

The adsorption of polydimethylsiloxane onto silica from the melt

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(Revised 10 October 1996)

N.m.r. relaxation and diffusion studies of the adsorption of polydimethylsiloxane polymers on silicas have been carried out as a function of particle concentration and polymer molecular weight. The structure of the adsorbed layer can be rationalized by a three-state model comprising bound polymer, polymer entangled or restricted by the adsorbed layer and free bulk polymer. In particular, n.m.r. relaxation and diffusion studies have enabled us to describe these regions quantitatively. At a loading of 10% particles, nearly 90% of the polymer segments in the dispersion have their mobility constrained, though only ~10% of these segments belong to chains that are adsorbed. The diffusion of the bulk polymer is also affected by the inclusion of particulates, and the overall mobility is reduced. © 1997 Elsevier Science Ltd.

(Keywords: n.m.r.; adsorption; polydimethylsiloxane; melt; relaxation diffusion)

INTRODUCTION

The use of inorganic particles as reinforcing materials for polymer melts is widespread in many commercial applications, in order to fabricate a large range of products whose strength/weight and cost are at a premium. However, the investigation of these systems is not straightforward and only a few techniques have been successful in studying these materials at the molecular level. These methods include n.m.r. relaxation^{1–5}, neutron scattering and reflection^{6–7} and various atomic/molecular scattering methods^{8,9}. Other routine methods such as FTi.r. and AFM can also give useful information. Bulk methods such as rheology are clearly important but the interpretation of the data relies on presupposed models of structure. Techniques that can discriminate between free and bound polymer on either a spatial or a dynamic scale are clearly the most incisive.

Theoretically, adsorption from polymer melts can be treated satisfactorily by either mean-field or scaling approaches¹⁰. For physically adsorbed polymers the simple arguments given by Joanny¹¹ as extensions to the general theory of adsorption from concentrated solutions are quite revealing. In this situation the adsorption is considered as comprising those chains which are sited within the radius of gyration (R_g) of the surface. A simple scaling argument (volume of coil/subtended area) then leads to an adsorption per unit area, θ , of $(R_g^3/R_g^2)a\phi_p$, where a is the monomer length and ϕ_p is the volume fraction of polymer in the bulk phase. In the melt, $\phi_p = 1$ and, assuming gaussian statistics,

$$\theta \approx N^{0.5}, \quad (1)$$

where N is the number of monomers.

Several studies have indicated that this behaviour is indeed found¹², though the systems have been eluted from bulk polymer in order to make the measurements. In this process it is assumed that the surface-bound polymer is irreversibly adsorbed; for low molecular weight polymers this may not be true. For polydimethylsiloxane (PDMS) the interaction of the polymer chain with the silica surface is very strong, due to specific hydrogen bonding. Under certain situations it is even possible that some chemisorption of the polymer may take place. For this system it may therefore be acceptable to use the residual bound amount of polymer as the equilibrium adsorbed amount if one can also assume that the strong binding does not preclude the system from reaching equilibrium in the first place. The direct measurement of the adsorbed layer structure in particulate systems dispersed in the same melt is rather difficult, though experiments on macroscopic surfaces using neutron reflection and selective deuteration have shown several interesting features with regard to the chain dimensions of the adsorbed layer¹³. Firstly, the adsorbed amount of an end-functionalized chain increased with its bulk concentration (in a higher molecular weight matrix), but the width of the adsorbed layer was virtually constant at approximately twice the unperturbed radius of gyration. In a second series of experiments the width was found to decrease with increasing matrix molecular weight (at fixed bulk concentration) even though the adsorbed amount increased. These data indicate extensive interactions between the grafted chains and the host melt. Indications from the extensive rheology measurements that have been carried out¹⁴ show that the incorporation of particles into PDMS melts leads to large changes in the bulk viscosity; i.e., the particles affect the structure of a region, extending well into the bulk phase. How these effects come about and how they

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are influenced by surface chemistry are highly pertinent. The aim of the present study is to use nuclear magnetic resonance (n.m.r.) relaxation and pulsed field gradient (p.f.g.) n.m.r.¹⁵ to quantify the different regions of mobility and structure in these composite materials in the presence of the host melt.

EXPERIMENTAL

The silica samples used in this study comprised aerosil and cabosil silicas obtained from Dow Corning (Barry, UK). Their physical characteristics are given in *Table 1*. The polymers used in this study were obtained from Petrarch and Dow Corning and their properties are given in *Table 2*.

