eXPRESS Polymer Letters Vol.6, No.3 (2012) 178–188
Available online at www.expresspolymlett.com
DOI: 10.3144/expresspolymlett.2012.20

Properties of casting solutions and ultrafiltration membranes based on fullerene-polyamide nanocomposites

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Received 7 July 2011; accepted in revised form 22 September 2011

Abstract. Poly(phenylene isophtalamide) (PA) was modified by fullerene C_{60} using solid-phase method. Novel ultrafiltration membranes based on nanocomposites containing up to 10 wt% of fullerene and carbon black were prepared. Properties of PA/C_{60} composites in solutions were studied by light scattering and rheological methods. The relationship between characteristics of casting solutions and properties of nanocomposite membranes was studied. Scanning electron microscopy was used for structural characterization of the membranes. It was found that increase in fullerene content in nanocomposite enhances the membrane rigidity. All nanocomposite membranes were tested in dynamic (ultrafiltration) and static sorption experiments using a solution of protein mixture, with the purpose of studying protein sorption. The membranes modified by fullerene demonstrate the best values of flux reduced recovery after contact with protein solution. It was found that addition of fullerene C_{60} to the polymer improves technological parameters of the obtained composite membranes.

Keywords: *nanocomposites, poly(phenylene isophtalamide), fullerene C_{60}, asymmetric membranes, ultrafiltration*

1. Introduction

Fullerenes exhibit a number of unique physicochemical properties. Particularly, being π-acceptor, fullerene molecule can be incorporated into a wide variety of polymers via formation of donor-acceptor [1, 2] or, in certain cases, covalent bonds [3, 4]. Polymer-fullerene complexes can be prepared either by synthesis or by mixing components in solvent or in solid phase; they exhibit properties different from those of the pristine polymer. Complexes obtained by mixing solutions usually contain 1–2 wt% of fullerene at the most [5, 6]. The solid-phase approach allows to increase fullerene content in the complexes appreciably (up to 10 wt%) [7–9]. The polymer-fullerene complexes have been extensively studied for several years, and the general view of their structure is still open to question. Polymer-fullerene complexes are studied using static (light scattering, NMR, diffusion, etc.) and dynamic methods. The static methods, which affect the solution structure very slightly, clearly indicate the existence of intermolecular associates [7, 10, 11]. Dynamic methods such as liquid chromatography, viscometry, sedimentation, and birefringence in flow characterize only individual macromolecules since intermolecular associates existing in solution are destructed by velocity gradients during the experiments [4, 7, 10, 12, 14, 15]. The change in polymer properties after modification by fullerene was demonstrated very clearly in the cases of poly(vinylpyrrolidone) (PVP)/fullerene and polystyrene (PS)/fullerene complexes. Properties of water-soluble PVP/C_{60} or

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PVP/C_{70} complexes were studied in detail [7, 10–12, 15]. The light scattering investigation showed that the sizes of intermolecular associates were one or two orders of magnitude higher than those of PVP molecules; the diameter of associate increased with increasing fullerene content in the complex. The majority of the data concerning supramolecular association in complex solutions was obtained using dilute aqueous solutions of polymer-fullerene complexes. According to [16], water soluble supramolecular structures are stabilized by dipolar interaction. The study of polystyrene/C_{60} complexes by liquid chromatography showed that destruction of the polymer chain followed by the formation of PS-C_{60} covalent bonds occurred during the preparation of the samples (mixing of C_{60} and PS solutions with subsequent solvent evaporation and re-dissolving of the complexes). The degree of destruction increases with increasing polymer molecular weight (M_w) and deterioration of the solvent quality for fullerene C_{60} [4]. Intrinsic viscosities of solutions of many polymer-fullerene complexes including polymers of different structure and M_w were determined in various solvents [7, 13, 14]. The decrease in intrinsic viscosity of the complex as compared with that of pristine polymer was mainly observed in experiments with polymers having high M_w. Dynamic methods using controlled velocity gradients are of particular interest. For instance, sedimentation [12] and rheological [17] experiments with aqueous solutions of PVP/C_{60} complexes and birefringence in flow experiments using PVP/C_{70} solutions [10] showed that increase in velocity gradient leads to the destruction of the clusters (even to the appearance of pristine polymer at the velocity gradient of 5700 s^{-1} [12]). The destruction of covalent bonds in the PVP chains took place at the velocity gradient of 3000 s^{-1} in dilute aqueous solutions [18]. These data give indirect evidence that the clusters are destructed at high velocity gradients. The inclusion of fullerenes, other carbon and metal oxide nanoparticles in different polymers modifies the properties of films and membranes based on these polymers [3, 9, 19–30]. For example, the addition of small amounts of fullerene (up to 2–10 wt%) to poly (phenylene oxide) (PPO), PS, and PA changes selectivity and permeability of membranes made from these polymers in gas separation and pervaporation processes [3, 28–30]. Ultrafiltration membranes made from polysulfone [25], poly(ethersulfone) [26] and poly(vinylidene fluoride) [27] containing nanoparticles of titanium or zirconium oxides demonstrate surface and performance properties which are distinctly different from those of unmodified membranes. However, there are few data on the studies of fullerene-containing polymer membranes intended for ultrafiltration (UF). The asymmetric membranes based on PPO/C_{60} were developed and used for removing estrogenic compounds from wastewater [31, 32]. In the previous works [33, 34] we compared the structure and functional characteristics of pristine PA membranes and PA membranes modified by 5 wt% of nanocarbon additives (fullerene, nanotubes or carbon black). The objects of the present study were to produce poly(phenylene isophtalamide) – fullerene C_{60} composites with different fullerene content, to form asymmetric membranes based on these composites, and to investigate the influence of fullerene C_{60} on the casting solution properties and membrane characteristics. To reveal the specific character of fullerene C_{60} influence on the functional properties of the membranes, a comparative study using membranes of similar polymers modified by carbon black was carried out.

