



Comparative studies on effects of silica and titania nanoparticles on crystallization and complex segmental dynamics in poly(dimethylsiloxane)

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ARTICLE INFO

Article history:

Received 18 August 2010

Received in revised form

20 September 2010

Accepted 20 September 2010

Available online 26 September 2010

Keywords:

Poly(dimethylsiloxane) nanocomposites

Segmental dynamics

Polymer crystallization

ABSTRACT

Effects of *in situ* synthesized silica and titania nanoparticles, 5 and 20–40 nm in diameter, respectively, on glass transition and segmental dynamics of poly(dimethylsiloxane) networks were studied by employing differential scanning calorimetry, thermally stimulated depolarization currents and broadband dielectric relaxation spectroscopy techniques. Strong interactions between the well dispersed fillers and the polymer suppress crystallinity and affect significantly the evolution of the glass transition in the nanocomposites. Next to the α relaxation associated with the glass transition of the bulk amorphous polymer fraction, two more segmental relaxations were recorded, originating from polymer chains restricted between condensed crystal regions (α_c -relaxation) and the semi-bound polymer in an interfacial layer with strongly reduced mobility due to interactions with hydroxyls on the nanoparticle surface (α' relaxation), respectively. Interactions with the polymer were found to be stronger in the case of titania than silica, leading to an estimated interaction length of around 2 nm for silica and at least double for titania nanocomposites.

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1. Introduction

The evolving needs for multifunctional materials aiming at complex applications, is a basic motivation for modern science to improve or, as a second step, to create good material properties. As a new option, the development of various composite polymeric materials [1] was a satisfactory solution for various needs and applications. For the last years, nanoscale composites are in the center of interest [2]. The use of nanoscale fillers in a composite material offers the great benefit that, in comparison with traditional composites, only a small amount of filler content is sufficient to induce tremendous improvements in desired properties [3]. The main reason for that is the surface to volume ratio of the nanoparticles, which is very high in the nanocomposites, in comparison with traditional composites. Specifically, the polymer fraction close to these surfaces (interfacial polymer) constitutes a significant fraction of the material and its behaviour affects significantly or even dominates the properties of the system. It is commonly accepted that the improvement of properties in polymer nanocomposites is related to modified polymer dynamics in the interfacial layer [4,5].

The presence of various nanofillers, such as silica, titania, nanoclays, typically leads to a restriction of polymer mobility and

thermal transitions ability, manifested in an increase of the glass transition temperature, and a decrease of the degree of crystallinity and of the crystallization temperature in semi-crystalline polymer matrices [6–8]. The extent of these effects depends on composition and preparation/processing conditions and can be further controlled by functionalization of either the polymer or the filler [9,10]. There are, however, several exceptions to this behaviour, depending on the type of polymer and filler [11] and/or the preparation/processing conditions [12]. It is referred that carbon nanotubes in polymer/carbon nanotube nanocomposites [13] and clays in polymer nanocomposites [9,14] act as crystallization nuclei or favor different types of crystals growth.

Similar to the picture described above for polymer nanocomposites, results in literature on effects of nanoparticles on glass transition and segmental dynamics in rubber/oxide nanocomposites, in particular rubber/silica nanocomposites, appear, at least at first glance, controversial [8,15–20]. Depending on composition, the method of preparation and the experimental technique employed, results on glass transition and segmental dynamics have often been described in term of a three layer model [15–17] or a two layer model [18–20] or a continuous distribution of glass transition temperatures as a function of the distance from the particle surface [21]. Rittigstein and Torkelson pointed to the significance of the type of polymer–filler interaction and, for a given composition, of the method of preparation [12]. Roland and

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coworkers pointed out that different experimental techniques may result to different pictures of dynamics in the nanocomposites, which are not necessarily contradictory [22].

In the present work we study polymer–filler interactions and their effects on molecular mobility in PDMS networks filled *in situ* with silicon and titanium oxide nanoparticles generated via sol–gel technique. To that aim, we employ differential scanning calorimetry (DSC), and two dielectric techniques, thermally stimulated depolarization currents (TSDC) and dielectric relaxation spectroscopy (DRS), covering together a broad frequency range of 10^{-4} to 10^6 Hz. Morphological characterization of the materials in a previous paper showed a good dispersion of nanoparticles, 5 and 20–40 nm in diameter for silica and titania nanocomposites, respectively, and revealed fine details of this dispersion [23]. The mechanical properties were significantly improved in a different way for the two oxides, and that was correlated with the different strength of polymer–filler interaction and details of the nanoparticle dispersion [23]. The results of the present study show significant effects of the nanoparticles on segmental dynamics associated with the glass transition, originating from the severe restriction of crystallization ability and the strong reduction of molecular mobility in an interfacial layer of a few nm in thickness around the nanoparticles. The extent of these effects depends on the type of the filler (stronger for titania than for silica) and the quality of particle dispersion. The effects are quantified and the results may provide a basis for understanding and modeling the improvement of mechanical properties at the molecular level.

