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Polymer-Inorganic Nanocomposites Based on Aromatic Polyamidoimides Effective in the Processes of Liquids Separation

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Abstract—The polymer-inorganic nanocomposites based on the aromatic polyamidoimides and the silicate nanotubes of chrysotile structure were developed. The polyamidoimides were synthesized from dicarboxyphenylphthalimide dichloride by the polycondensation with either 4,4'-diaminodiphenyl ether or 3,5-diaminobenzoic acid. The morphology, mechanical and transport properties of the nanocomposite films were studied. Distribution of nanotubes in the composites is shown to be defined by the chemical structure of the polyamidoimide. The conditions for the formation of the composites were optimized to provide a significant increase in selective permeability toward alcohol and water in the process of pervaporation at the introduction of the nanotubes in the polymer.

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An actual problem of the modern material science is the creation of new functional and structural materials with high performance. A promising direction in this regard is the development of hybrid organic-inorganic nanocomposites with new or improved properties compared to the initial components [1]. Their creation is stipulated by the requirements for high-performance catalysts, chemical sensors, opto-electronic and membrane materials [1–5]. The fundamentally important feature of the polymer-inorganic nanocomposites is the dispersion of inorganic components in the organic matrix where the functional properties of the material distinguishing it from the individual components is defined by the degree of mutual distribution and structural dependence of the phases [4, 5]. Therewith, each component can contribute specific characteristics to the nanocomposite.

The properties of the filled polymers associated with the processes of distribution in them of nanoscale inorganic particles are defined not only by the new structural characteristics of composites, but also by such factors as the number and nature of reactive groups of the composite components, as well as the presence of fragments in the polymer structure that can serve as the "potential ligand" for the selected filler. We suggest that the planned implementation of the discussed characteristics is the route to achieve the required functional properties, especially for the formation of diffusion membranes. The reason is that the mechanism of selective transport in a diffusion membrane is directly related to diffusion (as a consequence of structural features) and sorption (the ability to reversible interactions) capabilities of the material in relation to the penetrating substances [6].

At creating a polymer-inorganic nanocomposite for the membrane application, it is very useful to apply nanotubes (NT) of different morphology and size as the inorganic component [7]. There were works on the development of high-performance membranes based on the carbon and inorganic nanotubes oriented in thin

layers. In particular, it was attempted to create pervaporation membranes with the nanoparticles of tubular structure that allows to implement the mechanism of accelerated transport of the specific components [2, 8–10]. In this connection and due to several other factors the features were studied of the transport of liquids, especially of water, through the nanotubes and nanofibres of different chemical nature [11, 12].

Structure of nanotubes, their shape, length, ratio of inner and outer diameters, and surface chemistry can influence the morphological features of the composites 13]. However, the general principles at the combining the components, and the pattern of transport of liquids through the composites such as polymer–nanotubes have not been investigated to the moment.

Therefore a comparative study is of interest of the structure and transport properties of nanocomposites formed by the introduction of inorganic nanotubes into the polymer matrices of different chemical structure, and of the respective basic polymers. Our previous publications showed that the introduction of inorganic nanoparticles of tubular structure into the matrix of poly(diphenyloxideamido-*N*-phenylphthalimide) leads to the formation of nanocomposite material with improved mechanical and physical properties permeable to a greater extent than the original polymer in the process of pervaporation of polar liquids, in particular of water and alcohol [14]. Later on the nonporous composite films based on the aromatic polyamidoimides differing by the structure of diamine component, containing equal amounts of the silicate nanotubes of the composition $Mg_3Si_2O_5(OH)_4$ with the chrysotile structure were obtained and investigated in relation to the structure and transport properties.

The choice of this filler is defined, above all, by the fact that the physicochemical principles of the predefined synthesis of these hydrosilicates nanotubes under hydrothermal conditions are now known, and as a consequence the methods are known of the control over the structure, morphology and size of the tubes and their assemblies at varying the mode of synthesis and the composition of the reaction medium. The main reason for the choice of nanoparticles is the chemical composition of their surface, namely, the presence of the reactive polar hydroxy groups.

We studied the moderately hydrophilic polyamidoimides characterized by the ability to interact with the functional groups of magnesium-silicate nanotubes, as well as to the sorption interaction with the solvents used as a penetrating substance in the process of pervaporation. Thus, it became possible to study the influence of functionalization of the polymer matrix on the morphological and transport properties of formed nanocomposites, and the results obtained are presented in this publication.

