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MOLECULAR DYNAMICS IN NANOSTRUCTURED POLYIMIDE-SILICA HYBRID MATERIALS AND THEIR THERMAL STABILITY

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Summary: Molecular motion and thermal stability in two series of nanophase-separated polyimide-silica (PI-SiO_2) hybrid networks with chemically bound components were studied. The hybrids were prepared via a sol-gel process and differed in PI structure and chain length, and in SiO_2 content ranging from 10 to 50 wt.%. Differential scanning calorimetry, laser-interferometric creep rate spectroscopy, dielectric relaxation spectroscopy, thermally stimulated depolarization current techniques, and thermogravimetry were used covering, on the whole, the ranges of 100-900 K and 10^{-3}-10^{9} Hz. Silica domains influenced PI dynamics in two opposite directions. Loosened segmental packing in chains confined to nanovolumes resulted mainly in rise of small-scale motion below β-relaxation region, while anchoring of chain ends to 'rigid walls' caused, contrarily, a partial or total suppression of segmental motion above T_β, especially drastically at the temperatures close to and within glass transition. The latter resulted in a large change in thermal stability, e.g., 2.5-fold increasing of the apparent activation energy of thermooxidative degradation, and more than 100^0 rise of predicted long-term thermal stability for the hybrids as compared to that for PI.

Introduction

In recent years an increased attention has been paid to organic-inorganic polymer hybrids prepared via the sol-gel process, basically by hydrolysis-condensation reaction of alkoxysilane in the presence of a polymer or oligomer (Refs. 1-11). Of special interest are homogeneous hybrids with 10-100 nm size silica domains covalently bound with a polymer. The latter was attained by using of the 'end-capping agent' forming trialkoxysilyl groups at chain ends (e.g., Refs. 4, 5). The hybrids promise improvement on some of polymer properties and their potential applications to optical waveguides, biosensors, membranes,

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biocompatible and aerospace materials, etc. (Refs.1, 2, 4, 5, 10). However, there is only limited infomation on hybrid properties so far. In this research, two series of PI-SiO_2 hybrids were prepared, and their molecular dynamics and thermal stability were studied.

Experimental

The hybrids were prepared via a sol-gel process (Ref. 4). On the first stage, the starting materials, *p*-aminophenyl(trimethoxysilane)terminated poly(amic acid)s, based on (**I**) 3,3'-oxydiphthalic anhydride or (**II**) 4,4'- (hexafluoroisopropylidene) diphthalic anhydride, and 4,4'-diaminodiphenylether, were obtained as PI_1 and PI_2 precursors, respectively. In turn, tetramethoxysilane (TMOS) as silica precursor was used. Adding of TMOS and water to end-capped poly(amic acid) resulted in hydrolysis of methoxysilane groups. When heating, silanol condensation and imidization reactions simultaneously proceeded resulting in formation of nanostructured PI-SiO_2 hybrids where the silica domains of ca.50-100 nm size were covalently bound with PI chain ends (Ref. 4). Two series of transparent films of 0.2-0.5 mm thickness with various compositions, PI_1-*m/n* or PI_2-*m/n,* were prepared where m = 5 or 7.5, or 10 corresponded to M_n = 5.000 or 7.500, or 10.000 for PI, and n designated SiO_2 content ranging from 10 to 50 wt.%. To compare, microphase-separated PI-SiO_2 blend without chemical bonding between the components was prepared.

Differential scanning calorimetry (DSC-2, 300-640 K, heating rates of 5, 10, 20 or 40 K min^{-1}, correlative frequency $\nu_{corr} \approx 10^{-2}$ Hz) was used for estimation of temperature, T_g , temperature range, $\Delta T_g = T_g'' - T_g'$, heat capacity step, ΔC_P, and activation energy, Q, in the glass transition. Relaxation spectra below T_g were obtained by three methods: (a) creep rate spectroscopy (CRS), under tensile stress of 1 MPa, at 280-520 K; (b) dielectric relaxation spectroscopy (DRS), at 210-430 K and 10^{-2}-10^{9} Hz (a Schlumberger Frequency Response Analyzer FRA 1260), and (c) thermally stimulated depolarization current (TSDC) technique, at 100-300 K and $\nu_{corr} \approx 10^{-3}$ Hz. The original CRS was described elsewhere (Refs. 12-14). The apparatus for TSDC measurements was described in Ref. 15. Thermogravimetric analysis (TGA) was carried out by using of Du Pont 990 Thermal Analyzer, at heating in air over the range of 20-640°C, with the rates of 5, 10 or 20 K min^{-1}.