The melt samples were made up in two different ways: (1) by direct incorporation of the particles into the melt phase, using a Silverson mechanical mixer; and (2) from dispersions of silica in a concentrated polymer solution in toluene, followed by solvent evaporation in a vacuum oven. The solution samples were left for 2–4 days at $\sim 50^\circ\text{C}$ until they reached a constant weight. The mechanical samples were used as prepared but no significant ageing effects were observed, at least over the timescales of carrying out the experiments (2 weeks maximum).

The gravimetric experiments were carried out by washing the adsorbed melt samples with excess toluene

Table 1 Properties of silicas

| Particle | Surface area ($\text{m}^2 \text{g}^{-1}$) |
|----------|---|
| Aerosil | 211 |
| Cabosil | 380 |

Table 2 Polymer characterization

| Molecular weight, M_n (kg mol^{-1}) | Key | Polydispersity index, M_w/M_n |
|---|-------|---------------------------------|
| 3.5 | 3.5 K | 1.5 |
| 6.5 | 6.5 K | 2.4 |
| 20 | 20 K | 1.7 |

until no more polymer could be eluted. The dried samples were then analysed using standard analytical procedures for measuring the elemental carbon content. Thus, from the total mass of silica added, the fraction of bound polymer can be calculated.

The spin–spin relaxation data (T_2) were obtained using the Carr–Purcell–Meiboom–Gill sequence¹⁶, and the diffusion attenuations were measured using the Stejskal–Tanner 2-pulse and 3-pulse methods¹⁷. The spectra were recorded on a 100 MHz Jeol FX100 spectrometer with a Surrey Medical Imaging Systems RF console. The relaxation data were recorded with a typical 180° pulse separation of 5 ms. The self-diffusion measurements used typical field gradients of 0.068 T m^{-1} .

RESULTS AND DISCUSSION

In *Figure 1* we show the experimental transverse magnetization decays from aerosil silica dispersed in 20 K polymer prepared using mechanical mixing. The decay curves have been normalized to unit intensity to help make a comparison of the relative shapes. It is clear that the decay rate increases with increasing particle concentration. There are two possible mechanisms we can invoke to explain this. Firstly, the space filling of the particles means that the translational diffusion of the polymer will be limited. The particles have a nominal radius of 70 Å but do form strings of aggregates which can be broken down during processing. If the particles were fully dispersed, then at $\sim 12\%$ particle concentration the particles would be separated, approximately, by their own diameter. The radius of gyration of 20 K PDMS is $\sim 37 \text{ Å}$, so the adsorbed sheaths would overlap at this concentration provided the layer thickness is unperturbed. The translation of the free polymer would also be restricted. There is quite a large change in relaxation over this range of concentration as the amount of completely unperturbed polymer decreases rapidly. The second effect, which may be more important as a relaxation mechanism, is the change in the segmental correlation times brought about by the substrate and the anisotropy of the resultant motion; we shall return to this point later.

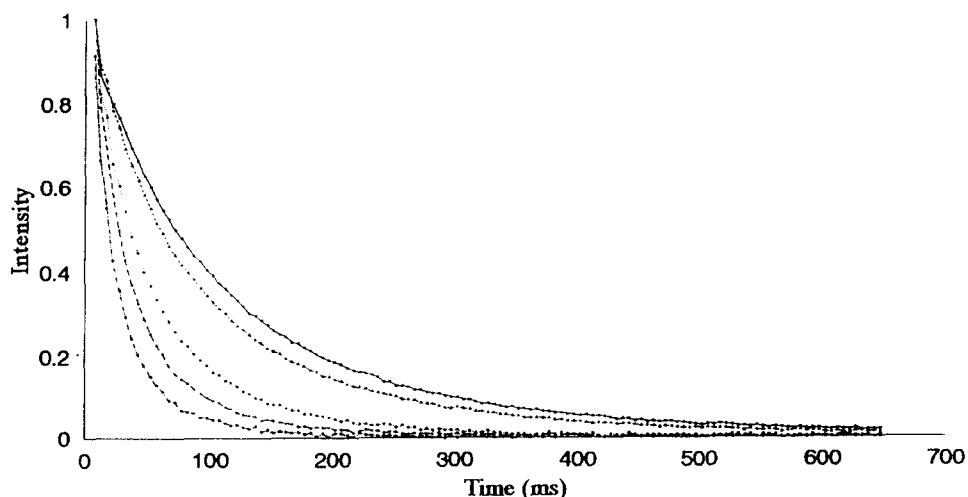


Figure 1 CPMG T_2 relaxation decays for Aerosil filled 20 K PDMS as a function of solids content 2.1%, 4.9%, 10.1%, 14.7% and 19.7% by weight, made by mechanical mixing. The curves are in order, the slowest decay corresponding to the 2.1% loading and the fastest to the 19.7% loading

