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Polyamide-Imide Membranes of Various Morphology – Features of Nano-Scale Elements of Structure

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1. Introduction

Polyamide-imides (PAI), having a valuable set of properties due to the presence in the main chain amide and imide groups of atoms, in addition to resistance to chemical environments and to processability at elevated temperatures, are very attractive materials for the formation of coatings, films and membranes of different applications [1]. Interest in polymers of this class periodically arose throughout several decades in various scientific schools of the world. First of all, a possibility of preparing from them isolating materials for microelectronic was considered [2, 3]. Workings out materials produced in industrial scale from polymers of commercial marks Torlon ® (Solvay Advanced Polymer), Tecamax ® (Graftech Industries, Inc.), Durimide ® (Fujifilm Electronic Materials, Inc.), Tecator ® (San Diego Plastics, Inc.) are known, and also along with them unique laboratory researches [4-6]. One of the most successful applications of polyamide-imides may be formation of materials for membranes, particular for membranes of composite type [7-8]. On a basis of polyamide-imides either their polymeric or polymer-inorganic compositions, membranes of a wide spectrum of classification groups, and consequently, different morphology are offered. In particular, microporous membranes with nano-scale pores in a skin-layer are discussed [9-11]. Investigations of the flat or the hollow fiber membranes, porous or dense non-porous films and composite multilayer structures are known. Last two of the listed above morphological types of films are widely used as diffusion membranes, these are membranes containing one or more non-porous separating layers. For example, on a basis of polyamide-imides with trade-mark Torlon ®, asymmetric and composite diffusion membranes for gas separation or pervaporation processes were developed [12-13]. Polyamide-imides have appeared selective for a wide spectrum of the separating problems solved in a pervaporation [14-16]. In particular, the film from Torlon 4000T has been offered for use at pervaporation separation of isomers (xylene isomers [17]).

At the same time, the spectrum of PAI applications is limited, that is connected with specificity of synthesis of these polymers. For preparation of membranes with a specific

morphology, it is necessary to choose an appropriate strategy to optimize the synthesis conditions for obtaining PAI so that the polymer could be formed into a material with desired properties. So, in case the need for self-supporting films, optimizing the synthesis conditions should result in the first place, to the preparation of stable polymer of high molecular weight with narrow molecular weight distribution. Complex requirements of chemical and thermal stability and mechanical properties needed to form flexible and strong self-supporting films satisfy PAI samples, obtained by polycondensation in solution at low temperature. Conditions of mentioned above reaction have been optimized at the Institute of Macromolecular Compounds Russian Academy of Sciences (IMC RAS) [18]. Main feature of the reaction consists in introduction in the reactionary environment at the lowered temperatures monomers, one of which contains in the structure an imide fragment. Such method gives the chance not only to obtain polymer with a necessary complex of properties, but also to avoid imidization as an additional stage of the process. Proposed in 1971 by researchers from the Romanian Academy of Sciences and optimized by chemists of IMC RAS method has found followers and has been successfully used to this day, as in Romania [19-20], and in Russia [21-23].

2. Asymmetric porous films based on polyamide-imides in the membranes of various morphological types

In focus of the authors of this paper were always materials with unique transport properties, or other characteristics, that allow the use these materials in the high-performance composite membranes. In previous our publications it has been shown, that with use of polyamide-imides as active (in the course of separation) materials of supporting or intermediate layers, membranes high-effective for separation of mixtures of gases or liquids can be generated. So, in [24-26] were considered gas separation properties of the composite membranes containing microporous supporting layers from polyamide-imides of a similar chemical structure, differing with a diamine fragment. In these membranes after the formation of structural components with the certain morphologies, the conditions of highly selective transport through the support material were achieved. As a result of this, the support from the category of passive substrates, which are responsible only for the mechanical strength of the composite material as a whole, passed into the category of active ones. The choice of the polyamide-imide for formation of such membranes became basic, as well as conditions preparing microporous films on their basis. On Fig.1 the schematic image of the typical multilayer composite membrane and microphotographs of low-temperature fractures of porous PAI membranes (supports in composite membranes) prepared in identical conditions of phase - inversion process from PAI's with similar chemical structure, but differing in diamine component, are presented.

Variations in the morphological features of microporous PAI films demonstrated in Fig. 1 correlate with their transport properties: for example, N_2 permeability in these PAI-films series is $(4 \div 95) \cdot 10^{-3} \text{ cm}^3/(\text{cm}^2 \text{ s (cm Hg)})$. This level of permeability shows the presence of cross-porous structure in all asymmetric films discussed above. The morphologies of all supports are similar: the finger-shaped conical macropores traverse the support, and the cone voids in cross section decrease towards the upper surface of the support (skin layer). The walls of the macropores have a network - morphology with a pore size of 50 - 100 nm. All supports, concerning SEM photographs in Fig.1, have almost perfectly smooth flat surfaces with pores in skin layer of less 20 nm in diameter.

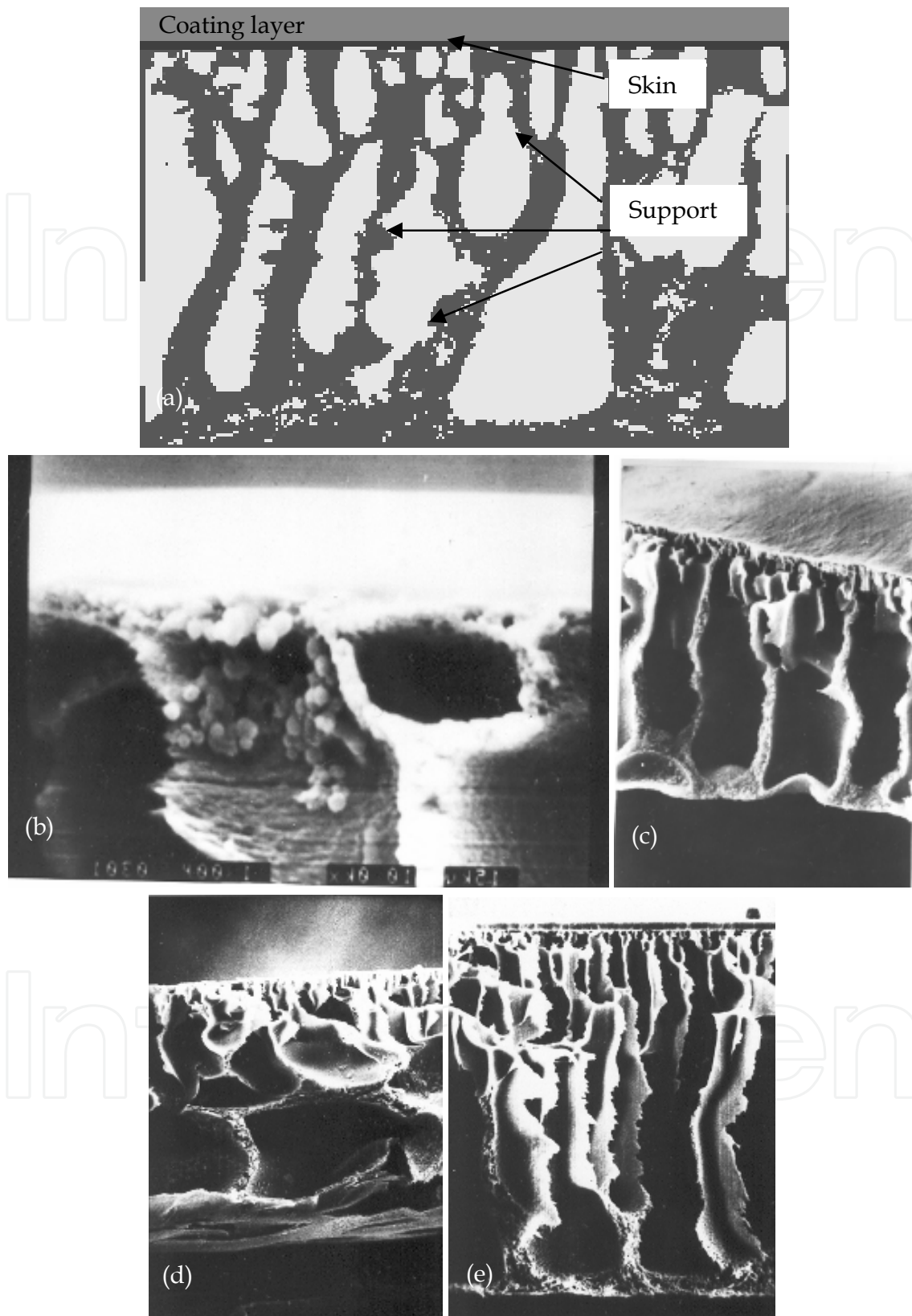


Fig. 1. (a) schematic representation of the cross section of a composite membrane; (b,c,d,e) microphotographs of low-temperature fractures of porous PAI's membranes prepared in the present work using water as non-solvent [26].

These features of morphology are illustrated well also by Fig. 2. In this Figure microphotographs of low-temperature brittle fracture (cross-section) and the top surface of the asymmetric porous film (support) are placed. Film was obtained by a method of wet formation from polyamide-imide synthesized at the Institute of Macromolecular Compounds of RAS from phthalimidobenzenedicarbonyl dichloride and diaminediphenyl oxide (PAI-1) by low-temperature polycondensation in solution [18].

