

Glass transition and molecular dynamics in poly(dimethylsiloxane)/silica nanocomposites

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Received 3 November 2004; received in revised form 18 May 2005; accepted 18 May 2005

Available online 21 June 2005

Abstract

The molecular dynamics of a series of poly(dimethylsiloxane) networks filled with silica nanoparticles synthesized in situ was investigated using thermally stimulated depolarization currents, broadband dielectric relaxation spectroscopy and differential scanning calorimetry. The techniques used cover together a broad frequency range (10^{-3} – 10^9 Hz), thus allowing to gain a more complete understanding of the effects of the nanoparticles on the chain dynamics. In addition to the α relaxation associated with the glass transition of the polymer matrix, we observe in dielectric measurements a slower α relaxation which is assigned to polymer chains close to the polymer/filler interface whose mobility is restricted due to interactions with the filler surface. The thickness of the interfacial layer is estimated to be about 2.1–2.4 nm. Differential scanning calorimetry shows a change in the shape of the glass transition step, as well as a decrease in both the degree of crystallinity and the crystallization rate by the addition of silica.

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Keywords: Nanocomposites; Glass transition; Cooperativity

1. Introduction

Polymer nanocomposites have attracted a great deal of attention in recent years due to their exceptional mechanical and barrier properties compared to conventional micro and macroscale composites, usually at very low filler contents. The materials used as nanoscale fillers include layered silicates [1], ceramic nanoparticles such as silica and titania [2], and carbon in the form of nanoparticles [3], graphite sheets [4] and carbon nanotubes [5]. Indeed although the terms ‘nanocomposite’ and ‘nanomaterial’ are recent [6], such materials in the form of rubber reinforced with carbon black, and more recently silica, have been widely used for many years, though not usually studied as nanocomposites. It is generally agreed upon that the improved properties of nanocomposites are related to the modification of the structure and dynamics of the polymer 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 significantly affect or even dominate the properties of the composite. However, experimental results on polymer dynamics and the glass transition in nanocomposites are not conclusive concerning the mechanism and the details of this modification.

Several studies [7,8] on polymer nanocomposites show an increase of the glass transition temperature T_g , suggesting that the mobility of the entire volume of the polymer is restricted by the presence of the nanoparticles. However, reduction of T_g has also been reported [9] in the case of weak interactions between filler and polymer, and in other cases the addition of nanoparticles causes no significant change to the glass transition of the polymer presumably because effects causing increase and decrease of polymer mobility are present simultaneously and effectively cancel out [10].

However, there are many experimental results suggesting that the restriction of chain mobility caused by the nanoparticles does not extend throughout the material but affects only the chains within a few nanometers of the filler surface. The existence of such an interfacial layer seems relatively well-established in the case of silica-filled

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elastomers such as the materials studied here, however, its exact nature is not well understood: experimental results have been described in terms of one or two distinct interfacial layers or a gradual change in dynamics with changing distance from the particle.

In the following we concentrate on the case of polymer/silica nanocomposites, which have been more extensively studied. Tsagaropoulos and Eisenberg [11,12], studying a wide range of polymers, including poly(dimethylsiloxane), filled with silica nanoparticles, observe in dynamic mechanical measurements a second peak in $\tan \delta$, 50–100 °C above the glass transition, which is attributed to the glass transition of an interfacial polymer layer with restricted mobility. Their results are interpreted in terms of a model where there are three types of polymer: a strongly bound, immobile layer immediately surrounding the particle, which does not participate in the glass transition; a second, loosely bound interfacial layer which is responsible for the second glass transition; and quasi-bulk polymer unaffected by the particle. This model is able to account for the observed reduction of the intensity of the second glass transition with increasing silica content. Kirst et al. [13], studying poly(dimethylsiloxane) filled with 50% by weight Aerosil by means of dielectric relaxation spectroscopy, observed in addition to the quasi-bulk α relaxation two additional relaxations which they attributed to the α relaxation of strongly and weakly bound polymer, in agreement with the above model. NMR measurements [14] also support the existence of three types of polymer in such materials, one strongly bound and almost immobile, one with restricted mobility and finally chains with quasi-bulk behavior.

