Diffusion of Poly(dimethylsiloxane) Mixtures with Silicate Nanoparticles

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ABSTRACT: Pulsed field-gradient (PFG) NMR has been used to measure self-diffusion coefficients in mixtures of silicate nanoparticles with poly(dimethylsiloxane)s as a function of volume fraction of particles and of polymer molecular weight. Two different sizes of nanoparticles were used: the smaller acted like a solvent, and the larger one acted more like a colloidal particle. In the former case, two distinct diffusion coefficients were obtained, corresponding to the particle and the polymer. In the second case, only a signal from the polymer was evident because of the short spin−spin relaxation time (T_2) of the particle. However, in this latter case the diffusional attenuation indicated the presence of both free polymer and locally mobile but translationally constrained polymer, characteristic of polymer adsorption from a liquid. The data have been interpreted as a function of particle loading, and calculations have been made to estimate the thickness of the polymer layer using a hydrodynamic model.

Introduction

Fillers are frequently added to commercial polymers to enhance their mechanical properties without great expense. Despite the widespread use of such systems, there remains a need to provide a fundamental understanding of how their mechanical properties are altered, and few techniques have proved suitable for studying such systems at a molecular level. Methods that have been used include NMR relaxation,[1−4] neutron scattering and reflection,[5,6] and other atomic/molecular scattering techniques.[7] Diffusion studies may also provide information about the dynamics of the system and how the presence of the filler particles and the adsorption of polymer onto the particles affect molecular motion. Theoretically, the adsorption of polymer melts may be studied using either a mean-field or a scaling approach.[8] Scaling theories of adsorbed polymer layers from solution[9] predict how the thickness of the polymer layer (δ) scales with the molecular weight of the polymer in either a good solvent ($\delta \sim M^{3/5}$) or a Θ solvent ($\delta \sim M^{1/2}$). To a first approximation in the melt, chain conformations are ideal and both the adsorbed amount and layer thickness are expected to scale as $M^{1/2}$.[10]

The system examined in this paper consisted of low molecular weight poly(dimethylsiloxane)s (PDMS) filled with trimethylsilyl-treated silicate nanoparticles. For the polymer, a regime was chosen such that the viscosity was proportional to molecular weight, where the dynamics can be adequately described by the Rouse theory. On the basis of sol−gel chemistry, silicates can be synthesized from different routes including acid-catalyzed hydrolysis and condensation of aqueous sodium silicate followed by treatment with trimethylchlorosilane[11] or through the cohydrolysis and condensation of trimethylchlorosilane and tetraethoxysilane.[12] Although these silicates were first prepared in the 1950s, little work has been published on either their physical properties or on their interactions with silicone polymers. A study by Langley et al.[13] concentrated on silicate particles with radii in the range 1−5 nm and showed that the particles were compact and exhibited little aggregation. High-resolution ^{195}Pt NMR has been applied to follow PDMS being cured using a silicate, containing platinum, as the catalyst.[14] Newmark and Copley[15] used ^{13}C and ^{29}Si NMR to study silicate-filled siloxane polymers; the relaxation times and nuclear overhauser factors obtained for the segmental motion of polymers suggested that the polymer chains were constrained within a solid composite at room temperature. Dynamic mechanical and dielectric relaxation techniques were used to provide insight into the molecular interactions and morphology when silicates are incorporated into a siloxane-based polymer matrix.[16,17]

In another paper in this series,[18] it was found by NMR spin−spin relaxation measurements that a high molecular weight polysilicate reinforced the PDMS polymers. Further spin−spin relaxation measurements showed that an oligomeric silicate appeared to "solvate" the PDMS.[19] The aim of this paper is to use pulsed field-gradient NMR (PFGNMR)[20−22] to study the mobility of the different components of such blends. The results are used in an attempt to estimate the hydrodynamic thickness of the adsorbed polymer layer and to compare the results with those predicted by scaling theory while varying the size of the silicate particles and the molecular weight of the polymer.

