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Polyamide Membranes Modified by Carbon Nanotubes: Application for Pervaporation

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New polymer nanocomposites consist of poly(phenylene isophtalamide) (PA) modified by carbon nanotubes (CNT) were obtained by the solid state interaction method to prepare dense membranes. The investigation of the PA/CNT nanocomposites was made by Raman spectroscopy. The morphology of the dense membrane was analyzed by SEM. The transport properties of the dense polyamide membranes modified by 2 and 5 wt% CNT were studied in pervaporation of methanol/ methyl *tert*-butyl ether mixture. It was shown that the selectivity with respect to methanol and permeability were the highest for membranes containing 2 wt% CNT as compared to membranes of pure PA and containing 5 wt% CNT. To analyze transport properties the sorption tests and contact angle measurements were employed.

Keywords carbon nanotubes; dense membranes; pervaporation; poly(phenylene isophtalamide)

INTRODUCTION

Incorporation of nano-size particles in known polymer membrane materials is one of the ways to develop new nanocomposite membranes with improved transport properties. Nanocomposite membranes find successful application in membrane technology, and in pervaporation, among other processes. The growing interest in pervaporation is connected with the possibility of using this membrane process for the separation of azeotropic mixtures and substances that have close boiling-points. Furthermore, pervaporation is a low energetic process, and therefore it is important for industrial application. In the present work the separation of methanol (MeOH) and methyl *tert*-butyl ether (MTBE) mixture is under study. The separation of this mixture is an important problem. First of all, MTBE is used to increase the octane number of gasoline and to increase the efficiency of combustion to achieve a cleaner burning process and thereby reduce the emission of compounds such as carbon monoxide and ozone. It has been shown that an addition of 10–15% MTBE to gasoline increases the motor octane number by 2–5 (1). MTBE is also used as a reagent in fine chemical production. For these reasons, the market demand for MTBE is rapidly increasing. MTBE is usually produced by the reaction between methanol and *iso*-butylene at moderate temperature and pressure. It is often desired to add methanol up to 20% excess to improve the reaction conversion. Therefore, the separation of methanol/MTBE mixtures constitutes an important unit operation. Another tricky problem is that methanol forms an azeotrope with MTBE at a composition of 14.3 wt% methanol at atmospheric pressure. Due to this fact, pervaporation is the best tool for the separation of this mixture.

So far, many polymers such as cellulose acetate and triacetate (2–4), chitosan (5), polyvinyl alcohol (6), acryl amide copolymers (7), and agarose (8) have been used as membrane materials for the pervaporation separation of methanol/MTBE mixtures. Every one of the above stated membranes has some advantages and disadvantages. One of the ways to improve the membrane properties is to modify polymer membranes by nano- or ultraparticles. Organic–inorganic hybrid membranes have attracted considerable recent attention as potential ''next generation'' membrane materials (9–11). Such hybrid membranes are typically composed of polymeric and inorganic materials,

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and have both membrane-forming properties of a polymer and physico-chemical stability of inorganics (12,13). Inorganic particles in organic–inorganic hybrid membranes are usually silica, zeolites, metal oxide nanoparticle, nanotubes, and so on. More recently, there has been a growing interest in exploring new applications of porous carbons because of their ability to interact with molecules not only at their surfaces but also within the bulk of the material (14). The announced effect was observed in the work (15) where properties of the cellulose acetate membranes were improved by filling them with metal oxide particles for the separation of methanol/MTBE mixtures. The permeation flux and the separation factor of blended cellulose acetate membrane were higher than those of pure cellulose acetate membrane. Also, it was shown (16) that the cellulose acetate membrane filled with 0.2 wt% zeolite showed the higher separation factor and permeation flux in pervaporation of 20 wt% methanol/MTBE mixtures as compared to the non-modified membrane.

The aim of the present work is to obtain poly(phenylene isophtalamide) (PA) membranes filled with carbon nanotubes (CNT) and estimate their pervaporation properties in the separation of the methanol/MTBE mixture. The PA is known as excellent commercial membrane material due to its chemical resistance and good mechanical properties.

EXPERIMENTAL

Materials

Poly(phenylene isophtalamide) with a molecular weight of 105 kD and density of 1.33 g/cm^3 was used for the work. It was purchased from Vecton (Russia). Multi-walled carbon nanotubes (Taunit®) were obtained by the chemical vapor deposition method at Innovation Technologies Center (Tambov, Russia).