On the other hand, there are both neutron scattering [15] and dynamic mechanical [16,17] data on polymer nanocomposites similar to the system studied here which are well described by a two-layer (interfacial and bulk) model. Arrighi et al. [16], for example, observe a second dynamic mechanical $\tan \delta$ peak in silica-filled styrene butadiene rubber, which increases in magnitude with increasing filler content, in contrast with the three-layer model of Tsagaropoulos and Eisenberg. Matejka et al. [17] prepared a series of rubbery epoxy/silica composites using a variety of sol–gel processes as well as conventional blending, and also observed for some of them a second mechanical $\tan \delta$ peak attributed to a single layer of polymer interacting with the silica surface, in this case via chemical bonding.

Finally, other studies support a continuous distribution of glass transition temperatures or polymer mobilities as a function of the distance from the particle surface. Berriot et al. [18] interpret the results of dynamic mechanical analysis on poly(ethyl acrylate)/silica nanocomposites using a gradient of glass transition temperatures near the particles. This kind of gradual change of dynamics has also been observed in molecular dynamics simulations [19].

In the present work, the polymer dynamics related to the glass transition in a series of poly(dimethylsiloxane)

networks filled with different amounts of sol–gel synthesized silica nanoparticles are investigated by means of dielectric techniques and differential scanning calorimetry. These materials, containing nanoparticles with a small and well-controlled size and with a known interaction with the polymer matrix (hydrogen bonding between the silanol groups on the silica surface and the oxygen on the main chain of PDMS) can serve as model systems in order to better understand the glass transition and polymer dynamics in more complex nanocomposites. The combination of experimental techniques used covers a wide frequency range (10^{-3} – 10^9 Hz) and allows us to gain a more complete understanding of the effect of the nanoparticles on the polymer mobility.

The traditional method of preparation of polymer/silica composites involves mixing of the silica either into the polymer before the cross-linking reaction, or into the polymer melt. The main difficulty in this process is always the effective dispersion of the inclusions in the polymer matrix, as these usually tend to agglomerate limiting the amount of surface area available to the polymer. One alternative preparation technique is to prepare such composites starting with a suspension of silica particles in the monomer before polymerization. The resulting materials are typically homogeneous with well dispersed silica particles [18]. Another alternative technique, which we have used here, is to synthesize the nanoparticles in situ within the polymer matrix by using sol–gel techniques, a method introduced by Mark et al. [2,20]. Using this method nanoparticles with diameters of 10–25 nm can be produced, their size and distribution depending on the conditions of preparation.

2. Experimental

2.1. Sample preparation

Several series of PDMS/silica nanocomposites were prepared differing in the catalyst used for the hydrolysis and condensation of the silica (dibutyltin diacetate, dibutyltin dilaurate or diethylamine) as well as the terminal groups of the precursor PDMS chains (vinyl-terminated or hydride-terminated). The details of the preparation and the results of the characterization by SAXS, SANS and transmission electron microscopy have been reported elsewhere [21]. In this paper we concentrate on one of these series, prepared using hydride-terminated precursor chains and dibutyltin diacetate as a catalyst.

The synthesis of the unfilled PDMS was carried out by mixing for 15 min at room temperature, stoichiometric mixtures of precursor chains of hydride-terminated PDMS ($M_w = 17,200$) from Gelest with 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane used as the tetrafunctional cross-linking agent. The synthesis was performed in the bulk in the presence of platinum-divinyltetramethylsiloxane

used as a catalyst. The reacting mixture is slowly cast into a Teflon mold and cured at 80 °C for 12 h. The films were extracted with toluene for three days to remove any unreacted materials. The sol fractions were between 3 and 5%.

In the in situ filling process, the dried PDMS films were allowed to swell in tetraethoxysilane (TEOS) (from Aldrich) in the presence of a tin catalyst, dibutyltin diacetate, present at 3 wt%. The swelling time determined the degree of TEOS absorption and thus the filler loading of the final composite. Both the TEOS-swollen film and a beaker containing water were then placed for 24 h into a desiccator maintained at a constant temperature (30 °C) thus exposing the swollen film to saturated water vapor. The hydrolysis and condensation of TEOS produced the silica phase. Finally, the film was vacuum-dried at 80 °C for several days to constant weight in order to remove any alcohol generated from the reaction and also the remaining TEOS which has not been hydrolyzed. The amount of filler incorporated into the network was calculated from the weights of the films before and after the generation of the filler (Table 1). The samples finally produced were films of about 1 mm thickness. Scanning electron microscope images on samples prepared with the same catalyst under identical conditions as the present series (differing only in the terminal groups of the precursor PDMS chains) have shown that the silica nanoparticles have diameter of about 10 nm [21].

