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C_{60} fullerene-containing polymer stars in mixed matrix membranes

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Star-shaped macromolecules with C_{60} fullerene branching centers were used as modifiers of poly(2.6-dimethyl-1.4-phenylene oxide) matrix to obtain mixed matrix membranes. Two types of star modifiers were synthesized *i*) six-arms star with six polystyrene arms grafted onto C_{60} center and *ii*) twelve-arms hybrid star with six polystyrene arms and six copolymer poly(2-vinylpyridine)-*block*-poly(*tert*-butylmethacrylate) arms grafted onto C_{60} center. The membrane structures were studied by scanning electron microscopy. The transport properties of the membranes were determined by using sorption and pervaporation tests toward methanol and ethylene glycol over a wide concentration range. All membranes showed high affinity for methanol. The separation factor reached its maximum level at 5 wt% modifier concentration in the membrane. Polar hybrid arms were shown to change the membranes' morphologies and considerably improve their transport properties.

Keywords: applications of carbon nanostructures, fullerenes, star-shaped polymers, mixed matrix membrane, pervaporation.

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1. Introduction

The development of membrane technologies promotes the search for novel effective membranes to solve important industrial ecological problems. The up-to-date methods consist of creating mixed matrix membranes generally obtained by the inclusion of nanoparticles into a polymer matrix. However, agglomeration of small nanoparticles (fullerenes, nanotubes, etc) may create selective delamination on the interface between the polymer matrix and the agglomerated nanoparticle phase, which can result in membrane structural defects. To prevent the agglomeration, different methods of nanoparticle modification could be applied.

In the present work, a C_{60} fullerene molecule was modified by anionic polymerization in order to serve as a branching center for polymer stars with six or twelve arms; these star-shaped macromolecules were used as fillers for mixed matrix membranes for pervaporation. In recent years, pervaporation, a widely-used membrane technique for the separation of nearly inseparable liquid mixtures (e.g. isomeric, azeotropic, etc.) [1]. The mechanism of the pervaporation process consists of the following steps: selective sorption of liquid molecules into the membrane surface on the feed side, selective diffusion of them through the membrane and desorption from the permeate side of the membrane as a vapor. Separation of organic liquids by pervaporation is based upon the selective permeation of one of the components.

Among the industrially important tasks that can be solved by pervaporation is the separation of methanol – ethylene glycol mixtures, regeneration of these alcohols, and their utilization. This task arises from the joint involvement of these alcohols in a number of syntheses or

technological processes; it is aggravated by the fact that these alcohols are very toxic. To separate the methanol – ethylene glycol mixture, membranes based on homopolymers (cellophane, polyphenylene oxide) [2,3], copolymers [4], and binary polymer blends with additional chemical linkage [5] were proposed. The most simple and available of them is poly(2.6-dimethyl-1.4-phenylene oxide) (PPO), however, it is not effective enough as membrane material [3].

To improve the membrane transport properties, a novel approach based on physical modification of PPO matrix by including C_{60} fullerene containing star-shaped macromolecules with arms of a different nature is proposed in the present work. Two samples of modifier were used. They are *i*) six-arms star with six polystyrene (PS) arms grafted onto the C_{60} branching center ($C_{60}(PS)_6$) [6, 7] and *ii*) twelve-arms hybrid star with six PS arms and six copolymer poly(2-vinylpyridine)-*block*-poly(*tert*-butylmethacrylate) (P2VP-PTBMA) arms grafted onto C_{60} branching center ($C_{60}(PS)_6(P2VP\text{-}PTBMA)_6$) [8].

2. Experimental

PPO with molecular weight 172,000 and density 1.06 g/cm^3 (Brno, Czech Republic) and C_{60} fullerene of 99.9 % purity (Neo Tech Product, Research & Production Company, Russia) were used. Chloroform, methanol, and ethylene glycol were purchased from Vecton (Russia).

The six PS arms star on C_{60} branching center $C_{60}(PS)_6$ and twelve-arms hybrid star $C_{60}(PS)_6(P2VP\text{-}PTBMA)_6$ (Fig. 1) were prepared by synthesis [9, 10].

