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Local dynamics of poly(dimethyl siloxane) in the presence of reinforcing filler particles

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The dynamics of poly(dimethyl siloxane) (PDMS) filled with very fine silica particles with surface areas equal to 90 and 300 $m^2 g^{-1}$ has been investigated by quasielastic neutron scattering (QENS). The elastic scattering intensity has been monitored as a function of temperature up to 275 K and momentum transfer Q for values corresponding to the first and second sharp diffraction maxima. A small dynamic effect is observed below 235 K, i.e. below the melting temperature of PDMS. Considerable decrease of molecular mobility in the filled systems is detected above 235 K as a result of the decreased entropy of the adsorbed segments. The extent of reduced mobility is such that part of the chains no longer contributes to the quasielastic broadening but gives rise to an elastic component. At 40 wt% silica content and 250 K the fraction of immobilized segments amounts to 0.072 ± 0.005 for the filler with 90 $m^2 g^{-1}$ surface area which corresponds to an adsorption layer of about 50 Å. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: poly(dimethyl siloxane); filler particles; dynamics)

INTRODUCTION

Composites containing reinforcing fillers exhibit improved mechanical strength compared to the polymer matrix[1–3]. The reinforcement effect strongly depends on the properties of the interfacial region between the two components, i.e. the interphase, and it is largely determined by the specific interactions between the polymer and the reinforcing additive. As a consequence, the structure and the mobility of the polymer within the interfacial region are altered compared to the bulk polymer.

The experimental results from n.m.r.[4–8], dielectric spectroscopy[9] and dynamic mechanical thermal analysis[10,11] (d.m.t.a.) revealed that the mobility of chain units adjacent to the adsorbent surface differs considerably from the bulk. Two and even three[12] regions of different chain mobility have been identified by n.m.r. experiments. This dynamic heterogeneity implies that chain relaxation in the adsorbed layer differs from the bulk. The chain mobility outside the absorbed layer, which was estimated to be about four times the van der Waals diameter of the molecules, is close to that of the unfilled polymer. In addition, the introduction of active fillers produces an insoluble gel of bound rubber whose content can be determined by extraction or pulsed n.m.r. measurements[13].

Tsagaropoulos and Eisenberg[10,11] have recently reported a study of the dynamic mechanical properties of various polymer–filler systems including poly(dimethyl siloxane) (PDMS). Most composites examined showed two peaks in tangent delta (tan δ) at silica contents above 10 wt% except PDMS/filler composites where a second tan δ peak was observed above 20 wt%. The low-temperature peak corresponding to the usual polymer glass transition did not shift with increasing filler content but decreased in magnitude indicating that fewer chains participate in this relaxation process with increasing filler content. The second tan δ peak was broader than the first, decreased in size with increasing particle content and was shifted to a lower temperature. These results were discussed in terms of a model first developed for ionomers, the EHM (Eisenberg, Hird and Moore) model. Within this model, the polymer–filler composites consist of silica particles surrounded by a layer of immobile polymer that does not participate in either of the two glass transitions. The second glass transition is identified with a layer of loosely bound polymer chains which is experimentally detectable only when the regions of restricted mobility overlap; as the average interparticle distance decreases with the addition of filler particles, the loosely bound polymer is gradually transformed to tightly bound with a decrease in the area of the second tan δ peaks.

In this work we present the first quasielastic neutron scattering (QENS) study of polymer–filler composites and explore the effect of reinforcing filler on the fast segmental dynamics and for length scales in the range from 3 to 25 Å which are the relevant length scales for the dynamically modified polymer.

The system chosen for our study consists of PDMS filled with hydrophilic Aerosil (fumed silica). This appeared to be an obvious choice due to the extensive literature available on the low-frequency dynamics of both filled and unfilled polymer. Furthermore, PDMS has a low glass transition (T_g) resulting in a pronounced quasielastic broadening at temperatures above the melting point. It is therefore very suitable for studying the effect of restricted mobility due to the 'slow' filler particles. In addition, among the elastomers, PDMS shows the greatest improvement in mechanical

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properties with the addition of fillers. A modification of the dynamics of the chain units adjacent to the adsorbent surface compared to units in the bulk is therefore expected.

NEUTRON SCATTERING[14,15]

In a scattering experiment using neutrons, the incident beam, which is characterized by the wavevector k_o of wavelength λ_o ($|k_o| = 2\pi/\lambda_o$) and energy E_o is scattered by the nuclei in the target material. Changes in both their energy and direction of travelling may occur upon scattering. If the scattered beam has energy E and wavevector k ($|k| = 2\pi/\lambda$), then by considering conservation of energy and momentum, the following relationships can be obtained:

$$\Delta E = E - E_o = \left(\frac{\hbar}{2m_n}\right)(k^2 - k_o^2) \qquad (1)$$

$$\hbar Q = \hbar(k - k_o) \qquad (2)$$

where $\hbar = h/2\pi$ (h is Planck's constant) and m_n is the neutron mass ($m_n = 1.675 \times 10^{-27}$ kg). For an elastic process, there is no energy change upon scattering: $\Delta E = 0$ and therefore $|k| = |k_o|$. In this case, the wavevector change Q (also termed scattering vector or momentum transfer) defined by equation (2) reduces to:

$$Q = |Q| = \frac{4\pi}{\lambda} \sin\frac{\theta}{2} \qquad (3)$$

where θ is the scattering angle.