All measurements were carried out on samples cooled from room temperature at a rate of 10 °C/min unless otherwise stated.

2.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were carried out in the temperature range -160 to 20 °C using a Perkin–Elmer DSC-4 calorimeter. A heating rate of 40 °C/min was used.

2.3. Thermally stimulated depolarization currents

Thermally stimulated depolarization currents (TSDC) [22] is a dielectric technique which is used extensively to study relaxation mechanisms in polymeric materials. The sample is inserted between the plates of a capacitor and polarized by the application of an electric field E_p at

temperature T_p for time t_p , which is large compared to the relaxation time of the dielectric relaxation under investigation. With the electric field still applied, the sample is cooled to a temperature T_0 (which is sufficiently low to prevent depolarization by thermal excitation) and then is short-circuited and reheated at a constant rate b . The discharge current generated during heating is measured as a function of temperature with a sensitive electrometer. TSDC corresponds to measuring the dielectric loss at a constant low frequency in the range 10^{-4} – 10^{-2} Hz. It is characterized by high sensitivity and high resolving power, and provides several variations to the experimental protocol which allow the separation of overlapping relaxations [22]. TSDC measurements were carried out using a Keithley 617 electrometer in combination with a Novocontrol Quatro cryosystem and a Novocontrol sample cell for TSDC measurements. Typical conditions were $E_p = 10^5$ V/m for the polarizing field, $T_p = 20$ °C for the polarization temperature, $t_p = 5$ min for the polarization time, 10 °C/min for the cooling rate to $T_0 = -150$ °C, and $b = 3$ °C/min for the heating rate.

Thermal sampling [22,23] is a standard variation on the TSDC experimental technique. This technique can be used on a complex TSDC peak to determine if it consists of distinct overlapping relaxation or a continuous distribution of relaxations. Thermal sampling consists of polarizing the sample at a temperature T_p and subsequently depolarizing at a temperature T_d a few degrees lower, thus ensuring that only the dipoles corresponding to this temperature window remain polarized. The sample is then cooled down and the depolarization current measured during linear heating as in normal TSDC. In the case where a complex TSDC peak consists of distinct components, the maximum current vs. polarization temperature shows multiple maxima.

2.4. Dielectric relaxation spectroscopy

Dielectric relaxation spectroscopy (DRS) [24] measurements were carried out in the frequency range 10^{-2} – 10^{-6} Hz and temperature range -130 to 40 °C 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 4291A impedance analyzer.

Table 1

Silica content by weight and volume, degree of crystallinity χ_c , volume fraction of interfacial polymer χ_{int} and estimated thickness d of the interfacial layer around the filler particles

Sample	wt%	vol%	χ_c	χ_{int}	d (nm)
PDMS	0	0	0.61		
PDMS + 9.7% silica	9.7	6.1	0.44	0.13	2.3
PDMS + 14.1% silica	14.1	9.1	0.37	0.21	2.4
PDMS + 15.3% silica	15.3	9.9	0.40	0.22	2.3
PDMS + 23.5% silica	23.5	15.7	0.34	0.29	2.1

3. Results and discussion

3.1. Characterization by differential scanning calorimetry

Fig. 1 shows the DSC thermograms obtained for pure PDMS and the nanocomposites during heating. The glass transition around -115°C and a single endothermic melting peak around -40°C are visible.

The glass transition temperature (determined as the temperature of half C_p increase) does not appear to change significantly with silica content. In the samples cooled at $10^\circ\text{C}/\text{min}$ the signal at the glass transition is weak, so quenched samples (cooled at $>100^\circ\text{C}/\text{min}$) were also investigated. In the quenched samples the degree of crystallinity is reduced so the glass transition is more clearly observed, although the results can be compared only qualitatively with those of the other techniques. The DSC thermograms for the quenched samples (Fig. 2) show that while the glass transition temperature is basically unchanged with the addition of silica, the shape of the corresponding step in the heat capacity changes and seems to have a double structure in the composites indicating an additional contribution at the high-temperature side. This effect is later confirmed and studied in detail by dielectric techniques.