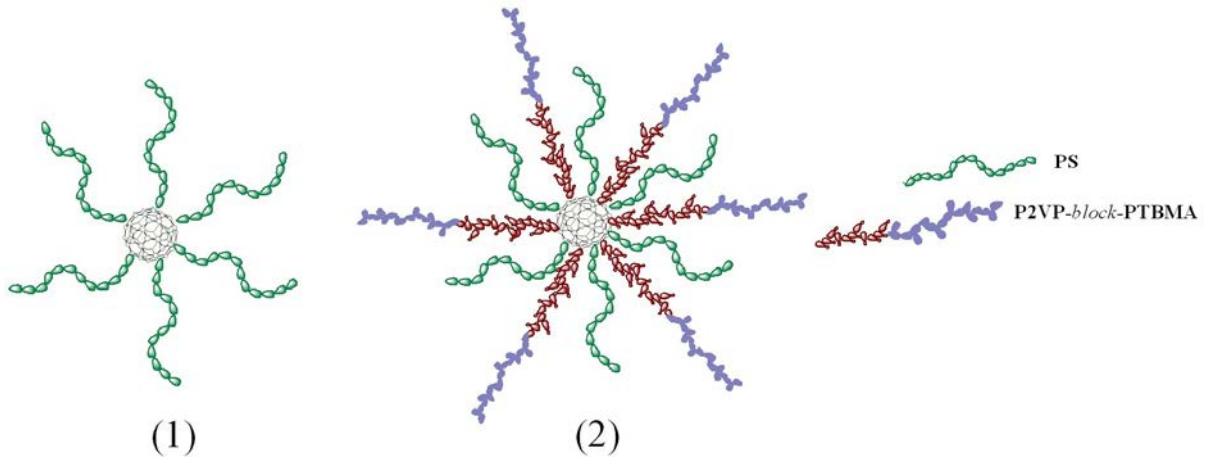

FIG. 1. C_{60} fullerene-containing polymer stars (1) $C_{60}(PS)_6$ and (2) $C_{60}(PS)_6(P2VP\text{-}PTBMA)_6$

The composites containing 1, 3, and 5 wt% PPO/$C_{60}(PS)_6$ or PPO/$C_{60}(PS)_6(P2VP\text{-}PTBMA)_6$ were prepared by mixing solutions of 3 wt% PPO in chloroform and 3 wt% star-shaped polymer in chloroform. Thin film membranes ($\sim$ 40 μm thickness) were obtained by casting the 3 wt% polymer solution in chloroform on a cellophane surface. Membrane morphology was studied by scanning electron microscope (SEM) Zeiss SUPRA 55VP (Carl Zeiss AG, Germany).

Pervaporation experiments were performed using a laboratory cell with an effective membrane area of 14.8 cm^2 at 50 °C, downstream pressure below 10^{-2} mm Hg was maintained. The permeate was collected into a liquid nitrogen-cooled trap, weighed and analyzed by chromatography "Chromatec–Crystal 5000.2" (Chromatec, Russia) with a thermal conductivity detector and refractometer IFR–454B2M. The total flux through the membrane was determined as the amount of liquid penetrated through the membrane area per time unit. The separation factor $\alpha_{\text{methanol/EG}}$ was defined by the following equation:

$$\alpha_{\text{methanol/EG}} = \frac{Y_{\text{methanol}}}{Y_{EG}} / \frac{X_{\text{methanol}}}{X_{EG}}, \tag{1}$$

where Y and X are the weight fraction of component in the permeate and feed, respectively.

Sorption experiments were performed by immersion of membrane samples in the individual liquid (methanol or ethylene glycol) at 20 °C. The weight change was determined gravimetrically. The sorption degree S was calculated by equation:

$$S = \frac{M_s - M_d}{M_d} \cdot 100, \tag{2}$$

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

Kinetic curves for the sorption as a function of $M_t/M_\infty = f\left(t^{1/2}/l\right)$ were plotted, where M_t is the amount of desorbed substance per time t, M_∞ is the equilibrium amount of desorbed substance that was determined as the difference between the weight of a swollen membrane and the weight of membrane dried to a constant weight, and l is the membrane thickness. The effective diffusion coefficient D was calculated by the equation:

$$D = \frac{\pi}{16}(\tan\beta)^2, \tag{3}$$

where $\tan\beta$ is the initial linear slope of the desorption kinetic curves when $M_t/M_\infty < 0.4$.

3. Results and discussion

Preparation of $C_{60}(PS)_6$ and $C_{60}(PS)_6(P2VP\text{-}PTBMA)_6$ star shaped macromolecules through covalent binding of the fullerene molecule with polymer chains prevents agglomeration of the modified nanoparticles and leads to their dispersion on the molecular level in the PPO matrix. PS and PPO blends are completely inter-soluble and the phase separation of these blends does not occur up to the temperature of their thermal destruction [11]. Therefore, one can expect that PS arms of both star types will be compatible with PPO matrix and this will facilitate the uniform distribution of star modifiers in the film.

