

Summary

This PhD Thesis, entitled '*Interfacial interactions and molecular dynamics in organic-inorganic nanocomposites polymeric materials*', deals with the systematic investigation of the effects of interfacial interactions between a polymer (polydimethylsiloxane, PDMS) and the solid surface of various metal oxide (silica, titania) nanoparticles on molecular dynamics and thermal transitions of the polymer. The main effort is paid on the study of the characteristics of the fraction of polymer interacting directly with the nanoparticles. This fraction is called '*interfacial polymer fraction*' and is widely thought to be responsible for the tremendous improvements in desired properties of polymer nanocomposites (NCs), as compared to those of traditional composites. Throughout the last decades it has been suggested that the modified properties of polymer NCs are dominated by those of the interfacial polymer fraction. Next to the physical properties of the polymer, also the characteristics of the interacting solid surface are of significance for interfacial interactions. It has been recently reported that the size and surface curvature of the solid surface strongly affect the strength of interaction. So far, the dependence of the characteristics of the interfacial polymer fraction (dynamics, cooperativity, chain segment conformations) on surface roughness has not been sufficiently considered in the literature. In the present work we show results which suggest that, at least for PDMS based NCs, the surface roughness of the particles in combination with the flexibility of the polymer chains dominate interfacial interactions, over other factors, such as the type and size of the primary particles.

This study involves morphological, thermal and dielectric measurements on PDMS/silica and PDMS/titania NCs (i) of various filler loadings, (ii) with a broad range of surface roughness and variety in size of the primary particles, (iii) with different molecular weight and structure (linear/crosslinked) of PDMS, and (iv) at various levels of NCs hydration. In order to quantify hydration level, water equilibrium sorption-desorption

measurements at room temperature were also performed. The materials studied can be classified into two series. The first series is that of ‘conventional’ polymer NCs type consisting of silica (SiO₂) and titania (TiO₂) nanoparticles, 5 and 20–40 nm in diameter, respectively, *in situ* synthesized and well dispersed (via sol–gel technique) in PDMS (*MW* ~18000) networks. The second series is that of ‘core–shell’ NCs type, as linear PDMS (*MW* ~2000 and ~8000) is adsorbed via hydrogen bonding on aggregates of fumed metal oxide particles of a wide range of surface roughness, S_{BET} . The metal oxides used are titania (~70 nm in diameter for primary particles, ~800 nm in size for aggregates, S_{BET} ~ 25 m²/g) and various silicas (8–85 nm in diameter for primary particles, 300–600 nm in size for aggregates, S_{BET} ~ 55–342 m²/g). Finally, we studied confinement effects of PDMS adsorbed in the cylindrical-like pores (of 6–20 nm in diameter) of silica–gel of high S_{BET} (~384 m²/g, affiliated mainly to intraparticle porosity). In selected samples, before adsorption of PDMS, the initial silica particle surfaces were partly modified by the chemical development of small zirconia nanoparticles, in an attempt to manipulate polymer adsorption.

Morphology was examined by scanning electron microscopy (SEM). Thermal transitions (focusing on glass transition) were monitored employing differential scanning calorimetry (DSC), while molecular dynamics was investigated in detail using two dielectric techniques, thermally stimulated depolarization currents (TSDC) and broadband dielectric relaxation spectroscopy (DRS), in wide frequency (10⁻⁴ to 10⁶ Hz) and temperature (–150 to 60 °C) ranges. All measurements were performed using instruments at the Physics Department of the National Technical University of Athens. Our results are discussed in relation to those obtained with Nitrogen adsorption-desorption isotherms (IPSD analysis), wide angle X-ray diffraction (WAXD), and Fourier transform infrared spectroscopy (FTIR), performed on the same materials in the laboratory where they have been synthesized.

The most important results that came out of this PhD Thesis may be described, in relation to hot soft matter issues in the literature, as follows. Extended measurements using different thermal treatments show that the good dispersion and strong interactions of the nanoparticles with PDMS restrict crystallization and segmental mobility of the polymer. 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 (dynamic glass transition), which was found to consist of three discrete and well defined relaxations. These relaxations arise from the bulk (unaffected) polymer (α relaxation), the mobility of polymer chains restricted between condensed crystalline regions (α_c relaxation)

and the segmental dynamics in an interfacial polymer layer around (or, in general, close to) the nanoparticles (α_{int} relaxation).

Compared with PDMS/silica, a shift of α_{int} to lower frequencies / higher temperatures and a larger thickness of the interfacial layer in the series of PDMS/titania conventional NCs, arise possibly from stronger polymer-titania hydrogen bonds as compared to PDMS-silica. This explanation is based on the different electrochemical properties of the surface hydroxyls of titania as compared to those of silica (-OH more acidic in titania). Taking into account recent literature, our results can be alternatively explained on the basis of the larger size of titania nanoparticles, as compared to silica. However, results obtained with core-shell NCs of titania and silica, both of low S_{BET} (surface roughness), demonstrate similar characteristics of α_{int} (dynamics, strength, cooperativity), being almost identical to those of PDMS/titania of the conventional type, independently of the initial particles dimension. Moreover, results by thermal annealing and dehydration of PDMS/silica show a slowing down and weakening of α_{int} . Additionally, the presence of the interfacial polymer fraction in the NCs results in increased internal polarization (e.g. high real part of dielectric permittivity, ϵ' , at very low temperatures) beyond additivity, while $\Delta\epsilon$ decreases systematically with temperature for low S_{BET} and increases for high S_{BET} . We recall that $\Delta\epsilon$ represents the population of the mobile (relaxing) molecular groups. Regarding the effects of molecular weight (MW) of PDMS, the interfacial polymer fraction is larger for the shorter polymer chains (lower MW), while α_{int} is slower, as compared to longer polymer chains (higher MW). Thus, combining all effects on the overall dielectric response (which is often not the case in the literature) we discuss results by employing a model that involves the formation of two types of segment conformations of the highly flexible PDMS chains at interfaces, namely (a) extended tails with bulk-like density but reduced mobility, and (b) loop-like chain segments with multiple contact points with the silica surface resulting in increased density and cooperativity. Obviously, both types of segments are characterized by increased orientation (order) and polarizability, as compared to segments in the bulk, which explains the increased dielectric response in the NCs beyond additivity. The loops / tails ratio increases with increasing S_{BET} . In addition, increase in surface roughness in the present work leads to increased number of contact points and, therefore, gradually denser interfacial layer. This implies reduction of the cooperativity length, thus, in the frame of Adam-Gibbs theory, faster and more cooperative segmental dynamics is expected, in agreement with results for α_{int} in the present thesis. Next to that, our results suggest that the tails to loops ratio should be larger for shorter PDMS chains (lower molecular weight), as compared to longer chains, due to increased concentration of free

polymer chain ends. Thus, we conclude that number and accessibility of contact points (surface properties of the particles) and structure and flexibility of polymer chain (polymer topology at the interfaces) dominate interfacial interactions.

Finally, measurements on PDMS adsorbed into the cylindrical-like pores of silica-gel (6-20 nm in diameter) show an additional glass transition step in DSC at lower temperature than that of bulk, while an additional segmental relaxation (α_p) faster than that in bulk was recorded by DRS. Both additional responses represent the spatially 2-D confined dynamics of PDMS, demonstrating, also, that the latter is sensitive to nanometric changes on spatial restriction of the polymer. On the contrary, thermal (crystallization) annealing did not impose any significant change on the respective glass transition (DSC) and dielectric process (α_p , DRS).

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