Results and Discussion

Fig.1 shows that silica domains influence PI dynamics in two ways: decrease the creep rates at temperatures $T>T_\beta$, especially near the glass transition, but much increase the creep rates

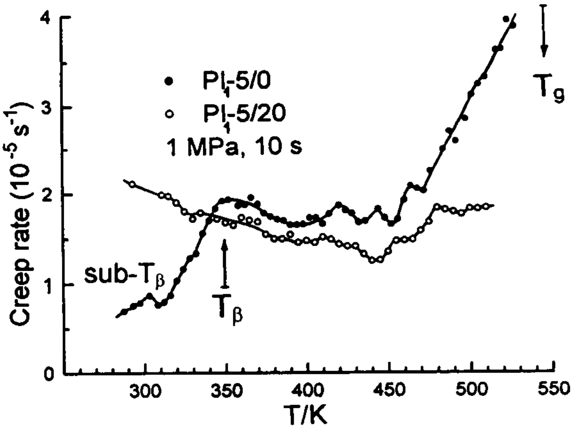

Fig.1. Creep rate spectra of PI_1 and PI_1-SiO_2 hybrid obtained under extension.

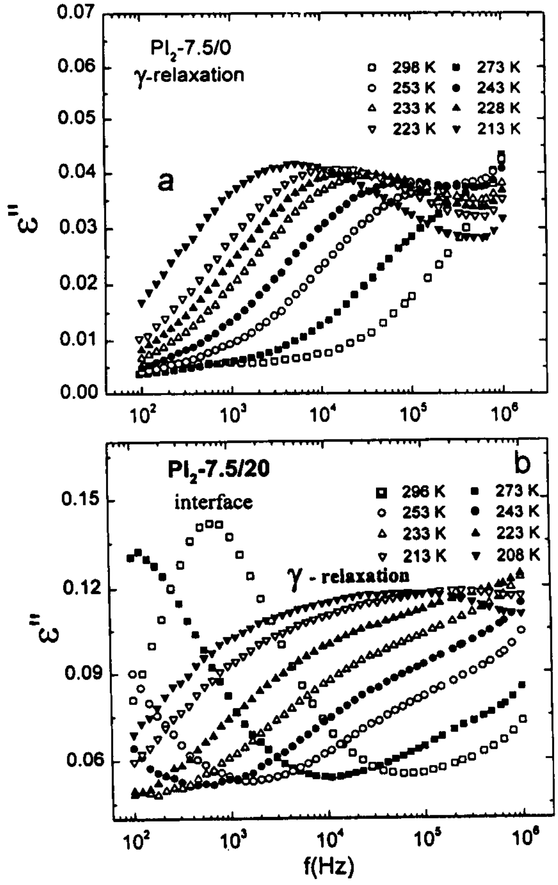

Fig.2. Dielectric loss vs. frequency plots measured for PI_2 (a) and PI_2-SiO_2 hybrid (b) at indicated temperatures.

measured at $T < T_\beta$. According to the concept of common origin of α- and β-relaxations (Refs. 16, 17), they are considered as intermolecularly cooperative or non-cooperative motion of Kuhn segments, respectively. We assumed that anchoring of chain ends to silica domains may suppress segmental motion but loosened segmental packing of chains confined to nanoscale volume may, contrarily, enhance small-scale motion below T_β and, sometimes, decrease the degree of cooperativity of segmental motion (Ref.16).

The DRS, TSDC and DSC data obtained validated this idea. Really, the dielectric loss $\varepsilon''(f)$ spectra indicate enhancing of γ-relaxation and arising of the new peak, at lower frequency, in the hybrids (Fig. 2). The latter may tentatively be associated with the same kind of motion as in γ-relaxation, e.g., imide cycle vibration (Ref. 18), but occurring at interfaces. Activation energies estimated for β, γ - and new relaxations equaled 140, 45 and 60-70 kJ mol^{-1}, respectively. TSDC spectra (Fig.3) also exhibit a new peak for the hybrid with 20% silica and an overall enhancing of small-scale motion with silica content.

