

Adhesion and surface energy of polyimide-based copolymer

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Abstract: *Adhesion and surface energy of polyimide-based copolymer.* Several sorts of block polyimide based copolymers, namely poly(imide-co-siloxane) (PIS) block copolymers containing siloxane blocks in their polymer backbone have been investigated. In comparison with pure polyimides the PIS block copolymers possess some improvements, e.g. enhanced solubility, low moisture sorption, and their surface reaches the higher degree of hydrophobicity already at low content of polysiloxane in PIS copolymer. This kind of the block copolymers are used as high-performance adhesives and coatings. The surface as well as adhesive properties of PIS block copolymers depends on the content and length of siloxane blocks. The surface properties of PIS block copolymers are strongly influenced by enrichment of the surface with siloxane-based segments. Micro phase separation of PIS block copolymers occurs due to the dissimilarity between the chemical structures of siloxane, and imide blocks even at relatively low lengths of the blocks. The surface analysis of PIS block copolymers using various methods of investigation e.g. contact angle measurements, SEM, TEM, AFM, ATR-FTIR, and XPS, was performed, and the strength of the adhesive joint to more polar polymer was studied. The surface and adhesive properties are discussed in view of the varied composition of PIS block copolymers.

INTRODUCTION

Polyimides present an important class of polymers, necessary in microelectronics, printed circuits construction, and aerospace investigation, mainly because their high thermal stability and good dielectric properties [1-4]. Poly(imide-co-siloxane) (PIS) block copolymers containing siloxane blocks in their polymer backbone have been investigated [5,6]. In comparison with pure polyimides the PIS block copolymers possess some improvements, e.g. enhanced solubility, low moisture sorption, and their surface reaches the higher degree of hydrophobicity already at low content of polysiloxane in PIS copolymer. This kind of the block copolymers are used as high-performance adhesives and coatings. The surface as well as adhesive properties of PIS block copolymers depends on the content and length of siloxane blocks. The surface properties of PIS block copolymers are strongly influenced by enrichment of the surface with siloxane segments [7]. Micro phase separation of PIS block copolymers occurs due to the dissimilarity between the chemical structures of both siloxane, and imide blocks.

EXPERIMENTAL

2-Aminoterminated ODPa-BIS P polyimides with controlled molecular weight were synthesized by solution imidization (first step in NMP at room temperature for 24 h, second step in NMP-BCB mixture at 180 °C). The number-average molecular weights of products were in the range $M_n = 2000-18,000$ g/mol (by ¹H NMR spectroscopy). The surface morphology (height image) and local surface heterogeneities (phase image) were measured 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 (NanosensorsTM Switzerland; spring constant 39 N/m, resonant frequency 160 kHz). The surface energy of PIS block copolymer was determined via measurements of contact angles of a set of testing liquids (i.e. re-distilled water, ethylene glycol, formamide, methylene iodide, 1-bromo naphthalene) using SEE (Surface Energy Evaluation) system completed with a web camera (Masaryk University, Czech Republic) and necessary PC software. The drop of the testing liquid ($V = 3 \mu\text{l}$) was placed with a micropipette ($0\text{--}5 \mu\text{l}$, Biohit, Finland) on the polymer surface, and a contact angle of the testing liquid was measured. The peel strength of adhesive joint (P_{peel}) to polyacrylate was measured by 90° peeling of adhesive joint using universal testing machine Instron 4301 (Instron, England) with 100 N measuring cell. The adhesive joints for peel tests were fixed in aluminum peeling circle.

RESULTS AND DISCUSSION

The AFM measurements of the PIS copolymers are shown in Fig. 1. AFM measurements of the surface topography (height image) and tip-sample interaction (phase image) of the samples containing 0–33 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 Fig. 1; sample containing 30 wt.% of siloxane is very similar in height and phase images to the sample with 33 wt.% siloxane and thus it is not shown here.