PA-CNT composites containing 2 and 5 wt% CNT were obtained by thorough mixing of powders of PA and nanotubes in porcelain mortar. After the solid-phase interaction the composites were dissolved in N,N-dimethylacetamide (DMAc) with ~0.7 wt% LiCl additives for solution stabilization. The PA/CNT solution was intensely stirred and sonified before membrane preparation.

Dense membranes of thickness ~30 μm were obtained by casting 8 wt% solution in DMAc on a glass support with the subsequent drying at 40°C and heating at 60°C in vacuum for a week. CNT-containing membranes had a grey color whose intensity depended on the quantity of CNT in the composites.

Characterization

Raman Spectroscopy

Raman spectra excited in the visible range with a HeNe 633 nm and argon-ion 514 nm lasers were collected on a Renishaw inVia Reflex Raman microscope. Research grade Leica DM LM microscope with objective magnification × 50 was used to focus the laser beam on the sample placed on a X–Y motorized sample stage. The scattered light was analyzed by the spectrograph with a holographic grating (1800 and 2400 lines mm^{-1}). A Peltier-cooled CCD detector (576 × 384 pixels) registered the dispersed light.

Scanning Electron Microscopy (SEM)

SEM micrographs were obtained with a microscope JSM 6400 (Jeol). Thin PA membranes were submerged in liquid nitrogen for 5 min and fractured perpendicularly to the surface. Then the specimens were fixed by conductive glue to metal supports, sputtered with a thin platinum layer (4 nm; Vacuum sputter coater SCD 050, Balzers), and the fracture surfaces were observed in the SEM microscope using secondary electrons at 15 kV.

Contact Angle Measurements

Contact angles of liquids on dense membrane surfaces were measured by the Wilhelmy plate technique, using the KRUSS installation. In the Wilhelmy plate technique, the advancing (θ_a) and receding (θ_r) angles are calculated from the force exerted as the sample is immersed or withdrawn from a liquid. A computer controls the stage velocity and movements and provides the software required for calculations. Liquids under study were water and methanol.

Sorption Experiments

The swelling of the membranes in methanol vapor was determined by measuring of the quantity of methanol adsorbed by the membranes at 20°C. The procedure was as follows: the membrane was put in a vacuum balance Sartorius type 4102 connected to a diffusion pump. The system was evacuated and heated for 3 hour. The vacuum was stopped and methanol was injected in the system at defined pressure (12 kPa). The change in weight of the membrane was recorded with a line recorder TZ 4100. The degree of swelling in methanol (or degree of methanol sorption) can be calculated by the following relation:

$$Sw = \frac{M_s - M_d}{M_d} \tag{3}$$

where M_s is the weight of a swollen membrane that reached equilibrium state (weight of swollen films became constant) and M_d is the weight of a dry membrane.

The diffusion coefficient, D (m^2/s), of methanol into a polymer membrane was determined from the derivatives of the sorption kinetic curve (17).

$$D = \frac{\pi}{16} \cdot R^2 \cdot \ell^2 \tag{4}$$

where R is the initial slope of the sorption kinetic curve and l is the thickness of a dry membrane.

To determine the polymer-solvent interaction parameter, the polymer volume fraction in swollen samples, φ_2, was calculated as

$$\varphi_2 = \frac{1}{1 + \frac{\rho_2}{\rho_1} \cdot Sw} \tag{5}$$

where ρ_1 and ρ_2 are solvent and polymer densities (g/cm^3), respectively.

Then, the Flory-Huggins theory equation was used (18):

$$\ln a_1 == \left[\ln(1 - \varphi_2) + \left(1 - \frac{1}{Z}\right)\varphi_2 + \chi\varphi_2^2 \right] \tag{6}$$

The interaction parameter, χ, was calculated in the ideal solvent approximation ($\ln a_1 = 1$) by the following formula (19):

$$\chi = \frac{-[\ln(1 - \varphi_2) + \varphi_2]}{\varphi_2^2} \tag{7}$$

The Flory-Huggins interaction parameter directly characterizes the solubility of a polymer in a given liquid.

Pervaporation

Pervaporation properties were measured using a laboratory cell having an effective membrane area of 14.8 cm^2 at 50°C with stirring. Downstream pressure below 10^{-1} mm Hg was maintained. The permeate was collected in a liquid nitrogen trap, weighed, and then analyzed by refractometry and gas chromatography. Methanol and MTBE were used as mixture components.

