

## **Povrchové vlastnosti polyimid-polysiloxánových blokových kopolymérov**

Štěpán Florián<sup>1\*</sup>, Igor Novák<sup>1</sup>, Petr Sysel<sup>2</sup>, Anton Popelka<sup>1</sup>, Milena Špírková<sup>3</sup>, Angela Kleinová<sup>1</sup>

<sup>1</sup>Ústav polymérov SAV, Dúbravská cesta 9, 845 41 Bratislava 45, Slovensko

<sup>2</sup>Ústav polymérov, Fakulta technologická, VŠCHT, Technická 5, 166 28 Prague 6, Česká republika

<sup>3</sup>Ústav makromolekulární chemie AV ČR, Heyrovského nám. 2, 162 53 Praha 6, Česká republika.

\*E-mail: upolnovi@savba.sk

**SÚHRN:** Morfológia polyimid-polysiloxánových (PIS) blokových kopolymérov závisí od segregácie siloxánových segmentov. Zistil sa výrazný rast drsnosti povrchu PIS kopolyméru pri zvyšovaní obsahu polysiloxánu v blokovom kopolyméri. Pri zvyšovaní obsahu polysiloxánu v blokovom kopolyméri výrazne rastú kontaktné uhly vody, ktorých hodnota sa pri ďalšom zvyšovaní koncentrácie polysiloxánu v PIS ustáli. S koncentráciou polysiloxánu v PIS rastie povrchová energia kopolyméru, polárne zložka povrchovej energie klesá a disperzná zložka povrchovej energie sa naopak zvyšuje. S rastom obsahu polysiloxánu v PIS kopolyméri sa pevnosť adhézneho spoja s epoxidom sa lineárne znižuje.

## **Surface properties of polyimide-polisiloxane block copolymers**

Štěpán Florián<sup>1\*</sup>, Igor Novák<sup>1</sup>, Petr Sysel<sup>2</sup>, Anton Popelka<sup>1</sup>, Milena Špírková<sup>3</sup>, Angela Kleinová<sup>1</sup>

<sup>1</sup>Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava 45, Slovakia

<sup>2</sup>Department of Polymers, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic,

<sup>3</sup>Institute of Macromolecular Chemistry AS CR, Heyrovsky sq. 2, 162 53 Prague 6, Czech Republic.

\*E-mail: upolnovi@savba.sk

**ABSTRACT:** The morphology of poly(imide-co-siloxane) (PIS) block copolymer depends on segregation of siloxane segments. A significant increase of roughness of PIS copolymer surface was observed, if the content of siloxane was growing. The contact angles of water extremely increased by rising of siloxane content in PSI block copolymer and at higher

composition were levelled off. The content of siloxane in PIS copolymer increased, the surface energy, and its polar component of copolymer diminished, but the dispersive component of the surface energy on opposite increased. The content of siloxane in PIS copolymer rises up, the strength of adhesive joint to epoxy decreased almost linearly.

## 1. 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]. In the last years, 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 [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 siloxane segments [7]. 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.

## 2. Experimental

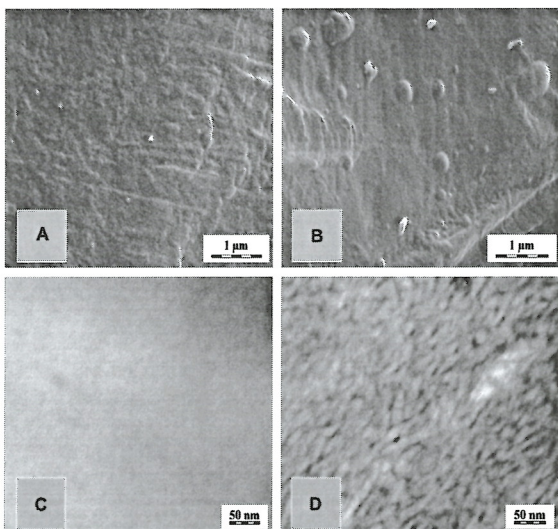
2-Aminoterminated ODPa-BIS P polyimides with controlled molecular weight were synthesized by solution imidization (first step in NMP at room temperature for 24 h, second step in NMP-BCB mixture at 180 °C). The number-average molecular weights of products were in the range  $M_n = 2000\text{--}18,000$  g/mol (by  $^1\text{H}$  NMR spectroscopy). The 1,4-bis(3-aminopropyl) polydimethylsiloxane was prepared by anionic ring-opening equilibrium polymerization of  $\text{D}_4$  initiated with potassium siloxanolate in the presence DSX. Their molecular weights were in the range  $M_n = 1000\text{--}5000$  g mol $^{-1}$  (by conductometric titration with HCl). Polyimide polysiloxane copolymers were prepared via transimidization route (120 °C for 3 h). Copolymers were characterized by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  and by viscometry (in chloroform at 25 °C). The copolymers were prepared with the theoretical molecular weight  $M_n = 40,000$  g/mol. Transparent foils with thickness 25  $\mu\text{m}$  were prepared from 5 wt.%

polymer solution in chloroform by spreading onto a glass plate and evaporating the solvent slowly at room temperature.