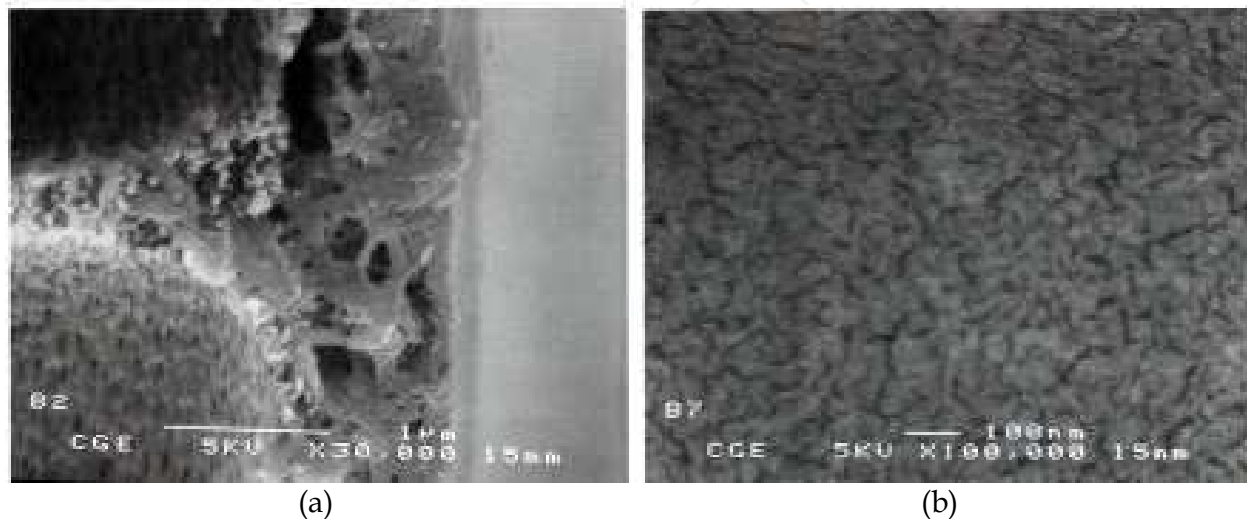


Fig. 2. SEM photographs of PAI-1 microporous support: (a) low-temperature fracture, (b) surface of skin-layer.

Formation of composite membrane by a method of coating the polymeric solution on a surface of skin-layer of the asymmetric support resulted, as is noted above, to formation of intermediate layers of complicated morphology, and in some cases - outwardly homogeneous layers of difficult structure. In [27] it is shown, that composite membranes presented in a Fig. 3 have diffusion separating layer, unlike porous support in their structure. On a surface of a skin-layer of the same PAI support (a microporous asymmetric film) from different coating polymers (polyvinyltrimethylsilane, polypropylmethacrylate) thin separating layers of various morphology can be generated in identical conditions [27]. Thus, obviously expressed "pores" and holes in coating layers are not through, and the internal intermediate layers generated on a skin-layer of support answer for the transport properties of composite membranes discussed in work [27].

It was demonstrated [26] with an example of poly(2,2,3,3,4,4,5,5-octafluoro-n-acylacrylate)/polyamide-imide composite membranes that highly selective diffusion layers, particularly of low-selective elastomers, can be realized on the support by optimization of the chemical structure of PAI, i.e., by varying the nature and (or) concentration of adsorption sites on the support surface and, therefore, its energy characteristics. This allows make diffusion membranes the separation characteristics of which differ from those predicted theoretically on the basis of the resistance model, so that they surpass the selectivity of all individual polymers composing the composite membrane. In similar conclusions about an essential role of internal intermediate layers resulted the analysis of characteristics of multilayer composite membranes, effective at separating pervaporation of liquids [28]. In this case the material of a porous support layer of PAI-1 played even more significant role and influenced essentially transport properties of a membrane.

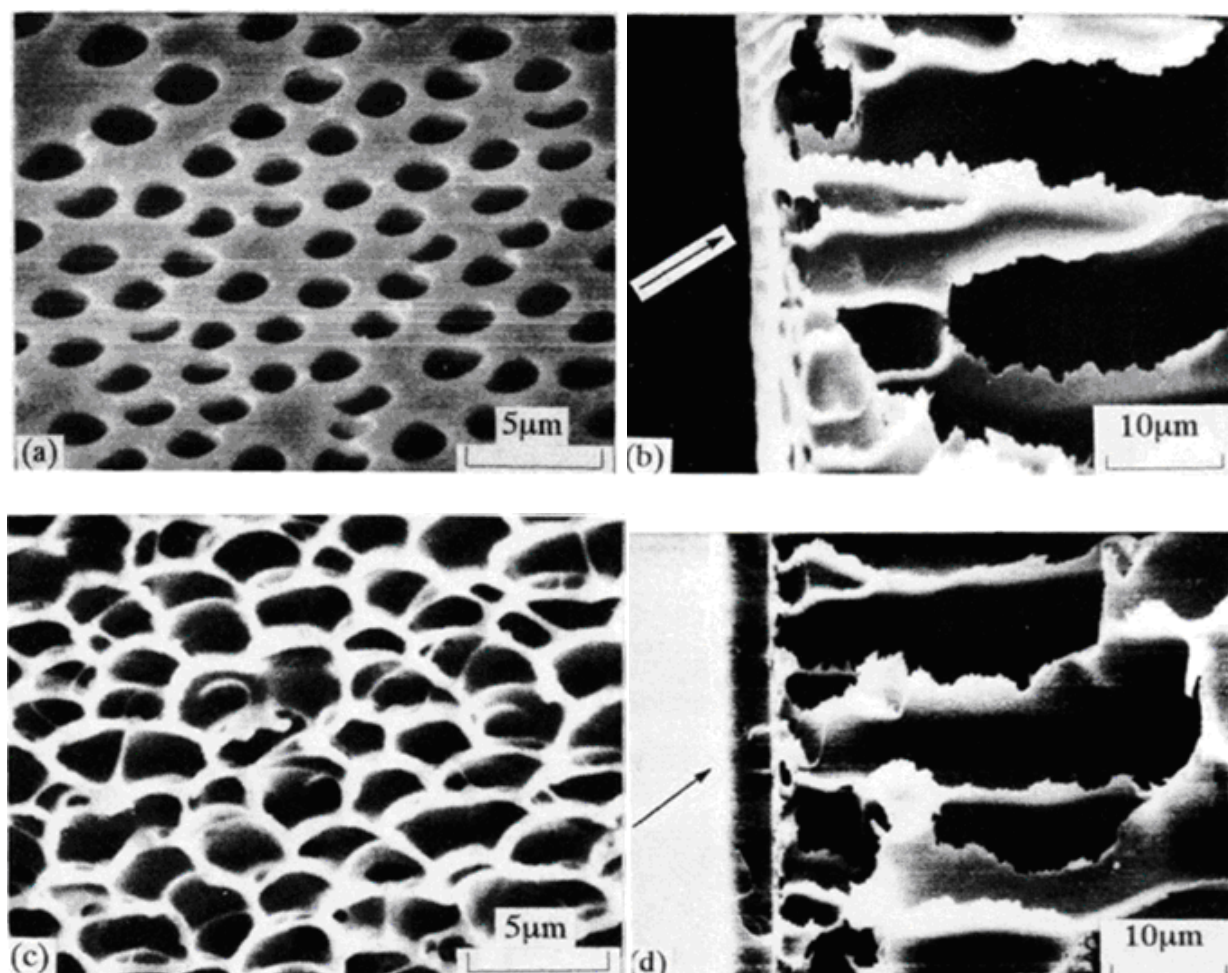


Fig. 3. SEM photographs of the surfaces (a, c) and of the cross-sections prepared by low-temperature cleavage (b, d) of the PVTMS-PAI-3 (a, b) and PPMA-PAI-3 (c, d) composite membranes. The arrow shows the upper surface.

We have studied the asymmetric porous membranes with ultra-thin diffusion layers of PAI-1 and also two - and multi-layered composite structures containing microporous polymer layers with a similar but looser morphology. These layers are characterized by penetrating porous structure with nano-sized pores in the skin layer and the nearby - layers. Unlike gas separation when glass transition temperature of coating polymer, the size of pores of a skin-layer, and also a parity of thickness of various layers of a composite membrane are the matter of principle, in a case of pervaporation last factor can have defining role for realization of transport properties of PAI, forming a microporous support of a membrane. As well as in a case of gas separation, the essential contribution to transport properties of multilayer membranes brings the boundary layer formed on a surface of a skin-layer of a microporous PAI film.

