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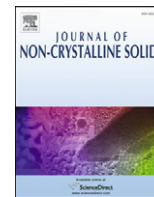
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Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrsol

Dielectric studies of segmental dynamics in poly(dimethylsiloxane)/titania nanocomposites

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ARTICLE INFO

Available online 17 August 2010

Keywords:

Dielectric spectroscopy;
Poly(dimethylsiloxane);
Titania;
Nanocomposites;
Segmental dynamics

ABSTRACT

Differential scanning calorimetry, thermally stimulated depolarization currents and dielectric relaxation spectroscopy techniques, covering together a broad frequency range of 10^{-4} to 10^6 Hz, were employed to investigate the effects of in situ synthesized titania nanoparticles on thermal transitions, segmental dynamics and interfacial interactions in poly(dimethylsiloxane)/titania nanocomposites. Titania particles (TiO_2 , 20–40 nm in diameter) were prepared and well dispersed into the polymer network through sol–gel technique, aiming at stable and mechanically reinforced systems. The interactions between polymer and fillers were found to be strong, suppressing crystallinity and affecting the temperature development of the glass transition. The segmental relaxation associated with the glass transition consists of three contributions, arising, in the order of decreasing mobility, from the bulk (unaffected) amorphous polymer fraction (α relaxation), from polymer chains restricted between condensed crystal regions (α_c relaxation), and from the semi-bound polymer in an interfacial layer with strongly reduced mobility due to interactions with hydroxyls on the nanoparticle surface (α relaxation). The thickness of the interfacial layer was estimated to be in the range of 3–5 nm. Measurements using different thermal protocols proved very effective in analyzing the origin of each relaxation and the respective effects of filler addition.

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1. Introduction

A main aim of modern science is to improve or create good material properties. For the last decades one way to achieve such results is through composite polymeric materials [1]. As a next step, nanoscale composites are in the center of interest [2]. The benefit of using nanoscale fillers in a composite material is that, in comparison with traditional composites, a small amount of filler content is sufficient to induce tremendous improvements on desired properties [3]. That is because the surface to volume ratio of the nanoparticles is very high, so that 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]. Very often the presence of various nanofillers, such as silica, titania, nanoclays, leads to a restriction of polymer mobility and thermal transitions ability, manifested in an increase of glass transition temperature and a decrease of the degree

of crystallinity and of the crystallization temperature in semi-crystalline polymer matrices [6–8]. There are, however, several exceptions to this behaviour, depending on the type of polymer and filler [9] and/or the preparation/processing conditions [10]. As an example, carbon nanotubes in polymer/carbon nanotube nanocomposites act as crystallization nuclei or favor different types of crystals growth [11].

In the present work we study the effects of filler–polymer interaction on the molecular mobility of PDMS networks filled in situ with titanium oxide nanoparticles generated via sol–gel technique. To that aim, we employ differential scanning calorimetry (DSC), thermally stimulated depolarization currents (TSDC) and dielectric relaxation spectroscopy (DRS) techniques, covering together a broad frequency range from 10^{-4} to 10^6 Hz. The effects observed are significant, obviously due to the good dispersion of the filler and the strong hydrogen bonding interactions between oxygens on the polymer backbone and hydroxyls on the nanoparticle surfaces. The results suggest that the effect of the fillers on segmental dynamics comes mainly through the restriction of crystallization ability and the strong polymer mobility restriction in an interfacial layer of a few nm thickness around the titania particles. Moreover, the results provide additional support and supplement conclusions drawn on the basis of other experimental techniques on the same materials, in particular the formation of an interpenetrating organic–inorganic network and the polymer–filler and filler–filler interactions strength [12].

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From the methodological point of view, the combination of thermal and dielectric techniques is proved a powerful tool for the investigation of effects of nanofiller on thermal transitions and molecular dynamics in the nanocomposites under investigation [6]. Evidence for complex behaviour of segmental dynamics and glass transition in similar systems has been provided also by other experimental techniques, including a second $\tan\delta$ peak in dynamic mechanical analysis measurements [13], changes in viscoelasticity [14] and DSC glass transition step [6] or via fluorescence/multilayer methods [10].