Morphology of the samples was studied by methods of electron microscopy – SEM and TEM. The surfaces of prepared block copolymers were observed using JSM 6400 (Jeol, Japan) microscope. 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 (Nanosensors™ 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 (0–5  $\mu\text{l}$ , Biohit, Finland) on the polymer surface, and a contact angle of the testing liquid was measured. The peel strength of adhesive joint ( $P_{\text{peel}}$ ) 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.

### **3. Results and Discussion**

SEM and TEM investigations were used for study of the morphology of PIS block copolymers. SEM micrographs of pure polyimide and PIS block copolymer with 30 wt.% of siloxane are shown in Fig. 1A and B. The changes on the surface of the PIS block copolymers in comparison with pure polyimide reflects the micro phase separation of the siloxane blocks forming a siloxane enriched circle places on the surface of the copolymer.



*Fig. 1. SEM (A, B) and TEM (C, D) micro photos of polymeric film containing: pure polyimide (A, C), PIS block copolymer with 30 wt.% of siloxane (B, D).*

SEM micrograph shows the surface of pure polyimide (Fig. 1A) containing very fine roughness. In the case of 30 wt.% of siloxane in PIS copolymer (Fig. 1B) the roughness is higher comparing to pure polyimide due to creation of the micrographs separated structure and it is manifested by forming of the hemispherical formations on the surface of PIS block copolymer. TEM micrograph of pure polyimide (Fig. 1C) is single-colored. The micrographs of the PIS block copolymer containing 30 wt.% of siloxane is beclouded, whereas very fine micro phase separated structure is observed. The black color in TEM micrographs (Fig. 1D) belong to siloxane blocks and white color to imide blocks in PIS block copolymer. TEM micrographs can be interpreted as a reflection of the conditions where polyimide constitutes the continuous phase and polysiloxane a dispersed one.

The AFM measurements of the PIS copolymers are shown in Fig. 2. 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. 2; 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.

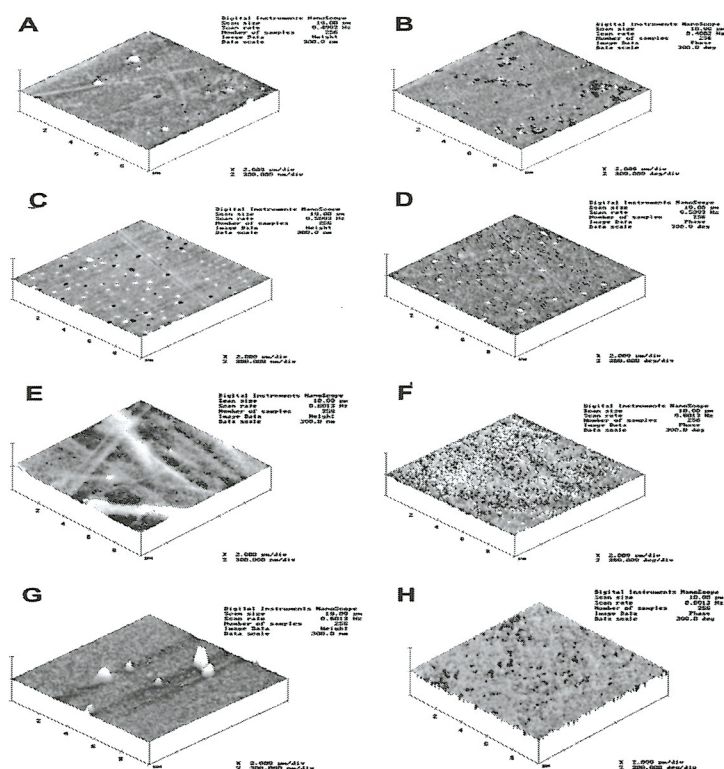


Fig. 2. AFM images of PIS block copolymers films: pure polyimide (A, B), 10 wt.% of siloxane (C, D), 20 wt.% of siloxane (E, F), and 33 wt.% of siloxane (G, H) Height images (A, C, E, G), and phase (B, D, F, H) images, respectively.