It is possible to consider the multilayer composite membranes presented on Fig. 4 as simple, but demonstrative examples. In this Figure SEM photograph (Fig. 4,a) of a highly effective multilayer composite membrane is resulted, in which on a surface of skin-layer of a microporous film intermediate layer of polydimethylamine ethylmethacrylate (PDMA) and a top-layer of polysiloxane are formed. Presented in [28], the transport properties of the

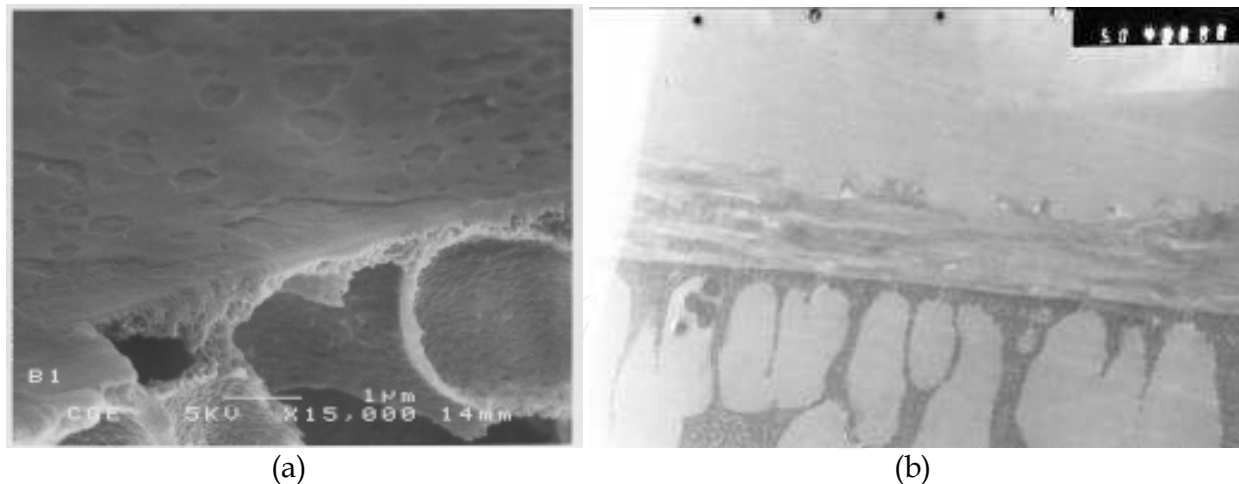


Fig. 4. Microphotographs of (a) the cross-sections prepared by low-temperature cleavage of multilayer composite membrane polysiloxane/PDMA/PAI-1, (b) ultra-thin cut of composite membrane with the coating layer of poly- γ -benzyl-L-glutamate.

membrane can be considered it one of the most effective membranes for the separation of mixtures of methanol - methyl tertiary butyl ether in different concentrations. However the Fig.4a shows a presence in a membrane structure of a faltering rough polysiloxane layer on border polysiloxane - air. It is possible to assume, that internal membrane layers boundary with a support top-surface provide diffusion separation.

The similar situation is created at formation of a composite membrane poly- γ -benzyl-L-glutamate (PBG)/PAI, the microphotograph of ultra-thin cut of which is presented in a Fig. 4,b. Despite formation of the thin intermediate layer having roughness, and external emptiness on border with air, the composite membrane is steady in pervaporation conditions and shows high selectivity at separation of mixtures of toluene and n-heptane [29].

Possibly, in a boundary region between polymers of various layers of a multilayer composite membrane, where interactions of adsorbed molecules with effective adsorption nodes on a surface of adsorbate (skin-layer polymer) are possible, in the process of the membrane formation a intermediate layer of the difficult structure is formed. This layer contains areas of the raised density, sites of domain character, and also the difficult architecture, consisting of coating polymer or both polymers. The morphology of the intermediate layer depends on conditions of formation of a composite. The laws found in works under discussion have led to necessity of detailed research of morphological, structural, physical and chemical characteristics of all layers in membranes, and first of all - of surfaces of skin-layers in PAI asymmetric films.

3. The surface morphology of the skin layer of asymmetric PAI film depending on the conditions of its preparation

In [30] the special attention has been given to PAI-1, containing diphenyloxyde fragments in structure of a molecular unit. PAI-1 concerns to moderate hydrophilic polymers. Phase separation at contact of its viscous solution in N-MP with strong for that polymer non-solvent - water - occurs with the high speed. Therefore the asymmetric microporous film with a skin-layer which thickness of 50 - 60 nm is formed. The SEM photographs of low-temperature

fractures and surface of skin-layers of asymmetric microporous PAI-1 films presented in [30] show obvious distinctions in density of packing of polymer in surface layers (top and bottom), such that the average size of a pores formed in them differ ~ in 100 times.

Comparison of the SEM photograph of the skin layer surface of PAI-1 asymmetric film, shown in Fig. 2b, and the data of atomic force microscopy (Figs. 5a, 5b) leads us to conclude that fiber-like polymer chain agglomerates are oriented mainly in one direction of the film plane (presumably along the direction of doctor blade motion during pre-formation of membrane) to form a complex texture whose fragments go under the surface plane or rise above it. The observed pattern resembles a knitted fabric where caves (voids) with different sizes are formed. It is difficult to reveal among the latter penetrating pores and estimate their average diameter; however, it is obvious that the average pore diameter does not exceed 15 nm [30].

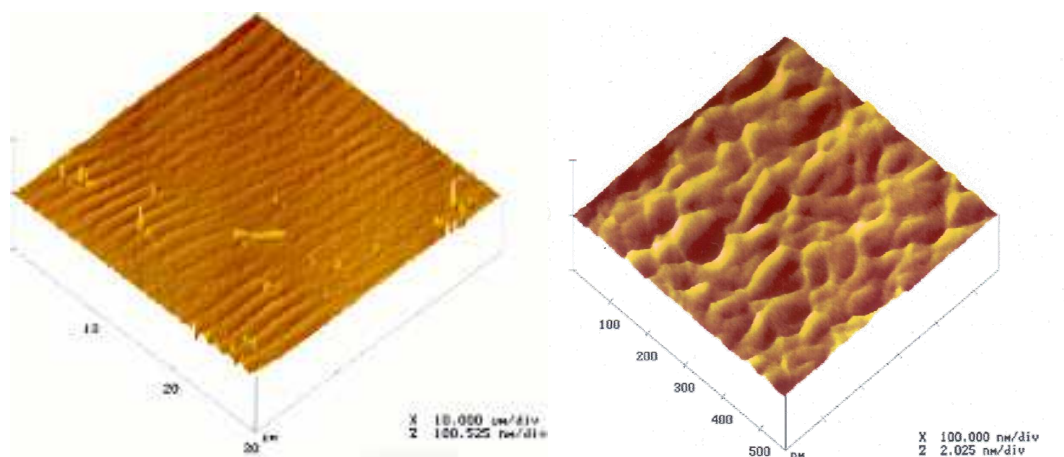


Fig. 5. Atomic force microphotographs of the top surface (skin-layer) of PAI-1 asymmetric film at different resolutions.

The increase in concentration of forming solution of PAI-1 in N-methyl-2-pyrrolidone (N-MP) leads to formation of microporous films with more dense skin-layers so since certain concentration, formation of non-porous skin-layers resulting preparation of asymmetric diffusion membranes is possible. Membranes of this type have been obtained by us and investigated in the conditions of pervaporation process at separation of aqueous-organic or organic liquids mixtures [31]. In our publications distinctions of physical, chemical and structurally - morphological characteristics of surface layers of asymmetric PAI-1 membranes [22], received in various conditions of phase-inversion process are shown.

It is of interest to compare data of atom-force microscopy of surfaces of skin-layers of asymmetric films on the basis of PAI-1, prepared from solutions with various PAI-1 concentrations, and also of a surface of non - porous dense film from this polymer. Mentioned the latter was obtained by a pouring technique with following slow removal of solvent from a solution during heating. In a Fig. 6 are presented SEM - photographs of low-temperature fractures of asymmetric diffusion PAI-1 membrane with non-porous dense skin-layer (Fig. 6a, 6b) and also the atom-force images (Fig. 6c, 6d) of a surface of this membrane in comparison with data of an atom-force microscopy for non-porous PAI-1 film (Fig. 6e, 6f). Formation conditions of asymmetric membranes (Fig. 3 and Fig. 6) differed only with concentrations of PAI-1 formation solutions.

