

Adhesive and surface behaviour of polyimide-polysiloxane elastomers

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Abstract: *Adhesive and surface behaviour of polyimide-polysiloxane elastomers.* The poly(imide-siloxane) (PIS) block copolymers containing siloxane blocks are suitable for industrial application, e.g. in microelectronics, and this kind of the block copolymers are used as high-performance adhesives and coatings. PIS block copolymers were studied with respect to their structure surface and adhesive properties relationship. The study of the morphology of PIS copolymers characterized by Atomic Force Microscopy (AFM) shows a growth of the surface roughness by increase of the content of siloxane. The relatively small amount of siloxane in PIS block copolymer, 10 – 20 wt. %, decreased significantly the surface energy of the PIS copolymer, as well as the polar component of surface energy. The increase of PIS the surface hydrophobicity reduced the peel strength of adhesive joints.

Keywords: surface properties, polyimide-polysiloxane elastomers, starch plasticizer

INTRODUCTION

The poly(imide-siloxane) (PIS) block copolymers containing siloxane blocks [1 – 4] are suitable for many industrial applications and they are used as high-performance adhesives and coatings. The surface as well as adhesive properties of PIS copolymers depend on the content and length of siloxane blocks. The surface properties of PIS copolymers are determined with content of siloxane segments in copolymer [5]. The PIS can be modified by starch containing a large amount of hydroxyl groups as the silica. Starch/plasticizer polymer composites have been suggested for use in elastomer composition for various purposes, including tires. In this contribution, the surface analysis of PIS copolymers using various methods of investigation was realised.

EXPERIMENTAL

Measurement methods

AFM

The surface morphology of the PIS copolymers were performed by AFM. All measurements were performed under ambient conditions using a commercial atomic force microscope (NanoScope™ Dimension IIIa, MultiMode Digital Instruments, USA) equipped with the PPP-NCLR tapping-mode probe (Nanosensors™ Switzerland; spring constant 39 N.m⁻¹, resonant frequency ≈ 160 kHz). Surface properties of all films were measured on size of x and y axis from 2 μm to 25 μm on different positions of the films in order to find out characteristic and significant surface features. TappingMode AFM technique was used for all images. This technique allows obtaining two- or three-dimensional information of both height and material heterogeneity contrast with high resolution when recording height and phase shifts simultaneously.

Surface energy

The surface energies of PIS block copolymer were determined by of contact angles measurements of testing liquids set (i.e. re-distilled water, ethylene glycol, formamide,

methylene iodide, 1-bromo naphthalene) using SEE (Surface Energy Evaluation) system containing a web camera (Masaryk University, Czech Republic). The drop of the testing liquid ($V = 3 \mu\text{l}$) was placed on the polymer surface, and a contact angle of the testing liquid was measured. The surface energies of the polymer were evaluated by Owens-Wendt-Rabel-Kaelble equation modified by the least squares method:

$$\frac{(1 + \cos \theta) \gamma_{LV}}{2} = (\gamma_{LV}^d \gamma_s^d)^{1/2} + (\gamma_{LV}^p \gamma_s^p)^{1/2} \quad (1)$$

where:

- θ = contact angle of testing liquid (deg),
- γ_{LV} = surface free energy (SFE) of the testing liquid ($\text{mJ} \cdot \text{m}^{-2}$),
- $\gamma_{LV}^d, \gamma_{LV}^p$ = dispersion component (DC), and polar component (PC) of SFE of the testing liquid ($\text{mJ} \cdot \text{m}^{-2}$),
- γ_s^d, γ_s^p = DC, and PC of SFE of the polymer ($\text{mJ} \cdot \text{m}^{-2}$).

Peel strength of adhesive joint

The strength of adhesive joint (P) to epoxy adhesive was carried out with 90 deg peeling of adhesive joint using 5 kN dynamometer Instron 4301 (Instron, England). The width of the adhesive joint was 20 mm, and its length was 160 mm. The adhesive joints were prepared from PIS copolymer foils bonding together using epoxy adhesive. The speed of peeling of the adhesive joint was $1.5 \text{ mm} \cdot \text{min}^{-1}$.

RESULTS AND DISCUSSION

Poly(imide-siloxane) block copolymers with the amount of siloxane moieties 10, 20 and 30 (and 33) wt. % were prepared. The imide/siloxane ratio was evaluated by using ^1H NMR spectroscopy. The theoretical molecular weight of these copolymers was $40,000 \text{ g} \cdot \text{mol}^{-1}$. The imide blocks were based on ODPa and BIS P (monomers). The polyimide control with $M_n = 40,000 \text{ g} \cdot \text{mol}^{-1}$ based on ODPa and BIS P was also synthesized.

