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Polyimide/silica nanocomposites with low values of dielectric permittivity

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Abstract. Polyimide nanocomposites prepared by the in situ generation of crosslinked organosilicon nanophase by sol-gel techniques were investigated by dielectric relaxation spectroscopy, thermally stimulated depolarization currents and dynamic mechanical analysis. Two series of samples were investigated with molar mass 5000 and 10000 of the polyimide chains. In both series a non-additive decrease of the dielectric permittivity with increasing amount of filler was observed, indicating a loose inner structure of the spatial aggregates of the organosilicon nanophase. The magnitude of the dielectric γ relaxation of polyimide was found to increase with increasing filler content for the shorter chains, whereas the opposite was observed for the longer ones.

1. Introduction

Increasing attention has been paid in recent years to organic-inorganic hybrid materials, in particular polymer-silica hybrids, prepared by sol-gel techniques[1]. Among them polyimide(PI)-silica nanocomposites attracted much interest as packaging materials and in membrane technology[2] due to the excellent thermal stability of polyimide, its chemical resistance, its mechanical properties and its high selectivity for separation of gas mixtures[3]. Less attention has been paid to the potential of such nanocomposites as low dielectric permittivity ϵ' materials, which could replace PI in microelectronics applications, the relative high values of intrinsic ϵ' of silica (3.8 – 4.0 at room temperature against values in the range 2.6 – 3.2 for PI[3]) being probably the reason for that. However, ϵ' values lower than 3.0 have been reported for PI-based nanocomposites at relatively high filler contents[4].

In a previous paper[5] dielectric relaxation spectroscopy (DRS), thermally stimulated depolarization currents (TSDC) and density measurements were employed to characterize PI nanocomposites prepared by the in situ generation of cross-linked organosilicon nanophase (ON) through the sol-gel process[6]. The dielectric data showed a non-additive decrease of ϵ' in the nanocomposites, which was treated in terms of effective medium theories (EMT) and attributed to a loose inner structure of the spatial aggregates of ON, in agreement with the results of density measurements[5]. At the same time, both the DRS and the TSDC data indicated an increase of the dielectric strength $\Delta\epsilon$ of the secondary γ relaxation of PI in the nanocomposites, observed

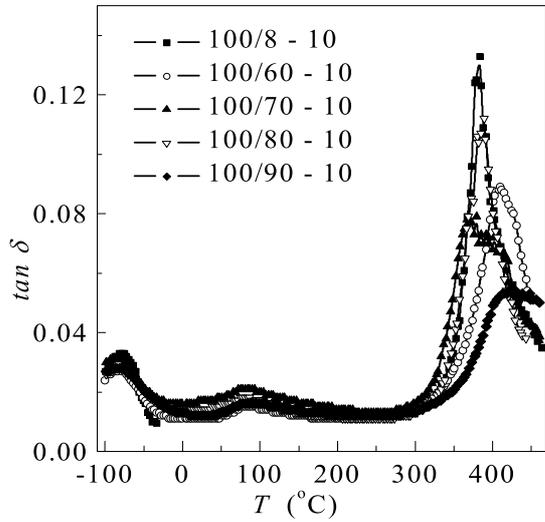


Figure 1. Loss tangent $\tan \delta$ for the nanocomposites of series 10 measured at a frequency of 10 Hz

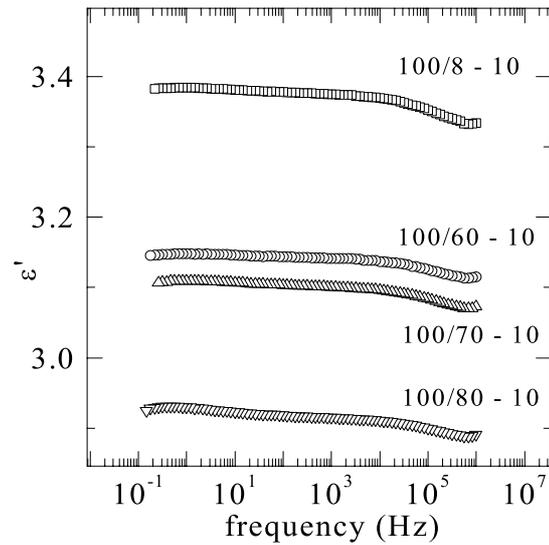


Figure 2. Dielectric permittivity ϵ' vs frequency f at room temperature for the nanocomposites of series 10

also in other PI-silica nanocomposites[7] and attributed to looser molecular packing of PI chain fragments adjacent to the filler particles. This point is of particular importance with respect to the efforts for preparing materials with reduced ϵ' values, because of the temperature/frequency range of the γ relaxation, and is further studied in the present paper.