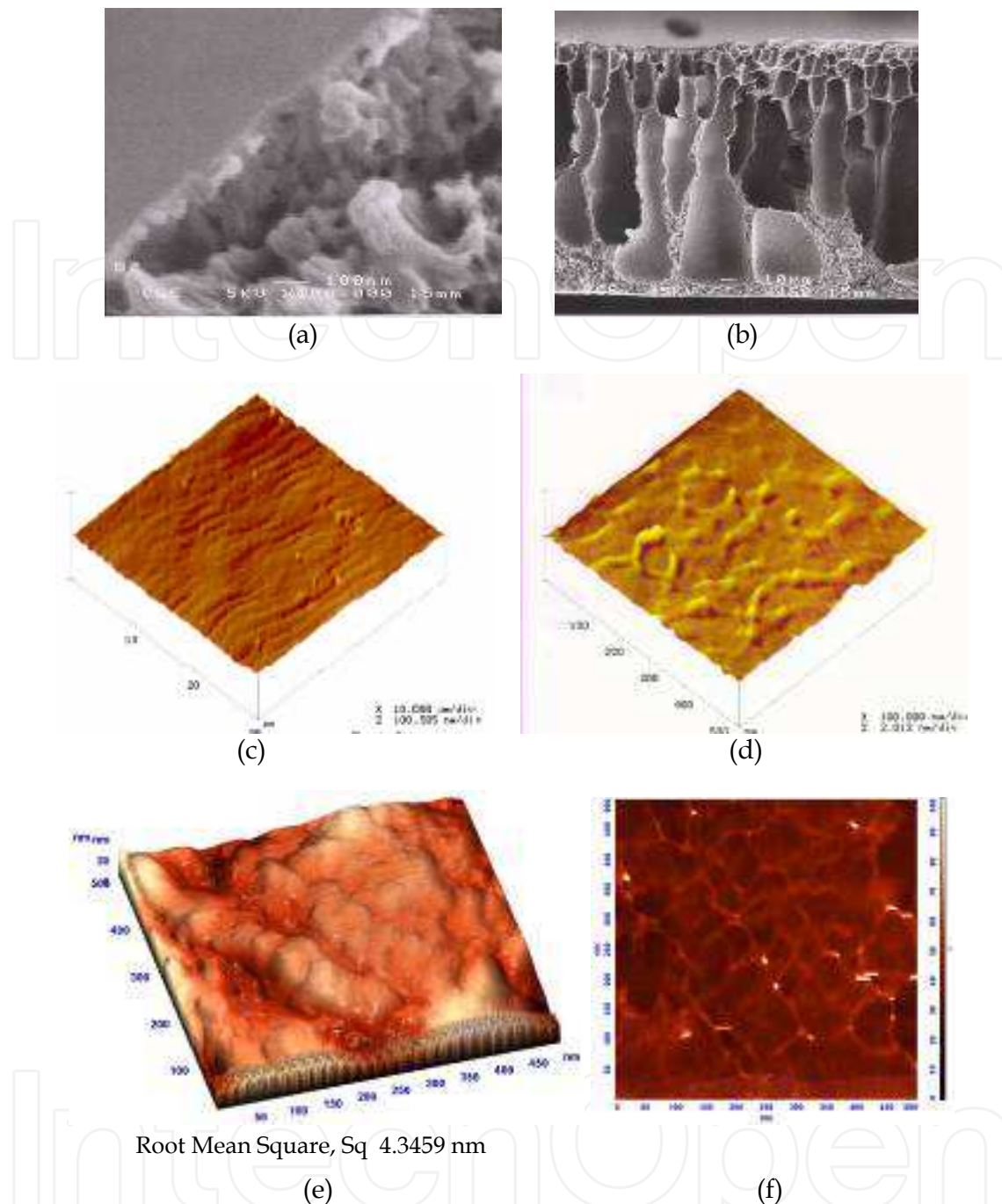
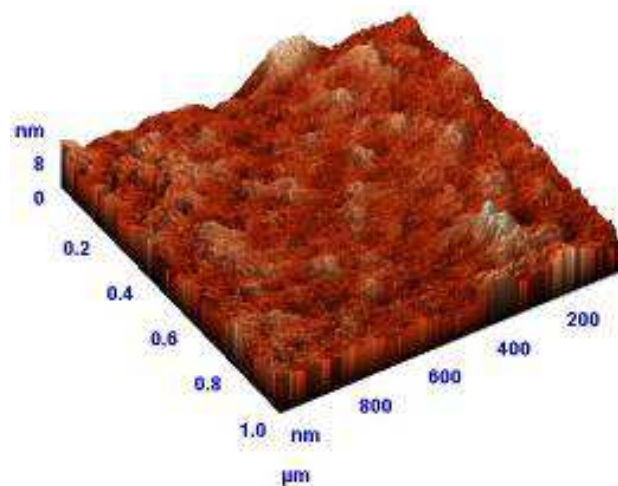


Fig. 6. (a, b) SEM - photographs of low-temperature fractures and AFM images of (c,d) asymmetric diffusion PAI-1 membrane and (e, f) non-porous dense film based on PAI-1 (e - 3D image, f - phase contrast image).

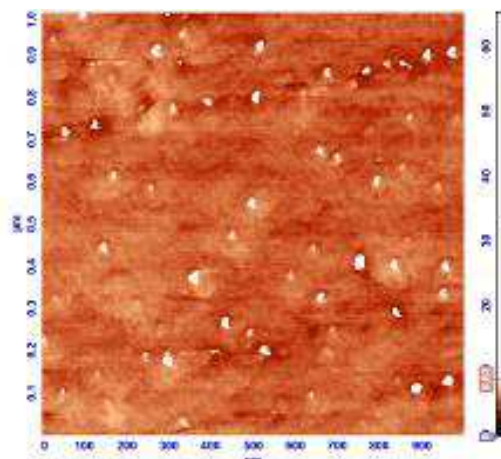
According to data of the atom-force microscopy, presented on Figs. 5 and 6, surfaces of all considered films are characterized by presence of the oriented polymeric domains. Their average size increases at transition from an ultrafiltration membrane (porous skin-layer) to diffusion one, that depends on increase in concentration and viscosity of a forming solution. Logical would be to expect the greatest smoothing of a surface at transition to non-porous polymeric film. On the contrary, in the case of PAI-1 film, most rough surface layer with the large oriented domains coming from a surface plane is observed.

Obviously, such unexpected effect is connected with ways of preparation of discussed samples. In case of asymmetric films of complex morphology of cross-section (Figs. 2a and 6a, 6b) the skin-layer is formed in process of “meeting head-on” of both the polymer solution and the precipitant (water), in the conditions of wet formation. At the same time at film formation on a surface of a smooth inorganic substrate (glass) there is a slow removal of solvent mainly in a direction, perpendicular the top surface. Polymer of top layer in these conditions “takes a great interest behind solvent” and takes a great interest behind it in that measure in which viscous polymeric gel formed already allows.

The similar picture can be observed at studying of a surface morphology of films of another polyamide-imide of PAI-2 synthesized by use of 3,5-diaminobenzoic acid as a diamine reagent in polycondensation. In a Fig.7 are presented AFM 3D image and phase contrast image to the top surface (it is generated on border polymer/air) of non-porous film of PAI-2. The film surface layer also is characterized by presence of the directed domains of polymer, but the smaller size, than at PAI-1. Carboxylic groups containing in a polymeric chain of PAI-2, more hydrophilic than PAI-1, takes a great interest in evaporating solvent so effectively that the craters which presence illustrates phase contrast image are formed.



(a)



(b)

Fig. 7. AFM images of non-porous dense film based on PAI-2 (a - 3D image, b - phase contrast image).

There is a question what reason of the formation of the oriented PAI domains, «as weaved» from polymeric chains. The results of X-ray researches showing are known, the structures of dense PAI films and asymmetric PAI-supports, as a whole, do not contain sites with notable degree of heterogeneity; fragments with high degree of crystallinity are absent [32-34]. In PAI-1 films obtained by a pouring on a solid basis of a solution of polymer with its subsequent drying, always there is a structure which is characterized by orientation of chains in a film plane (Fig. 8).

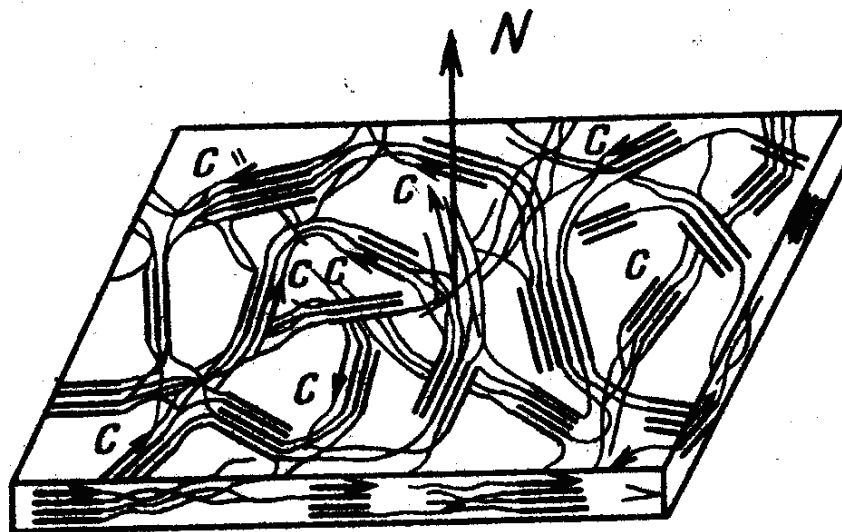


Fig. 8. Scheme of an arrangement of the ordered structures of macromolecules relative to the normal to a film surface [34].

In case of a film formation by pouring of a viscous solution of polymer on a surface of a glass plate with use of a doctor blade, it is necessary to expect a primary arrangement of the ordered fragments in a direction of movement of a knife, as illustrate Figs. 6 and 7. Thus, received by a pouring method on a surface of a smooth inorganic basis PAI films are characterized by the ordered structure, such that polymeric chains most typical allocate in a film plane, and in case of additional focusing influence are extended in the primary direction set by external forces. In case of wet formation of a microporous film the front of precipitant interferes with movement of chains of polymer in a direction of removal of steams of solvent therefore more smooth surface is formed, than in case of non-porous film.

4. Thermo-physical characteristics of PAI films

The assumptions discussed above are in agreement with the data of thermo-gravimetric analysis (TGA) of PAI-2 samples (curve 2, Fig.9). The Fig. 9 shows, that speed of weight loss increases for PAI-2 since 200 °C, and at 600 °C the weight loss attains 47 % of initial weight.

