Interfacial Effects in Polymer Nanocomposites Studied by Dielectric and Thermal Techniques

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I. INTRODUCTION

Organic/inorganic polymer nanocomposites have attracted much interest in recent years, as they exhibit significant improvement of properties at much lower filler factors, as compared to conventional composites [1]. The reasons for that improvement have not yet been fully understood, there is increasing evidence, however, that interfacial effects play a significant role [2]. Here we combine differential scanning calorimetry (DSC) and two dielectric techniques, thermally stimulated depolarization currents (TSDC) and broadband dielectric relaxation spectroscopy (DRS) to study thermal transitions and segmental dynamics associated with the glass transition (dynamic glass transition) of poly(dimethylsiloxane) (PDMS) in PDMS/silica and PDMS/titania nanocomposites over wide ranges of composition. Sol-gel techniques were employed for the generation of the nanoparticles in the presence of crosslinked PDMS, which ensures a fine dispersion of nanoparticles in the polymer matrix [2, 3]. In addition, the systems are characterized by hydrogen bonding interactions between the hydroxyls on the particle surface and the oxygens in the polymer backbone [2, 3], which are expected to be stronger in the case of titania (more acidic hydroxyls).

II. EXPERIMENTAL

Details of the preparation of the nanocomposites and their structural/morphological characterization have been given elsewhere [3]. The fraction of nanoparticles in the nanocomposites was varied from ~6 to 36 wt% in the case of silica, and from ~5 to 18 wt% in the case of titania. Films of ~ 1 mm in thickness were the finally produced samples. Transmission electron microscopy (TEM) and small-angle neutron scattering (SANS) measurements showed that nanoparticles (~5 nm in diameter for silica, 20 - 40 nm for titania) are well dispersed in the polymer matrix, whereas an interpenetrated polymer-oxide structure is obtained at higher filler contents. Mechanical and swelling measurements showed higher reinforcement of PDMS in the case of silica, due to the higher surface to volume ratio, although the hydrogen polymer/filler bonding is stronger for titania systems [3].

Thermal transitions were investigated in helium atmosphere in the temperature range from -170 to 40 °C at 10 °C/min using a TA Q200 series DSC instrument. For enhancing crystallization, measurements were carried out after a 30 min isothermal stay at the crystallization temperature (annealing). On the other hand, in order to suppress crystallization and its effects on glass transition, fast cooling (quenching) was employed [4].

For TSDC measurements in the range from -150 to 50 °C a Novocontrol TSDC sample cell in combination with a sensitive programmable Keithley 617 electrometer and a Novocontrol Quatro cryosystem were employed [4]. DRS measurements were carried out in the frequency range from 10^{-1} to 10^{6} Hz at temperatures from -150 to 20 °C. Details of the measuring procedures have been given elsewhere [4].

III. RESULTS AND DISCUSSION

Fig. 1 shows DSC cooling thermograms. In these, and the corresponding heating thermograms, we follow the glass transition and crystallization/melting events of PDMS. A significant suppression of crystallization in the nanocomposites is observed, which can be quantified in terms of decreasing crystallization temperature and degree of crystallinity and discussed in terms of the strength of polymer-filler interactions and specific surface area of the filler [4].

Fig. 2 shows results for the glass transition. No significant variation of the glass transition temperature is observed. Here we focus on the calculation of the rigid amorphous polymer fraction (RAF), defined as the fraction of amorphous polymer which remains immobilized, making no contribution to the glass transition [5]. RAF was calculated from the measured heat capacity step at the glass transition and the degree of crystallinity. It contains contributions from the presence of both crystallites and nanoparticles (inset to Fig. 2), as indicated by the complex dependence on the type and fraction of filler and the thermal history (processing) in Fig. 2.



Fig. 1. DSC thermograms for unfilled PDMS, PDMS/silica and PDMS/titania nanocomposites during cooling.



Fig. 2. Rigid amorphous polymer fraction of PDMS immobilized on the surfaces of the nanoparticles and within the polymer crystals, as calculated from DSC measurements, for the different crystallization treatments. The inset shows a simplified model of the estimated distribution of the different polymer phases and filler.

Comparative thermal and dielectric studies reveal the presence of three contributions to the glass transition, arising from the bulk amorphous fraction (α), small amorphous regions confined within the crystallites (α_c), and the rigid amorphous fraction around the filler particles (α). The most interesting result in Fig. 3, where DSC and TSDC thermograms in the region of the glass transition are compared to each other for the same composition and two different thermal histories, is that polymer "bound" to the filler does make a contribution not only to the dielectric response (TSDC, DRS) [2], but also to the DSC response.

Fig. 4 summarizes the results on the time scale of the segmental dynamics in the two types of nanocomposites studied in terms of the Arrhenius diagram. The striking result is the systematically slower dynamics of the α' relaxation in the titania nanocomposites, directly reflecting the stronger PDMS-titania as compared to the PDMS-silica interaction.



Fig. 3. Comparative DSC and TSDC thermograms for PDMS + 31,0 wt% SiO₂ during heating, after standard cooling (solid lines) and crystallization annealing (dotted lines).



Fig. 4. Activation diagram (Arrhenius plots) for PDMS, PDMS/silica and PDMS/titania systems, as recorded from isothermal DRS measurements. Lines are added as guides for the eyes.

IV. CONCLUSION

DSC and dielectric DRS and TSDC measurements in PDMS/silica and PDMS/titania nanocomposites reveal the presence of several contributions to segmental dynamics and the corresponding glass transition. Further work is needed to clarify as to whether this behavior is common to rubber nanocomposites, in relation to the high flexibility of the polymer backbone.

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