2. Experimental

2.1. Materials

PDMS networks filled with several contents of titania nanoparticles (~4 to 25 wt.%) and, for comparison, unfilled PDMS network were studied in this work. The unfilled network was prepared from hydroxyl-terminated PDMS (Gelest, $M_w = 18,000$) by end-linking reactions using tetraethoxysilane (TEOS) as cross-linking agent. The cross-linked PDMS was swollen for a given time in titanium (IV) *n*-butoxide (TBO). Then the sample was hydrolyzed during 48 h and vacuum-dried at 80 °C for several days to constant weight. The difference between the final and initial weights represents the amount of filler [12]. Films of ~1 mm in thickness were the finally produced samples.

Transmission electron microscopy (TEM), small-angle neutron scattering (SANS), stress–strain and equilibrium swelling measurements on the same systems show that titania nanoparticles are approximately spherical in shape with diameters between 20 and 40 nm and are well dispersed into the polymer matrix, leading to high mechanical properties improvement. In particular, the strong polymer–filler interactions and the almost interpenetrated PDMS and titania networks, even at low filler contents, lead to significant changes in the mechanical and swelling behaviour [12].

2.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were carried out in nitrogen atmosphere in the temperature range from –120 to 20 °C using a Perkin-Elmer Pyris 6 calorimeter. Samples of ~10 mg in mass, cut from the produced films, were closed in standard aluminium cups. For comparison with previous work on PDMS/silica nanocomposites [6], cooling and heating rates were chosen to 10 and 40 °C/min, respectively. Please note that at room temperature PDMS crystals are melted, so a first heating scan for erasing thermal history, typically needed in case of semicrystalline polymers [15], was not necessary here.

2.3. Thermally stimulated depolarization currents

The thermally stimulated depolarization currents (TSDC) method is a special dielectric technique in the temperature domain and is often used to study dielectric relaxations in polymeric materials because of its high resolving power arising from its low equivalent frequency (10^{-4} to 10^{-2} Hz) [16]. By this technique, the sample (12–15 mm in diameter, ~1 mm in thickness) was inserted between the brass plates of a capacitor (12–15 mm in diameter) placed in a Novocontrol 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), 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.

2.4. Dielectric relaxation spectroscopy

For dielectric relaxation spectroscopy (DRS) measurements [17] the sample (similar to that used for TSDC measurements) was placed between the plates of a capacitor and an alternate voltage was applied in a Novocontrol sample cell. The complex dielectric permittivity, $\epsilon^* = \epsilon' - i\epsilon''$, was recorded isothermally as a function of frequency in the range 10^{-1} to 10^6 Hz at temperatures –150 to 30 °C in steps of 2.5, 5 and 10 °C (depending on the process to be studied) using a Novocontrol Alpha analyzer. The temperature was controlled to better than 0.5 °C with a Novocontrol Quatro cryosystem. This measurement protocol will be referred to as *protocol A*. In order to investigate effects of crystallinity on the segmental dynamics, measurements were carried out after a 30 min isothermal stay (annealing) of the sample at a temperature between the onset and the peak of crystallization event, as it was defined from DSC measurements, this annealing leading to maximum degree of crystallinity. This measurement protocol will be referred to as *protocol C*.

3. Results

3.1. DSC measurements

DSC thermograms for unfilled PDMS and PDMS/titania nanocomposites recorded during cooling are presented in Fig. 1. In the temperature range –120 to 20 °C an exothermic peak is observed around –91 to –74 °C, representing the crystallization event of PDMS. In previous studies on PDMS systems [6,18] the glass transition temperature has been observed between –130 and –115 °C. The lower achievable temperature of the DSC means in the present work (–120 °C) was not low enough to record the whole glass transition step for these materials.

During heating of the samples, complex endothermic melting peaks were observed at temperatures between –46 and –38 °C. Complex melting peaks have been observed before in PDMS systems [18–20] and for the materials of the present work are still under investigation.