The comparison of height images: samples containing 20% (Fig. 2E) and 30% (not shown here) have rugged and funicular surface relief. On the other hand, surfaces of pure polyimide (Fig. 2A), 10% copolymer (Fig. 2C) and 33% copolymer (Fig. 2D) 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. 2A and C. Comparison of phase images: Fig. 2B vs. 2D, and 2F vs. 2H exhibit mutually similar relief. If compared the phase images with the relevant topography images, i.e. Fig. 2A 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. 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).

Fig. 3 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. 4 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. Since the surface energy of siloxane is very low as compared to polyimide, the siloxane segments aspired to migrate to the top of the surface to form a hydrophobic silicon-enriched layer. 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.

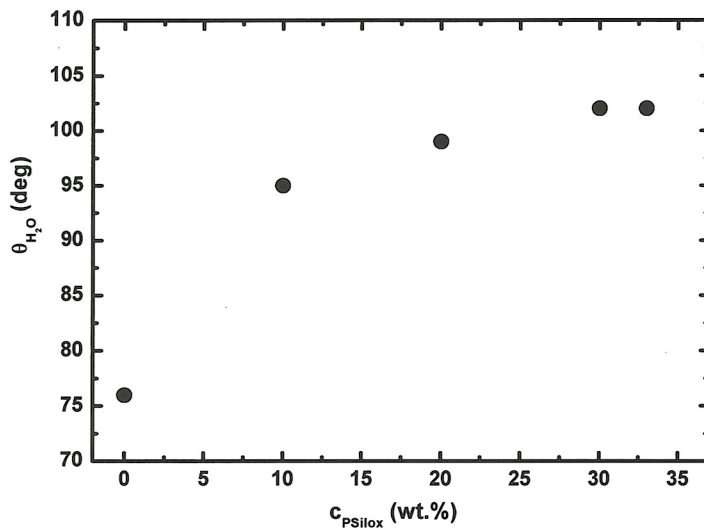


Fig. 3. Contact angles of water vs. siloxane content in PIS block copolymer.

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. 4. The surface energy of PIS block copolymer decreases significantly with the concentration of siloxane from 46.0  $\text{mJ.m}^{-2}$  (pure polyimide) to 34.2  $\text{mJ.m}^{-2}$  (10 % of siloxane), and to 30.2  $\text{mJ.m}^{-2}$  (30 % of siloxane). The polar component of the surface energy reached the value 22.4  $\text{mJ.m}^{-2}$  [pure polyimide], which decreases with content of siloxane in PIS copolymer to 4.6  $\text{mJ.m}^{-2}$  (10 % of siloxane) and 0.8  $\text{mJ.m}^{-2}$  (30 % of siloxane) The decline of the surface energy, and its polar component of PIS block copolymer with raising siloxane content are very intense mainly between 0 and 10 wt. % of siloxane in copolymer. In the case of further increase of siloxane concentration (above 20 % of siloxane), the surface energy of PIS copolymer, and its polar component is leveled off. The surface energy of pure polyimide is 46  $\text{mJ.m}^{-2}$ , while the value of the surface energy of poly (dimethyl siloxane) is only 20.9  $\text{mJ.m}^{-2}$ . 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. On the other hand 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.

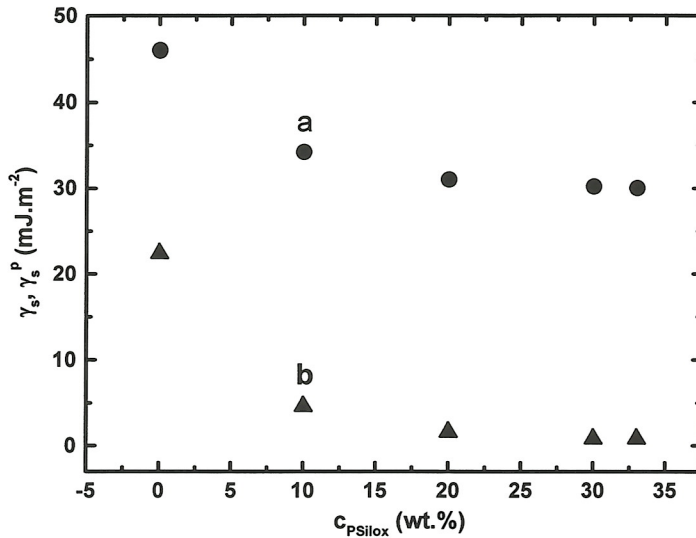


Fig. 4. Surface energy, and its polar component of PSI block copolymer vs. siloxane content.