AFM measurements

The AFM measurements of the PIS copolymers are summarized in Figure 1. AFM measurements of the surface topography (height image) and tip-sample interaction (phase image) of the samples containing 0 to 33 wt. % of siloxane monomer revealed differences in both characteristics. Only characteristic samples, i.e. 0, 10, 20, and 33 wt. % of siloxane are shown in the Figure 1; sample containing 30 wt. % of siloxane is very similar in height and phase images to the sample with 33 wt. % of siloxane and thus it is not shown here. The comparison of height images: samples containing 20 % (Figure 1e) and 30 % (not shown here) have rugged and funicular surface relief. On the other hand, surfaces of net polyimide (Figure 1a), 10 % copolymer (Figure 1c) and 33 % copolymer (Figure 1d) contain individual formations on the surfaces – “hills” of different size and height (tens to hundreds nm) and furthermore holes (tens of nm size) on 10 % sample.

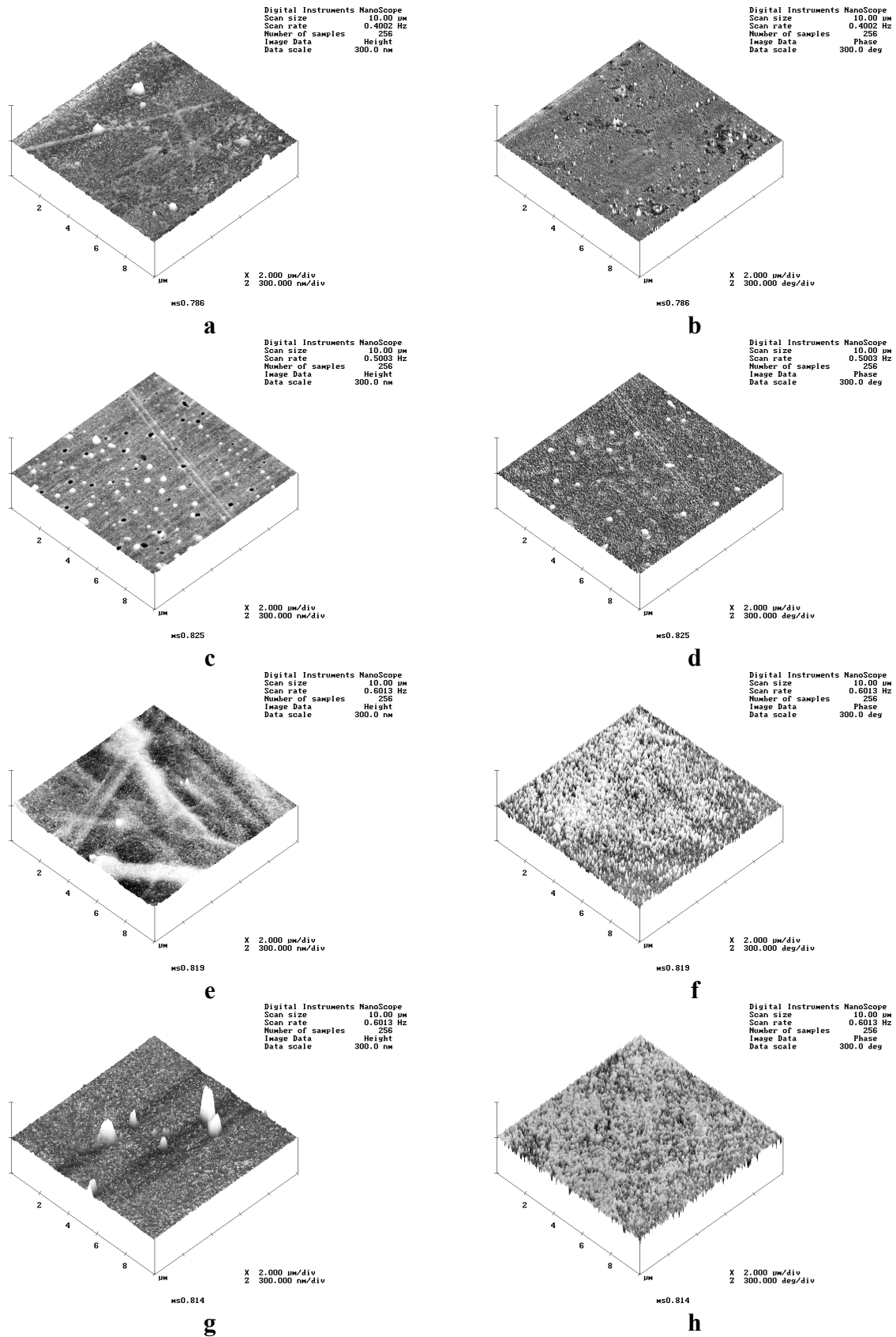


Fig. 1 AFM images of PIS block copolymers films: pristine polyimide (a, b), 10 wt. % of siloxane (c, d), 20 wt. % of siloxane (e, f), and 33 wt. % of siloxane (g, h). Height images (a, c, e, g), and phase (b, d, f, h) images, resp.

Moreover, funicular formations are shadowed also in the Figure 1a and 1c. Comparison of phase images: Figures 1b vs. 1d, and 2f vs. 2h exhibit mutually similar relief. If compared the phase images with the relevant topography images, i.e. Figure 1a vs. 1c and Figure 1e vs. 1g, it is evident: while height images are similar for first couple as well, significant differences for second couple exist. From these results follows that changes in tip sample interactions (phase images) jump between 10 and 20 % copolymer, and over 20 % remain practically identical in spite of surface topography changes of samples containing 20 % of siloxane and more (height images).

