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Polymer membranes modified by fullerene C_{60} for pervaporation of organic mixtures

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ABSTRACT

Modification of polymer properties by incorporation of nanoparticles is a way for the development of advanced membrane materials. New materials based on the compositions polymer – fullerene were developed for the use in pervaporation. Two polymers polyphenylene oxide (PPO) and polyphenylene isophtalamide (PA) were modified by fullerene C_{60}. Their transport properties were studied in pervaporation of two systems: the reacting mixture ethanol – acetic acid – water – ethyl acetate by fullerene-containing PPO membranes and the methanol/cyclohexane mixture with azeotropic point by fullerene-containing PA membranes. The experimental study of sorption-diffusion parameters were carried out in sorption tests to analyze transport properties of the modified membranes as a function of the fullerene content in membranes.

Keywords: Pervaporation; Fullerene-containing membranes; Poly(phenylene oxide); Poly(phenylene isophtalamide); Sorption; Selectivity

1. Introduction

Membrane technologies have been more and more frequently applied in modern industrial and environmental processes. The search of new membrane materials both polymeric and composite with high productivity and selectivity is an important task of membrane engineering [1]. Modification of polymer materials by incorporation of nanoparticles leads to a pronounced effect on material properties and accordingly on membrane separation efficiency. Fullerenes have attracted much attention due to its unique chemical and physical properties [2]. In the last few years, some research on polymer membranes modified by fullerenes came in to literature [3–11]. Among the first membrane methods for testing properties of polymers modified by fullerene was gas separation [3–10]. The study on polystyrene modified by dispersing 1–2% fullerene showed the prospects for polymer modification by fullerene to improve gas transport properties [5,6]. Membranes consisting of Matrimid and the dispersed benzylamine-modified fullerene exhibited higher He/N_2 selectivity but lower gas permeability than that of Matrimid due to the presence of benzylamine-modified fullerene that serves as impenetrable volumes and rigidifying elements within the polymer matrix [7].

The effect of fullerene C_{60} inclusion on gas separation properties of polyphenylene oxide (PPO) membranes was analyzed in detail in [8–10]. To improve gas transport properties, PPO modification by C_{60} was

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made by two different modes. Chemical modification by a three-step synthesis leads to obtaining PPO/C_{60} bonded covalently to methyl group of PPO [8,9]. Dispersion of fullerene C_{60} and PPO in solution or powder leads to PPO/C_{60} compositions with nonvalent binding [9,10]. The gas separation properties of bonded and dispersed PPO-C_{60} differ significantly.

However information on pervaporation properties of polymer membranes modified by fullerenes is limited. Therefore, we pay a peculiar attention on transport properties of polymer/fullerene C_{60} membranes in the processes of pervaporation. The aim of the report is to compare the effect of fullerene C_{60} addition on pervaporation properties of membranes based on hydrophilic polymer – polyphenylene isophtalamide (PA) and hydrophobic one – PPO. Detailed information on PPO/C_{60} system was given in our previous work [10]. Thermodynamic and transport properties: dependence of sorption parameters, selectivity and fluxes on the contents of fullerene additives in PPO and PA membranes are under the question in the present work.

2. Experimental

2.1. Materials and membranes

PA (commercial sample Fenylon®, Russia), PPO (Brno, Czech Republic) and fullerene C_{60} of 99.9% purity (Fullerene Technologies, Russia) were used for membrane preparation.

PA/C_{60} composites containing 2, 5, and 10 wt% C_{60} were obtained by thorough mixing PA and fullerene powders in porcelain mortar. Thereafter, the composites were dissolved in N,N′-dimethylacetamide with ~0.7 wt% LiCl additives for solution stabilization. The PA/C_{60} solution was intensely stirred and sonicated before membranes preparation.

To prepare PPO/C_{60} homogeneous membranes, compositions containing up to 2 wt% C_{60} were prepared by mixing toluene solutions of PPO and fullerene in the required quantity. The brown color appearance, when toluene solutions of colorless PPO and violet C_{60} mixed, demonstrated that C_{60} and PPO interact with complex formation.

Homogeneous membranes of thickness ~30 μm were obtained by casting 5 wt% polymer solutions on a support with the subsequent drying at 60°C in vacuum for 2 weeks. The membrane thickness was measured by micrometer with the accuracy ±5 μm.

2.2. Contact angle measurement

Contact angles, Θ (degree), of liquids on the surface of homogeneous membranes were measured by Wilhelmy plate technique, using the KRUSS installation at 20°C. Wilhelmy plate technique is a method for calculating average advancing and receding contact angles on solids of uniform geometry. Liquids under study were water with surface tension $\sigma = 72.4$ mN/m, methanol with $\sigma = 22.6$ mN/m, and cyclohexane with $\sigma = 25.1$ mN/m.

