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Interactions of poly(dimethylsiloxane) with nanosilica and silica gel upon cooling–heating

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ABSTRACT

To control the properties of poly(dimethylsiloxane) (PDMS, Oxane 1000) as a bio-inert material, the characteristics of Oxane 1000 were compared for PDMS alone and interacting with silica gel Si-100 and nanosilica PS400. Low-temperature ^{1}H NMR spectroscopy, applied to static samples at 200–300 K, and differential scanning calorimetry (DSC) at 153–393 K were used to analyze the properties of PDMS and composites. The NMR study shows that liquid and solid-like fractions of PDMS co-exist over a broad temperature range. The cooling–heating cycles give hysteresis loops of intensity of ^{1}H NMR signals of methyl groups of a liquid fraction of PDMS vs. temperature depending on the silica type. The loop width differs for PDMS alone and bound to silicas, and the samples preheated at 420 K are characterized by much narrower loops. DSC measurements of the samples show a significant difference in the thermograms on the first and second DSC scans that depend on the silica type. For PDMS confined in pores of silica gel, 3D spatial structure of the polymers can be more ordered than that of PDMS located in thin layers at a surface of nanosilica. Therefore, both melting endotherms and crystallization exotherms are observed for PDMS/silica gel. However, for PDMS/nanosilica, both thermal features are much weaker and observed during only the first DSC scan.

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1. Introduction

Poly(dimethylsiloxane) (PDMS) and related polymers are widely used in industry (as lubricants, rubbers, membranes, hydrophobic adsorbents, etc.) and medicine (as bio-inert materials in implants, adsorbents) [1–4]. Inert PDMS as a stable material can be used over a broad temperature range in different media including aggressive ones [5–7]. PDMS materials are used in medicine as implants in a liquid state [8–11]. Notice that intraocular PDMS implants can cause opacification of both implants and tissues at their boundary or even repeated retinal detachment [11]. This negative effect can be due to intraocular formation of microcrystalline calcium salts that is promoted by interactions with some biopolymers. Investigations of these formations are difficult both *in vivo* and *in vitro*. Therefore, interactions of biopolymers with silicone oils were frequently studied using model systems, e.g. emulsions of PDMS in aqueous solutions of biomacromolecules or other systems. The emulsion stability can be increased in the presence of biomacromolecules or solid nanoparticles, but elucidation of the

mechanisms of solidification of PDMS and the opacification of the implants needs additional investigations [7–11].

Intermolecular interactions between PDMS macromolecules are provided by relatively weak van-der-Waals forces with a small contribution of electrostatic interactions. The latter is small because the dipoles of Si–O bonds direct oppositely since the Si–O–Si angle is large and easily varied in the 142–170° range. Weak intermolecular interactions in PDMS cause low temperatures of freezing, melting, crystallization and glass transition. In solid state, PDMS forms molecular crystals and the crystallization temperature is very low ($T_c \approx 185$ K at molecular weight (MW) of 45–44 kDa). This temperature is lower at smaller MW of PDMS, e.g. $T_c \approx 180$ K at MW ≈ 15 kDa. For PDMS and other nonpolar polymers, low thermal effects are characteristic during liquid–solid phase transition [6,12–15]. For van-der-Waals liquids, approaching to the phase transition temperature upon slow cooling leads to a strongly increase in the viscosity, then crystallites appear but a certain fraction remains in a liquid state [16]. However, at a high cooling rate, PDMS could be frozen in amorphous state. Appearance of solid nanoparticles (modeled here by nanosilica) or microparticles (e.g. silica gel) in the PDMS medium can strongly change its temperature behavior and other properties as it is shown below.

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A significant difference in the mobility of molecules in liquid, solid-like and crystalline fractions of PDMS allows one to study polymer features in detail at temperatures close to the phase transition point using the NMR spectroscopy [17–20]. The application of low-temperature ^{1}H NMR spectroscopy to static samples (to analyze only a liquid fraction) is an effective tool to study the phase transition effects [21–24].

The mobility of macromolecules depends on confined space effects [21,24,25]. These effects can be elucidated studying interactions of the same polymer with the same solid material in the form of porous macroparticles (e.g. silica gel) and nonporous nanoparticles (fumed nanosilica) possessing similar specific surface area accessible for macromolecules. A helix shape of PDMS molecules with six $O-Si-O$ bonds in a cycle [7] restricts a number of the segments directly interacting with a silica matrix surface to form the hydrogen bonds such as $\equiv SiO-H \cdots O(Si(CH_3)_2-)_2$. The PDMS conformation can be changed in the adsorption layer depending on the PDMS content and the type and texture of adsorbent. These aspects are of importance for composites based on flexible linear polymers and particulate oxides [22,26–28]. Therefore, the aim of this paper is to study the phase state of PDMS (Oxane 1000) alone and interacting with silica gel (Si-100) or nanosilica (PS400), which have close specific surface area of meso/macropores, at different temperatures using ^{1}H NMR spectroscopy at 200–300 K and DSC at 153–393 K.

2. Materials and methods

2.1. Materials

Silicone oil (poly(dimethylsiloxane), PDMS) Oxane 1000 (Opsia, Labege Cedex, France, viscosity $\sim$1000 cs, molecular weight 44–45 kDa, polymerization order $\sim$600, crystallization temperature $\sim$184 K [13,29]), silica gel Si-100 (Merck) with beads of 0.2–0.5 mm in diameter, and pyrogenic silicas (nanosilicas) PS400 and PS300 ($S_{BET} = 409$ and 297 m²/g, respectively) (Pilot plant of Chuiko Institute of Surface Chemistry, Kalush, Ukraine) were used. To study the interfacial behavior of silicone oil alone or bound to a silica surface depending on temperature, different silicas were selected with close mesoporosity. Before NMR measurements, the silicas were heated at 520 K to remove adsorbed water (residual amount of water <0.5 wt.%).