The values of crystallization and melting temperatures, T_c and T_m respectively, are shown in Table 1 along with the respective enthalpies $\Delta H_{c/m, norm}$ as recorded through DSC and also normalized to the same polymer content for each sample (Eq. (1)). The degree of crystallinity X_c was calculated from the enthalpy of melting according

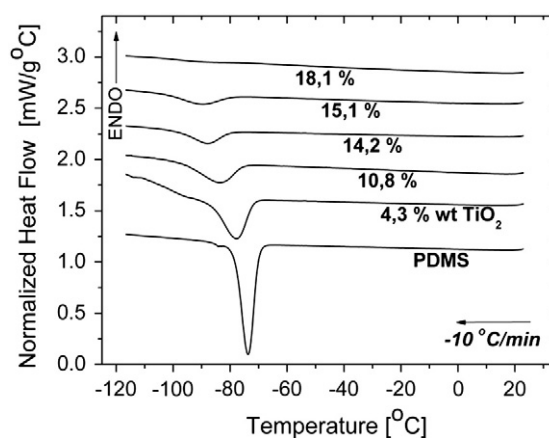


Fig. 1. DSC comparative thermograms for unfilled PDMS and PDMS/titania nanocomposites during cooling. Crystallization peaks are observed for all samples.

Table 1
Crystallization and melting temperatures T_c and T_m respectively, normalized respective enthalpies $\Delta H_{c/norm}$ and degree of crystallinity X_c for PDMS and PDMS/titania nanocomposites.

Filler content (wt.%)	T_c (°C) (± 1)	$\Delta H_{c, norm}$ (J/g) (± 2)	T_m (°C) (± 1)	$\Delta H_{m, norm}$ (J/g) (± 2)	X_c ($\pm 5\%$)
0	-74	30	-38	30	0.81
4.3	-78	29	-40	23	0.62
10.8	-83	18	-42	18	0.50
14.2	-88	11	-43	13	0.34
15.1	-90	9	-44	10	0.27
18.1	-91	2	-46	3	0.07

to Eq. (2), in which $\Delta H_{100\%}$ is the enthalpy of PDMS fusion, taken as 37.4 J/g [18].

$$\Delta H_{m, norm} = \Delta H_{m, DSC} / X_{polymer} \quad (1)$$

$$X_c = \Delta H_{m, norm} / \Delta H_{100\%} \quad (2)$$

The presence of the titania nanoparticles affects significantly the crystallization properties of PDMS in the nanocomposites.

3.2. TSDC measurements

The overall TSDC thermograms are presented in Fig. 2a. In the temperature range from -140 to -100 °C complex spectra consisting

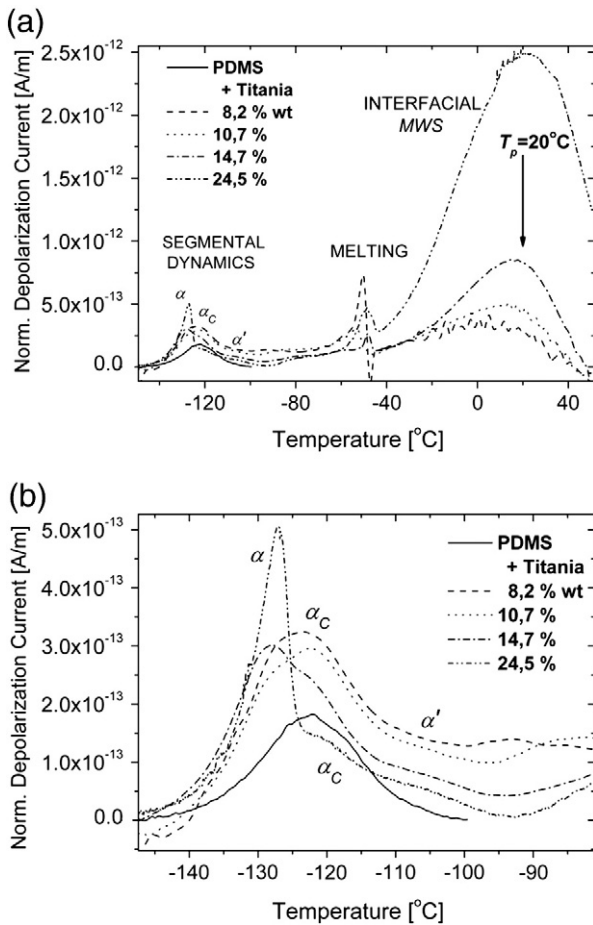


Fig. 2. TSDC comparative thermograms for unfilled PDMS and PDMS/titania nanocomposites (a) overall behaviour and (b) in the region of glass transition. The reduction of the degree of crystallinity with filler content depresses the height of α_c relaxation and at the same time α and α' relaxations arise.