DSC data showed drastic changes in PI glass transition characteristics for the hybrids. As seen from Fig.4, 3-4-fold broadening of ΔT_g range is observed. It is displaced to lower temperatures for the PI$_1$-SiO$_2$ blend but to both lower and higher temperatures in the hybrids with the longer PI$_1$ chains. For the hybrids with the shortest PI$_1$ chains (molecular mass of 5.000) consisting of 3-4 Kuhn segments only (Ref. 16), or for the PI$_2$-7.5/30 hybrid with more rigid chains, glass transition was displaced by ca.20-40K to higher temperatures. Accordingly, when reducing T_g the activation energy of segmental motion in ΔT_g range decreased from 500 kJ mol^{-1}, for PI, to ca.300 kJ mol^{-1}, but it attained of ~ 600 kJ mol^{-1} when T_g increased. This reflected the above tendencies of silica influence, viz., (a) of loosening of molecular packing resulting in some reduction of T_g and cooperativity degree, and (b) of anchoring the chain ends to 'rigid walls'.

Suppressive influence of silica domains on PI glass transition may also be seen from the ΔC_p vs. SiO$_2$ content plots (Fig. 5): ΔC_p step anomalously decreased with silica content and shortening of PI$_1$ chains as well as for more rigid PI$_2$ chains. For the hybrids with 40÷50 wt.% of silica and the shortest PI$_1$ chains, total suppression of cooperative motion in the glass transition was observed since ΔC_p step vanished (Figs. 4 and 5).

Finally, suppression of segmental motion in the hybrids led to their improved resistance to thermooxidative degradation. Figs. 6a and 6b show an increase in thermal stability with silica content, and temperature shift, by ca.100 K, of an onset of real chain degradation in the hybrid. As seen from Fig. 6c, the apparent degradation activation energy increased with silica

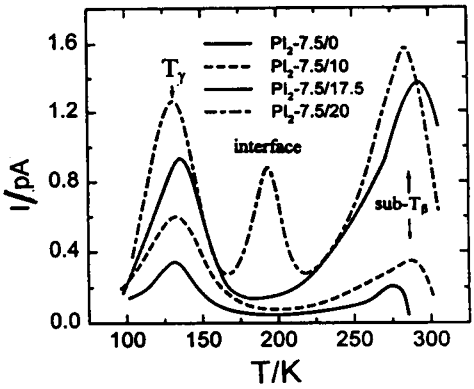

Fig. 3. TSDC thermograms of PI_2 and PI_2-SiO_2 hybrids measured at temperatures below β-relaxation region ($f \approx 10^{-3}$ Hz). Polarization conditions: V_p = 100V, T_p = 25°C, t_p = 5 min., cooling rate of 6°C/min. Heating rate equaled 3°C/min.

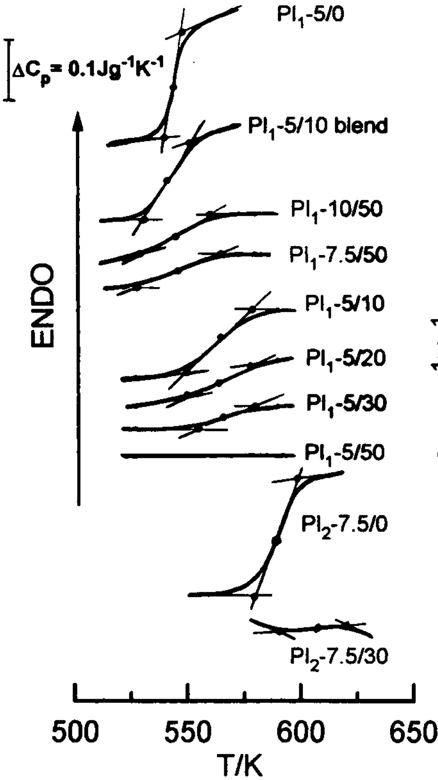

Fig. 4. DSC curves obtained in the glass transition region for PI and PI-SiO_2 hybrids differing in chain structure and length, and silica content. Measuring at scan II, after heating to 640 K and cooling to 300 K with the rate of 320 K/min. Heating rate 20 K/min.

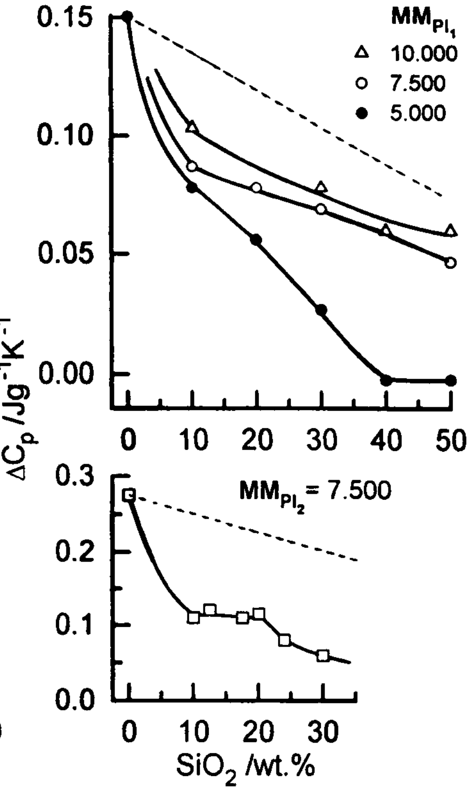

Fig. 5. Heat capacity step, ΔC_p, in glass transition vs. silica content plots for the PI_1-SiO_2 (above) and PI_2-SiO_2 hybrids (below). Dotted lines indicate calculated decrease in a step.