Membrane permeation flux, J (kg/m^2 h), was determined as an amount of liquid transported through the unit of the membrane area per time unit.

The selectivity or the separation factor, α, was defined by the equation

$$\alpha = \frac{y_i/y_j}{x_i/x_j} \tag{8}$$

where y_i and y_j are the weight fractions of components i and j in the permeate and x_i and x_j are the weight fractions of components i and j in the feed.

RESULTS AND DISCUSSION

Characterization of PA-CNT Composites

Membranes based on PA/CNT compositions prepared by solid phase interaction were characterized by SEM and Raman spectroscopy.

Raman Spectroscopy

Contrary to the infrared spectroscopy, the Raman spectroscopy is a good tool for the studying of carbonaceous materials (20). Two broad bands usually centered at about 1581 and 1341 cm^{-1} are typical for graphite and carbonaceous materials. The Raman-active vibrational mode of perfectly ordered graphite is situated at 1575 cm^{-1} (band labeled "G" for graphite). It originates from the ordered hexagonal rings consisting of conducting sp^2-bonded carbon. With increasing disorder, this band broadens and moves to a higher frequency, and a new band appears at 1350 cm^{-1} (band labeled "D" for disordered form) (21). The "D" peak in carbon-based materials has been observed for disordered graphite, such as the clusters of hexagonal rings. This band has a strong resonant character, as seen by dependence of the intensity and the position on the wavenumber (22).

Raman spectra of pure PA, its composites with 2 and 5 wt% CNT, and the spectrum of pure CNT powder obtained with 632.8 nm laser excitation are presented in Fig. 1a. The tangential G-band (derived from the graphite-like mode) is situated at 1583 cm^{-1} in the spectrum of the CNT sample. In contrast to the graphite Raman G band, which exhibits one single Lorentzian peak, this band has a shoulder at higher wavenumbers. Disorder- induced D- band is situated at 1329 cm^{-1} in the spectrum CNT. The spectra of PA nanocomposites with 2 and 5 wt% CNT are very similar to the spectrum of the pure PA membrane, in which a strong fluorescence background is also observed. It should be stressed that the bands of CNT overlap the band of the pure PA membrane. We suppose that CNT are not well dispersed in the PA membrane and no interaction between the PA and CNT molecules occurs. The corresponding Raman spectra obtained with 514 nm laser excitation are presented in Fig. 1b. The Raman active G- and D-bands of CNT are situated at 1595 and 1348 cm^{-1} respectively. They are also not observed in the spectra of nanocomposites with 2 and 5 wt% CNT that are similar to the spectrum of pure PA membrane.

Scanning Electron Microscopy

Internal morphology of PA/CNT membranes was studied by SEM microscopy of fracture surfaces (Fig. 2). The fracture surface of pure PA (not shown here) contained only a few fracture lines and plastic deformations of pure polymer matrix. Fracture surfaces of PA/CNT composites exhibited both plastic deformations of PA matrix (white lines) and agglomerates of CNT (white islands, mostly in between the plastic deformation lines). Increase in filler concentration was clearly visible at both low-magnification (Fig. 2a,b) and high-magnification (Fig. 2 c,d) micrographs. Moreover, the agglomerates were significantly bigger in the system with 5 wt% CNT, as documented at higher magnifications: In PA/CNT(2 wt%), the agglomerates were mostly smaller than 1 μm (Fig. 2c), whereas in PA/CNT(5 wt%) the agglomerates with sizes of several micrometers were not an exception (Fig. 2d).