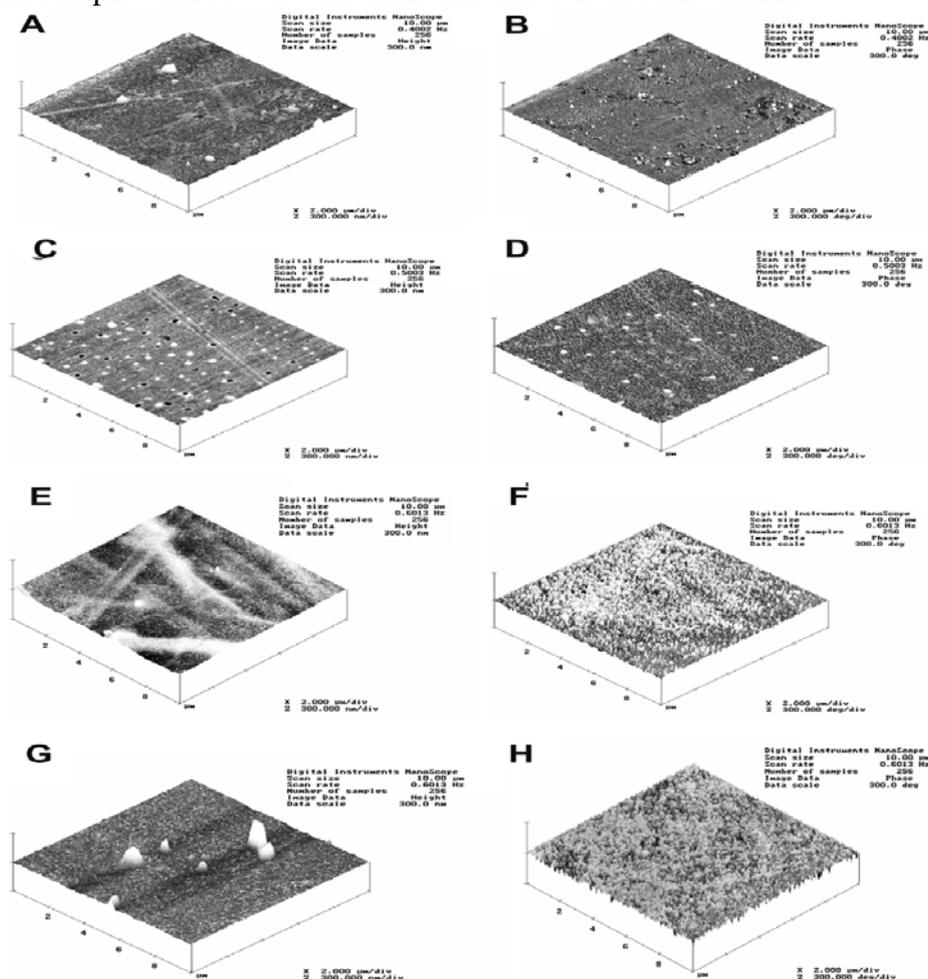


Figure 1 AFM images of PIS block copolymers films: pure polyimide (A, B), 10 wt.% of siloxane (C, D), 20 wt.% of siloxane (E, F), and 33 wt.% of siloxane (G, H) Height images (A, C, E, G), and phase (B, D, F, H) images, respectively.

The comparison of height images: samples containing 20% (Fig. 1E) and 30% (not shown here) have rugged and funicular surface relief. On the other hand, surfaces of pure polyimide (Fig. 1A), 10% copolymer (Fig. 1C) and 33% copolymer (Fig. 1D) contain individual formations on the surfaces – “hills” of different size and height (tens–hundreds nm) and furthermore holes (tens of nm size) on 10% sample. Moreover, funicular formations are shadowed also in the Fig. 1A and C. Comparison of phase images: Fig. 1B vs. 1D, and 1F vs. 1H exhibit mutually similar relief. If compared the phase images with the relevant topography images, i.e. Fig. 1A vs. C and Fig. E vs. G, it is evident while height images are similar for first couple as well, significant differences for second couple exist.