Inelastic scattering is observed when the nuclei are vibrating, rotating or translating in the time-scale of the scattering experiment. Because molecular vibrations involve changes between quantized energy levels which are large compared to neutron energies, a finite exchange of energy takes place between the neutrons and the nuclei giving rise to discrete peaks in the inelastic neutron scattering spectra.

For rotational and translation motion, small energy exchanges occur between the neutrons and the particles which are diffusing over a time scale of about 10^{-10}–10^{-12} s. Because the spacings between the energy levels are small compared to neutron energies, quantization can be neglected and molecular motion is detected as a broadening of the elastic line due to neutrons scattered without energy transfers. Because of the small energy changes involved, this type of neutron scattering technique is referred to as quasielastic neutron scattering (QENS).

The neutron–nucleus interaction is characterized in terms of two parameters, the scattering length b which represents the amplitude of the scattered wave and the scattering cross-section σ which gives the probability of a neutron being scattered in the 4π steradians. The relationship between the two parameters is: $\sigma = 4\pi b^2$ (the scattering cross-section is measured in barns, a unit which is equivalent to 10^{-24} cm^2).

The neutron–nucleus interaction depends not only on the type of nucleus but also on the total spin state of the neutron–nucleus system. This explains why values of scattering length b are of the same order of magnitude (10^{-12} cm) for all nuclei but differ from isotope to isotope of the same nucleus. As a consequence, the scattering cross-section can be separated into two contributions; a *coherent* cross-section: $\sigma_{coh} = 4\pi\langle b\rangle^2$ which is related to the mean value of the scattering length and an *incoherent* component $\sigma_{inc} = 4\pi(\langle b^2\rangle - \langle b\rangle^2)$, which is due to deviations from the mean scattering length.

Only the coherent scattering contains structural information on the position of the nuclei in the sample since it arises from interference effects between waves scattered from different nuclei. The incoherent part carries no structural information. Incoherent scattering arises from deviations in scattering length from the mean value and it is due both to the existence of different isotopes in the specimen and to the presence of nuclei in different spin states. Since the nuclear spin is usually uncorrelated with the position of the nuclei, incoherent scattering does not contain any structural information but can be exploited in dynamic studies.

Neutron scattering experiments carried out to investigate molecular motion in polymeric materials exploit the large incoherent cross-section of the hydrogen atoms ($\sigma_{inc}(H) = 80.26$ barns) compared to σ_{inc} of other nuclei ($\sigma_{inc}(C) = 0.001$ barns, $\sigma_{inc}(D) = 2.05$ barns and $\sigma_{inc}(O) = 0.000$ barns). For a hydrogen-containing polymer, the incoherent scattering cross-section relative to the monomer unit is also large compared to the coherent part and therefore the scattering is mainly incoherent.

The quantity measured experimentally is the double differential scattering cross-section, $\partial^2\sigma/(\partial E\,\partial\Omega)$. This gives the probability that a neutron is scattered with energy change dE into the solid angle $d\Omega$ at a fixed scattering angle θ. For a system of N identical nuclei, $\partial^2\sigma/(\partial E\,\partial\Omega)$ is related to the incoherent scattering law, $S_{inc}(Q,\omega)$ (ω being the angular frequency) according to:

$$\hbar\frac{\partial^2\sigma}{\partial\Omega\,\partial E} = \frac{N}{4\pi}\frac{k}{k_o}\sigma_{inc}S_{inc}(Q,\omega) \qquad (4)$$

The incoherent scattering law describes correlations between the same nuclei at time zero and t and it therefore provides information about the motion of individual nuclei. However, since $S_{inc}(Q,\omega)$ essentially arises from nuclei with different spins, nothing can be said about the spatial correlations of these nuclei.

Data analysis is generally performed by comparing a model function to the experimental data. This involves choosing an analytical expression to represent the scattering law $S_{inc}(Q,\omega)$, convoluting it with the instrumental resolution and fitting it to the experimental data. The disadvantage of this procedure is that the analytical form of $S_{inc}(Q,\omega)$ has to be known and needs to be a relatively simple mathematical function for the convolution to be performed.

To avoid making assumptions on the motion of the PDMS chains, we adopt a different method based on the Fourier transform of the QENS data. A detail study of the dynamics of PDMS will be reported in a separate publication.

The scattering function $S_{inc}(Q,\omega)$ is the time-Fourier transform of the intermediate scattering function $I_{inc}(Q,t)$:

$$S_{inc}(Q,\omega) = \frac{1}{2\pi}\int I_{inc}(Q,t)\exp(-i\omega t)\,dt \qquad (5)$$

which is defined as:

$$I_{inc}(Q,t) = \frac{1}{N}\sum\langle\exp(iQ\cdot R_i(t))\exp(-iQ\cdot R_i(0))\rangle \qquad (6)$$

where the brackets indicate a thermal average and $R_i(t)$ and $R_i(0)$ are the positions of the nuclei at time t and $t = 0$, respectively.