The melting temperature decreases with increasing silica content, and the melting peak broadens toward lower temperatures. The degree of crystallinity χ_c of the polymer in each sample is determined from the enthalpy of crystallization normalized by the percentage of polymer in the sample, ΔH_c , by $\chi_c = \Delta H_c / \Delta H_{100\%}$ where $\Delta H_{100\%}$ is the enthalpy of fusion of PDMS, taken as 37.43 J/g [25]. The degree of crystallinity, shown in Table 1 is 61% for the pure PDMS, and decreases with increasing silica content. During cooling at $10^\circ\text{C}/\text{min}$ (not shown), the pure PDMS crystallizes at -75°C whereas all the composites crystallize in the

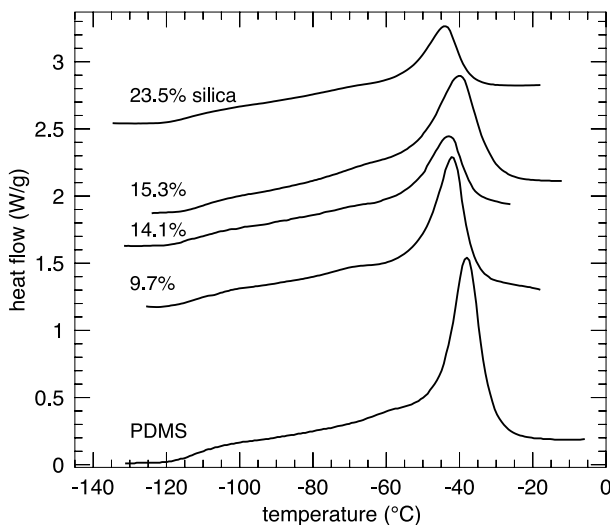


Fig. 1. DSC thermograms for unfilled PDMS and PDMS/silica nanocomposites, after cooling at $10^\circ\text{C}/\text{min}$.

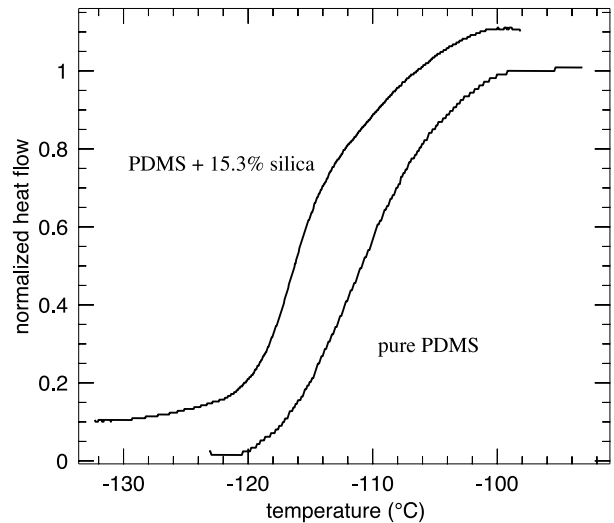


Fig. 2. DSC thermograms for unfilled PDMS and PDMS+15.3% silica nanocomposite in the region of the glass transition after quenching at $>100^\circ\text{C}/\text{min}$. In order to better compare the shape, the curves have been normalized to have $\Delta C_p = 1$ and the curve for the nanocomposite has been shifted vertically by 0.1 units.

range -80 to -83°C . This indicates that the rate of crystallization is reduced due to the presence of the silica particles.

