[a]	0.976[a]	0.21[c]
EO-600	600[a]	1.007[a]	0.0020[a]
EO-3000	3000[a]	1.07[a]	0.0080[a]
SO-1000	28 000[b]	0.971[a]	1.15[c]
SO-2000	35 000[b]	0.915[a]	1.94[c]

[a] Information provided by the manufacturers. [b] Calculated.[11] [c] Measured at 25 °C in our laboratory.

Results

Scaling of Moduli as a Function of Frequency. Freshly made samples are gel-like, with the elastic modulus (G') almost independent of frequency and larger than the viscous modulus (G''). Aged samples are liquid-like, with G'' linearly dependent on frequency and larger than G'. A crossover of moduli-vs-frequency curves is seen in the experimental frequency range during the aging process. As we have previously reported,[7] all G' and G'' curves can be scaled to a single set of master curves by multiplying the frequencies by a constant a and the moduli by a constant b. Figure 1a shows the scaled G' and G'' for all of our samples at different stages of aging; freshly made samples are represented by points at the left-hand side and aged samples at the right-hand side. Figure 1b shows an almost linear dependence of the scaling parameter b on a divided by the viscosity η of the base fluid.

This scaling behavior is similar to the pattern shown by Trappe and Weitz[12] for a system of carbon black in oil and can be understood in the following way. At low frequencies, the system is solid-like and G' is at a frequency-independent value, which we call the elastic plateau modulus G'_0. At high frequencies, the system is liquid-like and $G'' = \eta\omega$. The crossover of G' and G'' occurs at an angular frequency $\omega_c = G'_0/\eta$. For systems with different values of G'_0 and η, this crossover may or may not fall within the experimental frequency range. If the shapes of moduli-vs-frequency curves are the same for all samples, we can move the crossovers to a single point by multiplying the frequency by $a = 1/\omega_c = \eta/G'_0$ and the moduli by $b = 1/G'_0$. This also means that $b = a/\eta$, which is what we see experimentally. While master curves for the carbon black-oil system are obtained by using samples of different carbon black concentrations, our system's master curves comprise samples at different stages of aging with the same silica concentration. We will return to this point in the Discussion.

Effects of Surfactants. Because $G'_0 = 1/b$, the master curves allow us to extract G'_0 for all samples, including the aged ones for which G'_0 falls outside the experimental frequency range. Figure 2 shows G'_0 as a function of sample age for methyl-terminated SO-1000 with different concentrations of CMS-222 (molecular weight 6500, 20% nonsiloxane). Without surfactants, the aging time constant is 2.8 h. By adding only 5% (by weight) CMS-222, the aging time constant rises to 58 h, an impressive 21-fold increase. It seems that surfactants, even in small amounts, play a dominant role in the aging process.

It is interesting that at 100% CMS-222, the aging time constant is 99 h, substantially longer than that of samples made with pure SO-1000 (2.8 h). One might expect that CMS-222,

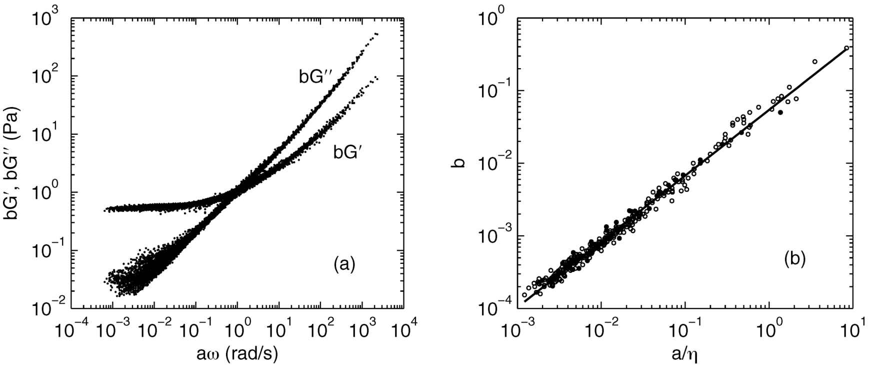

Figure 1. (a) Scaling of moduli as a function of frequency for all data sets: samples of different compositions at different ages (346 sets total). (b) Fitting parameter b as a function of the fitting parameter a divided by the base fluid viscosity η. The power law relationship has an exponent of 0.91.