The molar mass (MM) of polyamic acid (PA) used in the preparation of the PI-ON hybrids in the previous work [5, 6] was 5000. It has been observed that the molar mass of the chain fragments in PI-silica nanocomposites has an effect on morphology and molecular dynamics[7]. Thus, the previous work has been extended here with PI-ON nanocomposites prepared with PA of molar mass 10000. In addition to DRS and TSDC, dynamic mechanical analysis (DMA) was employed to study the relaxational behavior of the nanocomposites.

2. Experimental

The nanocomposites were prepared from polyamic acid of MM 5000 (series 5) or 10000 (series 10) with ethoxysilane end groups (PAAS) and methyl triethoxysilane (MTS). The PAAS/MTS mass ratio was systematically varied from 100/0 to 100/120, corresponding to PI/ON mass ratio varying from 100/0 to 64.4/35.6. Details of the preparation of the nanocomposites of series 5 have been given elsewhere[5], identical procedures were followed here for series 10. Samples are coded by the PASS/MTS ratio followed by the series number 5 or 10, e.g. 100/8-5.

Details of the equipment for DRS, TSDC and DMA measurements and the conditions of the measurements have been given elsewhere[5, 6].

3. Results and Discussion

Figure 4 shows results of DMA measurements for the nanocomposites of series 10. A reasonably strong and a weaker relaxation observed in the $\tan \delta$ vs. T plot for the pristine PI in the glassy state around $T_\gamma \sim -80^\circ\text{C}$ and $T_\beta \sim 90^\circ\text{C}$ can be attributed to the small-scale, local oscillations (γ process) and to the non-cooperative mobility (β process) of imide cycles, respectively[8]. The corresponding dynamic moduli E' (not shown here) smoothly decreased from 3.5 GPa

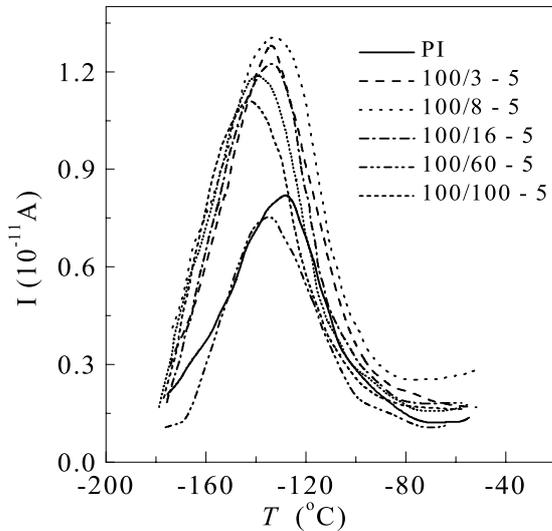


Figure 3. TSDC thermograms in the region of the γ relaxation obtained with the samples indicated on the plot

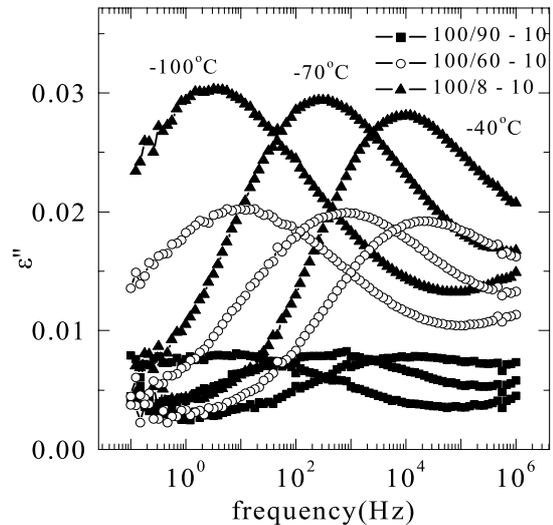


Figure 4. Dielectric loss ϵ'' against frequency in the region of the γ relaxation for the samples and the temperatures indicated on the plot.