Experimental Materials and Methods

Materials. The linear poly(dimethylsiloxane)s and the silicate-based materials were supplied by Dow Corning Corp. (USA). The polymer and silicate components were blended together at different weight ratios and measurements were conducted approximately 1 month after preparation.

An anionic polymerization process was used to obtain relatively monodisperse PDMS from hexamethylcyclotrisiloxane. The molecular and physical properties are given in Table 1. The information on molar and hydrodynamic size was obtained from size exclusion chromatography (SEC) which used Polymer Laboratories Mixed-D columns with a Waters 2690 HPLC+2410 refractive index detector coupled to a Viscotek T60a right-angle laser light scattering/viscometer dual detector and toluene as an eluent at 35 °C. The density was measured at 25 °C using an Anton PAAR DMA48 density meter. The zero-shear-rate viscosity of each fluid at 25 °C was obtained from a Rheometric Scientific RDAII using 50 mm-diameter cone-and-plate fixtures with a cone angle of 0.04 rad.

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Table 1. Molecular and Physical Properties of Poly(dimethylsiloxane)s[a]

sample	M_w/kg mol^{-1}	M_w/M_n	R_g/nm	R_h/nm	ρ/g cm^{-3}	η_0/Pa s
5K	5.2	1.07	2.0	1.5	0.960	0.047
12K	12.2	1.03	3.1	2.4	0.965	0.121

[a] M_w is the weight-average molecular weight, M_w/M_n the molecular weight distribution, R_g the radius of gyration, R_h the hydrodynamic radius, ρ the density at 25 °C, and η_0 the zero-shear-rate viscosity at 25 °C.

Table 2. Molecular and Physical Properties of Silicate Materials[a]

sample	M_w/kg mol^{-1}	M_w/M_n	R_g/nm	ρ/g cm^{-3}	η_0/Pa s
R1	0.5	1.15	0.35	0.88	0.0037
R3	14.1	2.99	2.2	1.17	$>10^{26}$ [b]

[a] M_w is the weight-average molecular weight, M_w/M_n the molecular weight distribution, R_g the radius of gyration, ρ the density at 25 °C, and η_0 the zero-shear-rate viscosity at 25 °C. [b] R3 is a glass at 25 °C; the value was extrapolated from data of blends of R3 with PDMS.

The molecular and physical properties of the silicate-based materials are given in Table 2. The lower molecular weight silicate, designated R1, was made from the acid-catalyzed hydrolysis and condensation of tetraethoxysilane and end-capped with hexamethyldisiloxane. Gas chromatography revealed that the R1 silicate was essentially a mixture of 68 wt % tetrakis(trimethylsiloxy)silane and 21 wt % hexakis(trimethylsiloxy)disiloxane plus residual amounts of larger oligomeric species. The trimethylsilylated silicate designated R3 was obtained from the acid-catalyzed polymerization of sodium silicate, followed by a reaction with trimethylchlorosilane in a process described elsewhere,[11] and was glassy at room temperature. The molar mass was determined by SEC equipped with Polymer Laboratories Mixed-D columns, with a Miran 1A-CVF HPLC infrared detector, calibrated with silicate molecular weight fractions and used chloroform as an eluent at 35 °C. The molecular size of R1 was calculated from molecular modeling [Cerius^2 Release 3.8, Molecular Simulations, San Diego, CA.] whereas the other silicate was measured from hydrodynamic considerations using the universal calibration SEC technique.

