



Morphology and molecular dynamics investigation of low molecular weight PDMS adsorbed onto Stöber, fumed, and sol-gel silica nanoparticles

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ABSTRACT

Morphology, glass transition and molecular dynamics of polydimethylsiloxane (PDMS) adsorbed onto three types of silica nanoparticles, namely Stöber, fumed-pyrogenic, and silica gel, were studied employing scanning electron microscopy (SEM), isothermal nitrogen adsorption–desorption, calorimetry (DSC) and broadband dielectric spectroscopy (BDS) techniques. The initial Stöber particles (specific surface area $S_{\text{BET}} \sim 240 \text{ m}^2/\text{g}$) form a quite loose silica network with mainly textural pores of $\sim 12 \text{ nm}$ in size. Fumed silica ($S_{\text{BET}} \sim 260 \text{ m}^2/\text{g}$) demonstrates denser aggregation and increased textural porosity ($\sim 11 \text{ nm}$), while silica gel ($S_{\text{BET}} \sim 850 \text{ m}^2/\text{g}$) exhibits tremendous intraparticle porosity (tubular-like pores of $\sim 6 \text{ nm}$). On adsorption of PDMS (at ~ 20 and $\sim 30 \text{ wt}\%$), the glass transition temperature (T_g) decreases as compared to the bulk, while the glass transition step broadens. Results suggest loosened molecular packing of the polymer chains accompanied by a broadening of the range of relaxation times in the composites as compared to the neat polymer. On the other hand, the heat capacity step at glass transition is significantly suppressed in the composites, suggesting the formation of a rigid polymer fraction (RAF) at the interfaces with nanoparticles due to strong physical interaction (hydrogen bonding). RAF increases in the order Stöber < fumed (A300) < silica gel, this increase following that of S_{BET} , in agreement with results in previous work on silica/PDMS systems. Next to the segmental dynamics (α relaxation) of the bulk-like polymer related to the glass transition, BDS allowed the detection of a separate segmental-like relaxation of the polymer in the interfacial silica-PDMS zone. In terms of timescale the interfacial relaxation is almost identical for Stöber and A300, and slightly faster for silica gel. Comparison of the results of the present work with previous results obtained with similar nanocomposites based on low molecular weight PDMS and silica, provides additional support to recently proposed 'S_{BET}–interfacial dynamics' and 'chain packing–polymer dynamics' correlations.

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1. Introduction

Polymer nanocomposites (PNCs) have attracted much interest during the last decades, mainly because they often exhibit a significant improvement of various properties of the polymer matrix [1]. It is generally accepted that interfacial effects play a significant role in that [2,3], nevertheless, there is no theory yet to account for the significant improvement of properties of PNCs. With the

interfacial effects, we mean changes in structure and organization, thermal transitions, molecular dynamics and properties of the polymer at the interfaces with the filler nanoparticles (NPs) extending up to a few nanometers into the polymer matrix [4,5]. Due to the large surface-to-volume ratio of NPs, the polymer fraction at the interfaces with the filler becomes a considerable fraction of the polymer matrix and may affect or even dominate the overall performance of the PNC. Methodologies involving computer simulations [6–9], structural characterization (e.g. FTIR [10,11]), calorimetry [12–14], and dielectric spectroscopy [10,11,15–18] have been developed for the study of interfacial polymer characteristics.

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They showed that modified polymer properties are observed in an interfacial zone of 1–10 nm in thickness [10,12,19–25]. Kumar and co-workers have demonstrated that the interfacial layer thickness depends on the size [17], curvature [20] and shape [26] of the filler. Pissis and co-workers showed a respective dependence on the type of particles [16,18], surface roughness of the nanoparticles [27], molecular weight of the polymer [18,28], and method of nanocomposites preparation [29]. Furthermore, they suggested an interfacial chain packing–polymer dynamics relationship (Scheme 1) [18,24,28,30–32]. By focusing on filler shape, Tadiello et al. [33] studied PNCs of styrene butadiene rubber (SBR) and shape-controlled spherical and rod-like silica NPs with different aspect ratios (AR 1–5) and evidenced that the amount of interfacial rigid polymer increases with the particle anisotropy [33]. In the same context, Klonos et al. studied [34] polylactide–based PNCs filled with a variety of nano-inclusions of different geometries and obtained a systematic increase of interfacial polymer fraction with increasing of AR of the nano-inclusions [34]. Regarding strength of polymer–filler interaction, dielectric results in rubber/graphene oxide NCs indicated stronger interfacial interaction for hydrogen than for ionic bonding [35]. Qu et al. demonstrated the potential to tune interfacial interaction in poly (methyl methacrylate)/silica PNCs as a function of either nanofiller surface chemistry or polymer reactivity [36]. In the same regard, Lin et al. [11] managed to manipulate the degree of polymer–filler interactions in PNCs based on poly (vinyl acetate) PVAc filled with silica NPs, by gradually replacing the hydrophilic sites of silica (surface silanols) with hydrophobic (calcined) ones.