3.2. Thermally stimulated depolarization currents

The samples were investigated using TSDC in order to characterize in more detail the glass transition. The TSDC thermograms obtained for the pure PDMS and the PDMS-silica nanocomposites in the temperature range of the glass transition are shown in Fig. 3. For the pure PDMS a single relaxation is observed at -123°C . This is the primary α relaxation associated with the glass transition of the amorphous phase of PDMS. The temperature T_α of the

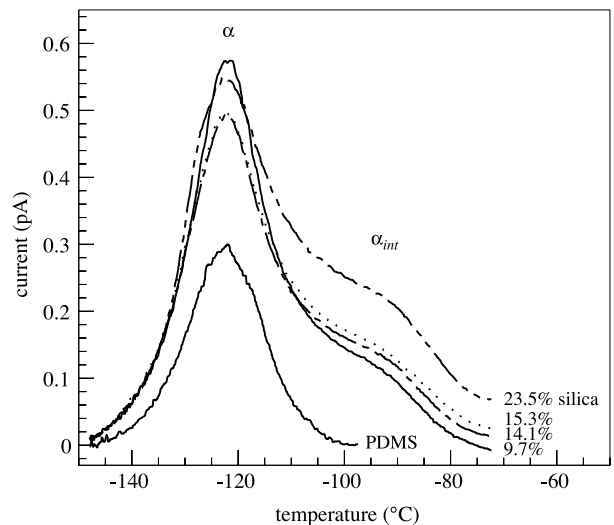


Fig. 3. TSDC thermograms for PDMS and PDMS/silica nanocomposites in the region of the glass transition.

peak maximum, which in general is found to be a good measure of the glass transition temperature [22,23], is in very good agreement with the calorimetric T_g the difference in heating rate (40 °C/min for DSC vs. 3 °C/min for TSDC) accounting, at least partly, for the difference between T_g and T_α .

For the composites the α relaxation is observed at the same temperature, but with higher intensity due to the decrease in crystallinity. In addition, a shoulder appears on the high-temperature side of the main peak extending up to approximately 30 °C higher, its intensity increasing with silica content. The shoulder in the TSDC thermograms of the composites is assigned to the α relaxation of PDMS chains in an interfacial layer close to the silica particles, where chain mobility is constrained due to interaction with the surface of the particles. The main relaxation at -123 °C in the composites is then assigned to the α relaxation of the PDMS chains that are sufficiently far from the filler surface as to exhibit quasi-bulk behavior.

Attempts to fit the TSDC thermogram with the sum of two peaks were not successful. However, by varying appropriately the experimental protocol it is possible to separate experimentally a complex TSDC peak into single responses [22]. In this case the thermal sampling technique was used in order to determine experimentally whether the TSDC signal corresponds to two distinct glass transitions or to a continuous distribution of T_g s. Fig. 4 shows the depolarization peaks obtained after polarizing the sample (in this case PDMS + 23.5% silica) in a series of 5-degree wide temperature windows. No sign of a double peak is observed in any of the thermal sampling responses. Moreover, the maximum current vs. polarization temperature shows a maximum, at the position of the bulk α relaxation, and decreases gradually at higher temperatures without showing a second maximum. Thus, we find that the

interfacial layer exhibits a continuous distribution of glass transition temperatures between the T_g of bulk PDMS (-123 °C) and approximately -90 °C.

The inset to Fig. 4 shows the corresponding apparent activation energies obtained from the initial rise portion of each peak [22]. The apparent activation energy in the temperature region of the shoulder is found to be smaller than the value in the region of the bulk α relaxation.

3.3. Thickness of the interfacial layer

The area of a TSDC peak is proportional to the dielectric strength $\Delta\epsilon$ of the corresponding relaxation. With the assumption that the dielectric strength of the α relaxation per unit volume is the same in the bulk and interfacial regions, the relative area of the main relaxation and the shoulder gives directly the relative volume of the interfacial and bulk phases. For each composite, the peak of pure PDMS is scaled so that its maximum coincides with that of the composite, and its area is taken as the contribution of the bulk α relaxation to the peak. This is subtracted from the total peak area to give the contribution of the shoulder. Assuming also that the polymer in the interfacial region does not crystallize (as was taken also by Aranguren [25] for a similar calculation), and taking into account the overall degree of crystallinity of the polymer obtained by DSC, we calculate for each sample the volume fraction χ_{int} of PDMS in the interfacial region (Table 1). χ_{int} ranges from 13 to 30% of the total amount of PDMS, depending on the silica content.

