

AFM Surface Studies of Polychloroprene/Piperylene-Styrene Copolymer Blends

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Films of a binary polymer blends comprising polychloroprene (PCP) and piperylene-styrene copolymer (PSC) have been prepared by solution casting. The dependence of the surface structure and morphology of the films on PSC content was investigated by atomic force microscopy (AFM). AFM imaging has shown that the changes of the surface morphology can be characterized as a function of interaction between blend components. It was obtained that up to 15 wt% PSC is distributed continuously in PCP bulk. However, the surface enrichment of PCP has been observed in the blends containing 25 wt% or more PSC. In these cases AFM images reveal distinctions between upside and underside of the blend films. It was been found that segregation of PCP on the upside favours the increase of PSC concentration at the film underside. The films underside morphology becomes similar to that of neat PSC, when PSC content reaches 40 wt%. The changes in the morphology results on PCP:PSC blend adhesion enhance to thermoplastic rubber surface. The adhesion properties of PCP:PSC blend mainly are determined by the increase of the compatibility between polymer film, used as adhesive, and substrate surface.

Keywords: polymer blends, segregation, AFM, adhesion.

1. INTRODUCTION

Some polymer combinations may exhibit more desirable properties than the parent polymers [1]. However, most polymer pairs are immiscible. Immiscible blends are known to have properties, which combine those of both the polymers, and also to have segregated structures with domains predominantly formed from the individual homopolymers. It was shown that changes of relative homopolymer proportion in such blends can vary the domain structure and surface morphology [2–4]. Another important aspect of the immiscible blends is the tendency for one of the homopolymers to be enriched at the surface in preference to the other. For example, in PC/PMMA blends, the surface segregation of PMMA has always been observed even when PC nodules are present in the bulk [5]. The driving force for this surface enrichment can be attributed to the incompatibility, molecular weight, bulk of composition, and difference between surface tension of mixed polymers [6]. In general, the component with lower surface free energy is enriched at the surface in order to minimize polymer-air surface tension. For polymer blends the equilibrium composition of the surface is often different from the bulk composition due to the asymmetrical environment composition at the air-polymer interface and larger thermal molecular motion of polymer chains in the surface region [6, 7].

For determination of enrichment phenomenon many methods, such as X-ray photoelectron spectroscopy, infrared spectroscopy, electron microscopy, etc., can be used. Atomic force microscope (AFM) imaging is a well-established technique for the characterization of polymer films morphology at sub-nanometer spatial resolution, also [8]. While of great utility, determination of film surface morphology alone is rarely sufficient to describe all important features of polymer systems. Significant efforts

have been made to develop AFM ability to probe local chemical and viscoelastic properties, with the ultimate goal of simultaneous morphological and compositional mapping. Some aspects of composition identification are intrinsic to AFM operation, as the interaction forces that exist between the tip and surface contain chemical and viscoelastic information about the sample. A number of novel imaging methods that monitor and exploit these interaction forces have recently been implemented [8–10]. Two of the most promising approaches for combined morphological and compositional mapping of polymer films that are gaining widespread use are friction force imaging and phase imaging.

Friction force imaging, also referred to as lateral force imaging, is a variation of contact mode AFM in which friction-induced torsion of the cantilever is used to construct an image of sample. Briefly, the AFM probe is scanned over the sample of interest maintaining constant tip-sample contact. The cantilever is scanned perpendicular to its main axis and torsion/lateral bending of the cantilever is measured. Torsion of cantilever reflects a complex convolution of effects, including coupling with sample topography, tip-sample adhesive force and viscoelastic deformation of the sample [11]. A number of important investigations have used friction force imaging to differentiate distinct chemical regions in polymer films [4,12,13].

Surface properties of polymers play a major role in their applications in various fields such as coatings, blending and adhesion, also. Kano *et al.* reported [14] that segregation of the fluoropolymer on the surface and acrylic type base polymer to the bottom of the blend led to use a new type of a pressure-sensitive adhesive without backing. The surface properties of epoxy resins could be modified using silicone polymer and fluoropolymer as additives [15]. The modified epoxy resin exhibited an excellent release property from the adherend due to the presence of low surface tension components (silicone polymer or fluoropolymer) on the surface of the resin.

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Polychloroprene adhesive surface properties also can be changed by addition of vinyl and styrene derivatives [16, 17]. The investigations indicate the relationship between adhesion and surface properties of the modified polychloroprene [18]. So, surface structure and properties of PCP play important role in the adhesion mechanism.

In this study the morphology of solvent-cast PCP:PSC blend films was analyzed by atomic force microscopy with the aim to reveal changes in the surface properties and to explain adhesion mechanism.

2. EXPERIMENTAL

2.1. Preparation of polymer films

Commercially available polychloroprene, Baypren 330 ($M_w = 300000$, Bayer AG) and PSC ($M_w = 35000$), obtained by radical polymerization mechanism [17], were used for investigations. Glass transition temperature T_g of PCP and PSC were $-45\text{ }^\circ\text{C}$ and $55\text{ }^\circ\text{C}$, respectively. Polymer solutions were prepared by dissolving each polymer in a mixture of ethyl acetate and *n*-hexane (2 : 1 by weight) in a laboratory mixer (150 rpm for 4 h). Polymer blend solutions were achieved by mixing solutions of the homopolymers in the desired proportions.