of three peaks are well discerned. Bearing in mind the similar range of equivalent frequencies of TSDC and DSC measurements [16], we suggest at this stage and will prove later that the three peaks (relaxations), called α , α_c and α' in the order of increasing temperature, are related with cooperative PDMS chain motions in the glass transition region. These three peaks contribute to the complex segmental dynamics view in a systematic manner (Fig. 2b). The α relaxation (between -95 and -110 °C) is present only in the nanocomposites and its magnitude increases with filler content. Observed at about -123 °C, α_c is slower and stronger than α and its position is not affected by the nanoparticles. The strength of this relaxation decreases with decreasing degree of crystallinity. Simultaneously with the depression of α_c the upcoming of α' relaxation is observed at -130 to -128 °C. The event that is recorded between -60 and -40 °C corresponds to the melting of PDMS crystals. The strong peak which follows at higher temperatures is due to the interfacial Maxwell–Wagner–Sillars (MWS) relaxation, arising from the trapping and the subsequent release of charges at the polymer–filler interfaces [6,21]. Both the melting and the MWS TSDC peaks will be further followed in future work.

3.3. DRS measurements

DRS results will be presented here in the form of the temperature (Fig. 3, isochronal plots) or frequency dependence of the imaginary part of dielectric permittivity (dielectric loss) ϵ'' (Fig. 4, isothermal plots). Data have been recorded isothermally and have been replotted in Fig. 3 to facilitate comparison with the TSDC thermograms of Fig. 2. A higher frequency of 1 kHz has been selected for the plots to suppress effects of conductivity [17]. The results agree well with those of TSDC, the slight shift to higher temperatures in Fig. 3 arises from the higher frequency of presentation [6].

In Fig. 4 one can observe the changes of α and α_c relaxations as the PDMS + 24.5 wt.% titania sample was measured under the thermal protocol A (almost amorphous polymer) and protocol C (annealed at crystallization temperature, semi-crystalline polymer). For the polymer allowed to get crystallized, the segmental dynamics is mainly expressed as the broadened, weaker and slower α_c relaxation. At higher temperatures (-97.5 °C) the α relaxation is observed at low frequencies, well separated from α and α_c .

The time scale of the three relaxations is best discussed on the basis of the Arrhenius plot (frequency of maximum of ϵ'' vs reciprocal temperature) shown for all samples and the two thermal protocols in Fig. 5. Included in the plot are also TSDC data at the equivalent frequency of 1.6 mHz [6]. The main observation is that α and α_c have very similar frequency–temperature development, typical for segmental dynamics

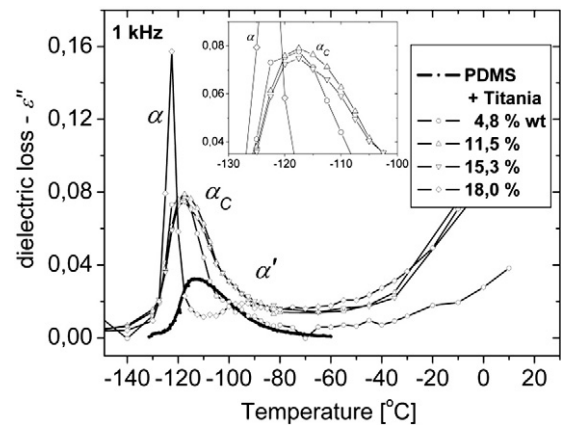


Fig. 3. Comparative isochronal plots of the imaginary part of dielectric permittivity ϵ'' , replotted from DRS measurements at 1 kHz for PDMS and PDMS/titania nanocomposites. The inset shows details in the glass transition region.