This study is a logical continuation of our previous work. Earlier we prepared a new nanocomposite material of tubular structure (PAI-1-NT) from poly (diphenyloxideamido-*N*-phenylphthalimide) (PAI-1) and layered magnesium hydrosilicate $Mg_3Si_2O_5(OH)_4$ [14]. PAI-1-NT is the result of optimization of the initial composition in respect of the composition, shape and morphology of the obtained nanotubes, the duration and method of combining components without additional modifiers and reagents, and the morphology of the obtained porous films studied by scanning electron microscopy (zoom up to 10000). It was shown in [14] that PAI-1-NT is the material permeable to a greater extent than the original polymer (PAI-1) in the pervaporation process in relation to polar liquids, in particular, water or water–alcohol solutions. It was proved that this effect cannot be a result of the influence on the permeability of the material of microinhomogeneities or microdefects (at nanoscale level or larger) in the nonporous matrix of the composite film. Although there is always a probability of appearance of the defects in the process of introduction of inorganic component, it does not occur at forming PAI-1-NT.

An essential difference between the obtained composite material PAI-1-NT and the typical polymer–inorganic filler composites should be also stressed in respect to the increase in its permeability at the introduction to PAI-1 of inorganic nanotubular additives. A typical result of introduction of inorganic particles in polymer matrix is the formation in the latter of an inorganic phase not permeable for gases and liquids, which leads to a decrease in mass transfer zone [15, 16]. For this reason, the introduction to the PAI-1 of the particles of MMT-15A (a commercial product Cloisite 15A, Southern Clay Products, Inc., USA) under the same conditions as the nanotubes, results in the formation of a composite material with low permeability by the named substances. The inorganic particles MMT-15A and silicate nanotubes are similar by chemical composition, and in these systems there are no other components, and the changes in the conditions of formation are excluded. Therefore it was

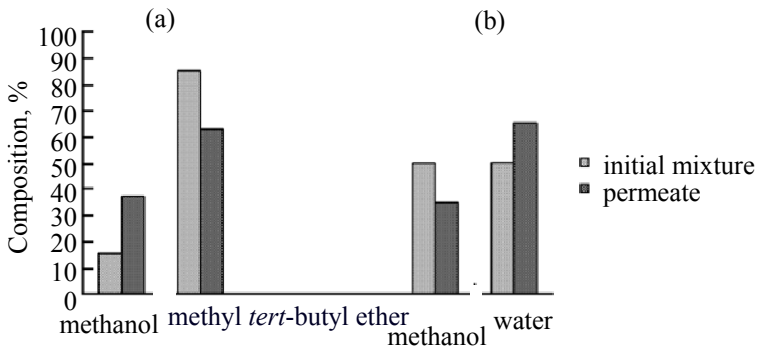

Fig. 1. Separation of (a) methanol–methyl *tert*-butyl ether mixtures at 40ºC and (b) methanol–water at 20ºC on PAI-1-NT.

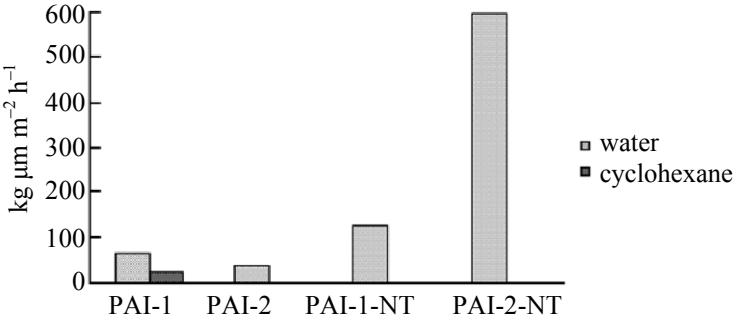

Fig. 2. Premeability by water and cyclohexane (at 40ºC) of non-porous membranes PAI-1, PAI-1-NT, PAI-2, and PAI-2-NT.

suggested that the decisive influence on the transport properties of these composite films is connected with their structural features on the nanoscale level [14].