2.3. Sorption experiment

Sorption tests were performed by immersing membranes in liquid individual components of tested mixtures at room temperature. The degree of equilibrium sorption, S (g/100 g polymer), was calculated by equation:

$$S = \frac{M_s - M_d}{M_d} \qquad (1)$$

where M_s is the weight of a swollen membrane upon equilibrium state and M_d is the weight of a dry membrane.

The diffusion coefficient, D (m^2/s), of penetrant in a polymer membrane was determined from the sorption kinetic curve [12] by equation:

$$D = 0.04939 \cdot \frac{l^2}{t} \qquad (2)$$

where l is the thickness of a dry polymer film and t is the time when gained weight M_t and $M_t/M_\infty = 0.5$ (M_∞ is the equilibrium uptake).

To determine the polymer-solvent interaction parameter, χ, the equation of Flory-Huggins theory [13] was used

$$\ln a_1 = \ln(1 - \varphi_2) + \varphi_2 + \chi\varphi_2^2 \qquad (3)$$

where a_1 is the solvent activity and ϕ_2 *is* a volume fraction of solvent in a swollen polymer sample that is expressed as:

$$\varphi_2 = \frac{1}{1 + \frac{\rho_2}{\rho_1}\Delta s} \qquad (4)$$

where ρ_1 and ρ_2 are solvent and polymer densities (g/cm^3), respectively, $\triangle s$ is amount of solvent (g/g polymer). The interaction parameter was calculated in the ideal solvent approximation ($\ln a_1 = 1$) by the following formula [14]:

$$\chi = \frac{-[\ln(1 - \varphi_2) + \varphi_2]}{\varphi_2^2} \qquad (5)$$

2.4. 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 13 Pa was maintained. The permeate was analyzed by refractometry (IFR – 454 B2M) and gas chromatography (Crystal 5000.2, ''Chromatech'' Russia).

Membrane permeation flux, J (kg/m^2 h), was determined as an amount of liquid transported through unit of the membrane area per time unit. Because J is inversely proportional to membrane thickness l, which varied from 20 to 40 µm, permselectivity strongly depends on it. Therefore, the product $J{\cdot}l$ (kg µm /m^2 h) so called specific permeation flux was used for comparing the permeability of membranes with different thickness, just as in [15].

The selectivity or the separation factor, α, was defined by the equation [16]

$$\alpha = \frac{y_i/y_j}{x_i/x_j} \tag{6}$$

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.

3. Results and discussion

It is known that pervaporation properties of membranes depend on interactions between components of the feed solution and the polymer of the membrane [17]. Transport of small molecules through a polymer membrane can be described by solution–diffusion mechanism. The permeability of liquids in pervaporation is significantly controlled by the solubility of penetrant in the polymer membrane. To give an exhaustive characterization of the transport process, besides pervaporation tests where membrane permeability and selectivity could be measured, membrane sorption toward individual components of liquid mixture should also be studied.

3.1. PA/C$_{60}$ membranes

The effect of C$_{60}$ inclusion in PA matrix was estimated in separation of methanol/cyclohexane mixture. During sorption test it was established that cyclohexane is not sorbed in membranes under study. The data on methanol sorption into membranes of pure PA and its composites, containing 2, 5 and 10 wt% C$_{60}$ are shown in Table 1.

Table 1
Diffusion coefficient (D), degree of sorption (S), and Flory-Huggins parameter (χ) for methanol-polymer systems

Membrane	$D{\cdot}10^{14}$, m^2/s	S,g/100 g polymer	χ
PA	2.3	17.38	1.20
PA /C$_{60}$ (2%)	3.3	17.93	1.18
PA /C$_{60}$ (5%)	7.2	18.20	1.17
PA /C$_{60}$ (10%)	10.5	20.16	1.12

As seen from Table 1, diffusion coefficient increases after inclusion of 2, 5, and 10 wt% C$_{60}$ in PA membrane, and the degree of methanol sorption has the same tendency. Data on equilibrium sorption allows calculating the Flory-Huggins interaction parameter that directly characterizes the solubility of a polymer in a given liquid [13]. As seen from Table 1, the values of methanol-polymer interaction parameter decrease with rise of C$_{60}$ content, i.e. affinity between the fullerene-containing polymer and methanol increases.

Membranes based on PA modified by C$_{60}$ were tested in pervaporation of methanol/cyclohexane mixture. This mixture is characterized by the azeotropic point, it contains 37.2 wt% methanol and 62.8 wt% cyclohexane at 20°C and 100 kPa. All membranes were essentially permeable with respect to methanol.