Fig. 2 shows the contact angles of re-distilled water deposited on PIS block copolymer surface vs. content of siloxane in copolymer. The contact angles of water by Fig. 2 increased by growth of siloxane content and/or Si/N ratio in copolymer. The contact angles of PIS block copolymer increase from 76° for pure polyimide, to 95° for 10% of siloxane in copolymer up to 102° for 30% of siloxane in copolymer. Micro phase separation in PIS block copolymer occurs even at relatively low block lengths due to dissimilarity between the chemical structures of the siloxane, and imide blocks.

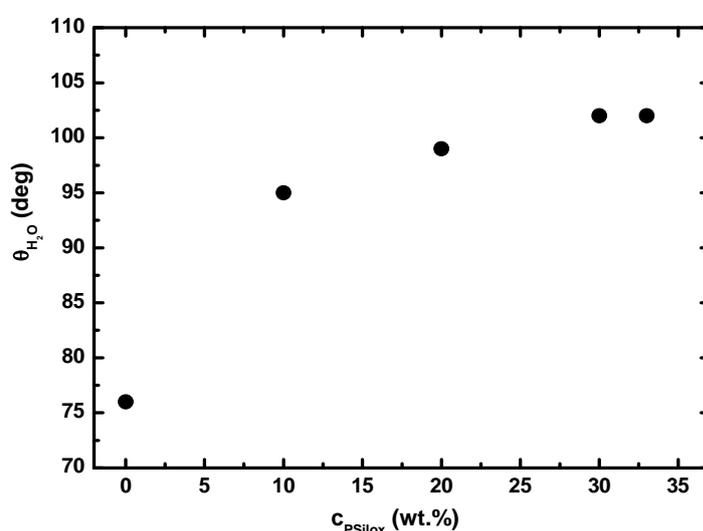


Figure 2 Contact angles of water vs. siloxane content in PIS block copolymer.

The dependencies of the surface energy, and its polar component of PIS block copolymer determined by OWRK (Owens-Wendt-Rabel-Kaelble) method [7] vs. content of siloxane in copolymer are shown in Fig. 3. The surface energy of PIS block copolymer decreases significantly with the concentration of siloxane from 46.0 mJ.m^{-2} (pure polyimide) to 34.2 mJ.m^{-2} (10 % of siloxane), and to 30.2 mJ.m^{-2} (30 % of siloxane). The polar component of the surface energy reached the value 22.4 mJ.m^{-2} [pure polyimide], which decreases with content of siloxane in PIS copolymer to 4.6 mJ.m^{-2} (10 % of siloxane) and 0.8 mJ.m^{-2} (30 % of siloxane) The surface energy of pure polyimide is 46 mJ.m^{-2} , while the value of the surface energy of poly (dimethyl siloxane) is only 20.9 mJ.m^{-2} . At room temperature the siloxane molecules are above their glass temperature, their segments are capable to migrate to the polymeric surface, so making it more hydrophobic. The surface of the PSI copolymer films should be covered with polysiloxane segments having their thickness in molecular order.

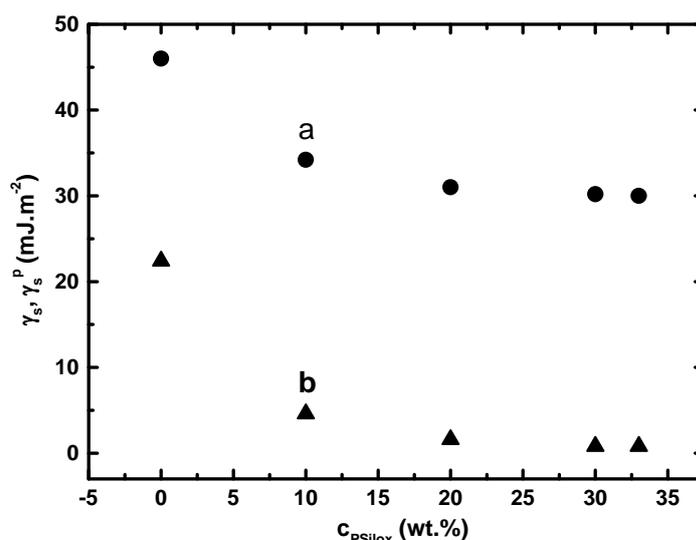


Figure 3 Surface energy, and its polar component of PSI block copolymer vs. siloxane content.