In the present study we examined the transport properties of PAI-1 and PAI-1-NT at the pervaporation in relation to a wide range of penetrating substances (water, methanol, cyclohexane, and methyl-*tert*-butyl ether). Figures 1 and 2 illustrate not only the difference in the permeability of porous films of PAI-1-NT with respect to polar and weakly polar liquids, but also the ability of the tested material to separate their mixtures. The separating ability of PAI-1-NT is evident even in the case of transport of mixtures of the strongly associated components (methanol–water), and the nanocomposite permeability by water is higher compared with the polymer constituting it (in Table 1 are listed the values of water permeability for PAI-1 and PAI-1-NT normalized to the film thickness).

The observed effects are typical for the membranes formed from non-porous nanocomposite films, in which the nanotubes are distributed within the volume of the polymer matrix and are not visible on the upper and lower surfaces of the film with electron microscopy at the zoom 18000, like shown in [14]. The photomicrographs of surfaces of extruded films show that the surface relief of PAI-1-NT is similar to the corresponding reliefs of homogeneous film of the basis polymer PAI-1. Thus, both the PAI homogeneous film and the composite film are characterized by a smooth upper and finely granular lower surface, on which are viewed clearly expressed band, the "fingerprints" of the relief of the glass substrate for molding the films, and not related to the presence of an inorganic component in the composite.

The above described method of preparation of composites applied in these works can lead to a specific orientation of nanotubes in the films. As is known from literature and discussed in several papers, the processes of accelerated transport of liquids or gases through internal channels of carbon or inorganic nanotubes oriented in the membrane structure in the direction of the penetrant motion can not play a decisive role in this case. But it is unclear how is formed and where is located the "priority transport channel" for the more polar components of the penetrating mixture. An assumption seems correct about the special role of the hydroxy groups located on the outer surface of the used nanotubes that are able to

interact with both amide and imide groups of the PAI-1 polymer chain, and with the polar groups of the transported molecules (water, alcohols). If this assumption is correct, then the introduction in the polymer chain of the functional groups capable to form hydrogen bonds with hydroxy groups or water dipoles should affect the transport properties of the composites.

To test this hypothesis we obtained the composite PAI-2-NT that differs from PAI-1 by the structure of the diamine component and contains carboxy group of diaminobenzoic acid (PAI-2). Figure 3 shows micro-photographs of (a) nanotubes, (b) upper, and (c) lower surfaces of the film PAI-2-NT. It is shown that, as in the case of PAI-1-NT, the lower surface of the film has a distinct grain structure, unlike the smoother upper surface. On both surfaces at the zoom 18000 were not found freely "lying" nanotubes, nor their fragments. All the elements of inorganic component were distributed in the inner layers of the composite film.

Tables 1 and 2 and Fig. 2 show the transport properties of the films PAI-2-NT and PAI-2. It is obvious that the PAI-2 (more hydrophilic polymers is twice more permeable by water than PAI-1, like in the case of PAI-1-NT compared to PAI-1. The introduction of nanotubes in the PAI-2 enhances the ability of the film to pass water more than 4-fold, which makes the material 5-fold more permeable for water than PAI-1-NT. It should be noted that the permeability of PAI-2-NT by a low polar penetrant cyclohexane remain as low as the permeability of PAI-2, in contrast to PAI-1, for which the introduction of nanotubes reduces the permeability of cyclohexane significantly (Table 2, nos. 1, 3). Nevertheless, note the possibility of selective separation of water from the mixtures with low polar components (Table 2, nos. 4, 5). From a practical point of view, this relates to drying weakly polar organic solvents. The effect is most clearly illustrated in the diagram shown in Fig. 2.

An interesting fact is that the use of homogeneous nonporous film PAI-2 for the water pervaporation, can lead to reducing the film permeability more than 3 times (Table 1, no. 2). This effect was not observed at the testing of pervaporation through the film PAI-2-NT. The introduction of nanotubes impedes the re-structuring of the polymer matrix as a result of interaction with the flow of penetrant.

Table 1. Permeability by water of the non-porous films in the pervaporation process at 40°C

Run no.	Type of sample	$C_{(NT)}$, wt %	l, μm	P, kg m^{-2} h^{-1}	Pl[a], kg μm m^{-2} h^{-1}
1	PAI-1	–	15	0.043	0.645
2	PAI-2	–	21	0.066 → 0.018	1.380 → 0.378
3	PAI-1-NT	2	15	0.084	1.260
4	PAI-2-NT	2	21	0.284	5.964

[a] Pl is permeability normalized to the sample thickness.