Polymer films were prepared by solution casting on a Teflon panel. The residual solvent from the polymer films was removed under vacuum at $50\text{ }^\circ\text{C}$ over 4 h. The thickness of dry films was $300 - 400\text{ }\mu\text{m}$.

2.2. AFM measurements

Atomic force microscopy (AFM) examinations were performed in air at room temperature using atomic force microscope NT-206 (Microtestmachines Co) and SPM processing software *SurfaceView*. Scanning operating in

contact mode with $12\text{ }\mu\text{m} \times 16\text{ }\mu\text{m}$ field-of-view was used. Images were obtained by scanning at a minimum loading force with a scan rate of $40 - 250$ points per second.

During scanning the cantilever bends not only in normal direction to the surface but also the its torsional (lateral) deformation occurs. So, topographical and lateral force images were collected simultaneously using a silicon cantilever with the tip of curvature radius $<10.0\text{ nm}$ and cone angle 20° . The lateral deformation depends on the frictional (lateral) force acting on the tip [19].

The cantilever deflections were registered by optical system of microscope. The measurements of cantilever torsion were carried out with constant force of 0.35 N/m condition, i.e. with constant vertical deflection of the silicon cantilever. As it is known, the lateral force microscopy is sensitive to chemical composition or structure of the surface [8, 9], so, it was possible to distinguish the areas with different friction that corresponds to different phases (Fig. 1). When moving over a flat surface with zone of different friction, the angle of torsion is changing in every new zone. This allowed to measure the local friction force.

If the surface is not absolutely flat, such interpretation is complicated. To distinguish zones of different friction and relief influence can be utilized by second pass on the same line in opposite direction. So, as it can be seen from Fig. 1, AFM images were obtained by scanning from left to right in each scan line, while the opposite scanning direction from right to left led to inverse image.

But the scanning from left to right sufficiently correlates lateral force signal with frictional value, i.e. the lateral force signal increases when frictional characteristics of the surface increase (greater torsions result from increased friction).

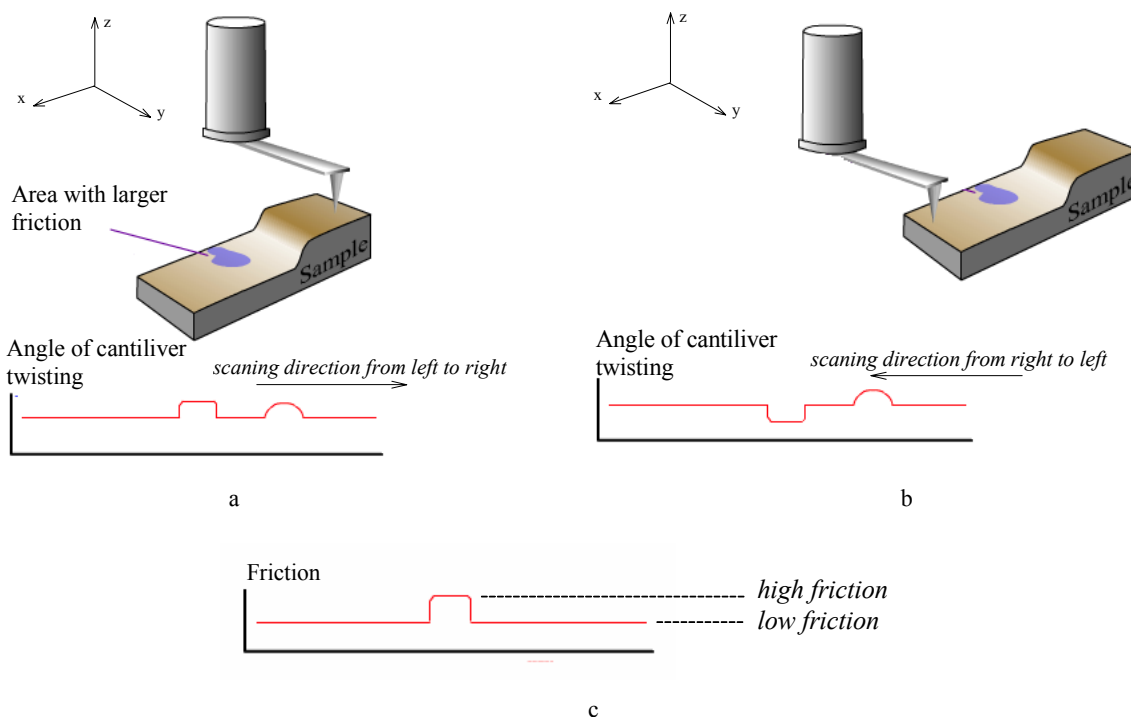


Fig. 1. Torsion deformation of the cantilever during scanning in contact mode: a – scanning from left to right; b – scanning from right to left; c – friction profile

3. RESULTS AND DISCUSSIONS

Thermoplastic rubber (TR) is non-polar substrate that requires chemical surface treatment prior to bonding with adhesive. Another economically acceptable alternative is the development of adhesives suitable for TR bonding. Extensive trials have shown that incorporation of styrene derivatives in the polychloroprene significantly alters its adhesion properties to TR surface [16]. It was found that piperylene styrene copolymer (PSC) could be used as an adhesion promoter for polychloroprene adhesive to make it suitable for TR bonding without its surface treatment procedure [20]. The adhesion properties of PCP were improved, when the amount of PSC was held at 25 – 30 wt%. In this case the peel strength increases more than twice and cohesive failure in TR is characteristic for these joints [16, 20].