From these values the thickness of the interfacial layer can be estimated. A first approximation is to consider the interfacial region as a spherical shell around each particle, neglecting the overlap of regions belonging to neighboring particles. One can, therefore, consider only a single particle in an appropriately sized box, and then calculating the volume of the interfacial layer and solving for its thickness d gives

$$d = [(p_{\text{int}}/f + 1)^{1/3} - 1]r \quad (1)$$

However, a rough calculation of the interparticle distance [26] yields values of 7–13 nm for the range of silica content investigated, therefore, some overlap of the interfacial regions is inevitable. Therefore, a simple computer simulation was done: spherical particles were placed randomly in a box with periodic boundary conditions and the volume fraction of the matrix lying at a distance less than d from any particle was calculated as a function of d . Thus, given the fraction of interfacial polymer one can obtain the thickness of the interface taking into account the overlap of the interfacial regions of different particles. The values obtained in this way for d are 2.1–2.4 nm for all samples (Table 1, Fig. 5). These values are 3–5% higher than those given by Eq. (1), the difference increasing with increasing silica content.

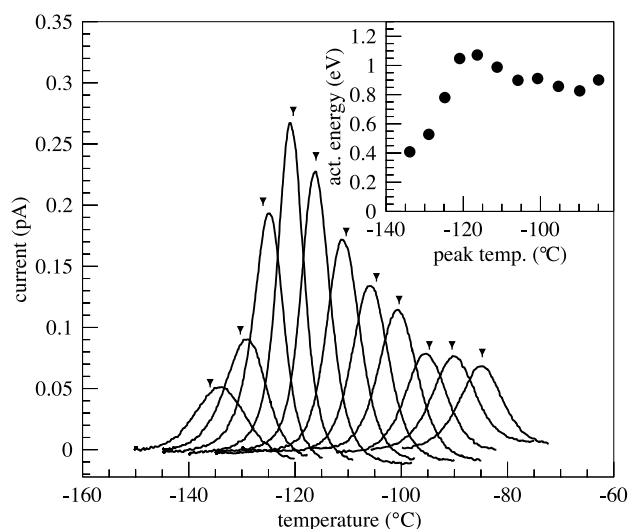


Fig. 4. Thermal sampling curves for PDMS + 23.5% silica and apparent activation energy calculated from them (inset). The arrows show the polarization temperature corresponding to each curve.

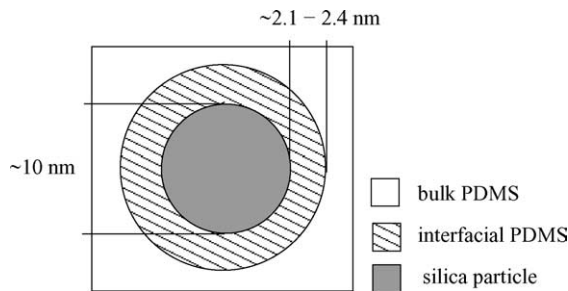


Fig. 5. Model depicting the morphology of the PDMS/silica nanocomposites.

The thickness of the interfacial layer calculated from the TSDC results is within the range of those reported in the literature in experimental studies of PDMS/silica systems (~ 5 nm using neutron scattering [15], 0.8 nm using NMR [14], 1–2.5 nm using DRS [13]) as well as for similar SBR/silica systems (~ 1.9 nm [16] and ~ 1.5 nm [27] using mechanical measurements). The presence of an additional completely immobilized layer such as the one in the model of Tsagaropoulos and Eisenberg cannot be excluded based on the present results. However, the model of Tsagaropoulos and Eisenberg predicts that the fraction of loosely bound polymer (the layer which gives the modified glass transition) decreases with increasing silica content as it is gradually transformed into immobile tightly bound polymer in contrast to the present results. Therefore, our results are better described by a simple two-layer model (interfacial and bulk).

3.4. Dielectric relaxation spectroscopy

Dielectric relaxation spectroscopy was used to investigate the molecular dynamics in the bulk and interfacial layers by following the temperature dependence of the corresponding dielectric relaxations. Note that DRS and TSDC are complementary to each other in the sense that the frequency range of TSDC is fixed at 10^{-2} – 10^{-4} –Hz [22], a frequency region where DRS measurements are very difficult to perform [24].