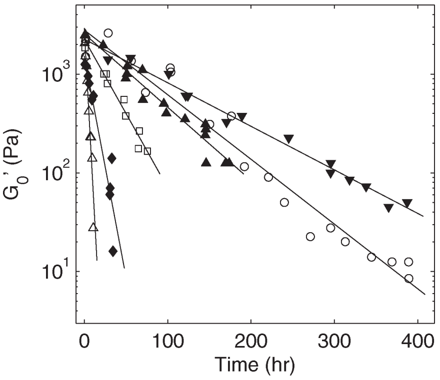

Figure 2. Elastic plateau modulus G_0' as a function of sample age for silica in SO-1000 with various concentrations of CMS-222: (Δ) 0 wt %, τ = 2.8 h; (♦) 1%, 9.7 h; (□) 3%, 29 h; (▲) 5%, 58 h; (○) 10%, 66 h; (▼) 100%, 99 h.

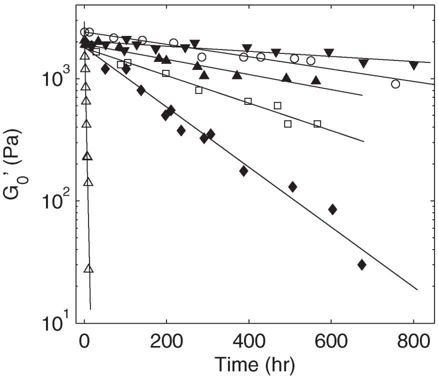

Figure 3. Elastic plateau modulus G_0' as a function of sample age for silica in SO-1000 with various concentrations of EO-3000: (Δ) 0 wt %, τ = 2.8 h; (♦) 1%, 180 h; (□) 1.5%, 390 h; (▲) 2%, 700 h; (○) 3%, 860 h; (▼) 10%, 2100 h.

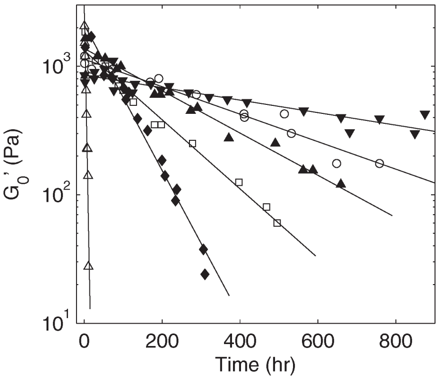

Figure 4. Elastic plateau modulus G_0' as a function of sample age for silica in SO-1000 with various concentrations of EO-600: (Δ) 0 wt %, τ = 2.8 h; (♦) 1%, 77 h; (□) 1.5%, 160 h; (▲) 2%, 260 h; (○) 3%, 410 h; (▼) 10%, 890 h.

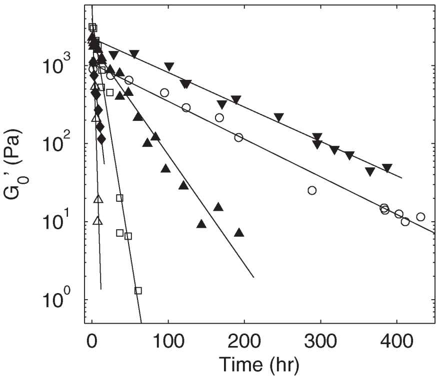

Figure 5. Elastic plateau modulus G_0' as a function of sample age for silica in SO-2000 with various concentrations of CMS-222: (Δ) 0 wt %, τ = 1.4 h; (♦) 2%, 5.1 h; (□) 3%, 7.2 h; (▲) 10%, 31 h; (○) 50%, 90 h; (▼) 100%, 99 h.

being a block copolymer with a hydrophilic section that is much more capable of forming hydrogen bonds with silica than methyl-terminated PDMS, would adsorb onto silica faster and produce a faster-aging gel. Yet the opposite is true. This most likely speaks to the importance of the molecular weight of base fluids in the aging process seen in our system.[7] With a molecular weight of 28 000, SO-1000 causes faster aging than CMS-222 (molecular weight 6500), despite the higher hydrophilicity of the latter.