It was supposed that the addition of PSC allows to manipulate the blend surface properties. To prove this proposition the contact angle measurements of blend film [18, 20] and surface tension determination by Wilhelmy plate method [21] were used to study the influence of additive content on the surface properties of PCP. It was shown that the effectiveness of PSC is related to surface tension difference with PCP. The investigation of surface tension of the blend film shows that the segregation of PCP at the surface occurs, while the film underside is enriched by high surface tension PSC. However, it is not easy to explain synergism of adhesion properties by the changes only in the surface properties of the binary blend or single blend components. The process of adhesion is complex and can involve several different mechanisms. The combination of these individual contributions leads to the final strength of adhesive joints, though individual mechanisms may dominate under specific conditions.

Therefore, to confirm or disprove additive content effect on the surface morphology of PCP:PSC blend films atomic force microscopy (AFM) was applied.

AFM images of neat PCP and PSC taken using contact mode in air are shown in Fig. 2. It is evident that film morphologies for PCP and PSC display quite different images. Neat PCP contains a large number of hills and valleys with features on the surface protruding (A) approximately 995.0 nm above the base level (Fig. 2, a). In contrast, neat PSC film exhibits flat surface with $A = 128.6$ nm (Fig. 2, b). Only some hill-like structures can be observed, which may be attributed to the impurities. Differences of films morphologies can be referred to the difference in the supermolecular structure of these polymers. The frictional forces are more than 3 times higher for the PCP film than that of the PSC (Fig. 2, I). It can be attributed to the lower PCP film hardness. A softer sample is more easily penetrated by the AFM tip and a higher lateral force is needed to move the tip through the sample [9, 12]. S. N. Mogonov has illustrated this effect and the importance of varying tip loading forces for determining relative polymer hardness in AFM by investigating friction force contrast behaviour in microlayered polyethylene samples [9].

From Fig. 2, III it is obviously that PCP films surface roughness is markedly higher (7 times) comparing to that

of PSC film due to significantly higher molecular weight of PCP.

The orientation of the films surface can be seen from the angular distribution of the surface elements (Fig. 2, IV). Directional distribution of the surface elements is characteristic for PSC. It may be related to the two-phase structure of copolymer, i.e. regular recurrence of the piperylene and styrene phases cause the constancy of the cantilever twisting distribution. Meanwhile for PCP angular distribution of surface elements is disordered. Besides, mostly repeated cantilever twisting angle for PSC film is equal to 1 – 2 degrees, while for PCP – it is in the range of 5 – 10 degrees with significantly large maximal angle (up to 40 degrees comparing to 5 degrees for PSC).

The considerable changes in the film surface morphology occur, when 15 wt% of PSC is blended (Fig. 3). In the PCP:PSC = 75 : 15 wt% blends formation of fine structure is observed. It is evident from lateral force and topographical images that composition surface consisted of bright and dark areas, i.e. showed the sea-island structure. The frictional images reveal higher friction (bright areas) in the surface matrix and lower friction (dark areas) with droplet-like areas (Fig. 3, I, II). Whereas friction with cantilever tip is lower for PSC than that of PCP, it may be assumed that bright areas, which occupied the largest area of the image, correspond to PCP-rich phase and dark areas that are 2 – 4 μm in diameter – to PSC-rich phase. Thus, the PCP : PSC = 85 : 15 wt% blend has two-phase structure, when PSC dispersive phase is continuously distributed in the PCP matrix.

The addition of 15 wt% of PSC causes the formation of the structure with higher local surface height ($A = 15432$ nm) comparing to that of neat PCP surface. It is also clearly evident from the cross-section along the line of the topographical image (Fig. 3, III).

As in the case of neat PSC, for PCP : PSC = 85 : 15 wt% blend surface elements distributed directionally, though their orientation has opposite direction. However, the maximal cantilever twisting angle is close to that of PCP (49 degrees), when mostly repeated angle are in the range of 9 – 12 degrees.

Surface investigation by AFM of the blend compositions with higher content of PSC – PCP : PSC = 75 : 25 wt% and PCP : PSC = 60 : 40 wt% – are presented in Fig. 4 and Fig. 5. Further to explore the capacity of the AFM for compositional mapping in these systems, friction force and topographical imaging of both upside and underside films surfaces were carried out and compared. It is evident that at higher content of PSC sea-island structures begin to coalescence and form continuous structures. The upside and underside of these blends display distinct AFM images with different cross-sections and angular distributions of surface elements.