The intermediate scattering function can be derived from the experimental data via deconvolution by considering that a convolution in ω-space corresponds to a multiplication in time.

EXPERIMENTAL

Materials

Poly(dimethyl siloxane) (M_w = 103 400 g mol^{-1}, M_w/M_n = 2.36) was purchased from Aldrich. Differential scanning calorimetry (d.s.c.) measurements were performed on a Metler DSC at a heating rate of 10 K min^{-1}. PDMS shows a T_g at 151 K, a cold crystallization at 188 K and a broad melting transition composed of two endothermal peaks at 227 and 233 K (see inset in *Figure 1(a)*).

Composite samples containing silica particles (Degussa) of two different surface areas were prepared: PDMS–A90 containing Aerosil A90 particles of 90 m^2 g^{-1} surface area (nominal diameter: 20 nm) and PDMS–A300 made from Aerosil A300 with 300 m^2 g^{-1} surface area (average diameter: 7 nm). The weight fraction of Aerosil in the mixtures was 40 wt% which corresponds to a volume fraction of 23 vol% as calculated from the densities of PDMS and Aerosil (0.982 and 2.20 g cm^{-3}, respectively).

PDMS–Aerosil mixtures were prepared by adding dried silica particles to a 0.5 wt% solution of PDMS in pentane. The suspension was stirred for 48 h and then the solvent was allowed to evaporate at room temperature under stirring. The powder was dried in a vacuum oven. Samples for QENS experiments were prepared by compressing the dried mixture at room temperature in a mould. The thickness of the films was approximately 0.2 mm.

The d.s.c. traces of the PDMS–filler samples showed broader transitions compared to PDMS but the transition temperatures are not substantially altered in the presence of filler. The main change is associated with the melting peak. A single peak was detected in the PDMS–filler samples at 233 K and the crystallization of the polymer matrix was found to be suppressed. In fact, earlier studies[4] have shown that addition of filler particles with volume fraction higher than 0.3 results in the complete suppression of crystallization. This effect is largely dependent on the type of filler used. The filler particles induce disorder by creating quasi-crosslinks at the physiosorbed points and slow down the chain diffusion which is necessary for polymer crystallization.
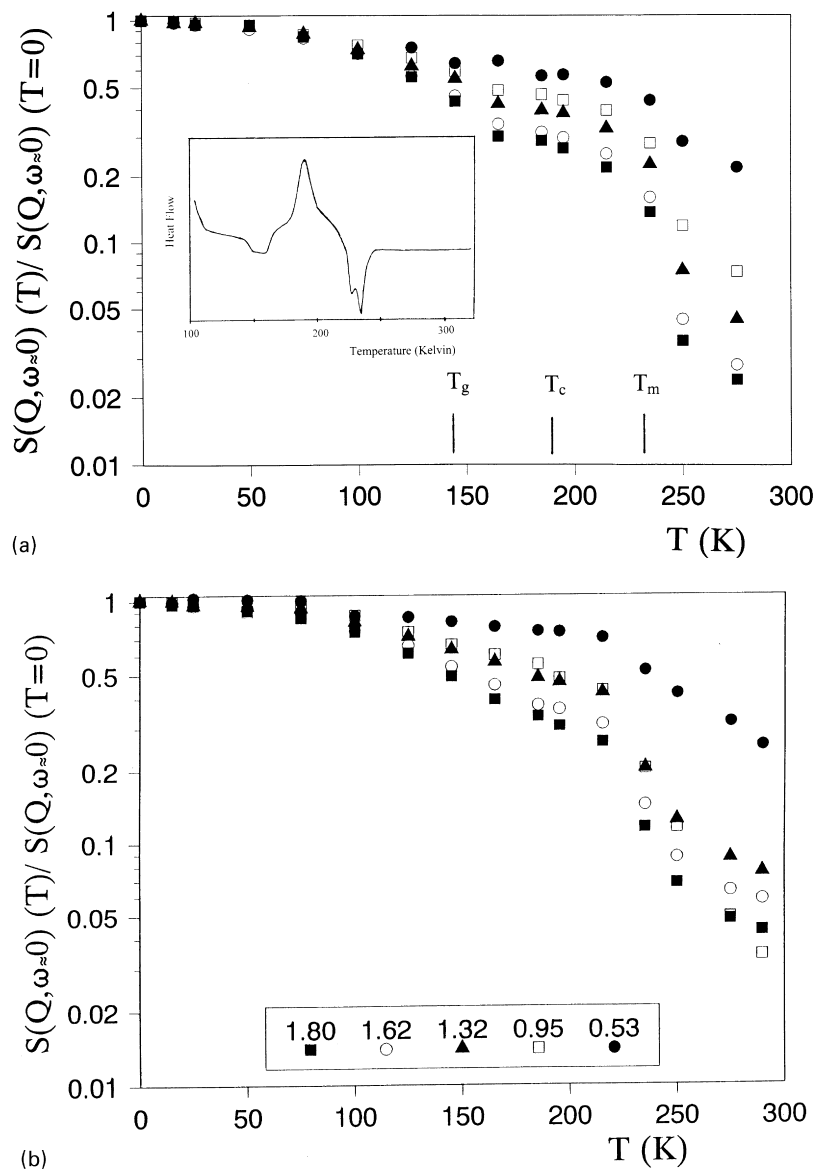
Figure 1 Elastic window scan, $S(Q, \omega \approx 0)(T)/S(Q, \omega \approx 0)(T = 0)$, *versus* temperature of (a) PDMS and (b) PDMS–A90 at (■) 1.80, (○) 1.62, (▲) 1.32, (□) 0.95 and (●) 0.53 Å^{-1}. In the inset of (a): d.s.c. trace of PDMS measured at 10 K min^{-1} showing the glass transition temperature, T_g, cold crystallization, T_c and melting peaks