When smaller surfactants are used, the slowing down of the aging process is even more pronounced. Figures 3 and 4 show G_0' as a function of sample age for SO-1000 with EO-3000 and EO-600 (molecular weights 3000 and 600, respectively). At 10 wt % surfactants, the aging time constant is 2100 h for EO-3000 and 900 h for EO-600 (750- and 320-fold increases, respectively, from no surfactants).

The same trend holds even when surfactants are added to hydroxyl-terminated SO-2000. Figure 5 shows G_0' as a function of sample age for SO-2000 with different concentrations of CMS-222. The aging time constant rises from 1.4 h at no surfactants to 31 h at 10 wt % CMS-222, a 22-fold increase. Since both hydroxyl-terminated PDMS and surfactants can easily form hydrogen bonds with silica, this drastic increase in aging time constant again shows the importance of the molecular weight of the polymer; polymers with a smaller molecular weight dominate the aging process over larger polymers when both are present.

When freshly mixed, pure CMS-222 and silica powder form a gel, but silica with pure EO-3000 or EO-600 is much more liquid-like, with G'' larger than G'. This reflects the fact that the hydrophilic sections in EO-3000 and EO-600 are much larger than the siloxane section (80% and 75% nonsiloxane, respectively), rendering these pure surfactants more hydrophilic. When mixed with these mostly hydrophilic base fluids, silica has less incentive to form a gel network. In contrast, only 20% of CMS-222 is nonsiloxane, and silica can form a gel network in this mostly hydrophobic base fluid.

Lattice Model of PDMS and Surfactant Adsorption on Silica. Similar to the "poison" model developed by Cohen-Addad and de Gennes,[9] we assume that binding sites on a silica surface are initially occupied by poisons, and a site only becomes available to PDMS or surfactant after the poison leaves. We assume that at time t, there are N binding sites on a silica surface that are *not* covered by either PDMS or surfactant. We further assume that the probability per unit time of a poison leaving its binding site is k_0, making this site available for adsorption by either PDMS or surfactant. If the probabilities of this site being occupied by PDMS and surfactant are p_p and p_s, respectively, then the rate equation for N is

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -k_0 N(p_p n_p + p_s n_s) \tag{1}$$

where n_p and n_s denote the number of sites that can be "covered up" by each adsorbed PDMS and surfactant, even when these sites are still occupied by poisons. (Of course, at least one binding site among them has to be free of poison for PDMS or surfactant adsorption to take place.) In other words, n_p and n_s take into account the sizes of the adsorbed polymers. The solution to this rate equation is

$$N = N_0 \mathrm{e}^{-t/\tau} \tag{2}$$

where N_0 is the number of sites at $t = 0$, and the adsorption rate constant is

$$\frac{1}{\tau} = k_0(p_p n_p + p_s n_s) \tag{3}$$

To find the probabilities p_p and p_s, we use a lattice model[13] to describe the process in which PDMS and surfactants compete for adsorption onto silica. Suppose that in the bulk fluid there are Ω_p lattice sites for PDMS and Ω_s lattice sites for surfactants, and there are N_p PDMS polymers and N_s surfactants. The binding energies of PDMS and surfactant to silica are ε_p and ε_s, respectively. We assume $N_p \ll \Omega_p$ and $N_s \ll \Omega_s$. After a poison leaves a silica binding site, there are three possible states for this site, and their contributions to the partition function are:

(1) The site remains unoccupied:

$$Z_1 = \frac{\Omega_p!\Omega_s!}{N_p!(\Omega_p - N_p)!N_s!(\Omega_s - N_s)!} \approx \frac{\Omega_p^{N_p}\Omega_s^{N_s}}{N_p!N_s!}$$