As it was mentioned earlier, the lateral force measurements are particularly useful for differentiating components of heterogeneous surfaces. Heterogeneity of materials elastic properties caused by material structure and presence of different components is mapped in images [8, 9, 12].

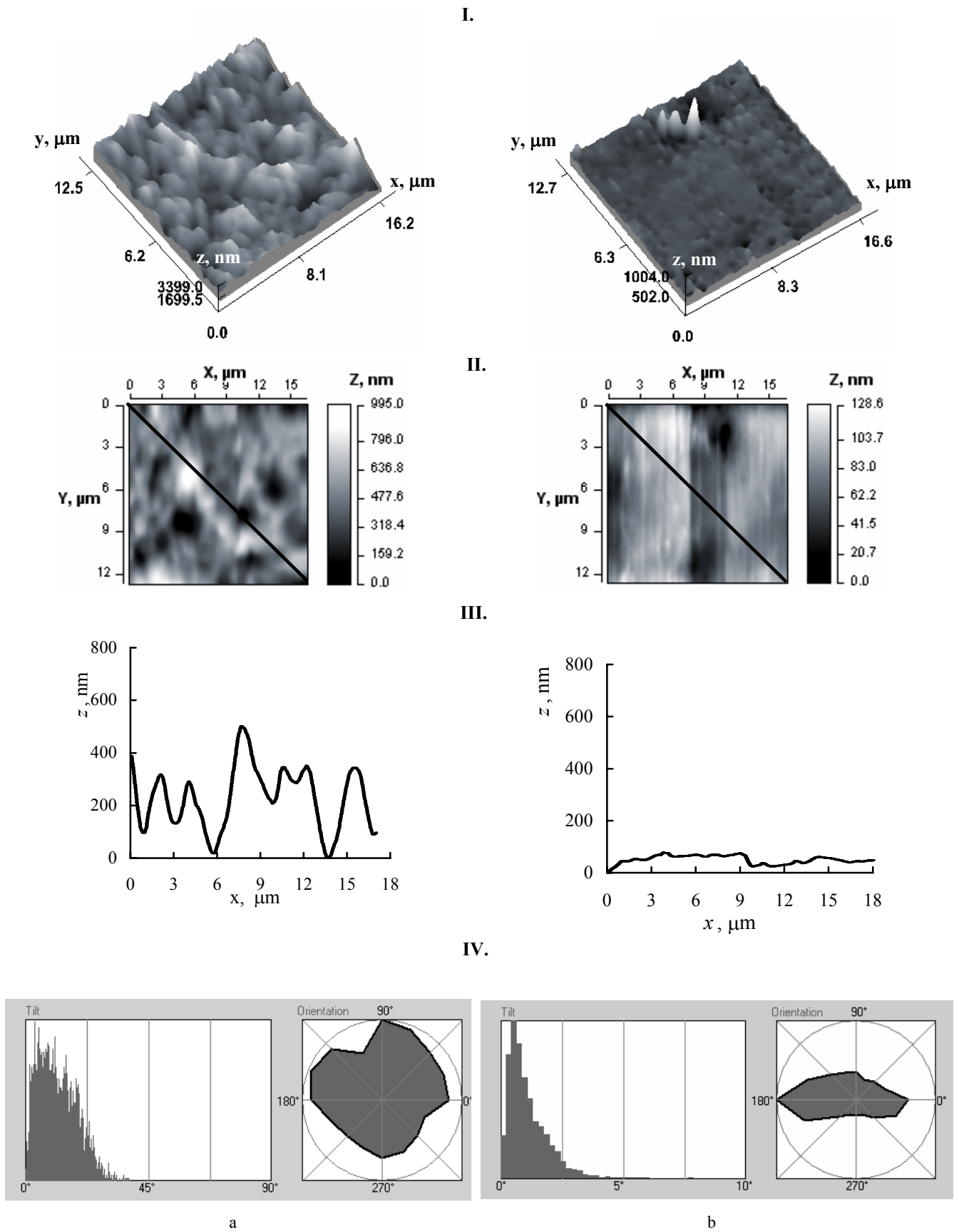


Fig. 2. AFM investigations of PCP (a) and PSC (b) films upside: I – lateral force images (PCP – $R_a = 322.7 \text{ nN}$, $R_q = 416.8 \text{ nN}$; PSC – $R_a = 26.4 \text{ nN}$, $R_q = 46.7 \text{ nN}$), II – topographical images; III – cross-sectional images, IV – angular distribution of surface elements