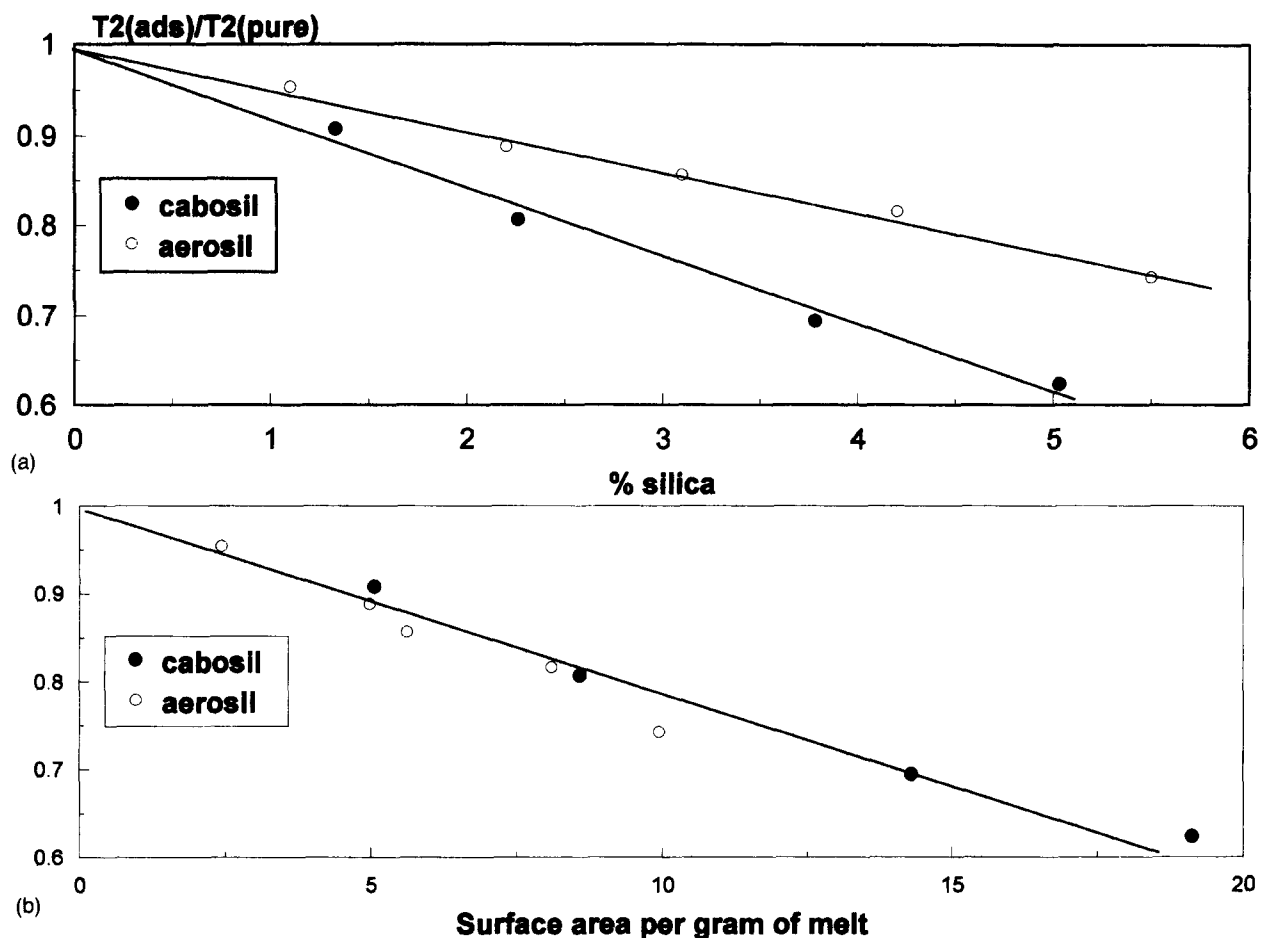


Figure 2 Variation of relative T_2 for Cabosil and Aerosil filled PDMS as a function of (a) % silica and (b) surface area, made by mechanical mixing