Thus, the introduction in a relatively low concentration of the nanotubes with the structure of chrysotile, with the reactive hydroxy groups on their surface, leads to a significant change in the transport properties of polyamidoimide material. Most important is the fact that the composites PAI-1-NT and PAI-2-NT obtained under similar conditions and containing nanotubes in equal amounts are similar by the trend of permeability of polar and weakly polar liquids, but differ by degree. The composite film PAI-2-NT, possessing high selectivity with good permeability (Table 2), may have practical importance as the membrane material, and even more so, as the material of the diffusion layer of the composite membrane.

The effect obtained requires attention and explanation. It obviously is associated with the appearance of a channel with facilitated transfer of the dipoles of water molecules or polar alcohols in moderately swelling matrix of the composite film. The nature of interaction of the polymer matrix with the nanoparticles, which determines distribution of the latter in the nanocomposite film affects the effectiveness of formation of the transport channel. In other words, the difference in the structure of the films on

Table 2. Permeability by cyclohexane [nos. (1)–(4)] and water (no. 5) of non-porous films in the process of pervaporation.

Run no.	Type of sample	$C_{(NT)}$, wt %	l, μm	T, °C	$P\times10^2$, kg m^{-2} h^{-1}	Pl, $\times10^2$, kg μm m^{-2} h^{-1}
1	PAI-1	–	24	19	0.85	20.40
2	PAI-2	–	22	20	0.05	1.10
3	PAI-1-NT	2	24	19	0.00	0.00
4	PAI-2-NT	2	22	18	0.06	1.32
5	PAI-2-NT	2	22	21	9.82	216.04

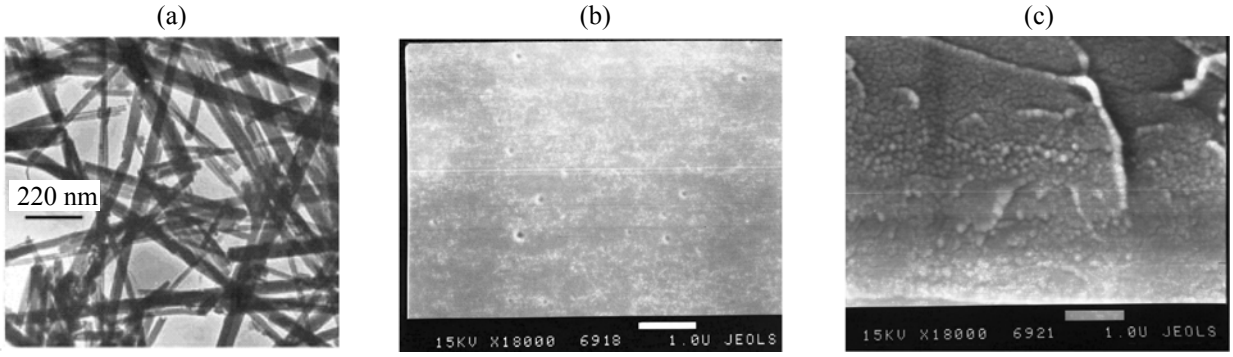

Fig. 3. Electronic microphptographs of (a) nanotubes, (b) upper, and (c) lower surfaces of the PAI-2-NT film.

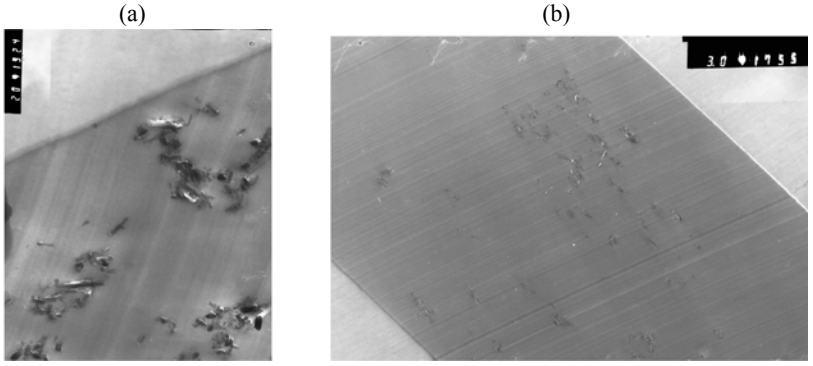

Fig. 4. Electronic microphptographs of ultrafine sections of the nanocomposites (a) PAI-1-NT and (b) PAI-2-NT.

the nanoscale level leads to a difference in their transport properties. Figure 4 shows ultrafine cross-sections of PAI-1-NT and PAI-2-NT films, allowing to judge about the nature of nanotubes and their agglomerates distribution in the inner layers of membranes. The image analysis shows that unlike the PAI-1-NT film, which is characterized by aggregates of 10 nanotubes randomly placed throughout the thickness of the sample, in the PAI-2-NT the aggregates are observed of 2–3 nanotubes that are uniformly distributed in the inner layers of the film. These morphological features correlate well with the data on pervaporation presented in this paper.