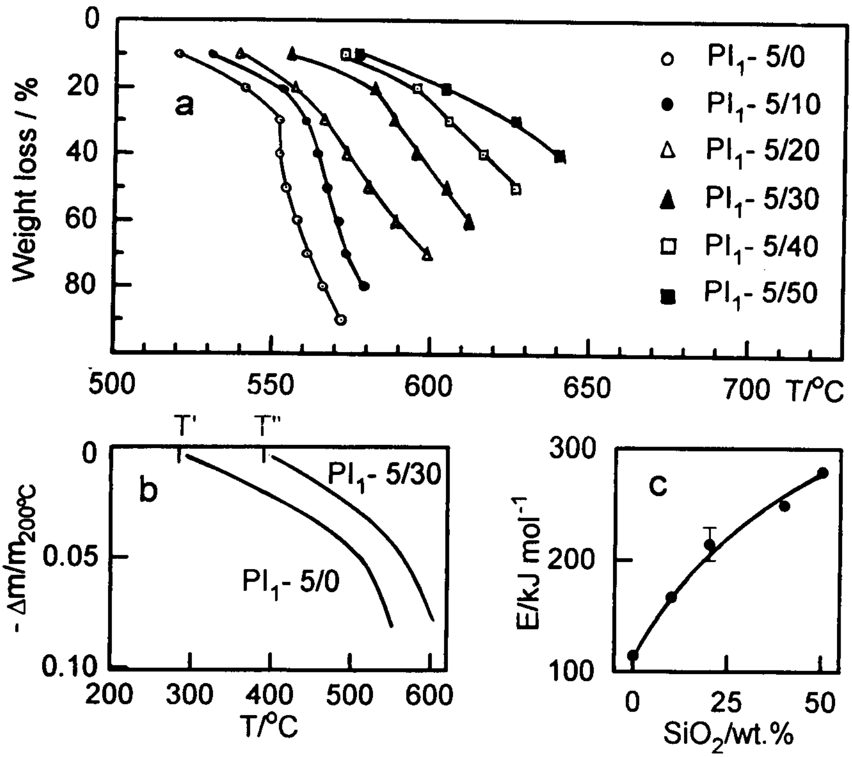

Fig. 6. Thermooxidative degradation of PI_1 and PI_1-SiO_2 hybrids.
a: TGA-curves, heating rate of 5 K/min; b: weight loss regarding sample weight at 200°C (T' and T" correspond to the onset of real chain degradation). c: apparent activation energy of the degradation process as a function of silica content in a hybrid

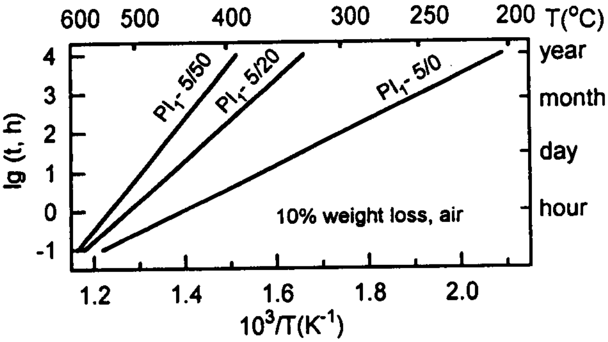

Fig. 7. Predicted thermal longevity vs. temperature plots obtained for PI_1 and the hybrids.

content in a hybrid, from 110 kJ mol^{-1} for PI up to 280 kJ mol^{-1} in the PI_1-5/50 composition. Assuming, for simplicity, the degradation process as the first-order reaction, we predicted the temperatures of long-term thermal stability of the samples under study. Fig. 7 shows large increase predicted for hybrid thermal stability. So, 10% weight loss may be attained for one year at 200^{0}C for PI but at 380^{0}C only for the PI$_1$-5/50 hybrid. Thus, introducing of inorganic nanodomains into a polymer, with covalent bonding of both components, may suppress segmental motion and substantially improve its thermal stability.

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