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Modified chain dynamics in poly(dimethylsiloxane)/silica nanocomposites

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Abstract

The molecular dynamics of a series of poly(dimethylsiloxane) networks filled with silica nanoparticles synthesized *in situ* was studied using dielectric relaxation spectroscopy. In addition to the α-relaxation associated with the glass transition of the polymer matrix, we observe a slower α-relaxation. This behavior is discussed in terms of a gradual increase of relaxation times close to the surface of the nanoparticles. The range of this effect is estimated to be around 3 nm at T_g, decreasing slightly with increasing temperature. The results are discussed in relation to molecular dynamics simulations of supercooled liquids close to an interface, as well as experimental studies of nanoconfined glass forming liquids and thin polymer films.

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Keywords: Dielectric properties; Relaxation, electric modulus; Glass transition; Nanoparticles; Polymers and organics

1. Introduction

Polymer nanocomposites, i.e. polymers containing inclusions with at least one dimension at the nanometer scale, have attracted a great deal of attention in recent years due to their improved properties (mainly mechanical and barrier properties) compared to traditional micro- and macro-scale composites.

However, our understanding of the relationships between the composition, structure and properties of these materials is still at an early stage: for example, the glass transition temperature of polymer nanocomposites has been reported to increase [1], decrease [2], or remain unaffected, compared to that of the pure polymer, and sometimes a second glass transition has been reported [3], while no existing model can reconcile these results in a satisfactory way.

It is generally agreed upon that many of the improved properties of nanocomposites are related to the modification of chain dynamics due to interaction with the filler surface. Due to the enormous surface-to-volume ratio of the nanoparticles, the polymer close to the interface constitutes a significant fraction of the material, and its behavior may significantly affect or even dominate the properties of the composite. In order to gain a more complete understanding of the relationship between composition, structure and properties of nanocomposites it is therefore necessary to understand the static and dynamic properties of polymers, and glass-forming liquids in general, in the vicinity of a solid interface.

In this study we investigate the molecular dynamics of a series of poly(dimethylsiloxane)/silica nanocomposites using dielectric relaxation spectroscopy. The silica nanoparticles were synthesized *in situ* using the sol–gel method, which typically produces small and well-dispersed silica nanoparticles [4]. These materials were initially prepared in order to study the effect of the silica phase on mechanical properties, hence the rather large silica contents used

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(6–16% by volume). The mechanical properties of these composites were found to be superior to those of composites prepared in the usual way i.e. by mixing already-formed nanoparticles with the polymer prior to crosslinking [5]. Our aim in this work is to study in detail how the presence of the silica particles affects the molecular dynamics of the polymer matrix in order to contribute to an understanding of the structure-property relationships in this type of materials.

2. Experimental

2.1. Sample preparation

The procedure used to prepare the samples has been described elsewhere [6]. Four samples containing, 6%, 9%, 10%, and 16% by volume of silica as well as an unfilled PDMS network were investigated. Scanning electron microscope images on samples prepared with the same catalyst under identical conditions as the present series have shown that the silica nanoparticles have diameter of about 10 nm [6].

Dielectric relaxation spectroscopy (DRS) [7] measurements were carried out in the frequency range 10^{-2}–10^{6} Hz and temperature range 143–313 K by means of a Novocontrol Alpha analyzer. The temperature was controlled to better than 0.1 K with a Novocontrol Quatro cryosystem. Supplementary dielectric measurements at high frequencies (10^{6}–10^{9} Hz) were carried out using a Hewlett–Packard 4291 A impedance analyzer.

3. Results

The glass transition of the pure PDMS and the nanocomposites has been characterized in a previous paper [8] by differential scanning calorimetry and thermally stimulated depolarization currents (TSDC). The TSDC α-relaxation, corresponding to the glass transition, remained at the same temperature position in all the samples in agreement with the calorimetric T_g, which was also found to be unchanged. In addition, a broad shoulder appeared on the high-temperature side of the peak in the composites, which was attributed to the α-relaxation in an interfacial region where the glass transition is increased (up to approximately $T_g + 30$ K due to interaction with the particle surface.