(2) The site is occupied by PDMS:

$$Z_2 = \frac{\Omega_p!\Omega_s!e^{-\beta\varepsilon_p}}{(N_p - 1)!(\Omega_p - N_p - 1)!N_s!(\Omega_s - N_s)!} \approx \frac{\Omega_p^{N_p - 1}\Omega_s^{N_s}}{(N_p - 1)!N_s!} e^{-\beta\varepsilon_p}$$

(3) The site is occupied by surfactant:

$$Z_3 = \frac{\Omega_p!\Omega_s!e^{-\beta\varepsilon_s}}{N_p!(\Omega_p - N_p)!(N_s - 1)!(\Omega_s - N_s - 1)!} \approx \frac{\Omega_p^{N_p}\Omega_s^{N_s - 1}}{(N_p)!(N_s - 1)!} e^{-\beta\varepsilon_s}$$

Here $\beta = 1/k_B T$, k_B is the Boltzmann constant, and T is temperature. The total partition function is $Z = Z_1 + Z_2 + Z_3$.

Thus, the probability of a vacated silica binding site being occupied by PDMS is

$$p_p = \frac{Z_2}{Z} \approx \frac{\frac{N_p}{\Omega_p}\mathrm{e}^{-\beta\varepsilon_p}}{1 + \frac{N_p}{\Omega_p}\mathrm{e}^{-\beta\varepsilon_p} + \frac{N_s}{\Omega_s}\mathrm{e}^{-\beta\varepsilon_s}} \tag{4}$$

and the probability of it being occupied by surfactant is

$$p_s = \frac{Z_3}{Z} \approx \frac{\frac{N_s}{\Omega_s}\mathrm{e}^{-\beta\varepsilon_s}}{1 + \frac{N_p}{\Omega_p}\mathrm{e}^{-\beta\varepsilon_p} + \frac{N_s}{\Omega_s}\mathrm{e}^{-\beta\varepsilon_s}} \tag{5}$$

Equations 4 and 5 closely resemble the Langmuir isotherm,[14] except that there are two Boltzmann factors in the denominators, representing the presence of both PDMS and surfactants. Furthermore, since in our system PDMS and surfactants have roughly the same density, we can write $N_s/\Omega_s = c_s$ and $N_p/\Omega_p = 1 - c_s$, where c_s is the surfactant concentration (wt %).

Computer simulation work by Tsige et al. shows that because methyl groups on the PDMS backbone sterically hinder hydrogen bonding between oxygen atoms in PDMS and hydroxyl groups on silica surfaces, PDMS most likely binds to silica through its end-groups.[15] Tsige et al. found that the binding energy of methyl-terminated PDMS to silica is in the range of −1 to −6 kcal/mol, depending on the simulation method used, and the binding energy of hydroxyl-terminated PDMS to silica is −16 kcal/mol. This puts the interaction between methyl-terminated PDMS and silica in the region of weak hydrogen bonds and that between hydroxyl-terminated PDMS and silica in the region of moderate hydrogen bonds.[16] Because $1/\beta = 0.6$ kcal/mol at room temperature, we assume $e^{-\beta\varepsilon_s} \gg e^{-\beta\varepsilon_p} \gg 1$. By substituting eqs 4 and 5 into eq 3, we can approximate the adsorption rate constant after some algebraic work:

$$\frac{1}{\tau} \approx k_0 n_s + k_0 \frac{n_p - n_s}{1 + c_s \mathrm{e}^{-\beta(\varepsilon_s - \varepsilon_p)}} \tag{6}$$

Equation 6 gives $1/\tau \approx k_0 n_p$ when $c_s = 0$, and $1/\tau \approx k_0 n_s$ when $c_s = 1$, as expected.