The integrated heat of fusion amounts to 31 and 10 J g^{-1} for PDMS–A90 and PDMS–A300, respectively.

QENS measurements

QENS measurements[14,15] were performed on the IRIS back-scattering spectrometer at the Rutherford Appleton Laboratory (ISIS pulsed neutron source)[16]. The temperature range investigated varied from 4 to 280 K. The energy range covered by the spectrometer was from − 0.4 to 0.4 meV with an energy resolution of 15 μeV (measured as FWHH) for the PG002 analyser and of 11 μeV for the MI006 analyser. The Q range varied from 0.25 to 1.9 Å^{-1}.

In all experiments, the elastic intensity scattered within a small frequency interval around $\omega \approx 0$ ($\Delta E = 14$ μeV) and corresponding to neutrons which are scattered at zero energy transfer, was first monitored in a wide temperature interval ranging from 4 to 280 K (elastic window scan). From these measurements the incoherent dynamic structure factor, $S(Q, \omega \approx 0)$, was determined and data were normalized with respect to the extrapolated value at 0 K for selected Q values.

In the absence of quasielastic broadening the decrease of the elastic intensity is described by the Debye–Waller factor:

$$\frac{S(Q, \omega \approx 0)(T)}{S(Q, \omega \approx 0)(T = 0)} \propto e^{-\langle u^2 \rangle Q^2} \qquad (7)$$

where $\langle u^2 \rangle$ is the mean square amplitude of vibrations which decreases linearly with increasing temperature, i.e. $\langle u^2 \rangle \propto T$. Therefore, by plotting $\ln[S(Q, \omega \approx 0)(T)/S(Q, \omega \approx 0)(T = 0)]$ *versus* temperature any non-linearity observed is due to molecular motions other than vibrations. This also gives rise to the appearance of a quasielastic broadened component in the QENS spectra.

Subsequently, a number of long time measurements were made at selected temperatures in the range between 100 and 280 K in order to determine the scattering law as a function of the energy transfer. To quantify the effect of filler on the mobility of the PDMS chains the frequency data were converted to the intermediate scattering function $I(Q,t)$[17].

WAXS measurements

The wide-angle X-ray (WAXS) measurements were carried out on a Siemens θ-θ diffractometer (Model D500T) in the reflection geometry. Cu Kα radiation measurements were used from a Siemens generator (Kristalloflex 710 H) operating at 35 kV and 30 mA and a graphite monochromator was utilized in front of the detector ($\lambda = 1.54$ Å). Measurements were performed in the θ range 1 to 20°, with steps of 0.01°, covering the Q range from 0.4 to 2.8 Å^{-1}. Experiments were performed at 300 K. *Figure 2* shows the static structure factor $S(Q)$ of PDMS, the filler particles (A90) and the PDMS/A90 sample used for QENS measurements.

The structure factors of the polymer and the filler show a main peak arising mainly from intermolecular interactions[18] at about 0.8 and 1.5 Å^{-1} for PDMS and A90, respectively. The peak position is related to an average intermolecular distance ($d = 2\pi/Q_{max}$) equal to 7.8 and 4 Å for PDMS and the filler particles (A90), respectively. Because the peak position reflects the average density (or specific volume) of the material[19], the difference between distances obtained for PDMS and A90 is then a consequence of the lower density (less efficient packing) of the polymer as compared to the filler particles (the nominal diameter of A90 is 200 Å). The structure factor for the composite (PDMS/A90) is the
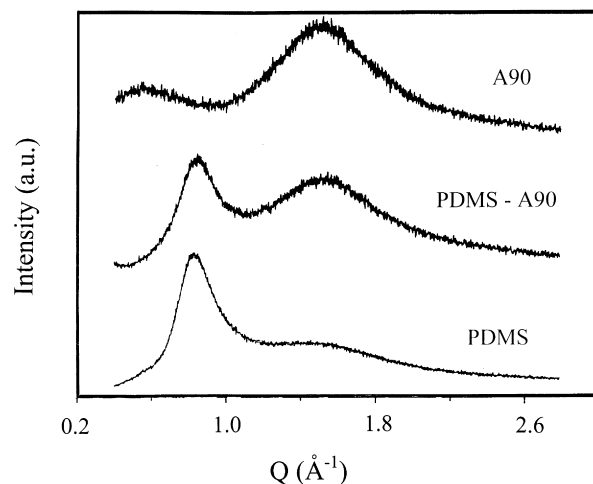