Fig. 6 shows a representative dielectric spectrum for a PDMS/silica nanocomposite in the temperature range of the α relaxation. The spectra for the other composites are similar, differing only in the relative magnitudes of the three relaxations. Two loss peaks are visible at each temperature. However, a sum of two Cole–Cole or two Havriliak–Negami [24] functions is unable to reproduce the shape of the spectra due to an additional contribution. Using a sum of three peaks, an additional weak relaxation is resolved. Symmetric Cole–Cole functions were chosen as a compromise between the quality of the fit and the number of parameters used, and only the frequency position of the peaks was quantitatively analyzed. The function fitted to the experimental data was

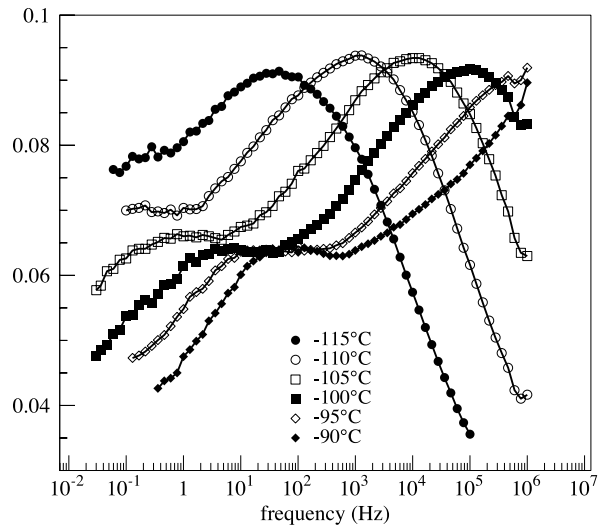


Fig. 6. Dielectric loss ϵ'' vs. frequency f for PDMS + 15.3% silica for the temperatures shown on the plot.

$$\epsilon^*(f) = \epsilon_\infty + \sum_{j=1,2,3} \frac{\Delta\epsilon_j}{(1 + if/f_{\max,j})^{\alpha_j}} \quad (2)$$

where for each relaxation f_{\max} is the frequency of the maximum, $\Delta\epsilon$ the relaxation strength and α a shape parameter.

Fig. 7 shows the Arrhenius plot containing the frequencies of the maxima of the three relaxations. Included also are data from TSDC measurements at an equivalent frequency of 1.6 mHz, corresponding to a relaxation time of 100 s [24]. The relaxation at high frequencies is in very good agreement with the quasi-bulk α relaxation in the TSDC data, while the low-frequency relaxation corresponds

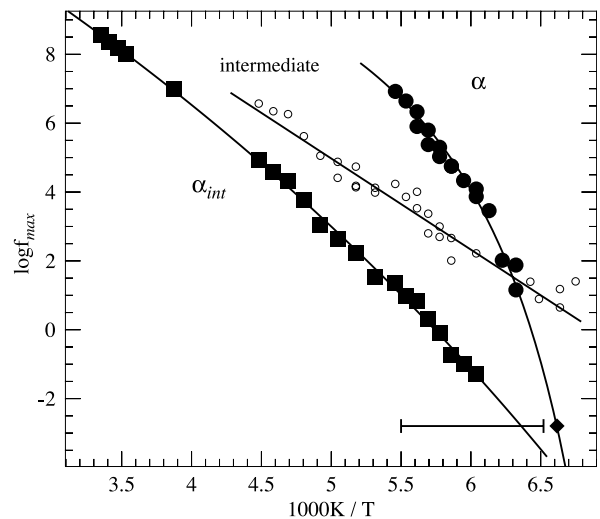


Fig. 7. Arrhenius plot for the sample PDMS + 15.3% silica. The filled diamond corresponds to the temperature of the main peak in the TSDC thermogram and the horizontal bar to the TSDC shoulder; both have been placed at an equivalent frequency of 1.6 mHz. The lines are fits to the DRS data of Eq. (4) for the two α relaxations and of Eq. (3) for the intermediate relaxation.

to the TSDC shoulder. The low frequency relaxation will be called the interfacial α or α_{int} relaxation. The relative dielectric strength of the two relaxations is similar to that calculated from the TSDC data for the main peak vs. the shoulder, and does not change systematically with increasing temperature suggesting that the thickness of the interfacial layer is relatively independent of temperature.