at 100°C to ~ 1 GPa at 320°C for all samples of series 10, similar to previous results for series 5[6]. The prominent main relaxation maximum around $T_\alpha \sim 400^\circ\text{C}$ is associated with the onset of cooperative mobility of chain segments. The patterns of $\tan\delta$ vs. T plots for the nanocomposites in the glassy state remained essentially similar, whereas the unimodal α relaxation at $T_\alpha \sim 400^\circ\text{C}$ broadened and shifted to higher temperatures, although its composition dependence was somewhat irregular. Apparently, the above effects reflected the composition-dependent morphological changes in the nanocomposites.

The DRS results for ϵ' at room temperature for selected nanocomposites of series 10 are shown in Fig. 2. Similar to the results for series 5 in our previous paper[5], ϵ' decreases with increasing amount of ON in the nanocomposite. The step observed in Fig. 2 at frequencies larger than about 1 KHz is due to the onset of the γ relaxation, as confirmed by isothermal measurements at lower temperatures to be discussed later. The ϵ' values at 1 KHz at room temperature for the series 5 nanocomposites were treated in ref.[5] in terms of EMT resulting in ϵ' values of the ON between 2.47 and 1.58 depending on the composition and the EMT formulae used and showing the same trend with composition, independently of the formula. These results were rationalized assuming that the ON is made up of nanoparticles of silica (intrinsic $\epsilon' = 3.8 - 4.0$) fused together into loose spatial aggregates with a considerable fraction of empty inner pockets ($\epsilon' = 1.0$) to give volume fractions of the latter in the range 0.40 – 0.65[5]. This type of analysis will be performed for the series 10 nanocomposites after completing the DRS measurements and the density measurements and will be also extended to DRS data recorded at lower temperatures / higher frequencies to eliminate the effects of the γ relaxation.

In the following we focus on the effects of the presence of ON on the dielectric γ relaxation of PI investigated by DRS and TSDC. Figure 3 shows TSDC thermograms recorded on the samples of series 5 in the temperature region of the γ relaxation. In terms of DRS these thermograms correspond to plots of dielectric loss ϵ'' against temperature at a fixed frequency in the region $10^{-2} - 10^{-4}$ Hz[5]. We observe in Fig. 3 a significant increase of the magnitude (relaxation strength $\Delta\epsilon$) of the relaxation in the nanocomposites and a slight shift to lower temperatures. Similar results were obtained also with DRS. They can be explained in terms of loosened packing

of PI chain fragments in the nanocomposites due to tehering on the ON particles, resulting in increase of free volume[7]. This effect is more pronounced in the case of short and rigid polymer chains, like PIs in the present study, and obviously overcompensates the reduction of molecular mobility imposed by the presence of the ON particles.

Figure 4 shows DRS results for selected nanocomposites of series 10: $\epsilon''(f)$ plots in the region of the γ relaxation at three temperatures. The results will be quantified in terms of time scale, magnitude and shape of the response and discussed in detail elsewhere. The main result to be discussed here is the significant reduction of the magnitude of the relaxation with increasing amount of ON and with respect to pristine PI (not shown in the figure) by far more than the presence of ON, which makes no contribution to the γ relaxation, and additivity would suggest. Our explanation for this behavior is that, with the longer PI chains of series 10, the increase of free volume due to loosened molecular packing of the chains is overcompensated by the decrease of molecular mobility due to constraints imposed by the presence of the ON particles.

4. Conclusions

The decrease of dielectric permittivity of the PI-ON nanocomposites with increasing filler content observed in a previous paper for a series of samples with polyimide molar mass 5000 was confirmed here also for a second series with molar mass 10000, indicating the suitability of these materials for low dielectric permittivity applications. The effect of the filler on the magnitude of the dielectric γ relaxation of polyimide was different for the two series of samples: increase for the shorter chains and decrease for the longer. This difference was explained in terms of two different effects on molecular mobility: increase due to loosened molecular packing of the chains and decrease due to constraints imposed by the filler particles, the former dominating for shorter chains. This hypothesis will be further tested in the future by measuring water sorption/diffusion on the same samples and by extending the study to samples with molar mass 15000.

Acknowledgments

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