Figure 2 Static structure factor $S(Q)$ obtained from wide-angle X-ray scattering at 300 K for PDMS, the polymer/filler composite and the filler particles (A90)
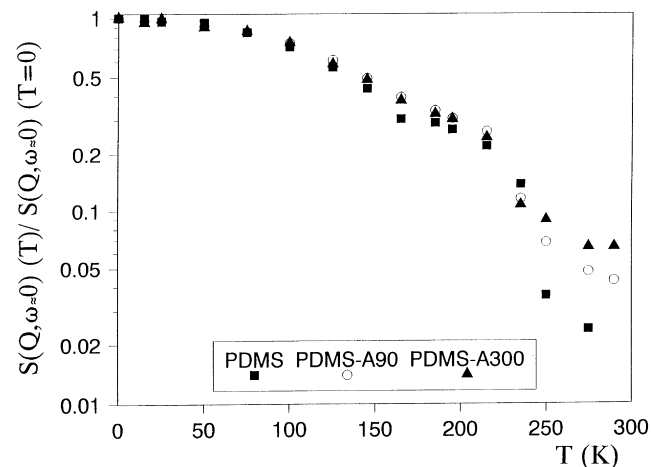

Figure 3 Elastic window scan *versus* temperature for (■) PDMS, (○) PDMS–A90 and (▲) PDMS–A300 at $Q = 1.80$ Å^{-1}

weighted average of the pure components, as shown in *Figure 3*.

RESULTS

Values of $S(Q, \omega \approx 0)$ normalized to the extrapolated intensity at 0 K are plotted in *Figure 1*(a) and *Figure 1*(b) as a function of temperature and momentum transfer Q for PDMS and a sample containing 40 wt% of Aerosil 90 (PDMS–A90), respectively. The temperature dependence of $\ln[S(Q, \omega \approx 0)(T)/S(Q, \omega \approx 0)(T = 0)]$ is a very sensitive probe of the mobility and hence of the transition temperatures in the unfilled and filled PDMS samples. Below 75 K, $\ln[S(Q, \omega \approx 0)(T)/S(Q, \omega \approx 0)(T = 0)]$ decreases linearly with increasing temperature, as expected by the absence of molecular motions other than vibrations. From 80 to 150 K the decrease of the elastic intensity beyond the normal Debye–Waller factor is attributed to the reorientational motion of the methyl groups in PDMS. Independent n.m.r. measurements made on similar systems assigned the dynamics around 95 K to the C_3 rotation of the CH$_3$ groups about the Si–C bond[4]. This is confirmed by the analysis of $S(Q, \omega)$ which will be reported in a separate publication[20].

In the vicinity of the glass transition temperature located at 150 K for both filled and unfilled samples, a pronounced decrease of the elastic intensity would be expected due to the onset of large-scale conformational rearrangements (α-relaxation)[21]. In practice, however, such a prominent decrease of $\ln[S(Q, \omega \approx 0)(T)/S(Q, \omega \approx 0)(T=0)]$ is observed only above the melting temperature, i.e. above 235 K for all samples investigated (*Figure 1(a)* and *Figure 1(b)*).

It is interesting to comment upon the behaviour close to 150 K in PDMS. As shown in *Figure 1(a)* and *Figure 1(b)*, just above T_g the elastic intensity appears to decrease more than at lower temperatures, but it soon stabilizes to a constant value up to 200 K. This is consistent with the d.s.c. measurements on PDMS (Section 3.1). Hence, the initial decrease of $S(Q, \omega \approx 0)(T)/S(Q, \omega \approx 0)(T=0)$ above T_g is associated with the onset of segmental motion. However, PDMS undergoes cold crystallization at 188 K (T_c) and molecular motion is now restricted due to the presence of crystalline regions up to the melting temperature. Above 235 K, the elastic intensity decreases steadily and shows a pronounced Q dependence (*Figure 1(a)* and *Figure 1(b)*) as usually observed in a polymer melt[22–26].

It is evident by comparing *Figure 1(a)* and *Figure 1(b)* that the presence of filler particles causes a slowing down of segmental motion. A direct comparison between filled and unfilled $S(Q, \omega)$ spectra at $Q = 1.80 \text{ Å}^{-1}$ is presented in *Figure 3*. Although the elastic intensity is generally higher for PDMS–A90 and PDMS–A300 up to 235 K compared to PDMS, the dynamic effect observed is very small. Above T_m this effect increases significantly (*Figure 3*) and depends on the particle surface area, at equal volume fraction of fillers. Aerosil 300, having the largest surface area ($300 \text{ m}^2 \text{ g}^{-1}$), is more effective in restricting the mobility of the polymer chains.