NMR Measurements. The PFGNMR experiments were performed on a JEOL FX-100 spectrometer at 25 °C using an external ^{2}D lock. Before performing the experiments the applied gradient was calibrated using water, which has a diffusion coefficient of 2.3×10^{-9} m^2 s^{-1} and the temperature of the sample controlled at 22 ± 1 °C. The results were analyzed using the basic equation for unrestricted diffusion

$$\frac{I(\delta,\Delta,g,\tau)}{I_0} = \exp\left(-\frac{2\tau}{T_2}\right)\exp\left[-\gamma^2 g^2 \delta^2\left(\Delta - \frac{\delta}{3}\right)D\right] + b \quad (1)$$

where I_0 is the initial signal intensity at time $\tau = 0$ in the absence of any gradient, τ the time between the 90 and 180° pulses, g the magnitude of the field gradient pulse, Δ the distance between the leading edges of the gradient pulses, δ the length of the gradient pulse, D the self-diffusion coefficient, T_2 the spin−spin relaxation time, γ the gyromagnetic ratio, and b a baseline when required. For example, b might be used to estimate the contribution from a component that is diffusing only very slowly, for example an adsorbed polymer layer, where there is no effective attenuation over the range of values of δ, g, and Δ used.

The attenuation obtained from a PFGNMR study of water was fitted using a nonlinear least-squares fitting routine, and the gradient g was estimated to be 0.33 ± 0.01 T m^{-1}. To fully attenuate the signal for the most viscous sample the δ range had to be extended to 16 ms. Measurements on other samples of intermediate values of diffusion coefficient showed that the calibration was reliable up to this value of δ. Care was also taken to avoid problems due to eddy currents.

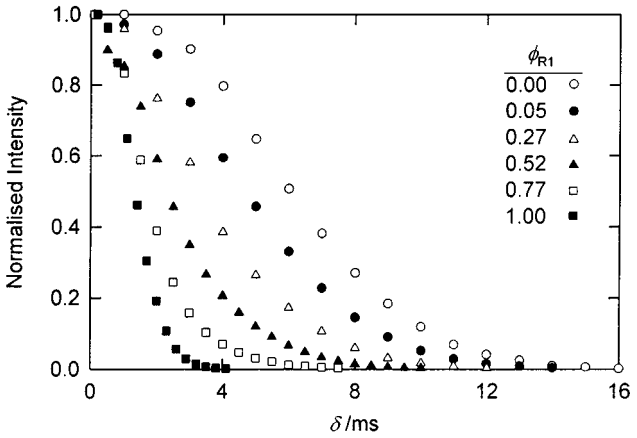

Figure 1. Attention functions at different volume fractions of the oligomeric R1 silicate ϕ_{R1} dispersed in 5K PDMS.

In all cases, four scans were carried out at each value of δ. The data were processed using *NUTSLite*,[23] and the attenuations were measured by studying the change in the integral of the PDMS peak in the spectrum and fitting the attenuation decays to eq 1 using nonlinear least-squares methods.

Viscosity Measurements. The zero-shear-rate viscosity of each silicate/polymer blend formulation at 25 °C was obtained from a Rheometric Scientific RDAII using cone-and-plate fixtures: 50 mm-diameter plates with a cone angle of 0.04 rad for low viscosity materials; 25 mm-diameter plates with a cone angle of 0.10 rad for viscosities greater than 1 Pa s.

Results and Discussion

Oligomeric Silicate, R1. Figure 1 shows a series of PFGNMR attenuation decays for mixtures of the R1 oligomeric silicate with the 5K PDMS over a wide range of concentrations. The self-diffusion coefficient D_s for pure R1 at 25 °C was 1.7 (±0.13) × 10^{-10} m^2 s^{-1}. Given the measured viscosity of R1 (η = 3.7 mPa s at 25 °C, Table 2), an estimate of the particle size (a) may be obtained from the Stokes−Einstein equation

$$D_S = \frac{k_B T}{6\pi\eta a} \quad (2)$$

where k_B is the Boltzmann constant and T the absolute temperature. This gave a hydrodynamic radius of 0.35 ± 0.03 nm. Since Table 2 gives R_g = 0.35 nm, a hydrodynamic radius of 0.44 nm could be expected using eq 3.[24]

$$R_g = (^3/_5)^{0.5} R_h \quad (3)$$

Therefore, the measured radius was slightly smaller than that predicted by modeling techniques. The diffusion coefficient of the 5K PDMS was found to be 0.81 (±0.05) × 10^{-11} m^2 s^{-1}.