Typical dielectric loss spectra for the nanocomposites are shown in Fig. 1. In addition to the α-relaxation, a second dielectric process, a few decades slower, is observed as a shoulder. Similarly to the TSDC results, the slower process is attributed to the relaxation of chains close to the polymer/particle interface and will be referred to as α_i. A third very weak relaxation, observed at a frequency intermediate between the two α-relaxations, is assigned to the rotation of hydroxyl groups attached to the silica surface [9].

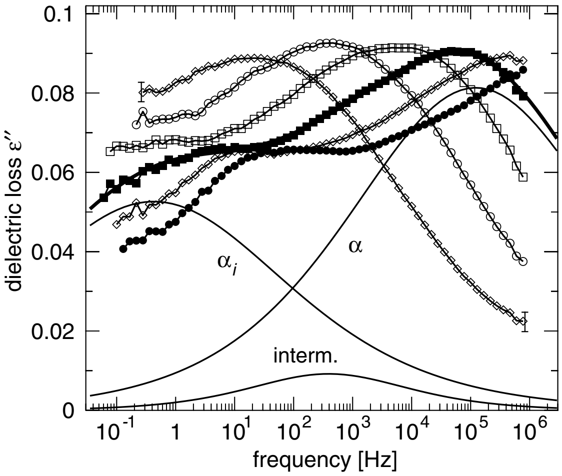

Fig. 1. Dielectric loss against frequency for the sample containing 10% silica. Temperatures are from 158 to 183 K in steps of 5 K. The bold line is a fit of Eq. 1 to the data for 173 K, the thinner lines are the individual HN terms.

To further analyze the data a sum of three Havriliak–Negami (HN) terms [7]

$$\epsilon^*(f) = \epsilon_\infty + \sum_{j=1,2,3} \frac{\Delta\epsilon_j}{[1+(\mathrm{i}f/f_{0,j})^{\alpha_j}]^{\beta_j}} \qquad (1)$$

was fitted to the $\varepsilon''(f)$ data. In this equation $\Delta\varepsilon$ is the relaxation strength, f_0 the characteristic frequency, α and β the shape parameters and ε_∞ is $\varepsilon'(f)$ for $f \gg f_0$. From the fits at various temperatures the fitting parameters f_0 and $\Delta\varepsilon$ were determined. The shape parameters α and β of all three relaxations was found not to change systematically with temperature. Therefore, in order to reduce the number of free parameters, a second fit was performed holding the shape parameters constant, at values equal to their mean values from the first fit. This second fit, with five free parameters, results in good agreement with the data, an example of the quality of fitting being given in Fig. 1, and provides more accurate values for the position and magnitude of the relaxations.

The frequency position of all three processes is independent of silica content. The evolution of the α, α_i and intermediate relaxations with temperature is shown in the activation plot (Fig. 2). Included also are data from TSDC measurements (at an equivalent frequency of 1.6 mHz, corresponding to a relaxation time of 100 s [7]) for the main α peak and the high-temperature shoulder.

The temperature dependence of the α process is well described by the Vogel–Tammann–Fulcher equation [7]

$$f_{\max} = f_0 \exp\left(-\frac{B}{T - T_0}\right) \qquad (2)$$

typical for cooperative relaxations, where f_0, B and T_0 are temperature-independent empirical parameters. The parameters obtained are $f_0 = 10^{13}$ Hz, $B = 716$ K and $T_0 = 131$ K, in good agreement with values previously reported for PDMS networks [10]. The α_i process shows

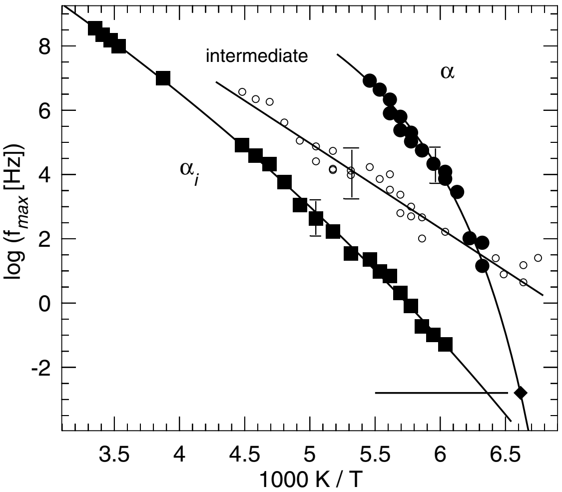

Fig. 2. Activation plot for the sample containing 10% silica. The filled diamond corresponds to the temperature of the main peak in the TSDC thermogram and the horizontal bar to the TSDC shoulder [8]; both have been placed at an equivalent frequency of 1.6 mHz.

a weaker temperature dependence which is almost Arrhenius-like, but it is better described by the VTF equation with parameters $f_0 = 10^{17}$ Hz, $B = 4530$ K and $T_0 = 56$ K, however the values of B and T_0 do not seem physically meaningful.