The morphologies of the membranes containing 1, 3, and 5 wt% star modifiers were studied by scanning electron microscopy. Fig. 2 shows that the inclusion of star modifiers in the PPO matrix leads to changes in the top surface and cross-section structures of membranes containing 5 wt% $C_{60}(PS)_6$ or $C_{60}(PS)_6(P2VP\text{-}PTBMA)_6$.

Figure 2(b) shows that the inclusion of $C_{60}(PS)_6$ stars in the PPO matrix does not affect the top surface structure as compared to the PPO membrane (Fig. 2(a)). On the contrary, inclusion of $C_{60}(PS)_6(P2VP\text{-}PTBMA)_6$ hybrid stars changes the membrane's morphology considerably (Fig. 2(c)). One can observe domain structures of a rounded shape formed due to the segregation of hybrid star-shaped macromolecules. In the previous work, data from small-angle neutron scattering analyses gave evidence for supramolecular structure formation in the case of these types of hybrid star-shaped macromolecules [10]. As can be seen from micrographs of the membrane cross-section (Fig. 2(d, e, f)), they acquire a cellular structure after modification.

The transport properties of hybrid membranes were studied by pervaporation and sorption tests toward two elementary alcohols: monohydric methanol and dihydric ethylene glycol (EG). The separation of a methanol – ethylene glycol mixture by pervaporation was studied over a wide concentration range of feed mixtures for both mixed-matrix membrane types at 50 °C. All membranes were more permeable for methanol than for ethylene glycol, thus the permeates were enriched by methanol. For both membrane types, the effect of methanol concentration in the feed was the same, namely, the growth of methanol concentration led to a decrease in the

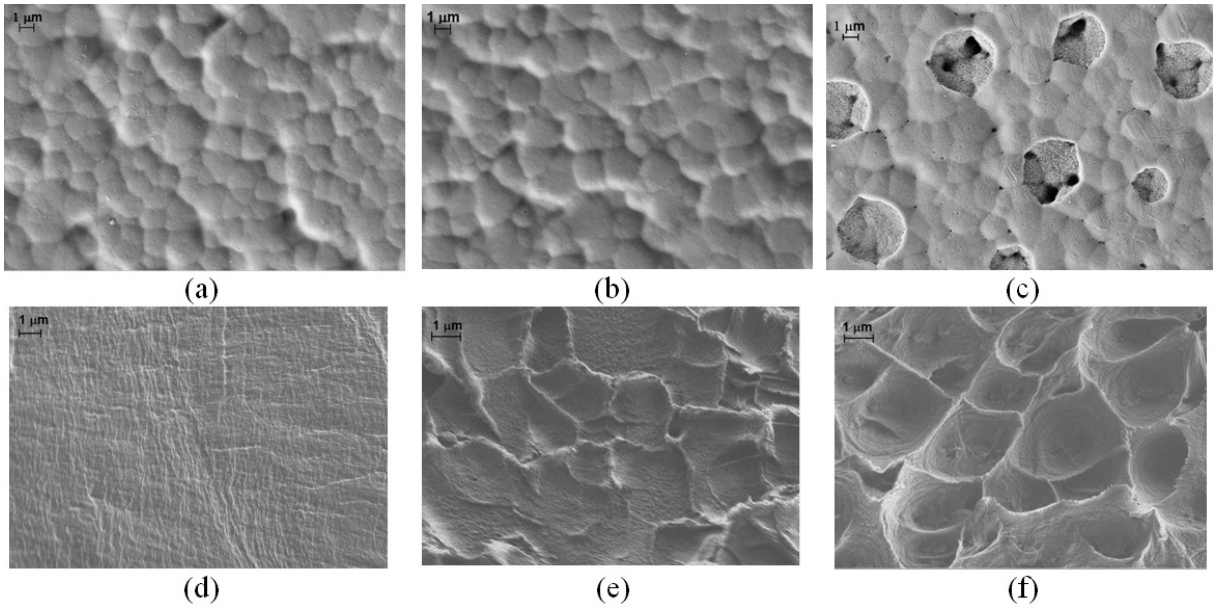

FIG. 2. SEM micrographs of (a, b, c) top surface and (d, e, f) cross-section of three membranes: (a, d) PPO, (b, e) PPO/$C_{60}(PS)_6$ (5 %), and (c, f) PPO/$C_{60}(PS)_6$(P2VP-PTBMA)$_6$ (5 %)

separation factor and increasing flux through membrane. However, the type of star modifier does have an effect on the quantitative characteristics of the membrane's transport properties. Fig. 3 shows the effect of $C_{60}(PS)_6$ content on the PPO matrix on the main pervaporation parameters: the total flux through the membrane and the separation factor (methanol/ethylene glycol). One can see that the separation factor increases but the flux through membrane decreases with increased star modifier content in the PPO/$C_{60}(PS)_6$ membrane.