The weak intermediate relaxation has an Arrhenius temperature dependence

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

with an activation energy of $E_{\text{act}}=0.52$ eV and pre-exponential factor of $f_0=10^{18}$ Hz. Its magnitude increases with increasing silica content. Based on its activation energy and frequency position it is assigned to conductivity on the surface of the silica particles due to adsorbed water molecules [13]. It is not observed in TSDC, where it would appear far below the temperature region of the measurement. This relaxation is not further discussed here but will be studied in the future, in relation to the water content of the samples.

The position of both α relaxations are independent of silica content. Their temperature dependence is well described by the Vogel–Tammann–Fulcher equation

$$f_{\text{max}} = f_0 \exp\left(-\frac{B}{T - T_0}\right) \quad (4)$$

characteristic of cooperative relaxations, where f_0 , B and T_0 are temperature-independent empirical parameters.

At high temperatures the α and α_{int} relaxations are well separated, their relaxation times differing by 3–4 decades. However, the interfacial relaxation has a weaker temperature dependence than the bulk α relaxation and a smaller curvature, having an almost Arrhenius behavior. Thus at lower temperatures and lower frequencies, approaching the glass transition, the α_{int} relaxation tends to converge with the bulk α . This behavior is in agreement with the TSDC results, which correspond to lower frequencies (10^{-3} Hz) than those accessible with DRS, and where the α_{int} relaxation appears on a shoulder on the α peak.

At first glance, there is an apparent inconsistency between the TSDC results, where there is no well-defined second T_g but a continuous distribution, and the DRS results where a distinct second α relaxation several decades slower is observed at high temperatures. A possible explanation for this behavior is the following: In polymer nanocomposites a layer of polymer close to the particle surface has been observed in molecular dynamics simulations [28,29], which has modified structure (increased average density, localized ordering of the polymer chains). The thickness of this layer is typically 1–3 nm. The α relaxation inside this layer is expected to be modified due to differences in density and restricted available chain conformations. On the other hand, the α relaxation is characterized by a cooperativity length ξ ,

which at T_g has a value of a few nanometers [30–32], and decreases with increasing temperature [33]. For PDMS networks in particular, this ξ has been determined to be around 1.4 nm [34] which is in the range (1–3.5 nm) of values generally found for polymers [31]. At or close to T_g , therefore, the cooperativity length is comparable to the thickness d of the interfacial layer. As a result, the α_{int} relaxation of the interfacial layer cannot appear separately since the movement of chains inside this layer must involve also chains outside it. The α_{int} relaxation takes, therefore, the form of a shoulder on the main α relaxation and a continuous distribution of T_g s is observed by TSDC. At higher temperatures, in the region of the DRS measurements, the cooperativity length becomes smaller than d and the interfacial layer is able to exhibit its own separate α relaxation, slower than the bulk α and with a different temperature dependence.

4. Conclusions

The molecular dynamics of a series of poly(dimethylsiloxane) networks filled with silica nanoparticles synthesized in-situ was investigated using differential scanning calorimetry, thermally stimulated depolarization currents and broadband dielectric relaxation spectroscopy. These experimental techniques are complementary covering together a large frequency range and allow the observation of segmental dynamics of the polymer in a large range of time scales, and gave results in very good agreement with each other.

In addition to the α relaxation associated with the glass transition of the polymer matrix, we observed an additional slower α relaxation which is assigned to polymer chains close to the polymer/filler interface whose mobility is restricted due to interactions with the filler surface. The presence of the interfacial layer is visible also in DSC results as a double structure of the step in heat capacity at the glass transition. The thickness of the interfacial layer is estimated from the TSDC data to be about 2.1–2.4 nm.

A well-defined second T_g was not observed by TSDC, the results being better described by a continuous distribution of glass transition temperatures. However, the bulk and interfacial relaxations at higher temperatures observed by DRS are well-separated, their relaxation times differing by several decades. These results can be reconciled by taking into account the interplay between the thickness d of the restricted interfacial layer and the cooperativity length ξ of the segmental relaxation. At the glass transition these two characteristic lengths are comparable, however, with increasing temperature d is found to be relatively constant but ξ decreases significantly, allowing the appearance of a second distinct relaxation.

Acknowledgements

Financial support from the Greek Ministry of Education and the European Union, through the research programs Heraklitos and Pythagoras, is gratefully acknowledged. We would also like to thank Prof. Kyriakos Vyras for assistance with DSC measurements.

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