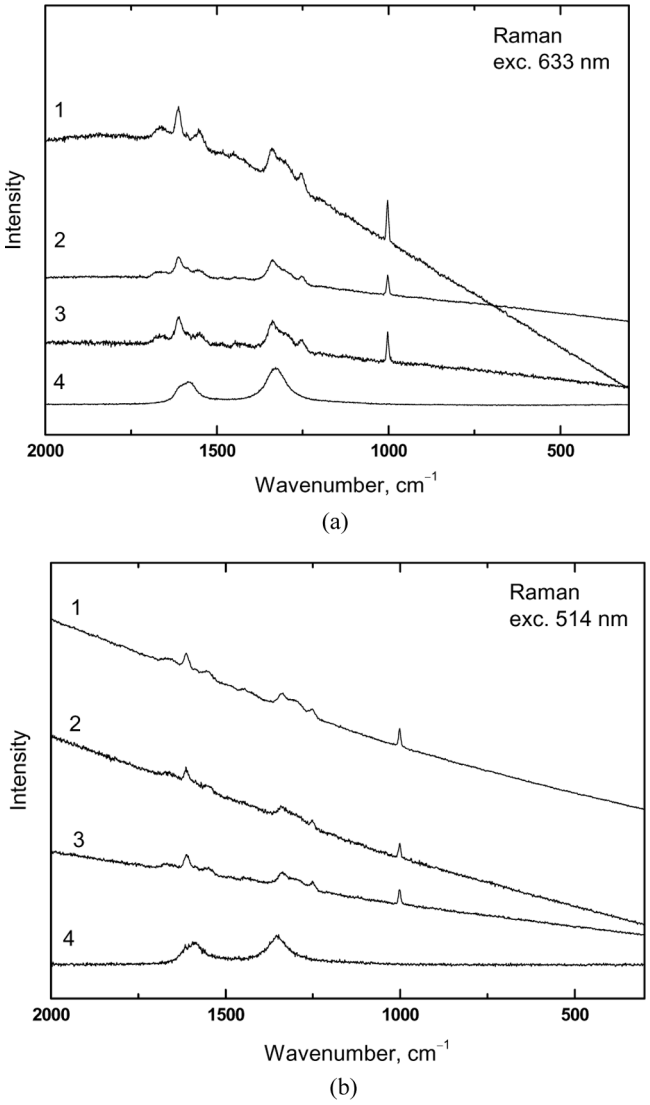

FIG. 1. The Raman spectra of (1) PA, (2) PA/CNT(2%), (3) PA/CNT(5%), and the spectrum of pure (4) CNT measured with (a) 633 nm, and (b) 514 nm laser excitation line.

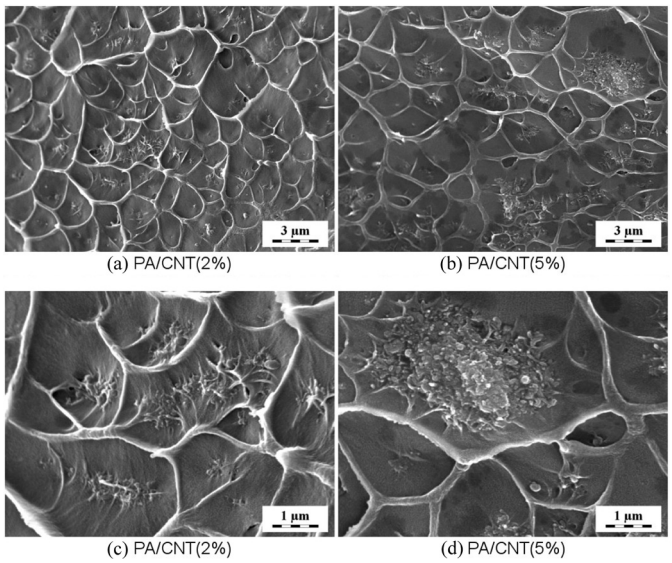

FIG. 2. SEM micrographs showing fracture surfaces of PA membranes filled with 2% CNT (a,c) and 5% CNT (b,d). The micrographs were taken at magnification x5000 (a,b) and x15000 (c,d). The fracture surfaces were perpendicular to membrane surfaces.

The presence of big agglomerates indicated poor interfacial adhesion between the matrix and the filler. This result was confirmed by Raman spectroscopy that did not reveal any strong interaction between PA and CNT. Therefore, the interfacial adhesion in the PA/CNT system was low and, as a result, the increase in CNT concentration of CNT resulted in big agglomerates of the filler, which were poorly fixed in the polymer matrix. This might be one of the main reasons why PA/CNT membranes with 5 wt% CNT exhibited worse pervaporation properties, as discussed below.

Pervaporation

Transport of small molecules through the polymer membranes is one of the characteristics sensitive to polymer modification. The transport properties of the PA/CNT membranes were studied in the separation of the methanol/MTBE mixture by pervaporation. The physico-chemical properties of the penetrants are presented in Table 1.

According to the solubility theory (23), the less is the difference in solubility parameters of polymer and penetrants $|\Delta\delta|$, the better is the solubility of this penetrant in the polymer. The solubility parameter of PA is equal to 27.7 $(J/cm^3)^{1/2}$. So, methanol solubility should be preferential as compared to MTBE.