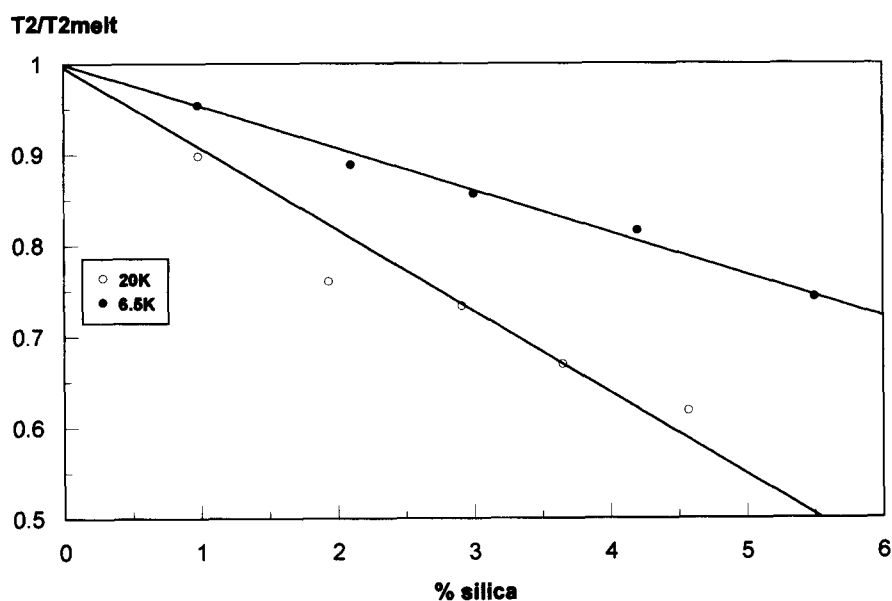


Figure 3 Variation of relative T_2 for Aerosil filled PDMS as a function of % silica for two different molecular weights, made by mechanical mixing

With mechanical mixing there must always be some concern about the reproducibility of the dispersions. To assess this, we have made samples with two different sized silica particles. The primary cabosil particles are smaller than those of the aerosil and hence, for a given mass of silica, the effects should be stronger for the latter (Figure 2a). As the nominal surface areas of the two

particles is known (Table 1) by BET analysis, and assuming that all of this area is accessible to the polymer, then replotting the data as a function of surface area should reduce all the points to a single line. This is shown in Figure 2b where it can be seen that the plots do superimpose. The relaxation data have been normalized by dividing by the T_2 of the pure melt [6.5 K in this case].

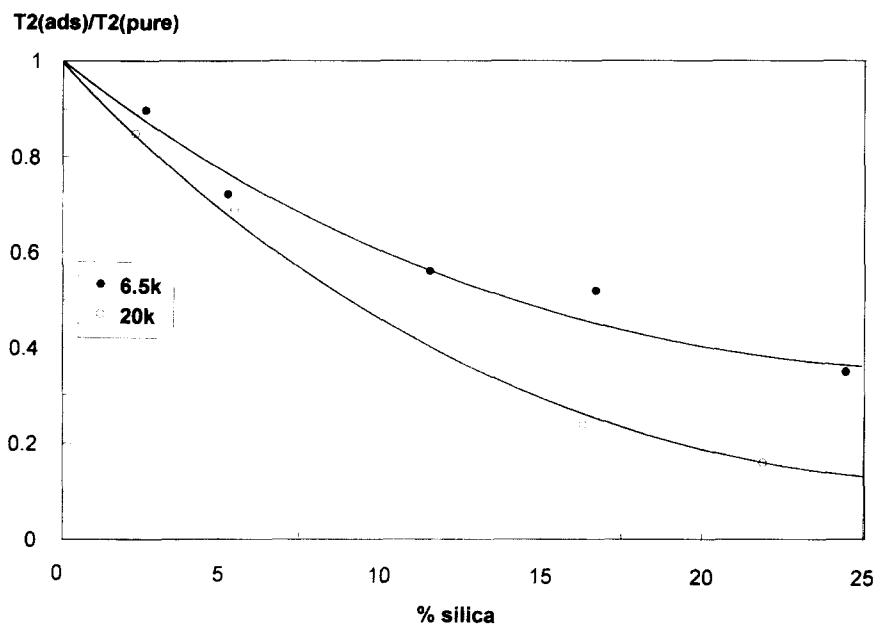


Figure 4 Variation of relative T_2 for Aerosil filled PDMS as a function of % silica for two different molecular weights, prepared from toluene solutions