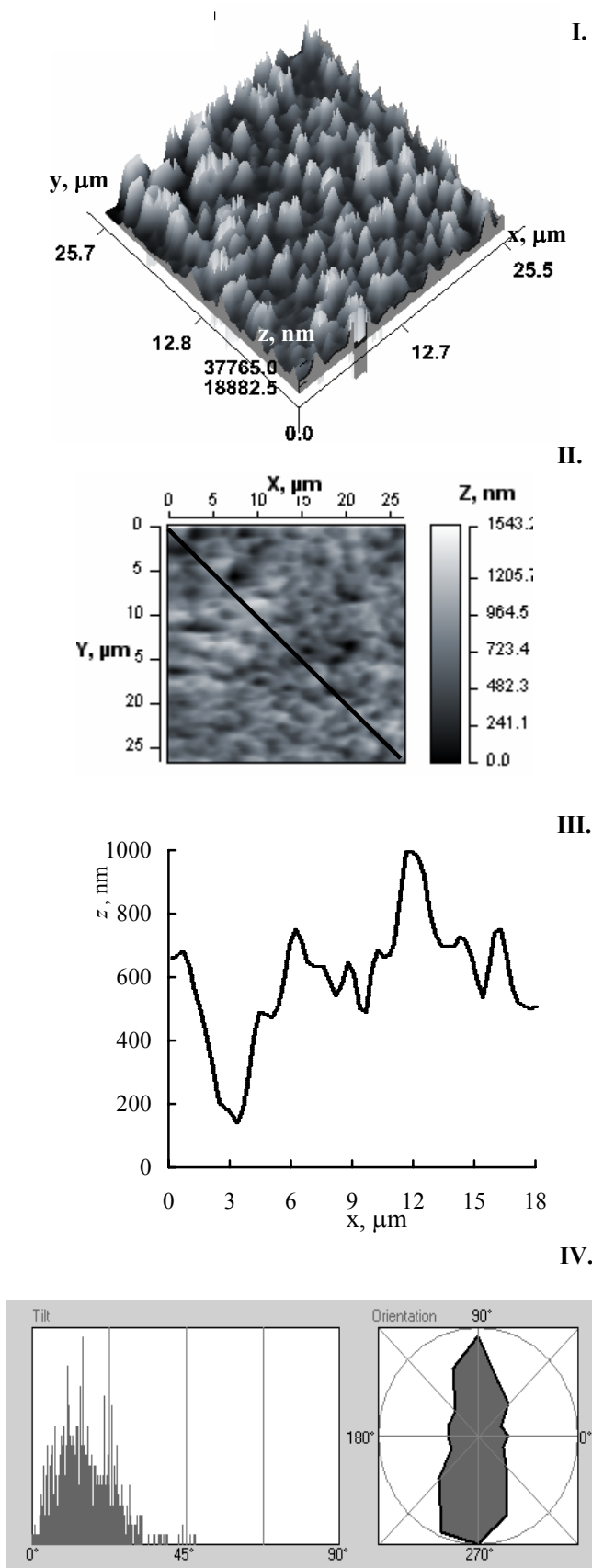


Fig. 3. AFM investigations of PCP:PSC=85:15 wt% films upside: I – lateral force image ($R_a = 6423.2$ nN, $R_q = 8084.9$ nN), II – topographical image; III – cross-sectional image, IV – angular distribution of surface elements

I. On the other hand, in the case of topographical images information gathered from the probe interaction with the surface can be as simple as physical topography. Consequently, the upside surface of PCP:PSC blends, casted on Teflon panel and exposed to air, was expected to reveal marked differences compared to the underside surface, because the underside of investigated blend films are relatively smooth and modelled the panel surface. Therefore, there no observable differences in morphology between topographical images with different blend compositions. The surface protruding A is 879.5 nm and 782.7 nm for blends with 25 wt% and 40 wt% of PSC, respectively (Fig. 4, b, III and Fig. 5, b, III). On the other hand, A of the upside of these blends also marginally depends on the composition (Table 1). It may be contributed to the segregation phenomenon at the film surface, which took place in the PCP:PSC blends at higher PSC content [18, 21].

Table 1. Dependence of films surface protruding A (nm) of blends

Film surface	PCP:PSC composition, wt%:				
	100/0	85/15	75/25	60/40	0/100
Upside	995.0	1543.2	1014.6	1230.7	128.6
Underside	–	–	879.5	762.7	–

III. This assumption confirms the relationship between frictional forces of the neat blend components and different film sides of compositions with 25 wt% and 40 wt% of PSC. As it can be seen, frictional forces of blend films upside increase 2.5 times (from 487 – 974 nN up to 1240 – 2480 nN), when PSC content increases (Fig. 4, a, I and Fig. 5, a, I). Friction forces of that blend composition were found to be similar to the friction forces of neat PCP film (Fig. 2, a, I). On the other hand, frictional forces of the films underside decrease 1.4 times, when PSC content increases (Fig. 4, b, I and Fig. 5, b, I). In this case frictional forces change from 1334.5 – 2669.0 nN down to 978.5 – 1957.0 nN, when blend compositions range from PCP:PSC = 75:25 wt% up to PCP:PSC = 60:40 wt%. So, according to the frictional force imaging, in the case of high content of PSC (40 wt%) the film upside surface morphology exhibit the images more close to those of pure PCP, while the morphology of the underside surface is more similar to that of neat PSC film.

IV. Further, the differences between the topographical images of the blends films upside and underside are clearly observable, also. It is evident that the plot of dark areas on the upside of the films decreases as copolymer content increases (Fig. 4, a, II and Fig. 5, a, II). Meanwhile, on the upside of PCP:PSC = 60:40 wt% blend film the dark areas practically is not observed. Therefore, it may be assumed that single phase is dominated on both sides of the film: on the upside – PCP-rich phase, while on the underside – PSC-rich one.