The methanol/MTBE mixture is characterized by an azeotropic point that contains 14.3 wt% methanol and 85.7 wt% MTBE at 20°C, 760 mmHg. It is known from Vrevsky's law that the azeotropic point position on a liquid-vapor diagram varies with pressure and temperature (24). Therefore, the pervaporation experiments were carried out in the concentration range of 14–70 wt% methanol in the feed that involves possible composition of the azeotropic mixture in pervaporation conditions (50°C and 10^{-1} mmHg).

Figures 3 and 4 show the results of methanol/MTBE mixture pervaporation by using membranes of pure PA and its composite containing 2 and 5 wt% CNT. For all feed compositions, the permeate was enriched with methanol, that is, all membranes are selective with respect to methanol. Figure 3 shows that the selectivity of all membranes decreases with the rise of the methanol amount in the feed mixture. It was found that the selectivity of PA/CNT(2 wt%) membrane is higher than that of pure

TABLE 1
Properties of penetrants

Penetrant	MW	Density, g/cm^3	Molar volume, cm^3/mol	Viscosity, m · Pa · s	Solubility parameter, (J/cm^3)$^{1/2}$
Methanol	32.0	0.792	40.4	0.55	29.7
MTBE	88.2	0.740	119.1	0.36	16.0

PA, whereas the selectivity of the membrane with 5 wt% CNT is the lowest. In the last case the decrease of the selectivity can be caused by two factors. The first one is the defects inside the membrane (see SEM micrographs). The second factor is high sorption of methanol that can promote the creation of additional transport channels for the permeability of small molecules.

Figure 4 shows the dependence of specific permeation flux, $J \cdot l$, on the methanol content in the feed. The total permeation flux, J, is inversely proportional to membrane thickness, l, which varied from 20 to 40 μm, and permselectivity strongly depends on it. Therefore, the product $J \cdot l$ was used for comparing the permeability of dense membranes with different thickness. Figure 4 shows that the permeability of membranes based on PA and containing 2 and 5 wt% CNT increases with methanol concentration in the feed; in doing so the penetrant flux across the membrane increases with the CNT content. To sum up, the membrane containing 2 wt% CNT exhibits the best transport properties in the case of pervaporation of methanol/MTBE mixture.

It should be mentioned that the values of transport parameters under the separation of the methanol/MTBE mixture strongly depend on the membrane polymer nature. For example, the membranes based on poly(ethylene-co-vinyl acetate) (25) exhibit lower values than that obtained in the present paper whereas using zeolite (HZSM5)-filled cellulose acetate membranes improves the known transport properties in separation of the methanol/MTBE mixture (16).

It is known that the mechanism of the pervaporation process can be described in terms of solution–diffusion mechanism, namely, permeability is directly proportional to solubility and diffusivity (26). Therefore, to account for the obtained pervaporation results, the sorption and diffusion parameters of penetrants in membranes was measured and analyzed.

Sorption

Sorption experiments showed that PA and its composites with CNT are adequately swelling in methanol. However, MTBE sorption was absent in these membranes.

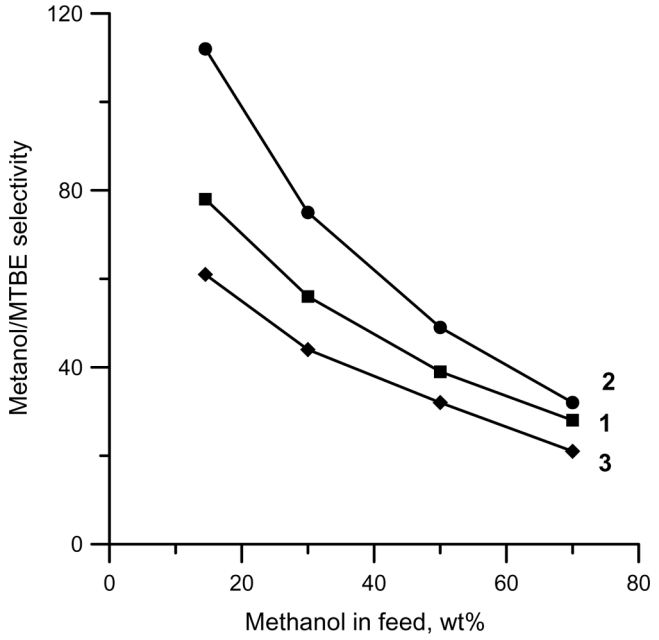

FIG. 3. Dependence of selectivity on methanol concentration in the feed for the pervaporation of methanol-MTBE mixture through (1) PA, (2) PA/CNT(2%), and (3) PA/CNT(5%) membranes.