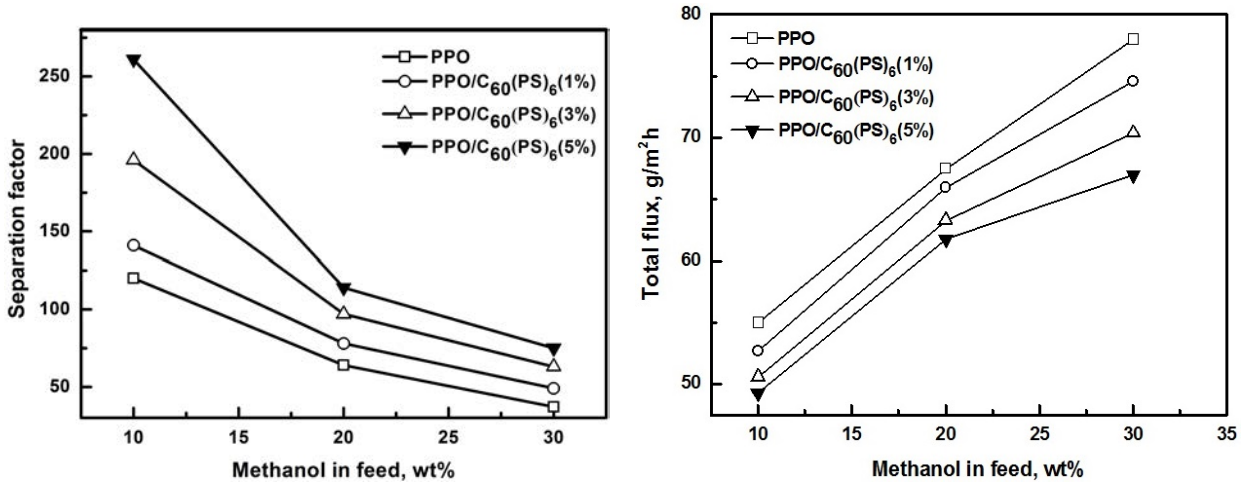

FIG. 3. Dependence of (a) separation factor and (b) total flux on methanol concentration in the feed for pervaporation of methanol – ethylene glycol mixture using PPO and PPO/$C_{60}(PS)_6$ membranes, 50 °C

A similar study of PPO/$C_{60}(PS)_6$(P2VP-PTBMA)$_6$ membranes showed that both the total flux and the separation factor increase with the inclusion of the hybrid stars. It should be noted that the magnitudes of both flux and separation factor are higher for membranes containing $C_{60}(PS)_6$(P2VP-PTBMA)$_6$ as compared with PPO/$C_{60}(PS)_6$. The best separation properties were obtained for membranes containing 5 wt% star modifiers. The PPO/$C_{60}(PS)_6$ (5 %) membrane exhibits a separation factor of 260, which is more than twice the level for the unmodified membrane (125).

Figure 4 shows data on the total flux and separation factor for the most efficient membrane, PPO/$C_{60}(PS)_6$(P2VP-PTBMA)$_6$ (5 %). The use of this membrane makes it possible to double the value of the total flux and to raise the separation factor more than four-fold in pervaporation of the feed containing 10 wt% methanol as compared with the unmodified membrane. The preparation and properties of PPO/$C_{60}(PS)_6$(P2VP-PTBMA)$_6$ membranes are claimed in the RU patent [12].