Figure 2 shows a typical blended sample, containing 0.27 volume fraction R1, fitted to a single diffusive process (- - -) and to a double diffusive process (——). The latter simply uses eq 1 twice.

$$I(\delta,\Delta,g,\tau) = \sum_{i=1}^{2} I_{0,i}\exp\left(-\frac{2\tau}{T_{2,i}}\right)\exp\left[-\gamma^2 g^2 \delta^2\left(\Delta - \frac{\delta}{3}\right)D_i\right] + b \quad (4)$$

Figure 2 clearly shows that the attenuation for the blends was best considered as a combination of two

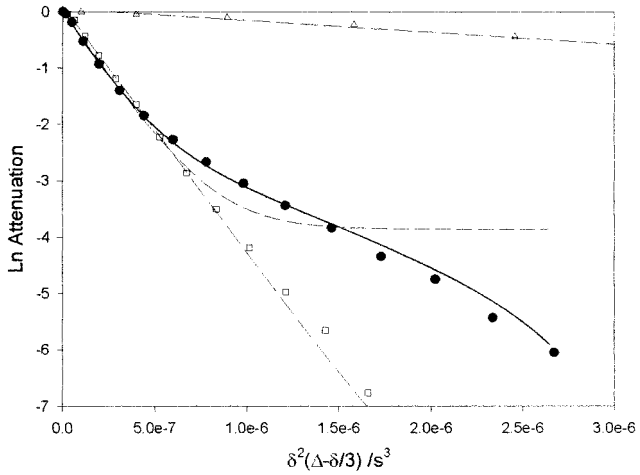

Figure 2. Single (− −) and double (—) diffusion fits for a 0.27 volume fraction R1 silicate (ϕ_{R1}) in 5K PDMS, compared with that of the pure components (△) PDMS and (□) R1.

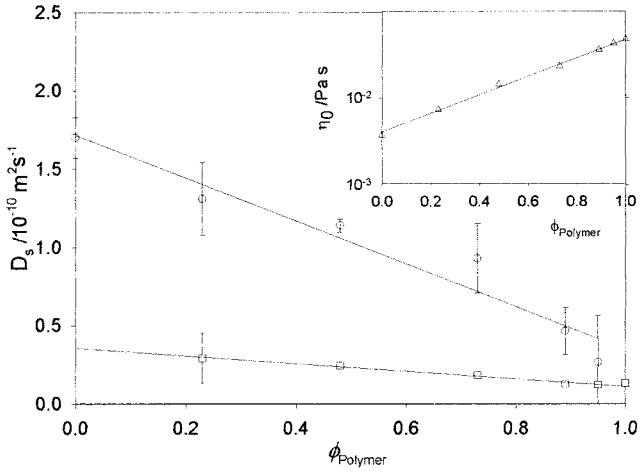

Figure 3. Self-diffusion coefficient (D_s) of the R1 silicate oligomer (○) and 5K PDMS (□), and the viscosity (η_0) as a function of the polymer volume fraction.

separate diffusive processes. The resolution of the spectrometer was insufficient in distinguishing the small chemical shift difference between the methyl resonance of the silicate and that of the PDMS; hence, this peak will contain contributions from both species. Therefore, it seemed appropriate to assign the two diffusion coefficients to the two species present. For comparative purposes, the pure polymer and silicate signals are also shown, both of which fit well to a single diffusive process. It is interesting to note that, although the polymer gives rise to a single diffusive process, two T_2 values were required to fully describe its relaxation behavior.[18]