Thus, in order to control the transport properties of the polymer-inorganic systems, we have investigated the factors influencing formation of their structure. These properties may include especially the nature and extent of interaction between the inorganic and polymer components of the nanocomposite. For this reason we studied conditions for the formation of nanocomposites based on aromatic polyamidoimides depending on the content in their molecules of functional groups capable of forming hydrogen bonds. The morphology and transport properties of the nanocomposite films in comparison with the homogeneous films formed from these polymers were studied. We also investigated distribution of nanotubes on surfaces and in the internal layers of the composite films.

Investigation of the transport properties showed that introduction into the polymer matrix of porous inorganic particles of tubular structure without additional processing (both chemical and orientation) leads to an increase flow of the water and lower aliphatic alcohols through the corresponding membrane film. The nanocomposite membrane PAI-2-NT showed practically significant transport properties such as high selectivity in the process of isolation of water from the water–organic mixtures.

The results obtained allow a conclusion that a new polymer-inorganic nanocomposite is obtained of considerable practical interest, especially in the light of the solution of a number of current problems associated with the purification of natural hydrocarbon raw material and respective products [17], in particular, from the contaminating them aliphatic alcohols and water.

EXPERIMENTAL

As a matrices for the preparation of hybrid composite materials were used polyamidoimides differing in the structure of diamine components. The polyamidoimides were synthesized by the low-temperature polycondensation of dicarboxyphenylphthalimide dichloride with 4,4'-diaminodiphenyl ether (PAI-1, M 68 000), or 3,5-diaminobenzoic acid (PAI-2, M 57 000) in solution, by the method described previously [18].

As the inorganic fillers of the composites were used the nanotubes of the composition $Mg_3Si_2O_5(OH)_4$ with the structure of chrysotile, synthesized under hydrothermal conditions. The nanotubes were obtained by hydrothermal treatment of precursors: magnesium oxide, silicon dioxide, and magnesium metasilicate $MgSiO_3$ with NaOH solution of concentration up to 3 wt % at 250–450°C under pressure 30–100 MPa using the method described in [19, 20]. For hybrid nanocomposites were used the nanotubes of the composition $Mg_3Si_2O_5(OH)_4$ with cylindrical morphology, of 20–25 nm outer diameter, 4 nm inner diameter, 200–500 nm length.

The composites were prepared in a medium of *N*-methyl-2-pyrrolidone by ultrasound action on the nanotubes dispersion while stirring with solutions of PAI-1 or PAI-2 (8 wt %), in air at room temperature. The duration of stirring of the nanotubes dispersions (up to 20 h) and their concentration in the compositions (2 wt %) are defined by the aim of obtaining the composites with uniformly distributed inorganic phase.

The obtained dispersions were applied on the surfaces of glass plates by extrusion, and after removal of the solvent in the process of heat treatment (up to 150°C) non-porous thin film ~20 μm thick was formed.

The morphology of the membranes was studied by scanning electron microscopy and transmission electron microscopy on a JSM-35C (Jeol, Japan) and a JEM 100-C instruments, respectively. For preparation of ultrathin sections of thickness 300–500 Å with ultratome (LKB, Sweden), the samples were preimpregnated with "Araldit" resin (polymerization at 60ºC for 8 h).

The pervaporation characteristics of continuous film membranes were determined with respect to water, methanol, ethanol, cyclohexane, *tert*-butyl methyl ether and their mixtures at temperatures up to 40°C on a pervaporation installation using the membrane working area 12.4 cm^2. The pressure under the dry membrane (before the process of pervaporation) was about 1×10^{-2} Pa. Knowing the working area of the membrane and the amount of the permeate passing through the membrane, we estimated the flow P [kg m^{-2} h^{-1}], as well as the flow normalized per unit of thickness (l) of the membrane, Pl (kg μm m^{-2} h^{-1}).

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