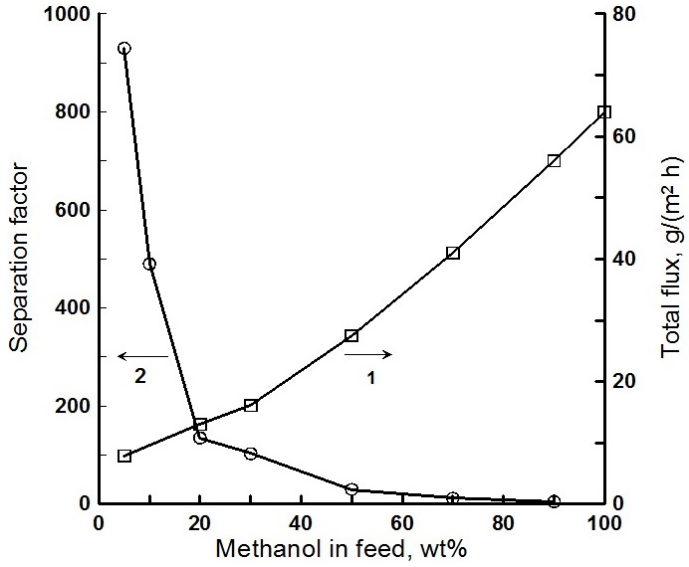

FIG. 4. Dependence of (1) total flux and (2) separation factor on methanol concentration in the feed for pervaporation of methanol – ethylene glycol mixture through PPO/$C_{60}(PS)_6$(P2VP-PTBMA)$_6$ (5 %) membrane, 50 °C

In pervaporation, the transport of small molecules through a membrane proceeds according to the "solution-diffusion" model i.e. the permeability is directly proportional to the solubility (sorption) and diffusivity [1]. Therefore, to explain pervaporation results, sorption and diffusion characteristics were determined on the basis of sorption experiments. Table 1 lists the data obtained for the sorption degree and diffusion coefficient for membranes containing 5 wt% star modifiers. The inclusion of $C_{60}(PS)_6$ stars into PPO matrix resulted in decreased values for the sorption degree and the diffusion coefficient for both methanol and ethylene glycol. Conversely, the inclusion of $C_{60}(PS)_6$(P2VP-PTBMA)$_6$ hybrid stars into the PPO matrix resulted in an increase in these parameters. The increase of the sorption degree may be related to the composition of hybrid stars which contain arms of copolymer poly(2-vinylpyridine)-*b*-poly(*tert*-butylmethacrylate) that are capable of higher affinity for alcohols than the PPO matrix.

Table 1 shows that the sorption degree for methanol is more than twice that of ethylene glycol for all mixed matrix membranes. The higher diffusion rate of methanol in comparison with ethylene glycol makes membranes selective for methanol. The enhancement effect is related to the architecture of the C_{60} containing polymer stars and structural peculiarity of C_{60}

TABLE 1. Membrane sorption and diffusion characteristics for methanol and ethylene glycol

Membrane	Sorption degree (%)		Diffusion coefficient D (m^2/s)	
	Methanol	EG	Methanol, $D \cdot 10^{12}$	EG, $D \cdot 10^{14}$
PPO	14.0	5.2	2.27	0.37
PPO/$C_{60}(PS)_6$ (5%)	12.4	5.0	2.10	0.05
PPO/$C_{60}(PS)_6$(P2VP-PTBMA)$_6$ (5%)	16.1	7.0	4.52	0.69

branching centers, which contain attached arms of different chemical nature which confer the ability to form different types of self-organization.

4. Conclusion

Two fullerene C_{60} containing star-shaped modifiers $C_{60}(PS)_6$ and $C_{60}(PS)_6$(P2VP-PTBMA)$_6$ were used for modification of PPO matrix to develop novel membranes for the pervaporation of methanol – ethylene glycol mixtures. The high affinity of the mixed matrix membranes for methanol and higher selectivity in separation of methanol – ethylene glycol mixtures were established as compared to that of unmodified membrane.

The improvement of transport properties occurs due to the favorable combination of matrix and filler properties. The effect of star-shaped modifier on the structure and transport properties requires an additional study, but the obtained results show that star modifiers provide a good compatibility for PS arms with matrix polymer, moreover, the segregation of $C_{60}(PS)_6$(P2VP-PTBMA)$_6$ polar arms promotes the formation of polar zones (domains) that provide high permeability and selectivity.

The fullerene C_{60} branching center and the nature of polymer arms of star modifiers have an effect on the interaction between the membrane and separable liquids, thereby affecting pervaporation transport properties of membranes. An appreciable effect of the C_{60} fullerene branching center on gas transport properties of membranes composed of the star shaped PS with C_{60} center has been established in our previous work [13]. We believe that the introduction of star shaped macromolecules with C_{60} branching centers in PPO matrix changes the system and the properties of transport channels, which leads to significant improvement of the membrane's transport characteristics.

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