Figure 3 shows the two diffusion coefficients obtained from fitting the entire data set, plotted as a function of composition, and the viscosity of the blends and each pure component is shown inset. The faster diffusing species can be identified with R1 and the slower process with the polymer. In a dilute polymer solution, the diffusion coefficient can be described by eq 5,

$$D_s = D_o(1 - \zeta\phi) \tag{5}$$

where D_o is the diffusion coefficient at infinite dilution, ζ a friction coefficient, and ϕ the volume fraction of the polymer. By fitting a linear function to the polymer D_s values and extrapolating to infinite dilution, D_o may be obtained [3.63 (±0.10) × 10^{-11} m^2 s^{-1}]. This allowed an estimate of the hydrodynamic radius of the polymer to be made using eq 2 and a value of 1.65 ± 0.05 nm was obtained which was close to the independently measured hydrodynamic value of 1.5 nm. The intensities of the two components roughly followed the weighted percentages in the mixture. However, the respective heights depended not only on their proton content but also on their individual T_2 values. The T_2 values obtained for the polymers were shorter than the T_2 of the particles, which may explain the slight deviation from linearity.

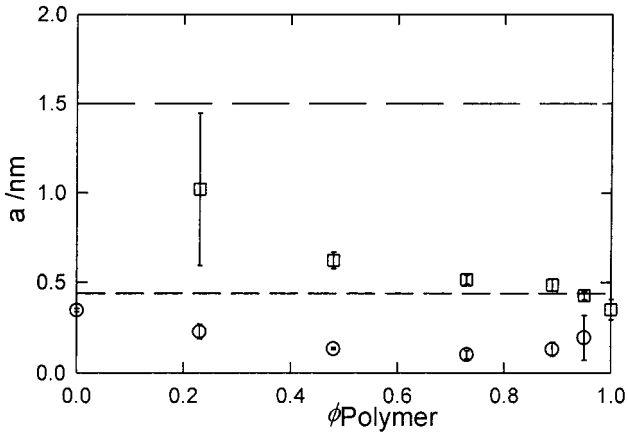

Figure 4. Hydrodynamic radius (a) of the R1 silicate oligomer (⊙) and 5K PDMS (□) as a function of the polymer volume fraction. Dashed lines represent values from Tables 1 and 2 for hydrodynamic sizes.

Figure 4 shows that the hydrodynamic radius for both the 5K PDMS and R1 silicate may be approximated at each blend composition by using the Stokes−Einstein relationship (eq 2). The hydrodynamic size of R1 remained essentially unchanged across the entire composition range, consistent with R1 behaving as a free-flowing solvent. As the polymer concentration increases, a decrease in size would be expected as the solvent was changing from "good" to "Θ" consistent with scaling theory.

An analogous series of experiments was performed where the PDMS molecular weight was increased to 12K. The results are not shown but the general trends were the same as those observed in the case of the 5K data. Using an extrapolated value for D_o [2.2 (± 0.4) × 10^{-11} m^2 s^{-1}] from a plot of diffusion coefficient as a function of volume fraction of PDMS, a hydrodynamic radius of 2.7 ± 0.4 nm was obtained for the polymer, which was in good agreement with the experimental value listed in Table 1.

The increase in blend viscosity with polymer concentration, shown inset in Figure 3, was significantly greater in the case of the higher molecular weight 12K PDMS as would be expected. For these two polymers, it appeared that $\eta_0 \sim M$,[1] the dynamics of which could be described by the Rouse theory.[25] The diffusion coefficients of the two polymers at different concentrations exhibited the same general trend: a linear decrease as a function of increasing polymer concentration with approximately the same gradient, which is proportional to the friction coefficient. However, the intercept was dependent upon the polymer molecular weight. This implied that the R1 silicate had the same effect on both polymers. Combining the diffusion coefficients