TGA/DSC investigations were performed simultaneously with analysis of volatile products, which rise during thermal treatment of PAI-2. In Fig.10 3D FTIR diagram in coordinate - temperature, wave length and intensity is presented. It was supposed that three main processes are observed here: release of water in temperature region 25-550 °C, removal of N-MP solvent in temperature region 250-420 °C and the beginning of thermal degradation (release of CO₂, starting with 400 °C).

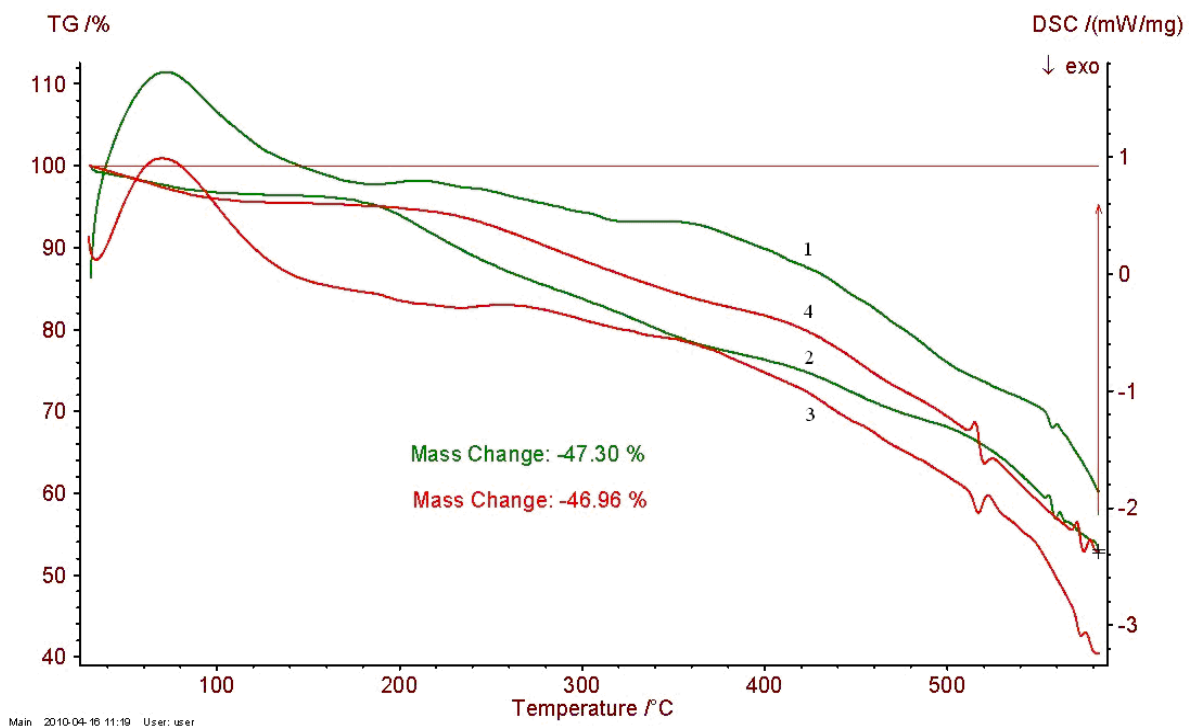


Fig. 9. TGA (2, 4) and DSC (1, 3) curves for PAI-2 (1, 2) and PAI-2 composite (3, 4) (2 wt% of nanotubes) non-porous films.

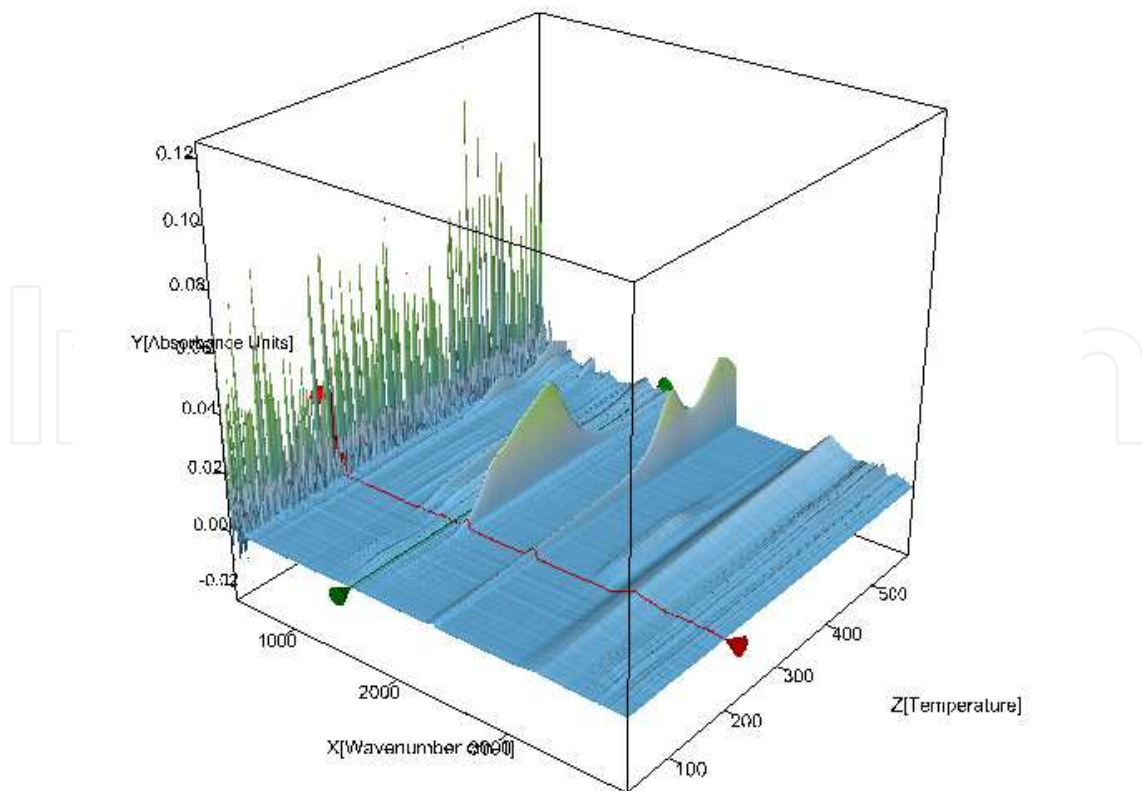


Fig. 10. 3D FTIR spectroscopy data for PAI-2 (simultaneously registered with TG-DSC).

The TGA curves related to the neat polymer (PAI-2) and the PAI-2-NT composite with the NT concentration of 2 wt% are presented in Fig. 9 (curves 2, 4). For PAI-2 (curve 2), two steps of the mass loss can be recognized: within (20-100) °C (the mass loss is about 5 wt%) and at 180 °C. The first step relates to the water evaporation, that confirmed by DSC data for polymer (curve 1, Fig 9). Endothermic peak is obviously observed on the DSC curve in this region. The next step of weight loss (curve 2) relates to the N-MP evaporation out of the inner layers of the sample (the boiling temperature of N-MP is 202 °C) and followed by thermal degradation of the sample.

The same behavior we observed in the PAI-2-NT composite (curve 4), but the beginning of the second step of mass loss is shifted to more high temperature (220 °C) compared with neat polymer matrix. It is interesting to note that in the region 200-400 °C the TGA curve for PAI-2-NT disposes above the TGA curve for PAI-2 matrix and mass loss does not exceed 20 wt% at 400 °C. This fact might be connected with NT's influence. Thus, introduction of NT's in polymer matrix promotes increasing thermal stability of PAI-2 and at the same time prevent of N-MP solvent and water removal from polymer-NT composite film.

5. Nanotubes with a chrysotile structure

The information on a chemical composition and structure of nanotubes, used in the given work is necessary for finding-out of the nature of the phenomenon discussed. Chrysotile $Mg_3Si_2O_5(OH)_4$ is the predominant fibrous form of serpentine. The crystal morphologies of the serpentines include cylindrical or conical rolls (chrysotile), planar structure (lizardite) and corrugated structure (antigorite). The structure of the chrysotile has been reviewed by Wicks and O'Hanley (1988) [35]. The first note concerning the tubular structure of chrysotile was by Pauling (1930) who suggested that the Mg-analogue of kaolinite should have a curved structure because of the misfit between the octahedral and tetrahedral sheets [36]. Later investigators confirmed this hypothesis and the tubular structure of chrysotile was demonstrated by electron diffraction and transmission electron microscopy (TEM) [37].

Chrysotile consists of sheets of tetrahedral silica in a pseudo-hexagonal network joined to a brucite layer in which Mg is in octahedral coordination with the apical oxygen of the SiO_4 layer and additional hydroxyl groups. The mismatch of the smaller lateral dimension of the SiO_4 sheet with respect to the $Mg(OH)_2$ layer is accommodated by the concentrically or spirally curled cylindrical chrysotile structure. This misfit results in a strain that can be relieved by curling of the double layer with tetrahedral part on the inner surface and the octahedral part on the outer surface [39]. As calculated by Whittaker (1955), the misfit is completely compensated at the ideal radius-of-curvature of 8.8 nm. There are several varieties of chrysotile, they differ mainly in the stacking of the double sheets and in the direction around which the sheets are rolled. Clinochrysotile and ortho-chrysotile are rolled around [100]. Para-chrysotile is rolled around the b axis. About 10 layers, each one 0.73 nm thick, constitute the wall thickness of the cylindrical rolls. The rolls possess hollow cores with a diameter of 4-5 nm because the layers energetically cannot withstand too tight a curvature. Figs. 11d and 12 present the schemes showing the incommensurate conformation between the smaller silica tetrahedra (light) and the sheet of darker $Mg(OH)_2$ octahedral.