From the methodological point of view, the results of the present study illustrate the power of the two dielectric techniques used in combination with DSC for the investigation of effects of nanofiller on thermal transitions and molecular dynamics in the nanocomposites under investigation [8]. In that respect, the dielectric techniques, implemented also in several other fields of macromolecular science [24,25], compete with and complement other methods employed, such as dynamic mechanical analysis measurements [8,15], changes in viscoelasticity [22] and DSC glass transition step [8,26,27], electron spin resonance [28] and fluorescence/multilayer methods [12].

2. Experimental

2.1. Materials

PDMS networks filled with several contents of silica (~6–36 wt %) and titania (~5–18 wt%) amorphous nanoparticles and, for comparison, unfilled PDMS networks were studied in the present work. The unfilled polymer network was prepared from hydroxyl-terminated PDMS (Gelest, $M_w = 18000$) by end-linking reactions using tetraethoxysilane (TEOS) as cross-linking agent. For composites preparation the unfilled extracted polymer network was swollen in TEOS for silica or in titanium (IV) *n*-butoxide (TBO) for titania, which were the precursors of the particles generation in the sol–gel process. Then the samples were hydrolyzed during 48 h and vacuum-dried at 80 °C for several days to constant weight. The amount of filler is represented by the difference between the final and initial weights. Films of ~1 mm in thickness were the finally produced samples [23].

According to the statistical equation $\langle r^2 \rangle = C_\infty/nl^2$ [29], by knowing the average number and length of the main-chain bond length, n and l respectively, the characteristic ratio C_∞ and considering that crosslinking involves only the endgroups of the PDMS chains, the end-to-end distance between crosslinks $\langle r^2 \rangle^{1/2}$ was calculated around 11.2 nm. Transmission electron microscopy (TEM), small-angle neutron scattering (SANS), stress–strain and

equilibrium swelling measurements were carried out on the same systems [23]. Results showed that silica nanoparticles are well dispersed in the polymer matrix with small domains around ~5 nm in diameter and rather diffuse surfaces. At higher than 10 wt% contents an interpenetrated polymer–silica structure is obtained. On the other hand, titania particles seem to be approximately spherical in shape with diameters between 20 and 40 nm and better defined interfaces with PDMS than in the case of silica. Even at the lowest titania content the particles are almost connected in a branched network structure. Distribution is better in case of silica giving a higher polymer–filler interfacial area but weaker bonds with PDMS, comparing with the strong PDMS–titania interactions. Mechanical measurements showed higher reinforcement of PDMS in case of silica. Tense transitions from linear (elastic) to sigmoidal (plastic) stress–strain behaviour for ~18 wt% SiO₂ and ~8 wt% TiO₂ were observed, due to the forming of the inorganic networks at these compositions [23]. The interactions of PDMS chain segments with the nanoparticles occur via hydroxyl groups (–OH) on the surfaces of the nanoparticles, which are proved by solid-state ²⁹Si NMR, Infrared (IR) and near-IR spectroscopy, as shown in previous work for PDMS/silica nanocomposites [30].

It is useful to note that the measurements described above were performed at room temperature, where this polymer, semi-crystalline at lower temperatures, is fully amorphous. So any effects in mechanical and swelling properties are affiliated only to filler–polymer and filler–filler interactions [23].

2.2. Differential scanning calorimetry

Thermal properties of the materials were investigated in helium atmosphere in the temperature range from –170 to 40 °C using a TA Q200 series DSC instrument. Samples of ~8 mg in mass, cut from the produced films, were closed in standard Tzero aluminium pans. Cooling and heating rates were fixed to 10 °C/min for typical measurements. In order to enhance cold crystallization event, affiliated to the suppression of crystallization (during cooling) due to the presence of nanoparticles, measurements were carried out also using different cooling rates (5, 10 and 20 °C/min) and fixed heating rate (at 10 °C/min). At this point it is useful to note that PDMS crystals are melted at room temperature, so a first heating scan for erasing thermal history [31] was not necessary here.

2.3. Thermally stimulated depolarization currents

Thermally stimulated depolarization currents (TSDC) is a special dielectric technique in the temperature domain, characterized by high sensitivity and high resolving power, the latter arising from its low equivalent frequency (10^{-4} to 10^{-2} Hz) [32]. By this technique, the sample (15–20 mm in diameter and ~1 mm in thickness) was inserted between the brass plates of a capacitor, placed in a Novocontrol TSDC sample cell and polarized by an electrostatic field E_p (~100 V/mm) with a home-made voltage source at polarization temperature $T_p = 20$ °C for time $t_p = 5$ min. With the field still applied, the sample was cooled down to –150 °C (cooling rate 10 °C/min, under nitrogen flow), sufficiently low to prevent depolarization by thermal energy, then short-circuited and reheated up to 50 °C at a constant heating rate $b = 3$ °C/min. Temperature control was achieved by means of a Novocontrol Quatro cryosystem. A discharge current was generated during heating and measured as a function of temperature with a sensitive programmable Keithley 617 electrometer.

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