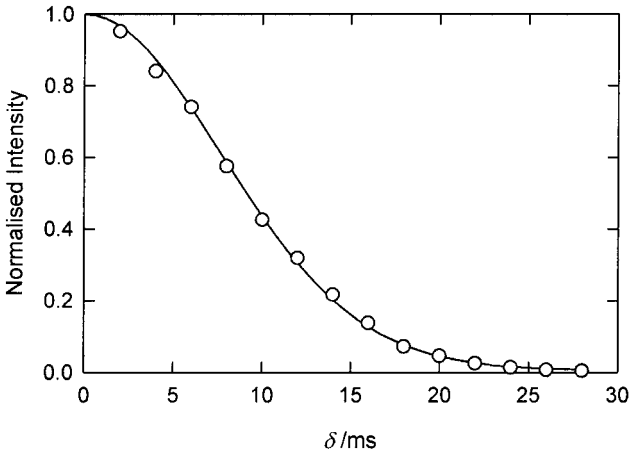

Figure 5. Attenuation function for a blend with 0.04 volume fraction R3 silicate in 5K PDMS. The solid line is a single component fit.

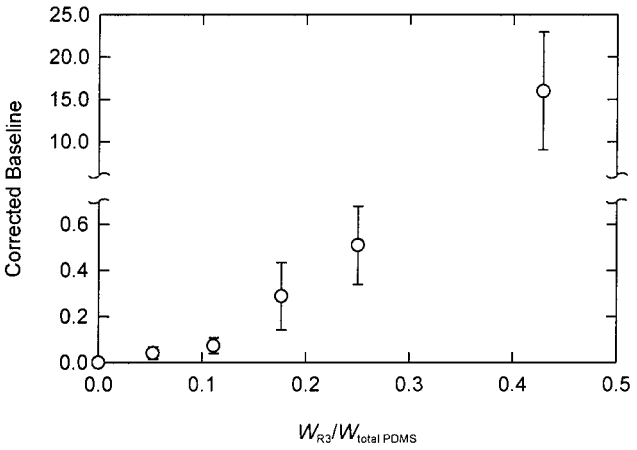

Figure 6. Corrected baseline intensity for the 5K PDMS as a function of the weight fraction of the R3 silicate normalized by the polymer weight fraction.

and the viscosity data allowed the hydrodynamic sizes of both the polymer and R1 to be estimated. The higher molecular weight example has the larger hydrodynamic radius as could be expected. The relationship between the hydrodynamic radius R_h and molecular weight ($R_h \sim M_w^{0.58}$) was closer to the scaling exponent of $^3/_5$, for a good solvent, than to $^1/_2$, for an ideal solvent. This suggested that R1 behaved as a good solvent for PDMS, which was not surprising due to the similarities in composition between the silicate and PDMS.

Polymeric Silicate, R3. A similar set of NMR diffusion data was obtained with the larger polymeric silicate, R3. Considering first the 5K polymer, Figure 5 shows a typical attenuation plot for one of the blend samples ($\phi_{R3} = 0.04$). Unlike the data for the R1 silicate, the decay fits well to a single diffusive process. This is because the R3 silicate is essentially an amorphous solid with a very short spin−spin relaxation time (T_2) on the order of 100−300 μs;[18] consequently, it was unseen in the spin echo experiment. Therefore, the single observed diffusion coefficient may be attributed solely to PDMS. All the data in this series were fitted to a single diffusion process. However, the silicate/PDMS blends exhibited a linearly increasing background signal as the R3 concentration increased. This corresponded to PDMS with a long T_2, but with a small value of D leading to a negligible attenuation with the current values of g, δ, and Δ. Candidates for this population would be loops and tails of an adsorbed polymer, which have a high local mobility, due to the flexibility of the siloxane backbone. From the absolute value obtained from the baseline, the corresponding adsorbed amount, Γ, due to this population can be estimated from eq 6,

$$\Gamma = \frac{R\rho W_{\text{polymer,adsorbed}}}{3W_{R3}} \qquad (6)$$

where W is the weight fraction, R the radius of R3, and ρ the density of R3. However, before applying this formula, the intensities and baselines were corrected for the effects of T_2.[18] Due to the nature of the pulse sequence used and the data acquisition capability, data collection began 200 ms after the first disturbance of the magnetization. Therefore, some of the intensity would have already decayed due to relaxation effects. This loss of intensity due to relaxation will not be constant across the composition range as the T_2 values