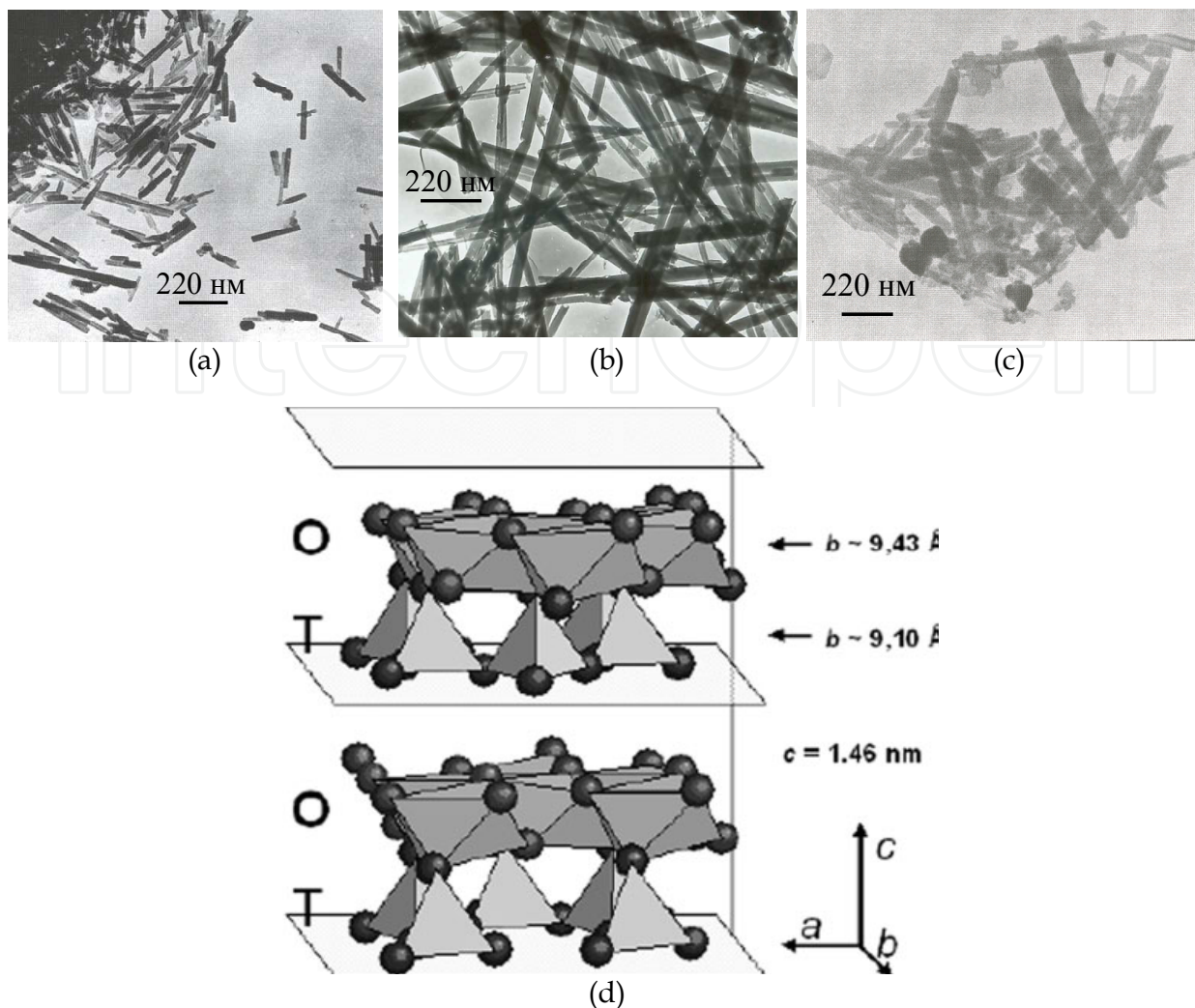


Fig. 11. (a, b, c) TEM photographs of $Mg_3Si_2O_5(OH)_4$ nanotubes of different sizes and morphologies [38]; (d) lattice of chrysotile (scheme 1) [37].

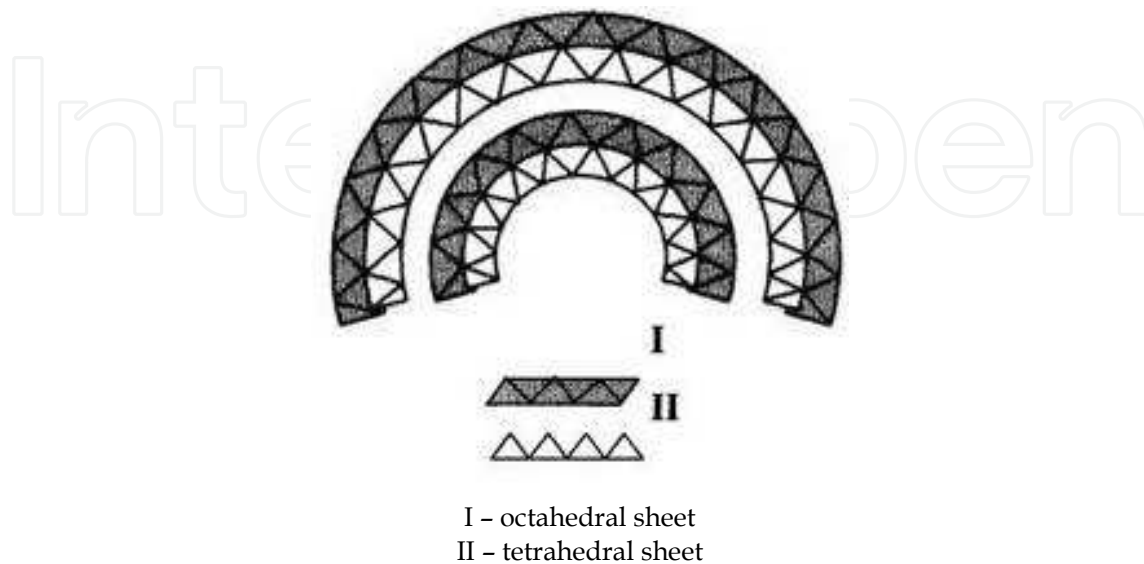


Fig. 12. Lattice of chrysotile (scheme 2) [40].

In the work, the following inorganic fillers were used in the composites: nanotubes (NT) of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ composition with a chrysotile structure. These NT were produced by hydrothermal treatment of various precursors: magnesium oxide, silicon dioxide, and MgSiO_3 with NaOH solutions at NaOH concentration of up to 3 wt% at temperatures of (250 - 450) °C and pressures of 30-100 MPa by the procedure described in [41, 42]. Nanotubes of composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ were used, with a cylindrical morphology and following dimensions: outer diameter $d_o = 20\text{-}25$ nm, inner diameter $d_i = 4$ nm, and length $L = 500\text{-}1000$ nm (NT).

Thus, introduction of described above nanotubes in a polymeric matrix of PAI means introduction of particles with a crystalline structure possessing the big area of a surface and having on their external surfaces reactionary-capable hydroxyl-groups.

6. Morphological peculiarities of PAI-NT composite films

In the paper [38] the morphology and mechanical and transport properties of the composites formed were analyzed, which enabled optimization of their synthesis conditions. It was shown an increase in permeability to liquids (pervaporation) upon introduction of inorganic nanotubular additives in PAI-1. These properties of PAI-1-NT composite material obtained are very different from those of typical composites consisting of polymer and inorganic filler. As a rule, introduction of inorganic particles into a polymeric matrix results in that an inorganic phase impermeable to gases and liquids is formed in the matrix and the mass-transfer zone becomes narrower. As a result, the permeability of non-porous films falls [43]. A study of the transport properties of the PAI-1-NT composite films (homogeneous membranes) during pervaporation demonstrated the following. Introduction into the polymeric matrix of porous inorganic particles with tubular structure without their additional treatment (chemical or orienting) leads to an increase in the flux of water across the film membrane. This effect is the most pronounced in the case of a good compatibility of components of the composite material. The results of tests of PAI-1 and PAI-1-NT films in dehydration of an aqueous ethanol solution (48 wt% ethanol) in the course of pervaporation at 40°C are shown that as the content of nanotubes in the composite increases from 2 to 10 wt%, the permeability of the material to polar liquids, such as water and ethanol, grows. Introduction of 2 wt% NT into PAI-1 film yields a composite for which the separation factor of the water/ethanol mixture even somewhat increases as compared with that for the homogeneous PAI-1 film.