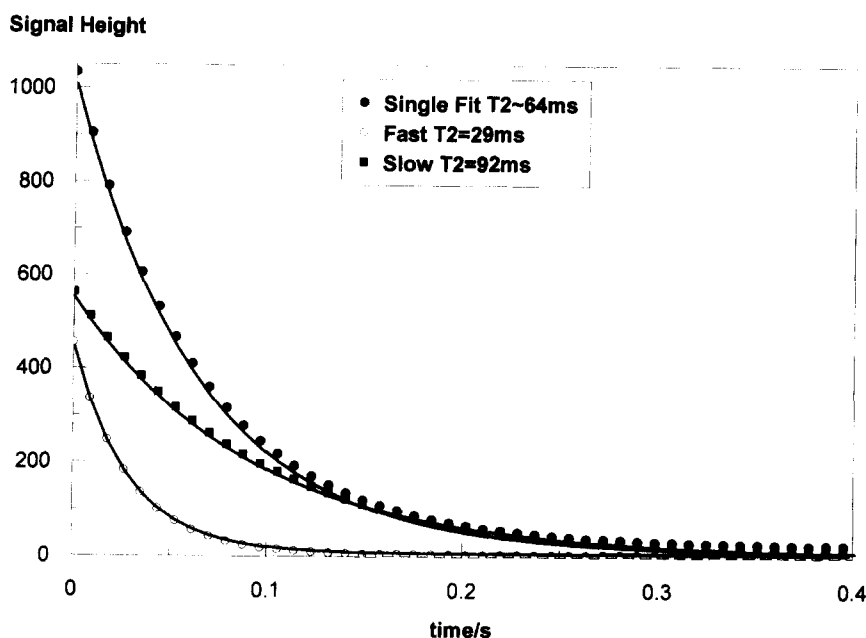


Figure 5 CPMG T_2 relaxation decay for Aerosil filled PDMS for 4.7% solids and 20K molecular weight showing deconvolution into two components, prepared from toluene solutions. Single fit $T_2 = 64$ ms. Double fit = 29 ms (fast) and 92 ms (slow). The solid lines correspond to the fitted functional forms

The effects of molecular weight on the viscosity of the particle/melt dispersions are known to be quite dramatic, and similar effects should be visible in the relaxation data. *Figure 3* shows a comparison between two different molecular weight samples: the higher molecular weight shows a much stronger change in the relaxation time with particle loading, and this can be attributed to an enhanced entanglement of the surface layer with the bulk matrix. The radius of gyration of the two polymers are 21 and 37 Å respectively and one would expect a larger effect for the higher molecular weight polymer at any given particle concentration. Assuming the particles are spherical and uniformly dispersed, and if the adsorbed layer stretches to $\sim 2R_g$, then it is

expected that a large change in relaxation time will occur at first overlap, i.e. at $\sim 25\%$ and 11% particle concentration respectively, for the two polymers. Mechanical mixing becomes very difficult above 12% and there is the possibility that the shear required may desorb, degrade or chemically graft the chains to the surface. In order to make higher concentrations the solvent method described earlier was used. For the lower concentrations the results for T_2 are virtually identical, and these are shown, together with the results for more concentrated dispersions, in *Figure 4*. The reduction in the normalized T_2 for a 25% dispersion occurs at a relative T_2 of 0.4 (6.5 K), and this is also approximately the same value for the higher molecular weight polymer at 11%

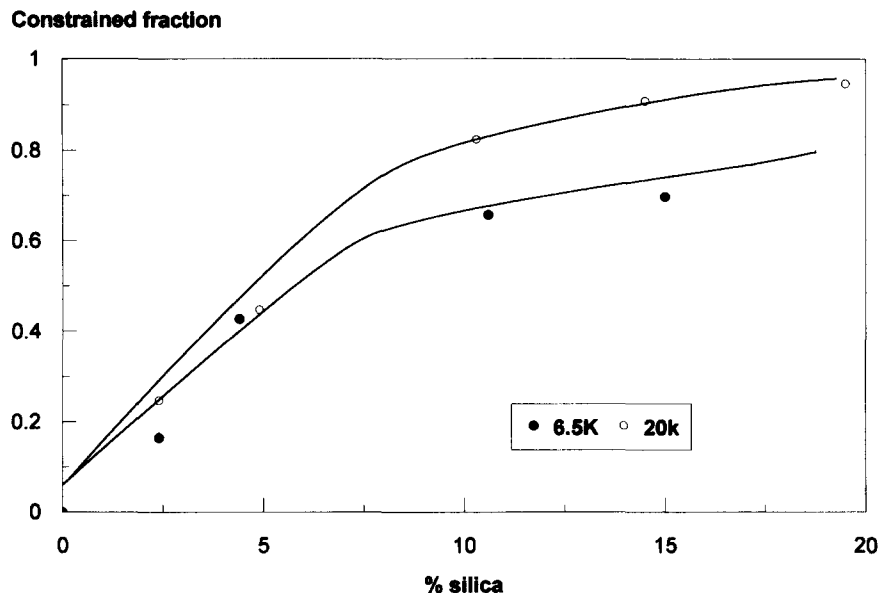


Figure 6 Constrained fraction from relaxation analysis for two molecular weights of Aerosil filled PDMS, 6.5 K and 20 K, prepared from toluene solutions