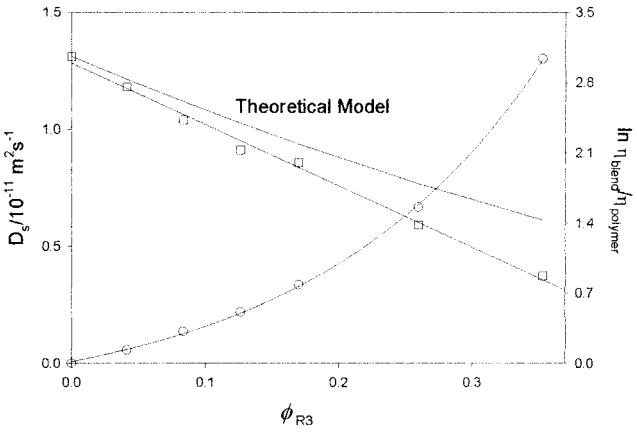

Figure 7. Effect of R3 silicate volume fraction on the self-diffusion coefficient of PDMS (□) compared to that obtained from a hydrodynamic model, and on the blend viscosity normalized by the viscosity of the polymer component (⊙). The dashed line is the fit to the Mooney equation.

alter.[18] Correcting for the intensity loss allows the $W_{\text{polymer,adsorbed}}/W_{R3}$ ratio to be obtained from a graph of baseline against $W_{R3}/W_{\text{polymer}}$ as shown in Figure 6. This weight ratio increased exponentially across the whole composition range, but the relationship was approximately linear at low weight fractions of R3. Assuming an intercept through zero, a value for the adsorbed polymer amount of 0.59 ± 0.02 mg m^{-2} was found which is similar to the adsorption of PDMS onto silica.[26]

Figure 7 shows the variation in the PDMS diffusion coefficient with increasing R3 content. The variation was almost linear, as was found with R1. However, in this case, the polymer was not solvated but reinforced as D_s decreased with increasing R3 concentration. In this situation the diffusion of soft spheres, in a polymer melt, should be considered. However, a model to describe this situation has not been found. If the system was approximated to the case of the diffusion of hard spheres, including three particle hydrodynamic interactions, the variation in D_s could then be described by eq 7[27] based on early work by Batchelor,[28]

$$D_S = D_0(1 - 1.83\phi + 0.91\phi^2) \qquad (7)$$

and this function is also shown in Figure 7. Clearly, the polymer was diffusing more slowly than this theoretical prediction. One interpretation is that the particles were

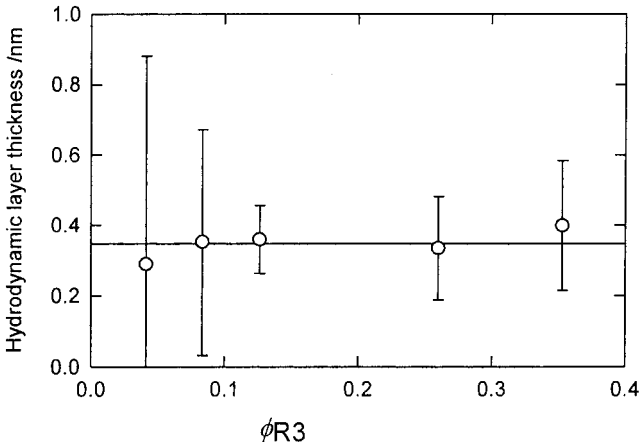

Figure 8. Estimation of the hydrodynamic layer thickness calculated using eqs 7 and 8 for 5K PDMS. The straight line represents the average value.

coated with a nondiffusing layer of polymer as was found for the adsorption of PDMS onto silica.[1] It is interesting to note that the experimental dependence of the diffusion coefficient upon volume fraction is approximately linear whereas the theoretical function is not. However, it is difficult to explain a simple linear dependence theoretically; this, therefore, suggests that higher order terms in volume fraction must partially cancel.[25]