Surface energy

The dependencies of the surface energy, and its polar component of PIS block copolymer determined by OWRK (Owens-Wendt-Rabel-Kaelble) (1) method vs. content of siloxane in copolymer are shown in Figure 2.

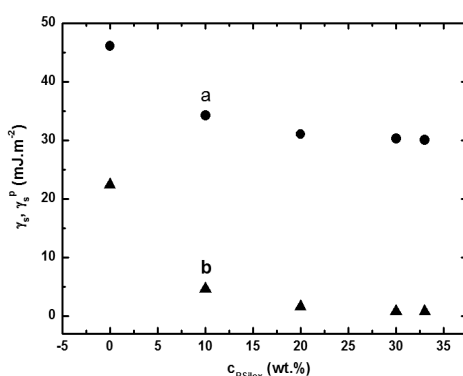


Fig. 2 Surface energy (a), and its polar component (b) of PIS block copolymer vs. siloxane content

The surface energy of PIS block copolymer decreases significantly with the concentration of siloxane from $46.0 \text{ mJ}\cdot\text{m}^{-2}$ (net polyimide) to $34.2 \text{ mJ}\cdot\text{m}^{-2}$ (10 % of siloxane), and to $30.2 \text{ mJ}\cdot\text{m}^{-2}$ (30 % of siloxane). The polar component of the surface energy reached the value $22.4 \text{ mJ}\cdot\text{m}^{-2}$ (net polyimide), which decreases with content of siloxane in PIS copolymer to $4.6 \text{ mJ}\cdot\text{m}^{-2}$ (10 % of siloxane) and $0.8 \text{ mJ}\cdot\text{m}^{-2}$ (30 % of siloxane). In the case of further increase of siloxane concentration (above 20 % of siloxane), the surface energy of PIS copolymer, and its polar component is levelled off. The surface energy of net polyimide is $46 \text{ mJ}\cdot\text{m}^{-2}$, while the value of the surface energy of poly (dimethyl siloxane) is only $20.9 \text{ mJ}\cdot\text{m}^{-2}$. The polyimide segments at room temperature are below their glassy temperature, thus these components of PIS copolymer are not mobile and their migration to the surface area is obviously restricted.

Adhesive properties

Figure 3 shows the dependence of the peel strength of adhesive joint PIS block copolymer-epoxy vs. content of siloxane. It is seen that the peel strength of adhesive joint PIS copolymer-epoxy decreases with growth in siloxane content in the whole concentration range. The fact that the strength of the adhesive joints decreases with increase in siloxane content reflects the increases hydrophobicity of the polymeric surface. The peel strength of adhesive joint to epoxy adhesive diminished from 1.2 N/mm (pristine polyimide), to 1.05 N/mm (10 % of siloxane), and to 0.65 N/mm (30 % of siloxane). This decrease of peel strength of adhesive

joint is relatively steady and almost linear for all investigated content of siloxane in block copolymer.

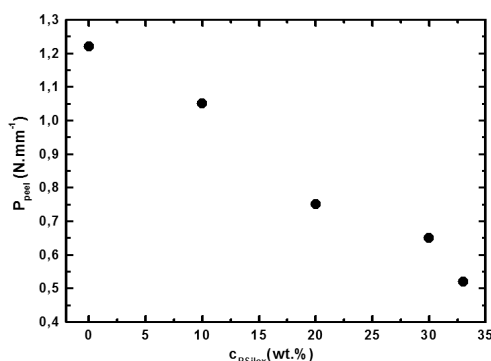


Fig. 3 Peel strength of adhesive joint PIS block copolymer-epoxy vs. concentration of siloxane

CONCLUSIONS

The significant increase of roughness of PIS copolymer surface, if the content of siloxane is growing, was observed. In the case of increasing the content of siloxane in copolymer, the surface energy, and its polar component of PIS copolymer diminished, the dispersive component of the surface energy on opposite increased. If content of siloxane in PIS copolymer rises up, the peel strength of adhesive joint to epoxy decreases almost linearly.

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Streszczenie: *Własności klejowe i powierzchniowe elastomerów poliimidowo-polisiloksanowych.* Kopolimery poliimidowo-polisiloksanowe (PIS) znajdują zastosowanie w przemyśle, przykładowo mikroelektronice, oraz używane są jako kleje i powłoki wysokiej jakości. Testowano kopolimery PIS pod względem struktury powierzchni i jej związku z własnościami klejowymi. Morfologia kopolimerów PIS opisana za pomocą mikroskopu sił atomowych (AFM) wykazuje wzrost chropowatości powierzchni przy wzroście zawartości siloksanów. Niska zawartość siloksanu (10-20% wagowo) w kopolimerze PIS znacząco zmniejsza jego energię powierzchniową. Zwiększenie hydrofobowości kopolimeru zmniejsza wytrzymałość na odrywanie połączeń klejowych.

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