The weak intermediate relaxation has an Arrhenius temperature dependence [7]

$$f_{\max} = f_0 \exp\left(-\frac{E_{\text{act}}}{kT}\right) \tag{3}$$

with an activation energy of $E_{\text{act}} = 0.52$ eV and pre-exponential factor of $f_0 = 10^{18}$ Hz. These values are in very good agreement with those reported in the literature for relaxations related to the hydroxyl groups on the silica surface [9,11].

The dielectric strength of the α and α_i processes are presented in Fig. 3. In the temperature range of our data, the dielectric strength of the α process increases slightly with increasing temperature and that of the α_i process decreases, while the sum of the two remains approximately constant.

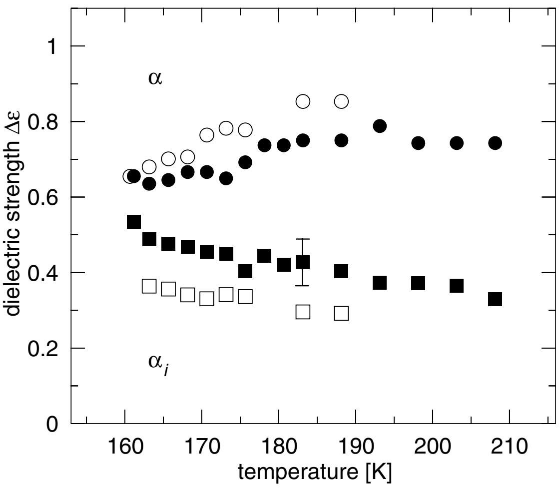

Fig. 3. Dielectric strength against temperature for the α (circles) and α_i (squares) relaxations, for the samples with 6% (open symbols) and 9% silica (filled symbols).

4. Discussion

The behavior of polymers and glass forming liquids in the vicinity of solid interfaces has been extensively studied using various types of model systems having an similarly large surface to volume ratio, such as ultrathin polymer films and polymers or glass forming liquids confined to nanopores [12]. Additional relaxation processes a few orders of magnitude slower than the main α-relaxation are often observed in such systems, and are usually discussed in terms of a layer of molecules with reduced mobility at the liquid/wall interface – this was also our original interpretation of the present results [8]. However there exist both molecular dynamics simulations [13–15] and experimental results [16,17] supporting a *continuous* distribution of relaxation times as we approach the interface. It has been demonstrated recently that such a continous distribution can lead to a double loss peak in the susceptibility, and this has been proposed as an alternative interpretation for this type of response [15]. Additional support for this interpretation in the case of the present results is provided by the TSDC data which indicate a continuous distribution of glass transition temperatures [8]. This would also explain the values obtained above for the VTF parameters of the α_i process: since this process is not related directly to the relaxation of a specific group of molecules, one would not expect these parameters to have a straightforward physical interpretation. However, the VTF equation provides a way to parametrize the shape of $f_{\max,\alpha_i}(T)$ and gives the expected $f_{\max,\alpha_i} < f_{\max,\alpha}$ for all temperatures where the equation is expected to hold ($T > T_g$).

In order to estimate quantitatively the length scale over which the reduction in mobility takes place, we distinguish – only for the sake of this calculation – two types of polymer chains: bulk-like and interfacial. We then assume that the relative dielectric strength of the two relaxations is a measure of the relative amount of bulk-like and interfacial polymer. Making the additional approximations that (i) the interfacial polymer does not crystallize and (ii) the particles are spherical with a diameter of 10 nm and are randomly distributed in the matrix, we can estimate [8] the fraction of interfacial polymer and from that the thickness d of the interfacial layer at each temperature (Fig. 4). The length d obtained in this way can be taken as a measure of the distance from the particle surface up to which the effect of the interface reaches.