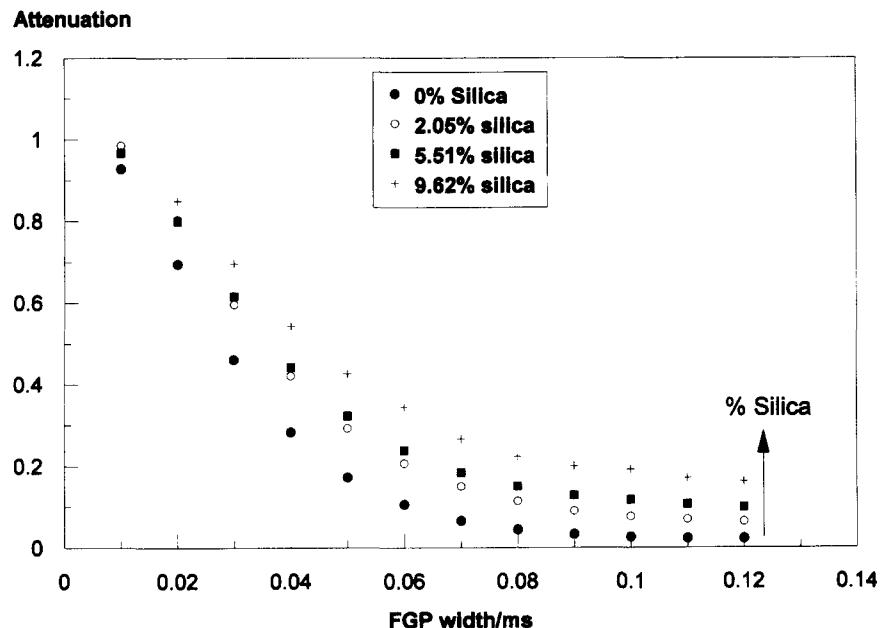


Figure 7 P.f.g. n.m.r. attenuation decays for Aerosil filled PDMS, 3.5 K molecular weight, for 0%, 2.1%, 5.5% and 9.6% silica, prepared from toluene solutions

(20 K), which is consistent with the overlap argument presented above.

The T_2 decays shown contain, of course, a contribution from the adsorbed layer segments in different environments as well as unperturbed segments of the free chains, and a single relaxation time fit to the data is clearly rather approximate. Exchange between the bulk and surface-perturbed populations is expected to be quite slow; we can therefore deconvolute the decays by fitting the slower component to that for the pure melt. This will then give the fraction of perturbed polymer: such a deconvolution is shown in *Figure 5*. The fit to a double exponential reproduces the experimental decay quite accurately. However, this is still an oversimplification as the response of segments in the perturbed region is certainly dependent on the distance from the

interface and a spectrum of relaxation times for segments in different environments with different anisotropies can be envisaged¹⁸. Also, segments strongly held at the surface will not contribute to the signal as their relaxation times are likely to be strongly damped by static dipolar interactions¹⁹. The CPMG sequence cannot refocus the dipolar Hamiltonian and so, although the intensity of the first data point will depend on the total PDMS content, the echo train will not contain any intensity from segments in 'solid-like' environments. Evidence for such environments can be found by using solid-echo methods^{2,19}. This latter approach can in principle give a method for finding the bound fraction of the adsorbed polymer (i.e. the fraction of segments in trains as compared to loops and tails)¹⁹, but this method will not be used here.

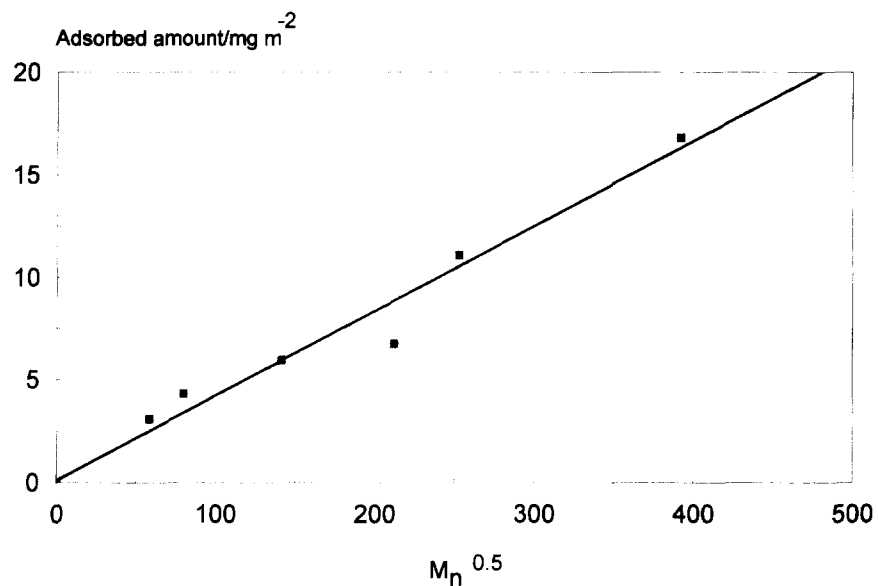


Figure 8 Molecular weight dependence of the adsorbed amount of PDMS on Aerosil at 2% solids concentration