Effect on methyl group rotation

In principle, the rotational motion of the methyl groups in PDMS influences the QENS spectra in the temperature range from 100 to 235 K. In practice, identification of methyl group rotation above 150 K is complicated by the onset of long-range motions and at higher temperatures by the cold crystallization of PDMS. In the temperature range between T_g and T_m the pure polymer spectral shape is complicated due to the filler and the amorphous and crystalline polymer dynamics. The analysis of the neutron scattering intensity as a function of energy transfer in terms of a Gaussian distribution of activation energies will be presented in a separate publication[20]. Here we note that any dynamic effect due to the fillers is negligible up to T_g and the slightly more pronounced effect which is detected between T_g and T_m (*Figure 3*) is probably due to differences in sample morphology, i.e. different amounts of crystallinity in the samples as discussed in Section Section 3. The extent of changes in molecular mobility in this temperature range is illustrated in *Figure 4* where the normalized $S(Q, \omega)$ spectra of the unfilled and filled samples at $Q = 1.78 \text{ Å}^{-1}$ and $T = 235$ K have been plotted. The good data overlap at this temperature indicates that the dynamics of the PDMS chains is unperturbed by the presence of the filler particles up to the melting point. In addition, the similarity between the two data sets confirms that the scattering of the filler particles is negligible compared to the scattering of the PDMS chains, as expected from a comparison of the cross-section of the repeat unit in PDMS (510 barns) and the cross-section of the silica filler (11 barns, calculated for the SiO_2 units).

Effect on segmental motion

The dynamics of PDMS has been investigated in the past by various techniques[4,27] including QENS[22–26]. Three relaxation processes have been observed: the segmental α-relaxation at $T > T_g$, and at $T < T_g$ two processes, β and γ, the latter being attributed to the methyl group rotation. Earlier QENS measurements on PDMS at $T > T_m$ showed that the segmental relaxation time-scaled with $\tau \approx Q^{-n}$ with n in the range 3 to 4. Although these results were interpreted in terms of the Rouse model, recent studies[28] demonstrated that the same $\tau(Q)$ scaling could result from the inherent non-exponentiality in the intermediate scattering function, i.e. $I(Q,t) \approx \exp\{-[t/\tau(Q,T)]^{\beta}\}$ with $n = 2/\beta$ where β is the Kohlraush–Williams–Watts (KWW) exponent.

PDMS and samples containing filler particles are semicrystalline up to 235 K and large-scale conformational rearrangements are severely hindered below this temperature. As a consequence, the QENS spectra up to T_m contain both elastic and quasielastic components (*Figure 4*), the latter probably consisting of contributions from the amorphous regions in addition to methyl group reorientations. The coexistence of amorphous and crystalline regions
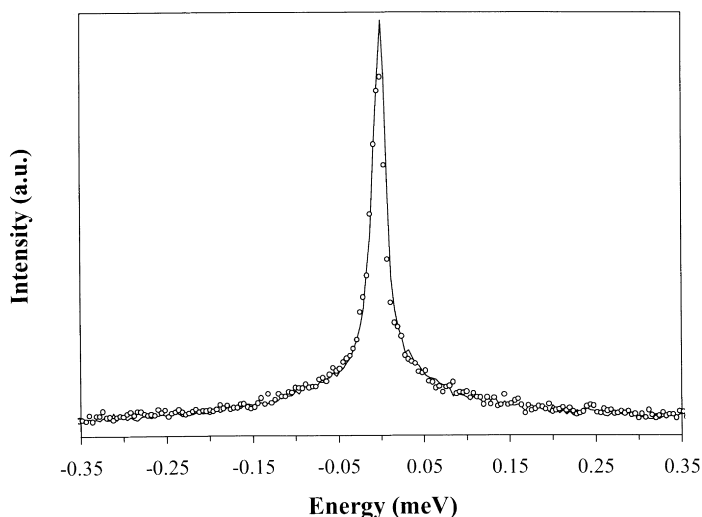

Figure 4 Normalized QENS spectra of (——) PDMS and (○) PDMS–A90 at 235 K and 1.78 Å^{-1}

having different mobilities, in addition to the underlying motion of the methyl groups, makes data analysis in this temperature range impractical. For this reason the following discussion will focus on the analysis of the neutron scattering data above T_m where the effect of the fillers on chain motion is greatest (*Figure 3*).

The reduced elastic intensity ($S(Q,\omega \approx 0)$) from the elastic window scan (*Figure 3*) in the filled polymers finds its counterpart in the $S(Q,\omega)$ spectra which are considerably narrower in the latter systems as compared to PDMS (*Figure 5*). This observation is in qualitative agreement with n.m.r.[4] and dynamic mechanical measurements[10,11].

In order to quantify the decrease of chain mobility in filled samples we have analysed in detail the intermediate scattering function $I(Q,t)$ derived from $S(Q,\omega)$ by performing a Fourier transform. An alternative fitting procedure of the QENS spectra is to treat the $S(Q,\omega)$ with a suitable choice of a model function to be convoluted with the instrumental resolution. However, in this approach assumptions about the scattering law are necessary. Bearing this in mind we have chosen a method of analysis which treats the intermediate scattering function and results in the spatial extent of confinement.

The restrictions of molecular mobility experienced by the chains has been clearly illustrated in *Figure 5*. The intermediate scattering function of PDMS and PDMS–A90 confirms this observation. The extent of the dynamic

effect is shown in *Figure 6* as an apparent elastic contribution to $I(Q,t)$. Whereas the intermediate scattering function of PDMS vanishes at long times due to the absence of fixed centre of mass, $I(Q,t)$ for PDMS–A90 tends to a finite value. This indicates that parts of the chains are immobilized, at least within the time-range examined in this experiment.