In [44] it is also shown by us, how pervaporation properties of PAI-2-NT differ from corresponding properties of PAI-1-NT and also of a homogeneous PAI-1 and PAI-2 films. As is known, distinction in pervaporation characteristics of samples can be connected with influence of several factors among which are considered to be the most important two factors: diffusion and sorption ability [45]. According to diffusion-sorption model, primary transport of water and polar liquids through discussed samples testifies about hydrophylic properties of studied polyamide-imides which increase at transition from PAI-1 to PAI-2, containing carboxylic groups in a polymeric chain. Introduction of nanotubes with hydroxylic groups on their surface only enhances effect of wetting ability of material. At the same time, introduction into a polymeric matrix of objects with crystal structure reduces an area of carrying over penetrating liquids through a composite film. Thereof followed expect

permeability decrease under the relation to all penetrants, in comparison with films of base polymer. Nevertheless, permeability on water only increases, and in case of PAI-2-NT exceeds permeability of film PAI-1-NT more than 5 fold, and PAI-2 film is twice more permeable by water than PAI-1. It is necessary to notice, that permeability of samples with NT in relation to a little polar liquids remains on a low level. Hence, speech does not go about substantial growth of free volume in a material or about occurrence of micro-defects in it as a result of introduction inorganic nanoparticles though it is impossible to deny their function of spacers. Apparently, NT's in a matrix of the semi-rigid polymer having ability to strong intermolecular interactions, fill free spaces which are arise at formation of non-porous film, not moving apart polymer chains in the visible extent. It is shown [38, 46] in our works, that the increase in quantity of nanotubes entered into a matrix PAI, according to the law of negation of negation, results, since certain quantity, to allocation superfluous NT on a surface of a polymeric film. Possibly, in this system intermolecular interactions of semi-fixed chains have appeared stronger, than interactions on border polymer – an inorganic phase.

It was of interest to investigate, how structural-morphological characteristics of a polymeric matrix PAI can change as a result of introduction in it NT's presented above.

On Fig. 13 data of atom-force microscopy are presented, obtained at surface research of nanocomposite film PAI-1-NT containing 2 wt% of NT. A surface more smooth, than in case of film PAI-1. On the image a presence of nanotubes in near-by-surface layers of a polymeric matrix is visible. This result will well be coordinated with the information received at the analysis of ultra thin cross-sections of samples of type discussed, which photo is presented on Fig. 14 (a, b).

The Fig. 14 shows that nanotubes are distributed in polymeric matrix PAI-1 non-uniformly, in most cases by groups in quantity to 10 pieces on group. In some places NT approach to a surface, but are kept by polymer. With increased concentration of filler to 5 wt%, NT's are going out on a surface of a composite film that illustrates Fig. 15.

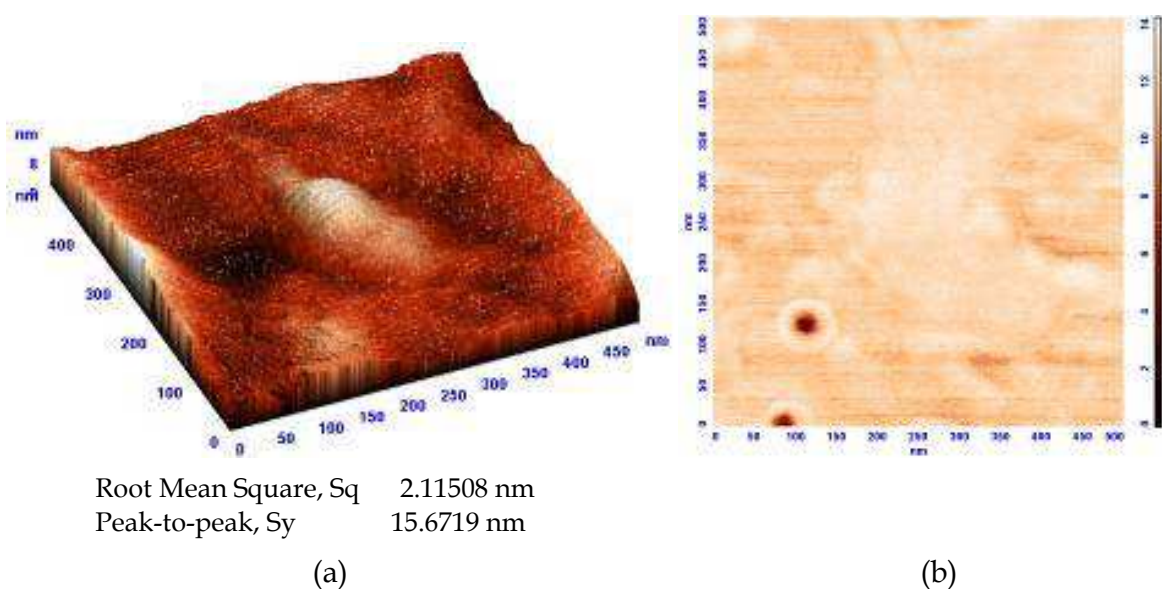


Fig. 13. 3D image (a) and (b) phase contrast image (b) for composite based on PAI-1 (2 wt% of NT).

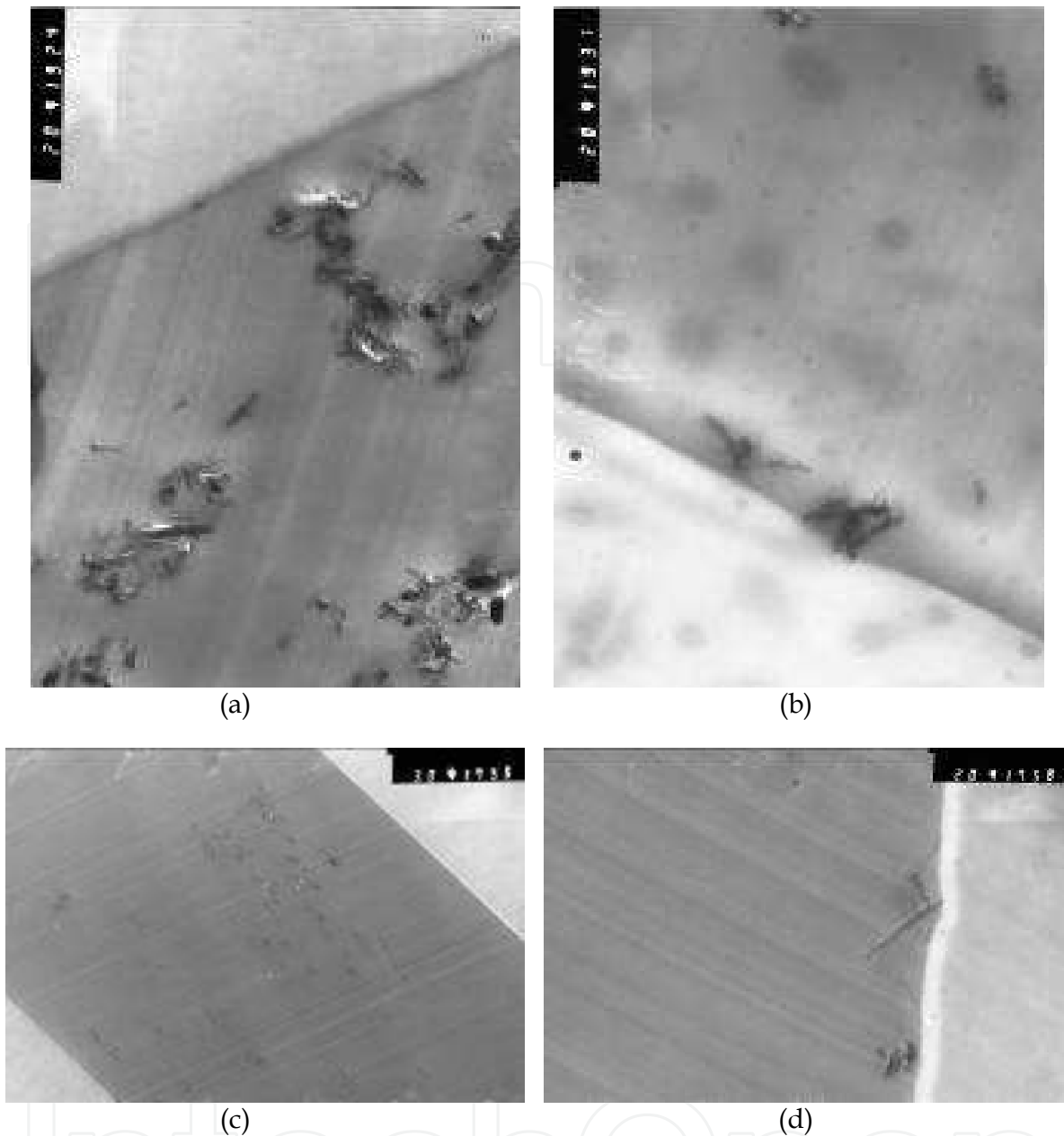


Fig. 14. Microphotographs of ultra-thin cross-sections for (a, b) PAI-1-NT (2 wt%) and (c, d) PAI-2-NT (2 wt%). Magnifications: (a, b, d) 20000, (c) 30000.