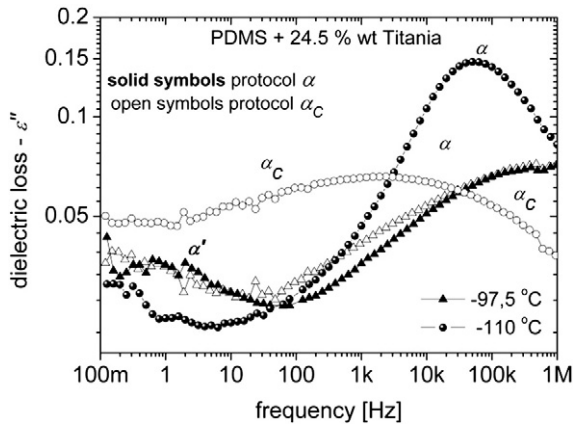


Fig. 4. Dielectric loss ϵ'' vs frequency for PDMS + 24.5 wt.% titania at -97.5 (triangles) and -110 °C (circles).

and practically not affected by the addition of titania nanoparticles. On the other hand, α tends to be strongly separated from α and α_c , and its time scale is practically described by a straight line characterized by lower activation energy (~ 0.50 eV), as compared to α and α_c . The behaviour is very similar to that observed for PDMS/silica nanocomposites [6].

4. Discussion

The results of DSC measurements (Fig. 1 and Table 1) show that, with increasing filler content the crystallization temperature, the degree of crystallinity and the melting temperature systematically decrease. These results indicate that the strong interactions (hydrogen bonds) between the particles and PDMS (hydrogen bonds between the oxygens on the polymer backbone and the hydroxyls on the nanoparticle surfaces) suppress the creation of crystallization nuclei and the growth and quality of the PDMS spherulites [22] in the nanocomposites. The depression of crystallization and melting enthalpy seems to become stronger as the titania content gets higher than ~ 10 wt.%, as compared to lower titania contents. Such behaviour could be explained in terms of the formation of an inorganic network throughout the polymer volume at this and higher filler contents. This network could be the main reason for the restriction of growing of crystals, due to the reduction of regions of free polymer mobility. The

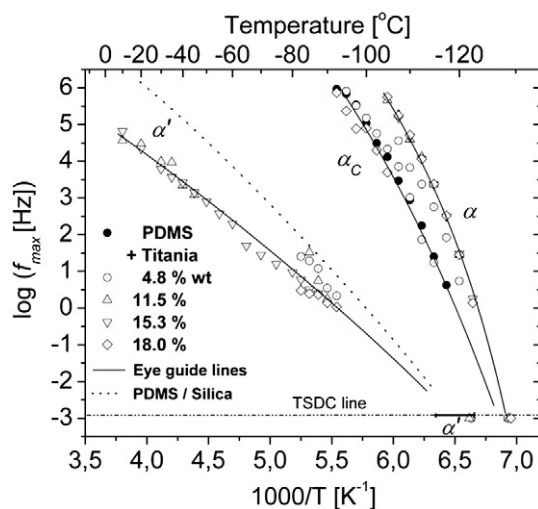


Fig. 5. Arrhenius plot of the segmental and interfacial dynamics for PDMS and PDMS/titania nanocomposites. The indicated α behaviour is similar to that of PDMS/silica nanocomposites (.....) [6].

above suggestions come in agreement with the results of TEM and stress-strain measurements on the same compositions [12]. Formation of an inorganic silica network was observed also in poly (hydroxyethyl acrylate)/silica nanocomposites, where, similar to here, silica particles were generated by sol-gel process [8].

In addition to calorimetry, the dielectric DRS and TSDC techniques provide significant information on the overall mobility, mostly on the segmental dynamics of the polymer in the nanocomposites. Through extended measurements using different thermal treatments, more than one dielectric relaxation mechanisms affiliated to glass transition are recorded. The results show that the fast α relaxation at low temperatures/high frequencies represents the segmental mobility of the bulk (unaffected) polymer. The slower α_c relaxation represents the mobility of polymer chains restricted between condensed crystalline regions [23]. Finally, the slowest α process represents the segmental dynamics in the interfacial polymer layer around the titania nanoparticles (or in general in a layer close to the surface of the nanoparticles) [6].

As X_c increases, it is observed in Figs. 2 and 3 that the whole dielectric response in the glass transition region gets lower. It is not clear at this stage to which extent the reduction of the fraction of the amorphous polymer and the constraints imposed by the polymer crystallites and the titania nanoparticles contribute to the reduction of the dielectric response. Experiments and analysis of the data by fitting model functions are in progress to quantitatively further follow this point.