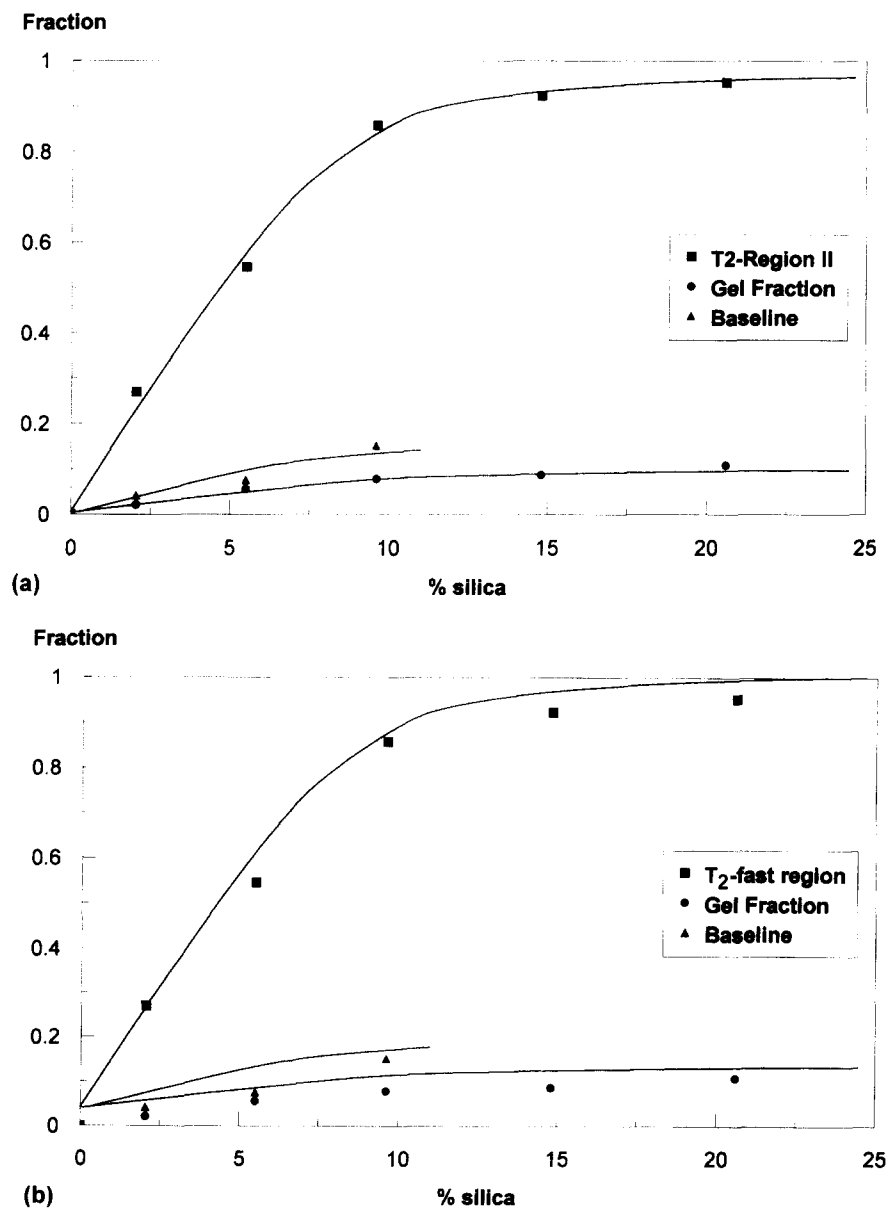


Figure 9 Fraction of PDMS in different environments in Aerosil filled PDMS, 3.5K molecular weight, as a function of % silica

The fraction of perturbed segments obtained by the simple two-state deconvolution is shown in *Figure 6* for the same two polymer samples as in *Figure 3*. Both of these curves show that a substantial fraction of the polymer is dynamically perturbed by the presence of the particles either directly, by being part of a bound chain, or indirectly, by being enmeshed with the bound layer which damps both the segmental dynamics and self-diffusion. At particle concentrations below that at which substantial chain overlap between polymer on adjacent particles occurs, one would expect a linear increase in the perturbed fraction with particle concentration. However, the data do not show distinct breaks at the expected volume fraction. This suggests that other factors, such as space filling by particles which also reduces the translational diffusion of the chains, play a role. The higher molecular weight sample certainly has more perturbed segments at all particle concentrations and does show a change in dependence on concentration. There is a similar break for the lower molecular weight sample, though the exact position where these changes take place is indicated only approximately by the present data.