Fig. 1 shows the dependence of selectivity in separation of methanol/cyclohexane mixture on methanol content in feed. Increase of methanol concentration leads to decreasing selectivity for all membranes. The highest selectivity was achieved in separation of feed with low methanol content. As compared with pure PA, the selectivity increases for membranes containing 2 and 5 wt% C$_{60}$, whereas the selectivity is all out of this proportion for PA/C$_{60}$ (10%) membrane. Evidently, these anomalous deviations are connected with inhomogeneity of the membrane containing 10 wt% C$_{60}$ where the part of fullerene is not bonded to PA

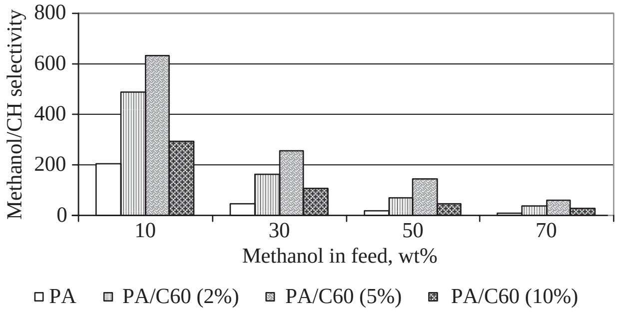

Fig. 1. Dependence of selectivity on methanol content in the feed for the pervaporation of methanol/cyclohexane mixture through PA/C$_{60}$ membranes.

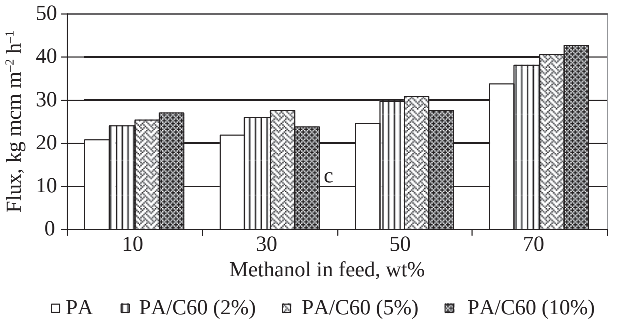

Fig. 2. Dependence of specific flux on methanol content in the feed for the pervaporation of methanol/cyclohexane mixture through PA/C_{60} membranes.

molecules. Membrane containing 5 wt% C_{60} exhibits the best selectivity in the separation of all feed mixtures including the azeotropic mixture.

Fig. 2 shows the dependence of specific permeation flux on methanol content in feed. Permeability of membranes based on PA and its composites containing 2 and 5 wt% C_{60} increases with methanol concentration in the feed; in doing so the penetrant flux across the membrane increases with C_{60} content. This is in agreement with the increasing sorption degree and diffusion coefficient of methanol. PA/C_{60} (10%) membrane did not show the stable results that is an additional evidence of the existence of the limiting concentration equal to 5 wt% C_{60}, excess of this concentration does not improve pervaporation properties of PA membranes.

In pervaporation the feed mixture contacts with membrane surface. So, to explain the mass transport of small molecules through the membrane the surface tension of a polymer film should be taken into account. To characterize surface tension of homogeneous membranes, contact angles of different liquids on membrane surfaces were measured by Wilhelmy plate technique, the results of these measurements are listed in Table 2. The contact angle of water decreases upon inclusion of C_{60} in PA matrix, suggesting that the membrane surface became more hydrophilic. The contact angle of methanol also decreases with a rise of C_{60} content up to 5 wt%; the surfaces are wet by methanol better than the surface of PA membrane. The contact angle of cyclohexane, a hydrophobic liquid, increases; this fact also implies the same change of membrane surface upon inclusion of C_{60} in PA matrix.

The data on contact angles of three liquids were used for calculation of critical surface tension. As the liquids exhibit different polarity, separately polar σ^p and dispersion σ^d contribution to critical surface tension had to be evaluated. Table 2 shows that the dispersion contribution decreases with fullerene addition. In contrary, the polar contribution to critical surface tension increases. These results indicate on the rise of hydrophilic properties due to fullerene inclusion in PA matrix. Such a trend correlates with sorption properties of fullerene-containing membranes toward the methanol and predominant selectivity with respect to methanol in pervaporation of methanol/cyclohexane mixture.

3.2. PPO/C_{60} membranes

The effect of fullerene addition on PPO transport properties was studied in the pervaporation of the quaternary mixture: ethanol – acetic acid – water – ethyl acetate. These compounds form the reaction mixture in ethyl acetate synthesis reaction:

$$C_2H_5OH + CH_3COOH = H_2O + CH_3COOC_2H_5$$

The shifting of the esterification equilibrium in hybrid process (reaction + pervaporation) may be one of the ways for the maximizing yield of ethyl acetate.