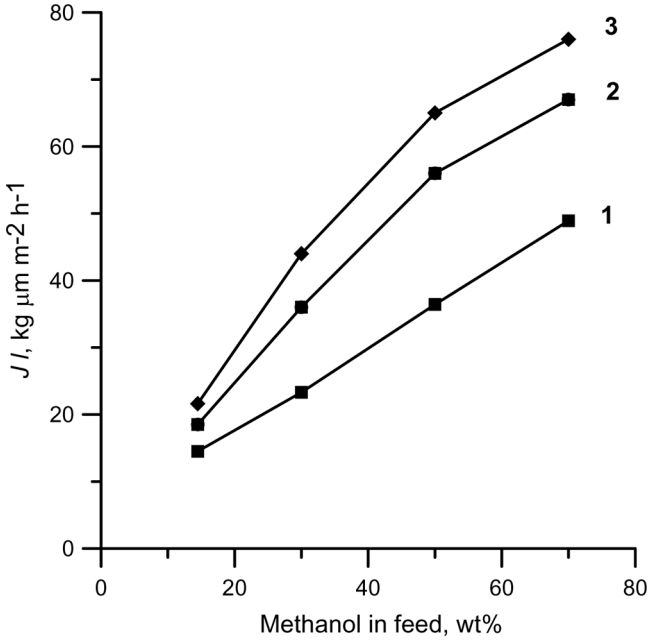

FIG. 4. Dependence of flux on methanol concentration in the feed for the pervaporation of methanol-MTBE mixture through (1) PA, (2) PA/CNT(2%), and (3) PA/CNT(5%) membranes.

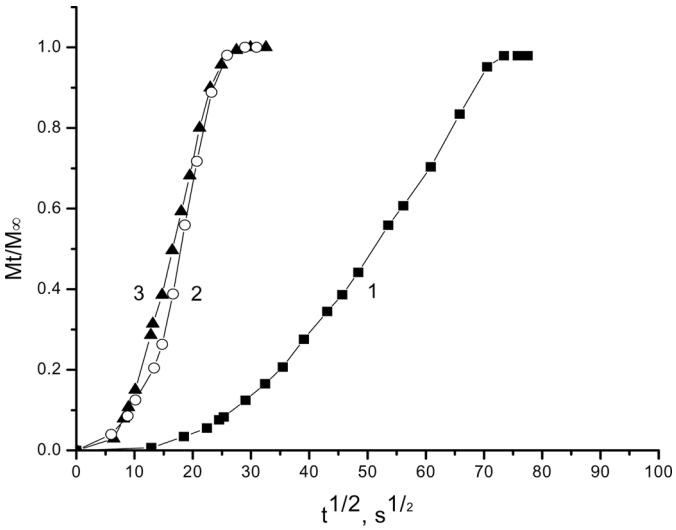

FIG. 5. Kinetic curves of methanol sorption into (1) PA, (2) PA/CNT(2%), (3) PA/CNT(5%) membranes.

The data on methanol sorption into membranes of pure PA and its composites containing 2 and 5 wt% CNT are shown in the kinetics curves as a function of M_t/M_∞ on the square root of time $t^{1/2}$, where M_t is the membrane weight gain at time t, M_∞ is the weight of a swollen membrane that reached equilibrium state (Fig. 5). In the initial stage of the sorption, the membrane weight increases rapidly, giving linear regions in the plots, then the sorption slows down and equilibrium is attained. Linear regions of sorption were used for the calculations of diffusion coefficients.

Table 2 lists the values of diffusion coefficients, the degree of sorption, and the Flory-Huggins parameters for methanol-polymer systems. It is seen that the diffusion coefficient increases after inclusion of 2 and 5 wt% CNT in membrane. The degree of methanol sorption also tends toward the increase. The Flory-Huggins interaction parameter characterizes the solubility of a polymer in a given liquid. It can be calculated from equilibrium sorption data. As seen from Table 2, the values of the interaction parameter decrease with the rise of the CNT content, i.e., the affinity between the CNT-containing polymer and methanol increases.