The values of the length scale d obtained in this way are in reasonable agreement with those calculated from the TSDC results [8], and are within the range of those reported in the literature for the thickness of the interfacial layer in experimental studies of PDMS/silica and similar systems, which ranges typically from 1 to 5 nm [18,11,19].

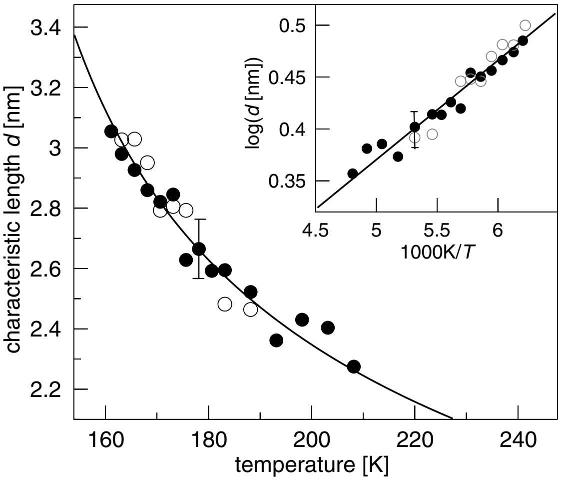

Fig. 4. Characteristic length d against temperature for the samples containing 6% (open circles) and 9% (filled circles) silica. The line is a fit of the equation $d = A(T - T_0)^{-\nu}$ (see text). The inset shows log$d$ against inverse temperature.

Since the dynamics of the polymer chains is cooperative, the slowing down of the dynamics at the interface will presumably extend into the material at least as far as the cooperativity length ξ defined in various theories and models of the glass transition [20]. However, one cannot simply identify d with the cooperativity length since there may be other factors contributing to the modification of the dynamics. Indeed there is evidence that for both ultrathin polymer films [12] and nanocomposites [2] the range of polymer/wall or polymer/particle interactions can sometimes be significantly larger than the cooperativity length, so d is in general only an upper bound of ξ. In our case, however, d is close to the values of ξ usually obtained for glass-forming substances in general (1–3.5 nm [21]) and for PDMS in particular (1.4 nm [10]), so it is reasonable to assume that the main factor that influences d is in fact cooperativity.

Most theoretical predictions for the temperature dependence of ξ take the form $\xi(T) \sim (T - T_0)^{-\nu}$ or variations thereof [20]. Taking the value of T_0 from the VTF fit of the α-relaxation, our data for $d(T)$ is well described by this equation with an exponent of $\nu = 0.31$ (fitting the data with all three parameters free results in very large uncertainty for T_0 and ν, but gives nevertheless very similar values). Although the value of $\nu = 1/3$ has been related to the predictions of the Adam–Gibbs theory of the glass transition, both theoretical considerations and experimental evidence seem to favor a stronger temperature dependence of ξ [22].

On the other hand, Scheidler et al., using a molecular dynamics simulation of a Van der Waals liquid close to a solid wall, find that the length scale of the liquid/wall interaction increases with decreasing temperature according to an Arrhenius law i.e. as $d \sim \exp(E/T)$ [15]. Interestingly, our results are also well described by this equation (inset to Fig. 4) although there seems at present to be no theoretical justification for this temperature dependence. One must also keep in mind that the simulations of Scheidler et al. correspond to temperatures above the T_c of mode coupling theory, i.e. slightly higher than the highest temperatures of our measurements. In order to decide between the two temperature dependences shown in Fig. 4, it would be necessary to have a wider range of d values.

5. Conclusions

The molecular dynamics of a series of poly(dimethylsiloxane) networks filled with silica nanoparticles synthesized *in situ* was studied using dielectric relaxation spectroscopy. The α-relaxation associated with the glass transition was found to have a distinctly double structure, which was attributed, following a recent proposal, to a gradual slowing down of chain mobility close to the silica particles. The range of this effect was determined from the relative dielectric strength of the two components of the relaxation, and was found to be around 3 nm. The value and temperature dependence of this length was discussed in relation to the concept of the cooperativity length as well as the results of molecular dynamics simulations.

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