Polymer dynamics at the interfaces is under intensive investigation, however, several questions remain still open [5,37]. In many studies interfacial polymer in PNCs shows no mobility, i.e. it makes no contribution, neither to the glass transition in DSC measurements (Scheme 1b) [12,13,16,38] nor to segmental polymer relaxation in BDS measurements [17,34,39]. On the other hand, in several other cases, BDS measurements show that interfacial polymer exhibits retarded dynamics accompanied by suppressed cooperativity, as compared to polymer in bulk [10,11,16,18,23]. Results suggest that this retarded dynamics is more often observed in PNCs based on rubber and rubber-like polymers [15,16,35,40], most probably in relation to lower polymer chain rigidity [30,37,41]. For a more in-depth interpretation of results, models involving multimodal chain conformations [42], developed mainly for thin supported polymeric films [43–47], have been adopted for PNCs [18,30,48] (Scheme 1b).

During the last decade we studied effects of various parameters on interfacial polymer characteristics of polydimethylsiloxane (PDMS), the polymer of interest in the present study, namely, the type and size of metal oxide nanoparticles [21], the size of initial silica particles and the subsequent surface modification of silica particles [24,31], spatial confinement in silica-gel nanopores [30,32], the nanometric roughness of the particles [27], the molecular weight of PDMS below the entanglement threshold [18], the method of nanocomposites preparation (dispersion of particles in the polymer matrix against polymer adsorption onto the particles) [29], the hydration/dehydration of PNCs [49] and thermal annealing related to changes in the degree of polymer crystallinity [24]. In all the cases described above, PDMS interacts with the nanoparticles via hydrogen bonding [50]. Quite recently, we recorded effects arising from another type of polymer–particle interaction, namely, the so-called ‘CH– π ’ bond, in addition to the geometry of particles, by studying PDMS physically adsorbed onto carbon nanotubes (CNT) and graphite sheets [51]. The overall results revealed that, compared to other characteristics of the particles, their surface properties (roughness/porosity) govern the structure of the interfacial polymer [18,27,32,49,51].

In the present work we focus on the dynamics of the interfacial polymer in PDMS composites based on three types of silica (SiO₂) with different preparation method of nanoparticles, namely, Stöber, pyrogenic, and sol-gel methods. PDMS of the low molecular weight of ~3 kg/mol was physically adsorbed onto silicas from a solution, at the relatively low weight fractions of ~20 and ~30 wt% PDMS. Structure and morphology are examined by scanning electron microscopy (SEM) and isothermal nitrogen adsorption/desorption technique. Glass transition and segmental dynamics, both sensitive means for studying interfacial effects in PNCs [5], are investigated by differential scanning calorimetry (DSC) and broadband dielectric spectroscopy (BDS), respectively. Next to standard routes, interfacial dynamics is further investigated by imposing a thermal annealing process, related to the enhancement of polymer crystallization. Similar treatment in previous studies proved quite illuminating [24,30,32]. Results are analyzed by widely adopted methods and are discussed in comparison with similar results obtained recently with other PDMS-based PNCs. An overall scope of this study is to further check recently proposed models in the frame of the interpretation of experimental findings in similar systems [18,24,28,31,49], involving an interfacial polymer structure – dynamics relationship.

2. Experimental

2.1. Materials

Three types of initial silica (SiO₂), namely, (a) silica spheres prepared by employing the Stöber method [52], (b) fumed pyrogenic silica A300 [53], and (c) silica gel prepared by the Sol-Gel method [54], were used as substrates for physical polymer adsorption. A detailed description regarding preparation method of Stöber and gel silicas is given in section S.M.1 of the Supplementary Material.

Commercial polydimethylsiloxane (PDMS) (Kremniypolimer, Zaporozhye, Ukraine, linear, –CH₃ terminated, code names PDMS-50, with molecular weight W_m ~2970 g/mol, degree of polymerization d_p ~38) was adsorbed onto silicas in the amounts of 23 wt% (30 phr) and 33 wt% (50 phr). First, the oxide samples were dried at 150 °C for 2 h in vacuum. Then, 1 g of dried silica was mixed with a toluene solution of PDMS-50 (0.3/0.5 g of PDMS, 4 ml of toluene). The suspension was mechanically stirred for 30 min and finally dried at 80 °C under low pressure for 10 h. Composite samples are in the form of powder, similar to the initial silica powders, while neat PDMS-50 is liquid at room temperature.

PDMS and silica particles are expected to interact physically with each other [18,28,31] via hydrogen bond formation between the oxygens (–O–) in the backbone of PDMS and the surface hydroxyls (–OH) of the particles (Scheme 1) [55].

2.2. Scanning electron microscopy (SEM)

The particulate morphology was examined by field emission Scanning Electron Microscopy employing a Quanta™ 3D FEG (FEI Company, USA). The chamber operated at room temperature under high vacuum mode using a Through Lens Detector (TLD) at a voltage of 3 kV. Prior to the measurement, a thin layer of gold was developed on the surface of the sample by sputtering.

2.3. Textural characterization

The textural characteristics of initial fillers and of filler/PDMS composites were studied employing low-temperature (77.4 K) nitrogen adsorption–desorption isotherms technique [56] using an ASAP 2420 N (Micromeritics Instrument Corp., USA) adsorption

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