In order to quantify the fraction of PDMS chains which experience restricted mobility we compare the intermediate scattering function of PDMS at 250 K with data from PDMS–A90. As shown in *Figure 6*, at this temperature the $I(Q,t)$ of PDMS can be fitted to the PDMS–A90 data after adding an elastic contribution, according to the following relationship:

$$I(Q,t)_{PDMS-A90} = A(Q) + (1 - A(Q))I(Q,t)_{PDMS} \quad (8)$$

where $A(Q)$ can be regarded as the non-ergodicity parameter representing the fraction of immobilized chains. By using equation (2) we implicitly assume that the dynamics of free segments, i.e. those giving rise to a quasielastic component, does not change significantly in the filled system. This is confirmed experimentally as shown in *Figure 6* where the match between data from the two samples is very good, within experimental error. Similar fits are obtained at other Q values and the $A(Q)$ values are reported in *Table 1* for PDMS–A90 at 250 and 275 K. It is worth noting that the $A(Q)$ values of *Table 1* have a broad maximum in the
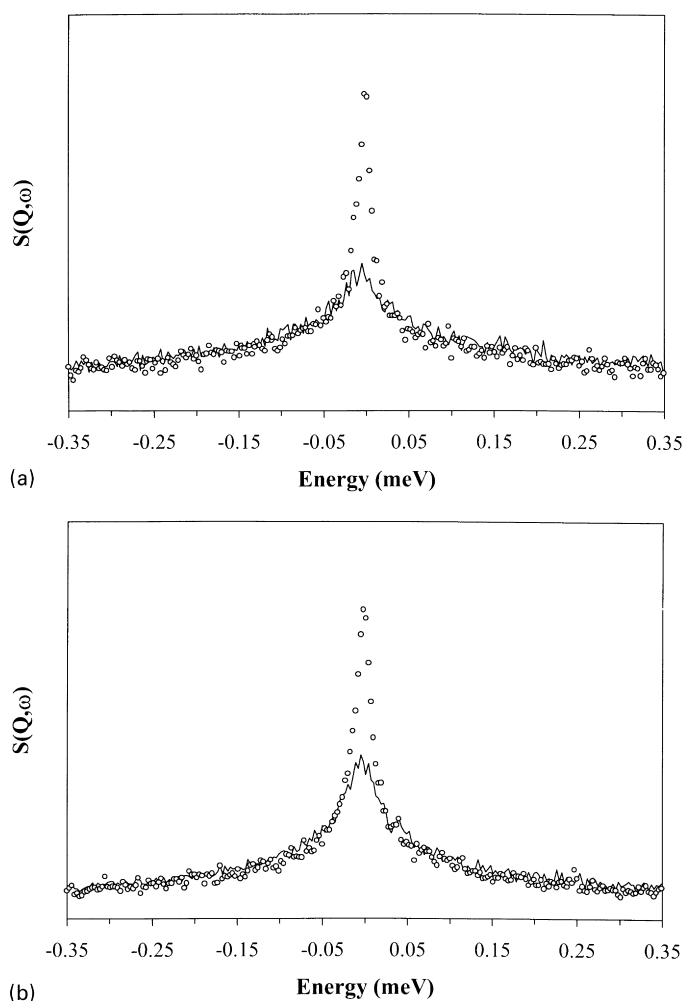
Figure 5 (a) Normalized QENS spectra of (———) PDMS and (○) PDMS–A90 at 275 K and 1.78 Å^{-1} and (b) QENS spectra of (———) PDMS and (○) PDMS–A90 at 275 K and 1.44 Å^{-1}
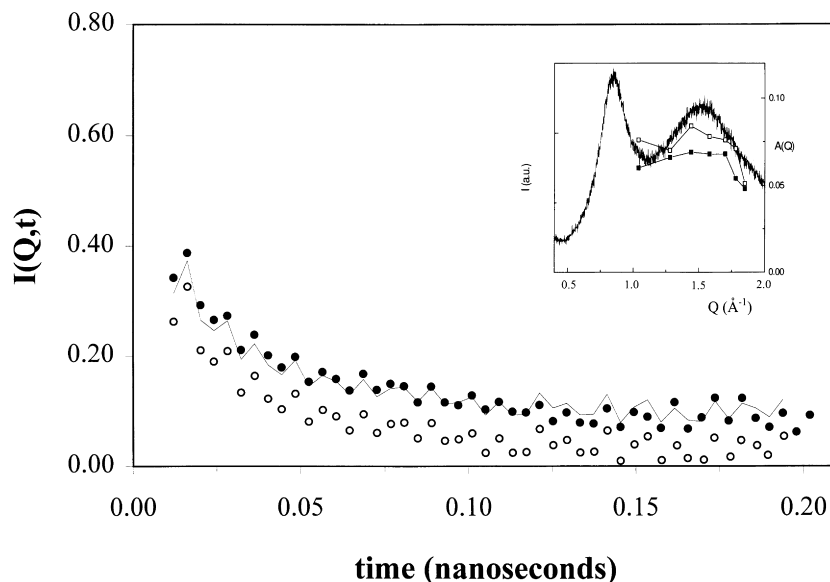
Figure 6 Intermediate scattering function determined from the QENS spectra after Fourier transform of (●) PDMS–A90 and (○) PDMS at 250 K and 1.2 Å^{-1}. The line represents the PDMS data corrected for an elastic contribution using equation (2) (see text). In the inset: comparison between the static structure factor $S(Q)$ obtained from wide-angle X-ray scattering at 300 K (*Figure 2*) and $A(Q)$ values at (□) 250 K and (■) 275 K (*Table 1*)