To estimate the binary polymer-solvent interaction, the equilibrium sorption of ethanol, acetic acid, water, and ethyl acetate in PPO and PPO/C_{60}(2%) homogeneous membranes was studied. Table 3 lists data on sorption tests that show a better sorption capacity of fullerene-containing membranes for ester, acid, and alcohol than that of PPO membranes. Ethyl acetate exhibits the highest sorption (the lowest value of χ), then acetic acid and ethanol come. Water appears to be absolutely inert to polymers under study. The

Table 2
Contact angles and surface tension

Membrane	Contact angle, degree			Critical surface tension, mJ/m^2	
	Water	Methanol	Cyclohexane	Dispersion contribution, σ^d	Polar contribution, σ^p
PA	79.7	18.8	25.5	17.44	7.64
PPO/C_{60}(2%)	78.9	17.7	26.3	17.3	8.01
PPO/C_{60}(5%)	77.5	16.9	27.7	16.84	8.76
PPO/C_{60}(10%)	76.8	16.5	29.1	16.48	9.28

Table 3
Degree of sorption and Flory-Huggins parameter for polymer membranes and components of esterification reaction

Component	S, g/100 g polymer		χ	
	PPO	PPO/C_{60} (2%)	PPO	PPO/C_{60} (2%)
Ethanol	13.0	15.0	1.45	1.34
Acetic acid	23.6	24.2	1.29	1.24
Water	0	0	–	–
Ethyl acetate	23.4	26.4	1.22	1.13

results of sorption tests are in good agreement with data on pervaporation.

Pervaporation of the quaternary system was studied for the feed composition (18.8 wt% acetic acid, 15.0 wt% ethanol, 56.3 wt% ethyl acetate, 9.9 wt% water) that is close to the chemically equilibrium state. Fig. 3 shows that initial reagents penetrate through the membrane only slightly. Ethanol penetrates partly through membranes; acetic acid almost completely remains in the reaction mixture in spite of high value of acetic acid sorption.

As seen from Fig. 3 reaction products penetrate through our membranes by different modes, water to a little extent, furthermore, its amount decreases in comparison with the initial amount. Hence, the main component of permeate becomes ethyl acetate. The use of membranes with C_{60} additives leads to decreasing water content and increasing ethyl acetate content in permeate. The ethyl acetate removal promotes shifting of the reaction equilibrium and the subsequent accelerating of esterification.

4. Conclusions

Polymer/fullerene composites can be obtained by dispersing fullerene C_{60} in polymer matrix by means of solid phase method and used for homogeneous membranes preparation.

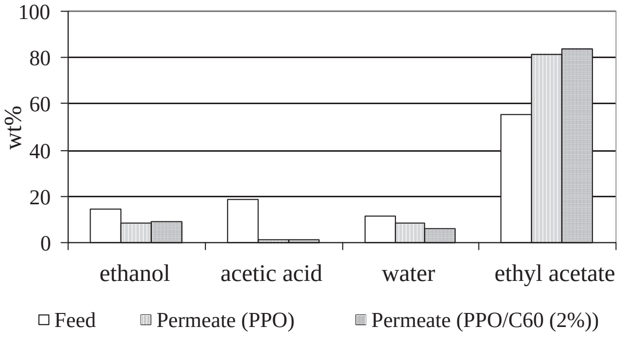

Fig. 3. Content of quaternary mixture in feed and in permeate after pervaporation through PPO and PPO/C_{60} (2%) membranes.

The inclusion of C_{60} molecules (up to 5 wt%) in PA matrix membrane improves transport properties in pervaporation of methanol/cyclohexane mixture, i.e. permeability and so-called inverse selective separation properties is higher for fullerene-containing membranes.

Membranes based on PPO/C_{60} (2 wt%) composites are more effective in ethyl acetate removal during pervaporation of the reacting mixture: ethanol – acetic acid – water – ethyl acetate as compared with pure PPO membranes.

List of symbols

S	degree of equilibrium sorption, g/100 g polymer
M_s	weight of a swollen membrane upon equilibrium state, g
M_d	weight of a dry membrane, g
χ	polymer-solvent interaction parameter of Flory-Huggins
ϕ_2	volume fraction of solvent in a swollen polymer sample
D	diffusion coefficient, cm^2/s
T	time, s
L	thickness of membrane, μm
$J{\cdot}l$	specific permeation flux, kg μm /m^2 h
α	selectivity or the separation factor
y_i, y_j	weight fractions of components i and j in the permeate
x_i, x_j	weight fractions of components i and j in the feed

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