In the Arrhenius plot (Fig. 5) the α relaxation trends look linear (Arrhenius behaviour), but judging from the respective TSDC temperature range we conclude that the Vogel-Tammann-Fulcher (VTF) equation [24] can be well fitted to the data giving low fragility values. Indeed, by fixing the pre-exponential factor f_0 of VTF to the phonon value 10^{13} Hz [17] and fitting the equation to our experimental data the average fragility index (m) values were calculated to be 110, 97 and 21 for α , α_c and α relaxations, respectively. The uncertainty for these fragility values is about 5. [25] This means that the α relaxation is indeed affiliated to segmental polymer chain motions (glass transition), but it is characterized by reduced cooperativity [24] in comparison with α and α_c relaxations [6].

Based on the interpretation of the origin of the relaxations given above and combining DSC and DRS results, we can calculate the reduced mobility polymer fraction X_{int} (the fraction of polymer in the interfacial layer, Fig. 6) by the following simplified equation

$$X_{int} = \frac{\Delta\epsilon_{\alpha'}(1-X_c)}{\Delta\epsilon_{\alpha'} + \Delta\epsilon_{\alpha + \alpha_c}} \quad (3)$$

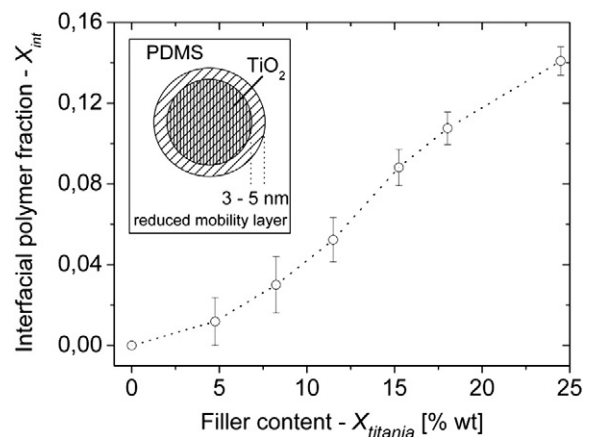


Fig. 6. The fraction of polymer with reduced mobility vs titania content obtained from Eq. (3). The line simply connects the data to guide the eye. The inset shows the simplified model used to calculate the thickness of the interfacial layer.

where $\Delta\varepsilon$ is the dielectric strength of each relaxation [17] and X_c is the degree of crystallinity for each sample. The results are shown in Fig. 6. The interfacial polymer fraction increases from 0 to 0.14 at the highest filler content, while at the same time the degree of crystallinity drops from 0.81 to almost 0.

As it was shown in previous work [6], it is possible to make an estimation of the thickness of the interfacial layer d_{int} , exploiting the information from TEM measurements on the morphology and the dimensions of the nanoparticles [12]. By using the following equation

$$d_{int} = \left[\left(v_{int} / v_{filler} \right)^{1/3} - 1 \right] r_{filler} \quad (4)$$

where v_{int} and v_{filler} are the volume fractions of the interfacial layer and fillers in the nanocomposites, respectively, while r_{filler} is the radius of the nanoparticles [26], d_{int} was calculated to be 3–5 nm (Fig. 6).

5. Conclusions

Molecular dynamics in a series of PDMS/titania nanocomposites were studied using calorimetry and dielectric techniques. Three discrete relaxations in the region of the glass transition were identified and studied, arising from the segmental mobility of the bulk (unaffected) polymer (α relaxation), the mobility of polymer chains restricted between condensed crystalline regions (α_c relaxation), and the segmental dynamics in the interfacial polymer layer around the titania nanoparticles (α relaxation). Compared with previous similar studies on PDMS/silica nanocomposites, the PDMS/titania nanocomposites are characterized by stronger polymer–filler interactions, reflected in a shift of α to lower frequencies/higher temperatures and a larger thickness of the interfacial layer.

Analysis of the experimental dielectric data in the present paper has been reduced to a minimum and results and conclusions are based mostly on the raw data. Work is in progress to critically analyze the complex dielectric data in the glass transition region by fitting model functions. Among others, this analysis will provide information on the temperature dependence of the thickness of the interfacial layer [6]. Also, thermal sampling TSDC analysis may provide quantitative

information on a possible distribution of relaxation times and glass transition temperatures in the interfacial layer [6,10].

Acknowledgments

The research leading to these results has received partial support from the European Community's Seventh Framework Programme [FP7/2007-2013] under grant agreement no. 218331 NaPolyNet.

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