TABLE 2
Diffusion coefficient (D), degree of sorption (Sw) and Flory-Huggins parameters (χ) for methanol-polymer systems

Membrane	$D \cdot 10^{14}$, m^2/s	Sw, g/100 g polymer	χ
PA	3.79	17.4	1.21
PA/CNT(2 wt%)	20.1	19.5	1.15
PA/CNT(5 wt%)	35.5	23.2	1.08

According to the solution–diffusion theory, the increase in solubility and diffusivity leads to increase of the permeability. As stated above, the permeability of the membranes increases with the CNT content. The obtained results are in good agreement with the theoretical description of the pervaporation process.

Contact Angles Results

To consider the methanol behavior on the surfaces of the PA membranes modified by CNT, advancing (θ_a) and receding (θ_r) contact angles both methanol and water were measured by the Wilhelmy plate technique. The results are listed in Table 3.

TABLE 3
Contact angles measured at 20°C

	Contact angle, degree			
	Water		Methanol	
Membrane	θ_a	θ_r	θ_a	θ_r
PA	83.6	34.9	19.5	15.5
PA/CNT(2 wt%)	79.9	27.2	12.6	10.5
PA/CNT(5 wt%)	79.2	26.1	11.8	8.4

Water is a standard liquid to start the contact angle measurements from. It helps to determine hydrophilic properties of surfaces. Table 3 shows that the advancing and receding contact angles of water are decreasing. It means that the surface becomes more hydrophilic with the rise of the CNT content in PA membranes. The same tendency was observed in case of methanol. The decrease of methanol contact angles with the rise of the CNT content in membranes correlates with the sorption data of the membranes. It should be added that contact angle reduction means the rise of the methanol affinity to material of the membrane.

CONCLUSIONS

New polymer nanocomposites consist of poly(phenylene isophtalamide) modified by carbon nanotubes were obtained by the solid state interaction method to prepare dense membranes. Their characterization by SEM and Raman spectroscopy showed slight interfacial adhesion and bad dispersion of CNT in the PA matrix. Increase in the CNT content leads to defective structure that takes place in membrane containing 5 wt% CNT.

Transport properties of membranes based on pure PA and its composites with 2 and 5 wt% CNT were studied in the separation of methanol/MTBE mixture by pervaporation. It was found that all membranes are essentially

permeable with respect to methanol. As compared with pure PA, the selectivity and permeability increase for membranes containing 2 wt% CNT, whereas these transport parameters are all out of this proportion for membrane containing 5 wt% CNT. Evidently, anomalous deviations are connected with inhomogeneity of the membrane containing 5 wt% CNT. Hence, the inclusion of nanotube molecules in the PA matrix improves pervaporation properties, i.e., an increase of permeability and so-called inverse selective separation properties of fullerene-containing membranes, only in concentration up to 2 wt% CNT.