Fig. 5 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 surface energy of epoxy and polyimide are very close. The surface energy of crosslinked epoxy was 44.2 mJ.m<sup>-2</sup> and the surface energy of polyimide reached the value of 46 mJ.m<sup>-2</sup>. The presence of siloxane in PSI block copolymer caused the more hydrophobic surface of copolymer (surface energy of

copolymer containing 10 % of siloxane was  $34.2 \text{ mJ.m}^{-2}$ ), the surface energies of copolymer and epoxy are more different and peel strength of adhesive joint to crosslinking epoxy resin diminished.

The dependence of peel strength of adhesive joint PIS copolymer-epoxy vs. polar fraction of the copolymer is shown in Fig. 6. The steepest gradient reaches the dependence by Fig. 6 to 15 wt% of siloxane in copolymer and then it is leveled off. This relation allows the determination of the relationship between adhesion properties of PIS block copolymer and polar fraction of the copolymer. The non-linear dependence in Fig. 6 complies with exponential decay of the first order.

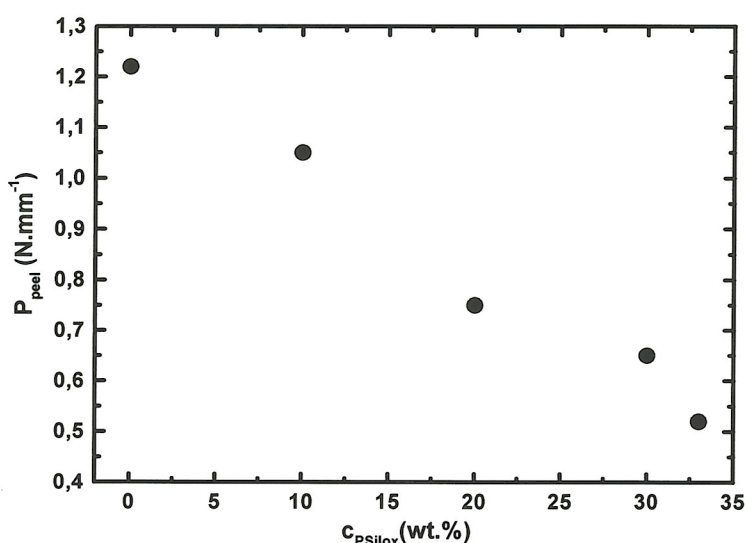


Fig. 5. Peel strength of adhesive joint PSI block copolymer-epoxy vs. concentration of siloxane.

#### 4. Conclusions

- (i) morphology of PIS block copolymer has been changed due segregation of siloxane segments; constitution of polyimide continuous phase in copolymer was affirmed,
- (ii) significant increase of roughness of PSI copolymer surface, if the content of siloxane is growing, was observed,
- (iii) values of contact angles of water extremely increased by rising of siloxane content in PSI block copolymer and at higher composition were levelled off,



(iv) content of siloxane in copolymer increased, the surface energy, and its polar component of PSI copolymer diminished, the dispersive component of the surface energy on opposite increased,

(v) content of siloxane in PIS copolymer rises up, strength of adhesive joint to epoxy decreased almost linearly.

### **Acknowledgements**

The research was supported by Slovak Scientific Agency project VEGA, No. 2/0185/10, and co-financed with the European Fund for Regional Development (EFRD). Grant: ITMS 26220220087: The development of ecological methods to control chosen forest pests in vulnerable montaineous regions of Slovakia.

### **References**

- [1] F. Niklaus, P. Enoksson, E. Kälvesten, G. Stemme, J. Micromech. Microeng. 2001, 11, 100.
- [2] M. B Chan-Park, S. S. Tan, Int. J. Adhes. Adhesives 2002, 22, 471.
- [3] Engel, J Chen, C Liu, J. Micromech. Microengn. 2003, 13, 359.
- [4] P. Sysel, R. Hobzová, V. Šindelář, J. Brus, Polymer 2001, 42, 10079.
- [5] P. Sysel, D. Oupicky, Polym. Intern. 1996, 40, 275.
- [6] J. E. McGrath, D. L. Dunson, S. J. Mecham, J. L. Hedrick, Adv. Polym. Sci. 1999, 140, 61.
- [7] I. Novák, M. Števiar, I. Chodák, I. Krupa, T. Nedelčev, M. Špírková, M. M. Chehimi, J. Mosnáček, A. Kleinová: Polym. Adv. Technol. 2007, 18, 97.