Data obtained above are in consistent with the PCP:PSC blends surface tension results presented in [18, 21].

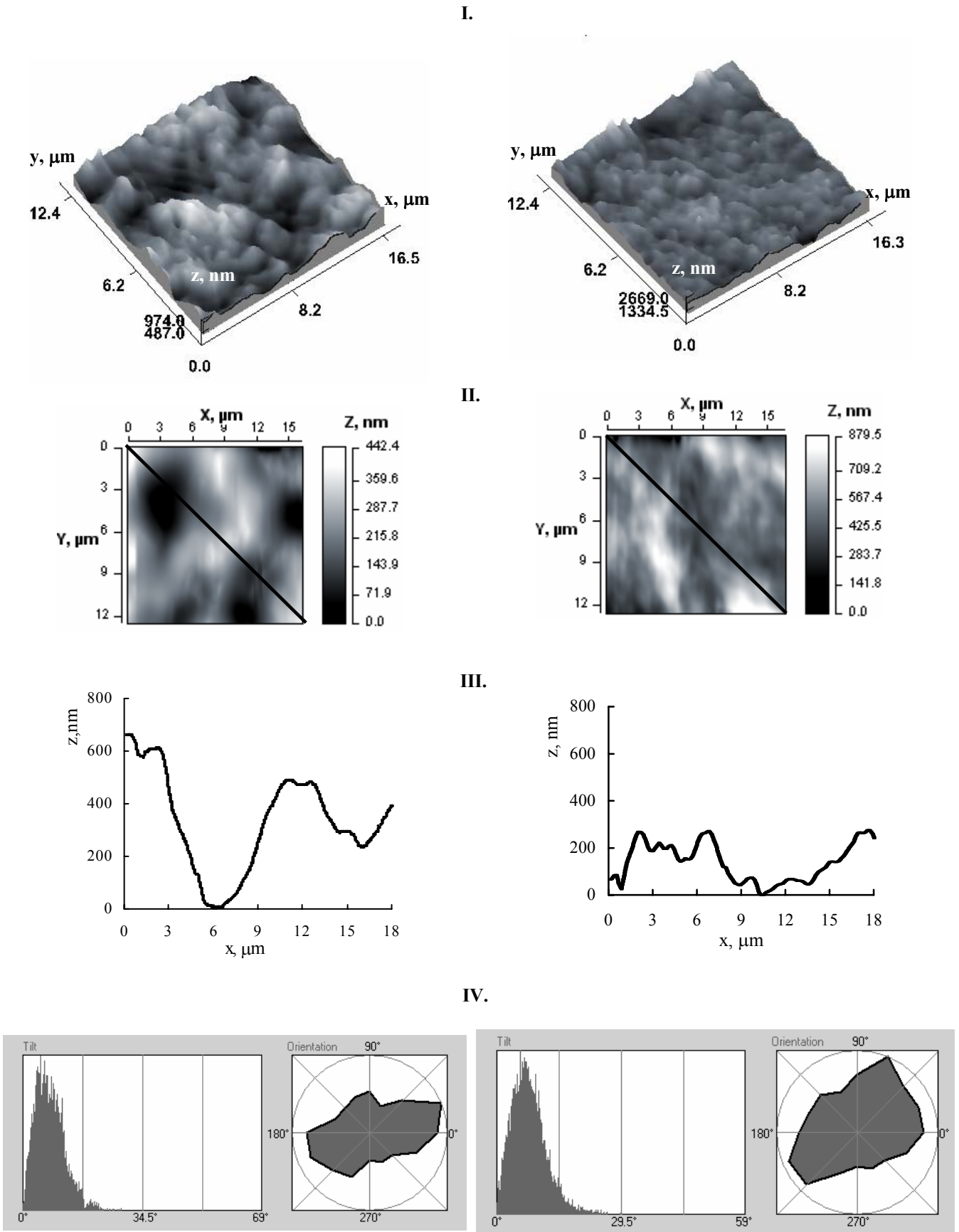
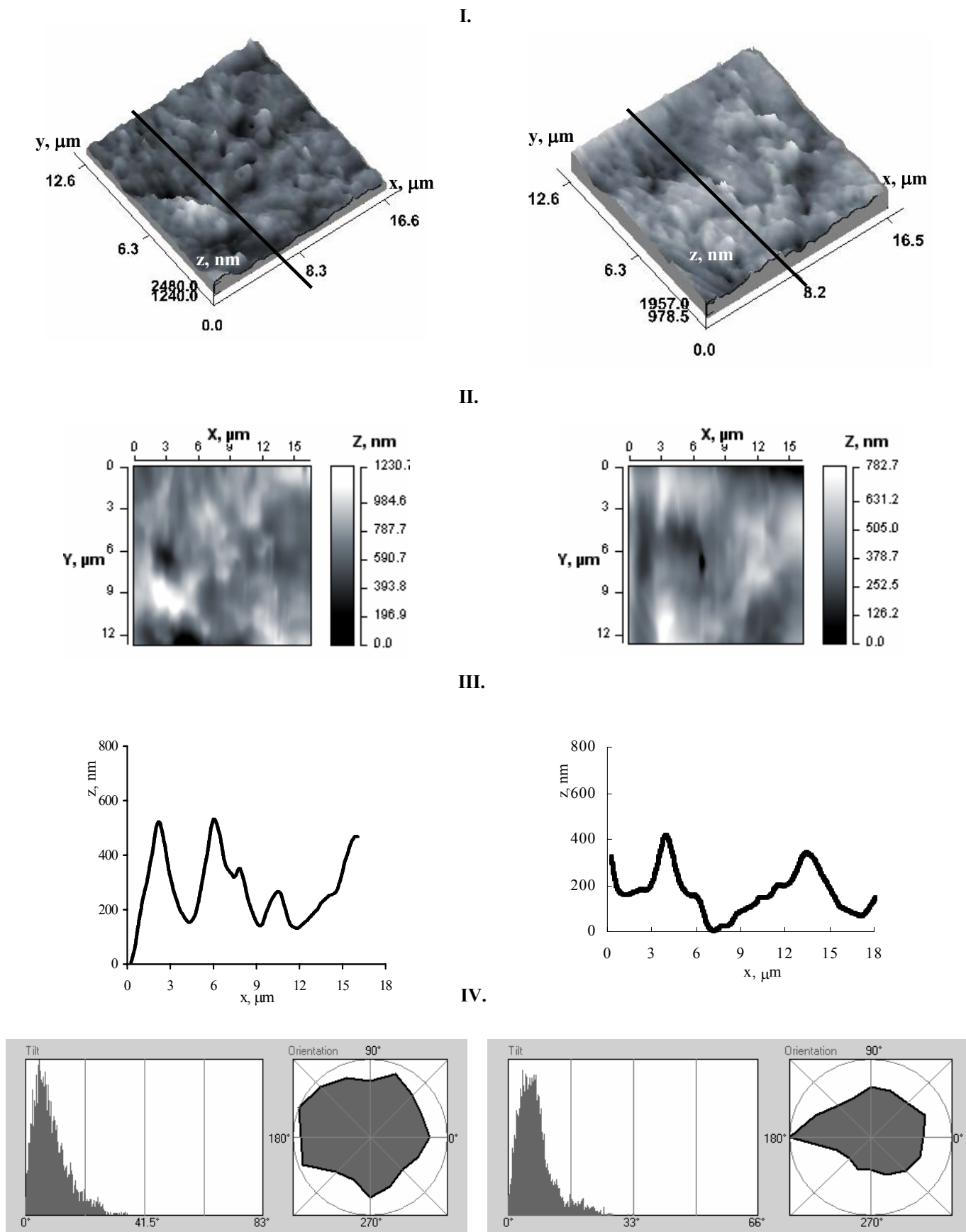