The analysis of images Fig. 15 leads to a conclusion, that at going of NT out on a surface of film adhesion between NT and a polymer matrix (that is well visible on the three-dimensional image and on profile) is broken, that negatively affects on transport properties and on values of durability of a composite [38]. In case of PAI-2-NT (2 wt%), nanotubes are distributed in a film in more regular intervals by small groups. Near to a surface they are strongly kept by polymer that illustrates a Fig. 14 (c, d). The topology of a surface of composite film PAI-2-NT (2 wt%) essentially differs from that at a surface of film PAI-2. If at AFM - image of surface of PAI-2 film craters from a solvent exit are shown (Fig. 7), the surface of composite PAI-2-NT (2 wt%) has absolutely other appearance - the same relief from more or less similar hills that illustrates a Fig. 16.

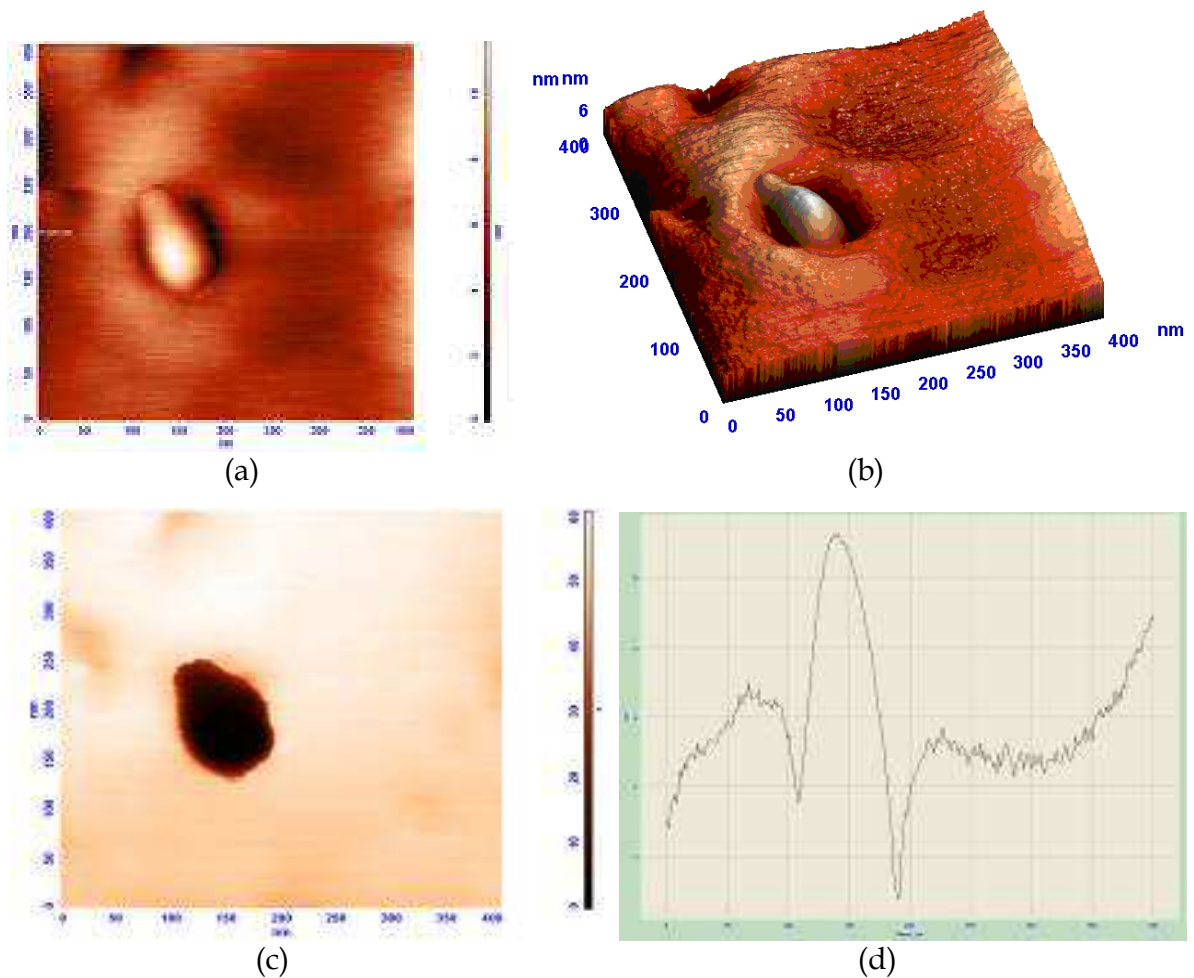


Fig. 15. AFM - images of magnesium hydrosilicate NT on the surface of polymer matrix at 5 wt% of nanofiller content: topography (a), 3D image (b), phase contrast (c) and profile (d).

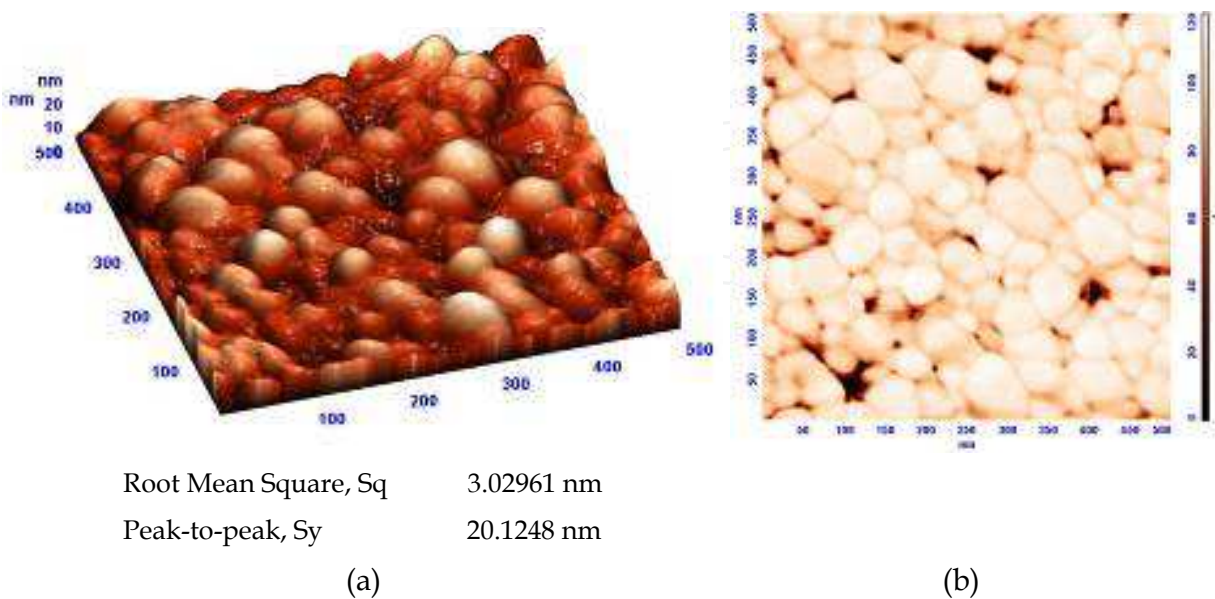


Fig. 16. 3D image (a) and phase contrast image (b) for composite film based on PAI-2 (2 wt% of NT).

On microphotographs of surface of PAI-2-NT top layer nanotubes are not visible, that confirms phase contrast image. In this case strong adhesion between nanoparticles and polymer thanks to interaction of hydroxyl groups (on the surface layers of nanotubes) and carboxylic polymer groups leads to that all nanotubes settle down in a polymeric film, and the surface relief is formed at allocation of solvent at a stage of heating of a film (Figs 9,10). Distinctions in pervaporation characteristics of PAI and PAI-NT films lead to thought that the reason of the primary accelerated transport of water through PAI-NT not differences in hydrophilic properties of samples can be only. Apparently, located in small groups in a polymeric film, nanotubes form areas of the raised permeability on water [44].

7. Conclusions

The present publication urged not only to show primary features of polyamide-imides as polymers for formation of a wide spectrum of actual materials of different morphology, but also to note once again a role of interphase border in formation of materials for composite membranes. Being formed on border polymer/polymer, polymer/air or polymer / inorganic filler, these boundary regions are capable to influence essentially on distribution of transport streams of penetrants and unexpectedly to change characteristics of diffusion membranes. Structural and morphological properties of the composite boundary layers, as well as the number of active sites of adsorption in them are characteristics that are extremely difficult to study because of problems obtaining the necessary data. Apparently, it is necessary to come nearer, methodically and carefully investigating the general morphology of membranes in a complex with their properties. Apparently, in order to get closer to the result, we need to methodically and thoroughly investigate the general morphology of the membranes together with their properties. In this context, atomic force microscopy was indispensable method, which in combination with electron microscopy, thermo-physical methods and techniques for evaluating the transport properties allow for a fresh look at the processes in the composite membranes.

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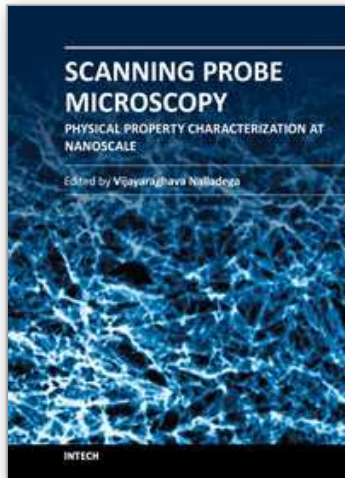
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