In order to quantify further the structure of these systems, two other experiments were undertaken: n.m.r. self-diffusion and gravimetric analysis. The self-diffusion studies require making measurements as a function of the field gradient intensity or duration. For unrestricted diffusion the attenuation of the signal should follow the equation given by Tanner¹⁷:

$$A = A(0) \exp(-\gamma^2 G^2 D (\Delta - \delta/3) \delta^2) \quad (2)$$

where the attenuation function $A/A(0)$ depends on D , the self-diffusion coefficient, δ , the width of the field gradient pulses, Δ , their spacing, G , the applied field gradient and γ , the magnetogyric ratio. For a fixed value of τ , the radio frequency pulse spacing, the effect of T_2 is constant and, in these experiments, Δ was also held constant. Hence, the ratio of the echo height with and without the field gradient gives a value for the self-diffusion coefficient D . However, if there is no diffusion but segments still have long spin-spin relaxation times (indicative of rapid segmental motion), a constant baseline signal should be observed at larger values of δ . The level of this baseline should then reflect the proportion of protons which are segmentally mobile but whose translation is restricted. This will include all chains which are in contact with the surface and a small set which are entangled for sufficiently long times (greater than ~ 100 ms) with the adsorbed layer. A typical set of data for the 3.5 K sample is shown in *Figure 7*. The effect of increasing the particle concentration is clearly seen in the increasing baseline signals. Of course, other effects such as bounded diffusion between particles must also be considered at concentrations near the overlap region. The fraction of non-diffusing polymer can be estimated from the difference in the baseline values and the initial heights. The data have been fitted to a gaussian function (equation (2)) and a floating baseline. At a solids loading of 10%, the fraction of non-diffusing polymer is $\sim 15\%$, which is substantial. Further data are plotted in *Figure 9*.

The fraction of polymer directly attached to the surface can be estimated by gravimetric analysis. One would expect that the adsorbed amount or 'gel' fraction should increase linearly with particle concentration up

to the overlap concentration. For the higher molecular weight polymers shown these concentrations are $\sim 6\%$, 4% and 1.7% respectively. The adsorbed amounts are approximately linear at lower concentrations (below 8% loading), and choosing 2% as a threshold and plotting the results as function of $M^{0.5}$ (equation (1)) gives a reasonably straight line (*Figure 8*) as expected. The washing process would therefore seem to remove only bulk polymer.

In *Figure 9*, we compare all of the data for the different motional regimes. Several interesting features emerge. Firstly, the fraction of chains that are in contact with the surface is only about 10% of the total, even at 25% particle concentration, indicating a very efficient screening of the surfaces. However, 95% of the chains are affected dynamically by the incorporation of particles (T_2 fast). This indicates a strong interaction between the adsorbed layer and the bulk phase, in agreement with other data¹⁴. The number of segments that are immobilized completely is greater than the physically adsorbed amount but still significantly less than the total perturbed amount. This indicates that it is a change in segmental mobility rather than translation restrictions which determines the spin relaxation time, and shows that the chains in these dispersions are still highly mobile on a segmental basis, even up to high particle concentrations. The populations measured by these three experiments of course overlap partially as extended tails form the adsorbed layer, and will be seen both as non-diffusing (from the baseline measurements) and as segmentally restricted (T_2 fast).

CONCLUSIONS

N.m.r. experiments have been used to probe the chain dynamics in concentrated particulate dispersions. The structure of these systems can be described in terms of a three-state model. Firstly, at the interface (region I) there is an immobile fraction of chains which have very long correlation times and diffuse with particles. The segments in region II are perturbed, probably quite strongly, by adsorption, both segmentally and translationally. In region III the chains can diffuse but their mobility is reduced. The fraction of segments whose mobility is unaffected either translationally or on a segmental scale is very low at solids loadings greater than 10% .

ACKNOWLEDGEMENTS

MJT would like to acknowledge Dow Corning (Barry) for the provision of a grant to undertake a PhD. The authors are also indebted to Dr T. C. Kendrick for his continued support of this work.

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