Discussion

The elastic modulus of a gel can be strengthened by increasing the connectivity between elements in the gel network. For example, the Young's modulus of a polymer gel is proportional to the cross-link density of the gel.[17] In a particle gel, such connectivity is related to particle concentration. It has been shown experimentally and theoretically that the elastic modulus G' of colloidal gels has a power law dependence on the volume fraction of colloidal particles ϕ ($G' \sim \phi^x$). The exponent x, usually in the range of 4−5, is related to the fractal dimension of the gel network.[18,19] In our system, the connectivity between silica particles is reduced when their surfaces adsorb PDMS or surfactant polymers. Thus, it is not surprising that the moduli of our aging samples can scale to a set of master curves, just as samples with different particle concentrations can, as mentioned earlier in the Results. It is therefore not unreasonable to expect that in our experiment, G' may also have a power law dependence on the "bare" silica area that has not been covered by PDMS and surfactants (which is proportional to the quantity N in eq 2). Consequently, we would expect the rate constant in eq 6 to be proportional to the aging rate constant in our experiment. Indeed we see that G'_0 decays exponentially with time, following the same functional form as eq 2. Furthermore, we can fit the data for aging rate constant as a function of surfactant concentration to eq 6 (Figure 6). Table 2 shows quantities in eq 6 extracted from nonlinear least-squares fitting parameters.

We next examine the fitting parameters. Given that $|\varepsilon_p|$ is likely to be significantly smaller than $|\varepsilon_s|$, the binding energies extracted from the fitting parameters certainly fall into the right range of moderate hydrogen bonds (4−15 kcal/mol). EO-600 and EO-3000, with 75%-80% nonsiloxane sections, bind more strongly with silica than CMS-222, which only has a 20% nonsiloxane section; this is also consistent with the values of $\varepsilon_s - \varepsilon_p$ in Table 2.

We can estimate k_0 from the fitting parameters. The surface of porous silica typically has about a few silanol groups per nm^2.[20] These silanol groups are sometimes called chemisorbed "bound water," which can be removed from silica surfaces only when heated at high temperatures (above about 200 °C).[21] The desorption activation energy of chemisorbed water is highly dependent on silanol density, because it is a second order reaction that involves two silanol groups. In addition to this layer of chemisorbed water, water molecules can also be physically adsorbed

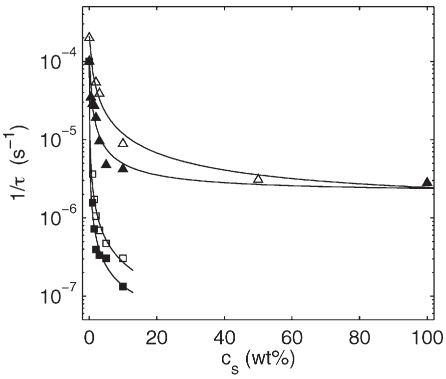

Figure 6. Aging rate constant as a function of surfactant concentration. The solid curves are nonlinear least-squares fits of the data to eq 6. Fitting parameters are listed in Table 2. (△) SO-2000 with CMS-222; (▲) SO-1000 with CMS-222; (□) SO-1000 with EO-600; (■) SO-1000 with EO-3000.

Table 2. Fitting Parameters to Equation 6 in Figure 6

	$\varepsilon_s - \varepsilon_p$ (kcal/mol)	$k_0 n_s$ (s^{-1})	$k_0 n_p$ (s^{-1})
CMS-222 with SO-2000	−3.1	1.3×10^{-6}	2.1×10^{-4}
CMS-222 with SO-1000	−3.5	2.1×10^{-6}	1.0×10^{-4}
EO-600 with SO-1000	−5.0	1.8×10^{-8}	1.0×10^{-4}
EO-3000 with SO-1000	−5.5	2.7×10^{-8}	1.0×10^{-4}

onto silanol groups; the desorption of these water molecules is a first order reaction.