Figure 7 also shows that the zero-shear-rate viscosity of the blend, $\eta_{0,b}$, increased exponentially with ϕ_{R3}. At low silicate content ($\phi_{R3} < 0.4$), this change in viscosity can be described by the Mooney equation[29]

$$\ln \frac{\eta_{0,b}}{\eta_{0,\text{polymer}}} = \frac{k_E \phi_{R3}}{1 - \phi_{R3}/\phi_m} \tag{8}$$

where $\eta_{0,\text{polymer}}$ is the zero-shear-rate viscosity of the polymer, k_E is the Einstein coefficient, and ϕ_m is the maximum packing fraction (true volume/apparent occupied volume). The Einstein coefficient is $^5/_2$ for dispersed spheres if there is no slippage at the interface, but drops to 1 if there is slippage. For the R3/5K series, $k_E = 3.2 \pm 0.1$ and $\phi_m = 0.56 \pm 0.01$ for $0 \le \phi_{R3} \le 0.36$. The calculated maximum packing fraction was consistent with the observation of a poorly packed silicate structure.[13] That k_E was not equal to 2.5 could be explained in part by the particle geometry, which was not completely spherical but had an average aspect ratio (length/diameter) of 1.8 ± 0.2.[13]

An estimate of the volume fraction (ϕ_{calc}) that would be required to obtain the experimental diffusion coefficient using eq 7 was made. The calculated volume fraction was always greater than ϕ_{R3}, and the difference between the two values was attributed to adsorbed PDMS. Since the hydrodynamic size of R3 is known (2.75 nm), an estimate of the hydrodynamic radius of the adsorbed layer can be made using eq 9. However,

$$R_{\text{layer}} = \left[\left(\frac{\phi_{calc}}{\phi_{R3}}\right)^{1/3} - 1\right] 2.75 \text{ nm} \tag{9}$$

this may not provide an accurate measure of the layer thickness, even assuming that eq 7 was correct, since ϕ_{calc} could contain contributions from free PDMS entangled with the adsorbed layer as well as the adsorbed layer itself. The results from this calculation are shown in Figure 8 and are approximately independent of ϕ_{R3} as would be expected at these solid concentrations. The average hydrodynamic thickness, δh (0.35 ± 0.04 nm), is close to the hydrodynamic size of the pure polymer (0.35 ± 0.06 nm) shown in Figure 4.

An equivalent series of experiments were performed using a higher molecular weight polymer (12.2 kg mol^{-1}). The general trends in the data were the same as those observed in the case of the 5K data. Unfortunately, the baseline errors were too large for a meaningful value to be obtained for the adsorbed amount, which was a result of having to work at the limitation of the available gradient range of the spectrometer. However, it was possible to gain an estimate of the diffusion coefficients and these were analyzed in the same way as for the 5K data giving a larger layer thickness (0.47 ± 0.11 nm). The exponent for the relationship $\delta \sim M^x$ may be estimated from the two values of δh using the equation

$$\ln\left(\frac{\delta_1}{\delta_2}\right) = x \ln\left(\frac{M_1}{M}\right) \tag{10}$$

and x was found to be 0.34 ± 0.14; a value of 0.5 would be expected for a polymer in a bulk melt.[9] The diffusion coefficients obtained for both the pure melts were in agreement with previous studies.[30]

Conclusions

Self-diffusion NMR and viscosity experiments have been performed on blends of PDMS and polysilicate particles where the molecular weight of the polymer and the size of the particles have been varied. The small particle was observed to behave as a "solvent" whereas the larger particle acted as a reinforcing agent for the polymer. Increasing the molecular weight of the polymer slowed the dynamics and the results were consistent with scaling theories. For the reinforced system, estimates of the adsorbed amount and the hydrodynamic thickness of the adsorbed polymer layer were obtained.

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