2.2. ^{1}H NMR spectroscopy

^{1}H NMR spectra of static samples (i.e. non-MAS) were recorded at 200–300 K using a Varian 400 Mercury spectrometer (magnetic field of 9.4 T) of high resolution with probing 90° pulses with duration of 3 μs with eight scans and 2 s delay between them.

Relative mean errors were smaller than ±10% for ^{1}H NMR signal intensity for overlapped signals and ±5% for single signals, and ±1 K for temperature. Repeated measurements of PDMS/silica gel and PDMS/nanosilica samples give a similar spectral picture at the same temperature. The ^{1}H NMR spectra were recorded during cooling of samples from 280–290 K to 200–210 K and then during heating to 290–300 K at a step $\Delta T = 10$ K and a heating rate of 5 K/min for 2 min and maintained at a fixed temperature for 7 min [21–24].

^{1}H NMR signal intensity was determined for static samples (non-MAS) to control only mobile molecules. This is due to short transverse relaxation time of solids (e.g. OH groups of silicas) and frozen adsorbates, i.e. frozen Oxane 1000 (melting temperature $T_m \approx 231$ K), and the use of a relatively narrow bandwidth of the spectrometer (20 kHz) [24]. This approach can be effectively used in NMR cryoporometry [24]. To determine chemical shift of the proton resonance (δ_H), tetramethylsilane (TMS) was used as an internal standard (δ_H errors < ±0.25 ppm).

2.3. Differential scanning calorimetry (DSC)

The thermal properties of the PDMS/silica samples were investigated in a nitrogen atmosphere at temperatures from 293 K to 153 K (cooling) and then to 393 K (heating) using a Perkin Elmer Pyris 6 DSC instrument (calibrated using indium). Samples ($\sim$8 mg) in aluminum pans were cooled and heated at the same rate of 10 K/min. For the first scan, the samples were cooled from 293 K to 153 K, held for 4 min, heated to 393 K and held for 2 min. For the second scan, the samples were cooled from 393 K to 153 K and heated again to 393 K.

2.4. Textural characteristics

The textural characteristics were determined from low-temperature (77.4 K) nitrogen adsorption–desorption isotherms recorded using a Micromeritics ASAP 2405N adsorption analyzer or a Quantachrome Autosorb adsorption analyzer. The specific surface area (S_{BET}) was calculated according to the standard BET method [30]. The total pore volume (V_p) was evaluated from the nitrogen adsorption at $p/p_0 = 0.98–0.99$ (p and p_0 denote the equilibrium and saturation pressure of nitrogen at 77.4 K, respectively).

The nitrogen desorption data were used to compute the pore size distributions (PSDs, differential $f_V(R) \sim dV_p/dR$ and $f_S(R) \sim dS/dR$) using a self-consistent regularization (SCR) procedure under non-negativity condition ($f_V(R) \geqslant 0$ at any pore radius R) at a fixed regularization parameter $\alpha = 0.01$ with a complex pore model including slit-shaped and cylindrical pores and voids between spherical nonporous nanoparticles packed in random aggregates (the SCV model was used with modified Nguyen-Do (MND) method) [31,32] for nanosilica and a model of cylindrical pores for silica gel. The differential PSDs (with respect to pore volume $f_V(R) \sim dV/dR$, $\int f_V(R) \, dR \sim V_p$) were re-calculated as incremental PSD (IPSD, $\sum \Phi_{V,i}(R) = V_p$). The differential $f_S(R)$ functions were used to estimate the deviation (Δw) of the pore shape from the model [24]. The $f_V(R)$ and $f_S(R)$ functions were also used to calculate contributions of nanopores (V_{nano} and S_{nano} at $0.35 < R \leqslant 1$ nm), mesopores (V_{meso} and S_{meso} at $1 < R \leqslant 25$ nm), and macropores (V_{macro} and S_{macro} at $25 < R < 100$ nm) to the total pore volume and surface area. Additionally, nonlocal density functional theory (NLDFT, Quantachrome software, a model of cylindrical pores) method was used to calculate differential PSDs converted into IPSDs.

2.5. Quantum chemical calculations

Quantum chemical calculations of PDMS fragments were carried out using *ab initio* and DFT (B3LYP and wB97XD) methods with the 6-31G(d,p) basis set using the Gaussian 09 [33] program suit to full geometry optimization. The gauge-independent atomic orbital (GIAO) method [33] with the DFT method (B3LYP) and the 6-31G(d,p) basis set was used.

Silica clusters modeling a porous silica particle ($\sim$1 nm in radius, 1624 atoms) with PDMS (18 units) and water molecules adsorbed in pore or at the outer surface were calculated using the PM7 method (MOPAC 2012 package) [34–36]. To calculate the $f(\delta_H)$ functions using the PM7 results, the calibration functions were used to describe the dependence between atomic q_H charges (PM7) and the δ_H values (GIAO/B3LYP/6-31G(d,p)) calculated for a small fragment of PDMS with seven units and water clusters with 8–64 molecules [16,24].

To analyze interaction features between PDMS molecules the interaction energy decomposition was carried out using the Morokuma method with basis set superposition error (BSSE) correction