vicinity of the second sharp diffraction maximum of $S(Q)$ (*Figure 2*), i.e. at 1.5 Å^{-1}, implying that there is a small contribution to the total scattering due to a characteristic distance in filler particles. This is illustrated in the inset to *Figure 6* where $A(Q)$ and $S(Q)$ are compared. To obtain an estimate of the fraction of immobilized chains at 250 K we use the average $A(Q)$ of 0.072 ± 0.005. This indicates that approximately 7.2% of the chains are tightly bound to the fillers when the particle content is 40 wt% (23 vol%). Assuming that every polymer chain has segments in the filler vicinity and that the adsorbed segments retain their Gaussian shape (which is an oversimplification resulting in the highest possible estimate), we find that the thickness of the adsorbed layer is about 50 Å.

DISCUSSION

In this section we attempt to reconcile our experimental observation with other studies reported in the literature for polymer–filler systems. Early studies of PDMS–silica particles[29] (200 m^2 g^{-1} surface area) reported that at a filler content of 14 vol% three tan δ peaks are observed by mechanical measurements. Two peaks are located at the same temperature found in the unfilled polymer and correspond to the glass transition ($T_g = 150$ K) and melting (213 K). A third broader peak was detected at an intermediate temperature of 182 K.

The existence of an additional tan δ peak appears to be a common feature of filled polymers as recently pointed out by Tsagaropoulos and Eisenberg[10,11]. This additional relaxation process is attributed to the glass transition of loosely bound polymer. For PDMS containing 40 wt% silica particles (380 m^2 g^{-1}) the difference between the position of the two peaks is 53 K. (No melting transition was detected for this polymer which contained 7 mol% methylphenyl monomer units to prevent crystallization). Due to the larger surface area used in the mechanical measurements we expect that the difference between the two glass transitions in PDMS–A90 should be considerably less than 50 K, at 40 wt%. We therefore expect the second glass transition in filled PDMS to occur within the temperature range from 150 to 235 K. Because of the semicrystalline nature of PDMS and PDMS–A90, this glass transition, in addition to the usual polymer glass transition, is not detectable by QENS. At 250 K, both the unperturbed chains and those which were loosely bound to the filler are expected to contribute to the quasielastic component.

The elastic intensity measured from the intermediate scattering function of PDMS–A90 (*Figure 6*) and the increase of the elastic contribution observed in PDMS–A90 and PDMS–A300 (*Figure 3*) are consistent with the existence of a layer of immobile chains. The fraction of immobile chains for PDMS–A90 is found to be equal to 7.2% at 250 K and 6.2% at 275 K. This is close to the amount of tightly bound silicone rubber measured after extraction with hexane[13] at similar filler content.

CONCLUSIONS

Chain adsorption at a filler surface results in a decrease of the free energy of the system and a decrease of the entropy through the loss of translational and rotational degrees of freedom of the adsorbed segments. Although this effect is known from low-frequency experiments it is the first time that direct evidence for the dynamically modified interface is provided in the GHz and THz frequency range with the relevant spatial resolution.

Our QENS study of filled PDMS clearly shows that the presence of the filler particles restricts the mobility of the polymer chains. A very small dynamic effect is observed in

Table 1 $A(Q)$ factor as defined by equation (2) as measured from the intermediate scattering function of PDMS–A90 at 250 and 275 K

Q (Å^{-1})	$A(Q)$ at 250 K	$A(Q)$ at 275 K
1.04	0.076	0.060
1.28	0.070	0.066
1.44	0.084	0.069
1.58	0.078	0.068
1.70	0.076	0.068
1.78	0.071	0.054
1.85	0.051	0.048

PDMS filled with nanosize silica particles between 100 and 235 K. Changes due to the presence of the filler within this temperature range are probably related to the effect of the filler on crystallization of the polymer matrix. However, above 235 K, the segmental motion is considerably hindered. Data analysis of the intermediate scattering function evidences two dynamic processes: chains which are unaffected by the presence of the filler and chains whose dynamics are severely hindered. These give rise to an elastic contribution to the QENS spectra and are therefore immobile within the resolution of our experiment. It is suggested that the dynamics associated with loosely bound chains responsible for the second glass transition in dynamic mechanical measurements could not be detected in this experiment. This is a consequence of the semicrystalline nature of PDMS which renders the two T_gs undetectable. The elastic contribution which amounts to 7.2% at 250 K is attributed to the formation of a tightly bound layer of reduced mobility.

PDMS, with its low T_g and broad quasielastic spectrum at GHz frequencies is suitable for such studies both from the fundamental and application viewpoint. However, one major drawback is that it undergoes cold crystallization which hinders the dynamics below the melting temperature, although this deficiency can be overcome by using higher filler contents.

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