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REFERENCES

1. Mohammadi, A.T.; Villaluenga, J.P.G.; Kim, H.J.; Chan, T.; Rauw, V. (2001) Effects of polymer solvents on the performance of cellulose acetate membranes in methanol/methyl tertiary butyl ether separation. *J. Appl. Polym. Sci.*, *82*: 2882–2895.
2. Yang, J.S.; Kim, H.J.; Jo, W.H.; Kang, Y.S. (1998) Analysis of pervaporation of methanoI-MTBE mixtures through cellulose acetate and cellulose triacetate membranes. *Polymer*, *39* (6–7): 1381–1385.
3. Niang, M.; Luo, G. (2001) A triacetate cellulose membrane for the separation of methyl *tert*-butyl ether/methanol mixtures by pervaporation. *Separation and Purification Technology*, *24*: 427–435.
4. Cai, B.; Zhou, Y.; Hu, J.; Zhu, L.; Wu, C.; Gao, C. (2002) Solvent treatment of CTA hollow fiber membrane and its pervaporation performance for organic/organic mixture. *Desalination*, *151*: 117–l21.
5. Huang, R.Y.M.; Moon, G.Y.; Pal, R. (2001) Chitosan/anionic surfactant complex membranes for the pervaporation separation of methanol/MTBE and characterization of the polymer/surfactant system. *J. Membrane Sci.*, *184*: 1–15.
6. Hilmioglu, N.D.; Tulbentci, S. (2004) Pervaporation of MTBE/methanol mixtures through PVA membranes. *Desalination*, *160*: 263–270.
7. Ray, S.; Ray, S.K. (2006) Synthesis of highly methanol selective membranes for separation of methyltertiary butyl ether (MTBE)–methanol mixtures by pervaporation. *J. Membrane Sci.*, *278*: 279–289.
8. Yoshikawa, M.; Yoshioka, T.; Fujime, J.; Murakami, A. (2000) Pervaporation separation of MeOH/MTBE through agarose membranes. *J. Membrane Sci.*, *178*: 75–78.
9. Merkel, T.C.; He, Z.; Pinnau, I. (2003) Effect of nanoparticles on gas sorption and transport in poly(1-trimethylsilyl-1-propyne). *Macromolecules*, *36*: 6844–6855.
10. Uragami, T.; Okazaki, K.; Matsugi, H.; Miyata, T. (2002) Structure and permeation characteristics of an aqueous ethanol solution of organic–inorganic hybrid membranes composed of poly(vinyl alcohol) and tetraethoxysilane. *Macromolecules*, *35*: 9156–9163.
11. Smaihi, M.; Jermoumi, T.; Marignan, J.; Noble, R.D. (1996) Organic–inorganic gas separation membranes: Preparation and characterization. *J. Membr. Sci.*, *116*: 211–220.
12. Mauritz, K.A.; Payne, J.T. (2000) Perfluorosulfonate ionomer/silicate hybrid membranes via base-catalyzed in situ sol–gel processes for tetraethylorthosilicate. *J. Membr. Sci.*, *168*: 39–51.
13. Hibshman, C.; Cornelius, C.J.; Marand, E. (2003) The gas separation effects of annealing polyimide–organosilicate hybrid membranes. *J. Membr. Sci.*, *211*: 25–40.
14. Sakintuna, B.; Yurum, Y. (2005) Templated porous carbons: A review article. *Ind. Eng. Chem. Res.*, *44*: 2893–2902.
15. Wang, Yu.; Yang, L.; Luo, G.; Dai, Y. (2009) Preparation of cellulose acetate membrane filled with metal oxide particles for the pervaporation separation of methanol/methyl *tert*-butyl ether mixtures. *Chemical Engineering Journal*, *146*: 6–10.
16. Ma, X.; Hu, C.; Guo, R.; Fang, X.; Wu, H.; Jiang, Z. (2008) HZSM5-filled cellulose acetate membranes for pervaporation separation of methanol/MTBE mixtures. *Separation and Purification Technology*, *59*: 34–42.
17. Malkin, A.Ya; Chalyh, A.E. (1979) *Diffusity and Viscosity of Polymers. Methods of Investigations*; Chemistry: Moscow.
18. Flory, P.J. (1953) *Principles of Polymer Chemistry*; Cornell Univ. Press: New York.
19. Khayet, M.; Villaluenga, J.P.G.; Godino, M.P.; Mengual, J.I.; Seoane, B.; Khulbe, K.C.; Matsuura, T. (2004) Preparation and application of dense poly(phenylene oxide) membranes in pervaporatio. *Journal of Colloid and Interface Science*, *238* (1–4): 269–272.
20. Trchová, M.; Matějka, P.; Brodinová, J.; Kalendová, A.; Prokeš, J.; Stejskal, J. (2006) *Polym. Degrad. and Stab.*, *91*: 114–121.
21. Robertson, J. (2002) Diamond-like amorphous carbon. *Mater Sci Eng R*, *37*: 129–281.
22. Colomban, P. (2003) Raman analyses and "smart" imaging of nanophases and nanosized materials. *Spectroscopy Europe*, *15* (6): 8–15.
23. Barton, A.F.M. (1991) *CRC Handbook of Solubility Parameters*; CRC Press: Boca Raton, FL.
24. Toikka, A.M.; Jenkins, J.D. (2002) Conditions of thermodynamic equilibrium and stability as a basis for the practical calculation of vapour-liquid equilibria. *Chem Eng J.*, *89* (1–3): 1–27.
25. Gozzelino, G.; Malucelli, G. (2004) Permeation of methanol/methyl-*t*-butyl ether mixture through poly(ethylene-co-vinyl acetate) films. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, *235*: 35–44.
26. Mulder, M. (1999) *Basic Principles of Membrane Technology*; Mir: Moscow.