Fig. 4 shows the dependence of the peel strength of adhesive joint PSI block copolymer to 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 MPa (pure polyimide), to 1.05 MPa (10 % of siloxane), and to 0.65 MPa (30 % of siloxane). This decrease of peel strength of adhesive joint is relatively steady for all investigated content of siloxane in block copolymer. Comparing polyimide with PSI block copolymer containing 30 % of siloxane shows that the peel strength of adhesive joint to epoxy decreased more than two times. The presence of siloxane in PSI block copolymer caused the more hydrophobic surface of copolymer (surface energy of copolymer containing 10 % of siloxane was 34.2 mJ.m⁻²).

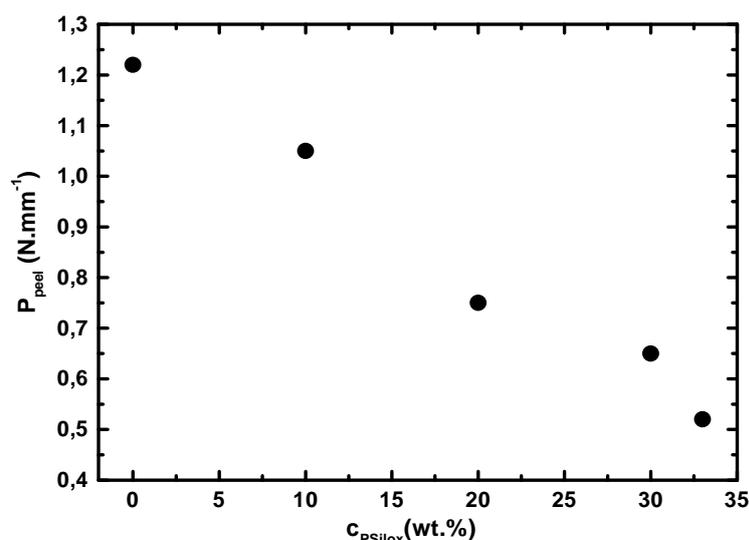


Figure 4 Peel strength of adhesive joint PSI block copolymer-epoxy vs. concentration of siloxane.

CONCLUSION

The morphology of PIS block copolymer has been changed due to segregation of siloxane segments; the constitution of a polyimide continuous phase in the copolymer was affirmed. A significant increase in the roughness of the PSI copolymer surface, as the siloxane content increased, was observed. The values of contact angles of water increased significantly with the rising siloxane content in the PSI block copolymer, and at higher compositions, they leveled off. As the siloxane content in the copolymer increased, the surface energy and its polar component of the PSI copolymer decreased, while the dispersive component of the surface energy increased. Furthermore, as the siloxane content in the PIS copolymer increased, the strength of the adhesive joint to epoxy decreased almost linearly.

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Streszczenie: *Adhezja i energia powierzchniowa kopolimerów poliimidowych.* Badano kilkanaście typów kopolimerów poliimidowych zawierających cząstki siloksanowe. Kopolimery PIS mają kilka zalet w stosunku do czysto poliamidowych, lepszą rozpuszczalność, mniejszą sorpcję, i lepszą hydrofobowość nawet przy nieznacznej zawartości siloksanów. Testowane polimery badano metodami powierzchniowymi, oraz na wytrzymałość połączeń klejowych, wyniki opisano w zależności od typu kopolimeru.