SO-1000, with a molecular weight of 28 000, has a radius of gyration of about 5 nm.[22] This means that n_p, the number of silanol sites a PDMS polymer can cover, is on the order of 10. Therefore, we estimate that k_0, the probability of a water molecule desorbing from silica per unit time, is on the order of 10^{-5} s^{-1}. Standard kinetic theory for desorption predicts that k_0 obeys the Arrhenius equation:[23,24]

$$k_0 = A e^{-\beta E_{des}} \tag{7}$$

where E_{des} is the desorption activation energy and A the pre-exponential factor. Using a mass spectrometric thermal analysis method, Zhuravlev found that for physically adsorbed water on amorphous silica pretreated at room temperature, $E_{des} = 6$ kcal/mol and $A = 0.8$ s^{-1}, and for chemisorbed water, E_{des} is in the range of 21−50 kcal/mol and A in the range of 10^4−10^8 s^{-1}.[21] Substituting these values into eq 7, one finds $k_0 = 10^{-5}$ s^{-1} for physically adsorbed water, which is in excellent agreement with our results. (k_0 for chemisorbed water, on the other hand, is in the range of 10^{-11}−10^{-28} s^{-1}, much smaller than the rate constants measured in our experiment.) Thus, we conclude that the poisons in our system are water molecules physically adsorbed onto silanol groups on silica surfaces.

It is worthwhile to mention some differences between our model and that by Cohen-Addad and de Gennes.[9] In our model, the adsorption of PDMS and surfactants follows the desorption of poisons, and the time dependence of PDMS adsorption is $e^{-t/\tau}$, which agrees with our experimental findings. In the model by Cohen-Addad and de Gennes, poisons diffuse on silica surfaces, which leads to a $e^{-(t/\tau)^{1/2}}$ time dependence for the PDMS adsorption, where τ is related to the diffusion constant of the poisons. Furthermore, Cohen-Addad and de Gennes assume that a PDMS polymer coil binds with silica at multiple sites along its backbone. In our model, the adsorption of a PDMS or surfactant polymer on silica only requires a single bond. Suppose PDMS binds with silica only through its end groups, as suggested by Tsige and coworkers.[15] Then it follows that larger PDMS polymers will adsorb at a faster rate. This is because the availability of binding sites for PDMS on silica is dictated by the desorption of poisons from its surface, which is a thermodynamic process that occurs at a constant rate at a given temperature. If a large PDMS polymer takes over a binding site vacated by a poison, it will cover up many nearby sites, including those still occupied by poisons. This more efficient coverage of the silica surface makes the adsorption of larger PDMS appear faster. Although we do not have direct proof that this is indeed what happens, the good agreement between our model and data suggests that this scenario is highly probable.

Conclusions

When silicone oil and precipitated silica are mixed together, the initial gel that forms is mechanically unstable and transforms into a viscous fluid over a period of a few days. We believe this aging effect occurs when PDMS slowly adsorbs onto silica, causing the silica gel network to deteriorate. We are able to slow down this aging process significantly by adding small amounts of surfactant-like block copolymers to the system. A model of competing adsorption of surfactants and PDMS onto silica seems to give an excellent fit to our experimental measurements. The physical picture that emerges from our model is the following. Initially, the silica surface is fully covered by poisons, and polymers are not able to bind with the silica. The poisons then desorb with a rate constant k_0, making some sites available for binding with PDMS or surfactant polymers. Surfactants, which can bind more strongly with silica than PDMS, are much more likely to take the available binding sites. But because of its small size and significant hydrophilic section, the surfactant cannot “cover up” the silica surface as effectively as PDMS, resulting in a much slower aging process. The agreement between our data and this model is excellent; our analysis indicates that the poisons are water molecules physically adsorbed on the surface silanol groups on silica.

If the purpose is to slow down the aging process, small surfactants with a large hydrophilic section seem to work best. But the size should not be too small, because very small surfactants have high diffusivity and possibly less binding energy. (It would be like trading one poison for another.) Among the three surfactants we tested, EO-3000 gives the best result in decreasing the aging rate constant, by a factor as large as 750 at 10 wt % surfactant concentration in the SO-1000-silica system.

It is well-known that aging effects are common in precipitated silica-filled rubbers.[25] This is not surprising since water is often used as a compounding agent to obtain a uniform dispersion of silica in elastomers. We believe that our current experimental findings and analysis may be helpful to the understanding of aging effects in silica-filled rubbers in general.

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