Fig. 4. AFM investigations of PCP:PSC = 75:25 wt% films upside (a) and underside (b): I – lateral force images; (upside – $R_a = 137.2$ nN, $R_q = 166.3$ nN; underside – $R_a = 188.7$ nN, $R_q = 245.2$ nN), II – topographical images; III – cross-sectional images, IV – angular distribution of surface elements



Investigations of angular distribution of surface elements upon PCP:PSC composition range show that increase of PSC content determines the decrease of the angle of cantilever twisting. However, the intensity of that parameter change is different on the upside and underside of film. The angular distribution of surface elements on the upside is similar to that of neat PCP film, while on the underside – to neat PSC. Besides, in the case of PCP:PSC = 60:40 wt% blend orientation of surface elements on the film upside again becomes disordered, as in the case of neat PCP film. Meanwhile, the directional distribution of surface elements is characteristic for all blend surfaces, where PSC phase may be detected.

The roughness parameter was used to characterize the PCP:PSC blend surface. The surface roughness calculation is based on the finding a median surface level for the image and then evaluating the standard deviation within the $N \times N$ range. For this three-dimensional $N \times N$ image of data heights $z(x, y)$, discrete approximations to root mean square (RMS) roughness, R_q is given by:

$$R_q = \sqrt{\frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N (z_{ij} - z_{av})^2}, \quad (1)$$

where i and j are pixel locations on the AFM image, z_{ij} and z_{av} are the height values at i and j locations and average height value within the given area, respectively.

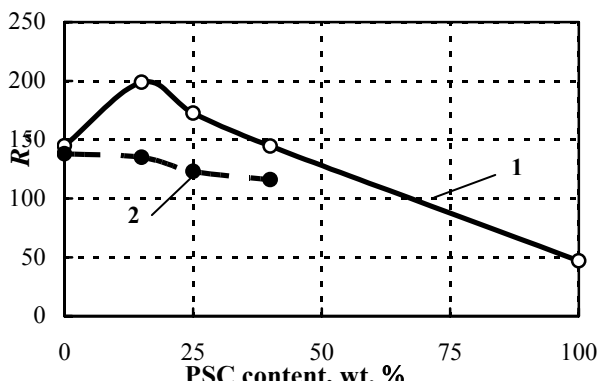


Fig. 6. Dependence of RMS roughness parameter on PSC content in blend: 1 – upside of the film; 2 – underside of the film

RMS values have been determined as a function of PSC content in the blend composition (Fig. 6). Significant changes of the roughness were observed when 15 wt% of PSC is blended. As it can be seen from the curve, this

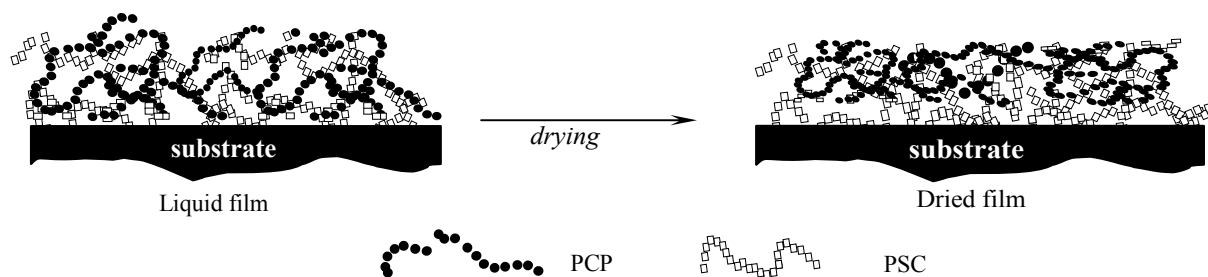


Fig. 7. PCP : PSC adhesive film formation on the TR substrate surface

amount of PSC increases roughness of the film upside from 145 nm up to 200 nm. In the cases of PCP:PSC blends 75:25 wt.% and 60:40 wt.% film roughness decreases (down to 172 nm and 144 nm, respectively). However, the roughness of the film underside negligibly depends on the composition ranges due to influence of Teflon panel during the film formation.

Thus, AFM images reveal distinctions between upside and underside of the PCP:PSC blend films. Segregation of PCP on the upside favours the increase of PSC at the film underside. The films underside morphology becomes close to that of neat PSC, when its content reaches 25 wt.% or more. So, the blending of PSC in the PCP composition allows to manipulate its surface properties and to enhance strength of adhesive joints.

The obtained data allow to conclude that the use of solvent-born PCP:PSC blend as an adhesive causes the increase of adhesion strength of TR joints due to the increase of compatibility between rubber and adhesive. During adhesive film drying PCP segregates at the film surface simultaneously increasing PSC concentration at the film underside (Fig. 7). So, it may be supposed that PSC acts as primer and intensifies the PCP adhesive film interaction at the interface with rubber.

To confirm this proposition the adhesion strength of TR joints, performed in two ways, was compared. Obtained results are presented in Fig. 8. In the case of the joints obtained by using PCP:PSC blend, the adhesion properties were markedly improved, when the amount of PSC was held at 25 – 30 wt% (Fig. 8, I). In this case the adhesion strength of TR joints increases more than twice – from 4.1 kN/m up to 9.9 kN/m; cohesive failure in rubber is characteristic for these joints.

As it can be seen from Fig. 8, II, the use of PSC as primer, i.e. formation of PSC layer on surface before PCP one, provides 20 – 40 % stronger bond strength comparing to that obtained by solution of neat PCP. It is obvious that PSC primer provides high adhesion strength of TR joints as in the case of PCP:PSC blend containing effective amount (25 – 40 wt.%) of PSC.

It can be supposed that in the case of neat PCP solution use at the interface poor molecular contact exits due to limited wetting of substrate surface with adhesive. However, quite different state at the interface occurs when PSC is used. In this case good wetting of TR surface by adhesive and high interaction at the interface is characteristic.

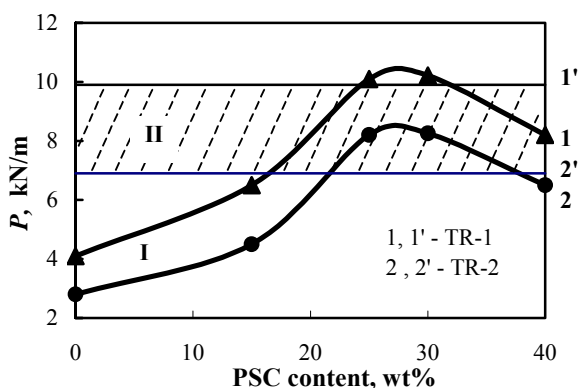


Fig. 8. Adhesion strength P of TR joints obtained using: I – PCP:PSC blends; II – PSC primer (PCP adhesive layer formation on dry PSC one)

CONCLUSIONS

The adhesion properties of polychloroprene can be improved by addition piperylene-styrene copolymer (PSC).

Atomic force microscopy (AFM) mapping of blends film obtained by solution casting have been used to study the influences of the content on the surface morphology and adhesion properties of the blends.

AFM investigations show that during adhesive film formation PCP segregates at the film upside and simultaneous increase PSC concentration at the film underside. Therefore, PCP:PSC blend used as adhesive causes the increase of adhesion strength of thermoplastic rubber joints due to the increase of compatibility between substrate and adhesive.

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