2. Experimental

Poly(phenylene isophtalamide) (PA, commercial Fenylon® sample, Vecton, Saint Petersburg, Russia), fullerene of 99,9% purity (C_{60}, Fullerene Technologies, Saint Petersburg, Russia), and carbon black (Fullerene Technologies, Saint Petersburg, Russia) were used for membrane preparation. Composites containing 2, 5, and 10 wt% of nanocarbons were obtained by intensive and thorough mixing of PA with fullerene or carbon black powders in porcelain mortar for one hour. After the solid-phase interaction, these composites were dissolved in N,N-dimethylacetamide (DMAc) containing ~0.7 wt% of LiCl added for stabilization of the solution; the solutions were kept during two days in a refrigerator. The prepared solutions were intensely stirred up before membrane preparation.These final solutions were used for the formation of asymmetric membranes by phase inversion technique, i.e. by immersion precipitation in the water bath at ambient temperature. The thickness of polymer layers before immersion and that of dried membrane were 0.35 mm and 0.20–0.22 mm, respectively. Fullerene-containing

membranes were brown in color, and membranes containing carbon black were grey. The color intensity depended on the content of additives.

Static light scattering studies of polymer solutions were carried out using photogoniodiffusometer (FPS-3M, Science and Technical Association RAS, Saint Petersburg, Russia) equipped with a photoelectrical system of light scattering intensity registration at scattering angles in the 40–140° range and at the incident light wavelength λ = 578 nm. Calibration was made with respect to benzene (Rayleigh ratio at the given wavelength was $13.06 \cdot 10^{-6}$ cm^{-1}). Two parameters of scattering medium were calculated on the basis of the Debye-Stein theory [35] using the method described elsewhere [36]. The parameter av (the mean correlation radius of the polarizability fluctuation) is related to the dimensions of clusters, and the parameter $<v^2>$ (the average square of polarizability fluctuations) is related to the optical heterogeneity of solution.

The intrinsic viscosities ([η]) of different polymer-fullerene complexes were determined using Ubbelohde capillary viscometer in benzene or chloroform solution at 25°C. The dynamic viscosity (η) measurements of pristine polymer solution and the similar solution kept for twenty days were performed using rheogoniometer (PIRSP, Institute of Petrochemical Synthesis of RAS, Moscow, Russia) with cone-plate (cone angle 1°, diameter 40 mm), at the temperature of 25°C and different shear rates.

N,N-dimethylacetamide of ultra-pure grade (DMAc, Sigma-Aldrich Inc), benzene and chloroform of pure grade (Vecton, Saint Petersburg, Russia) were used without further purification.

Scanning electron microscopy (SEM) micrographs of membrane samples were obtained using electron microscope (JSM-35, Jeol, Japan). Ultrafiltration experiments were carried out in a dead-end stirred cell (FM-01, Science and Technical Association RAS, Saint Petersburg, Russia) (membrane diameter 25 mm, initial filtration volume 10 ml, transmembrane pressure 0.1 MPa, stirring speed 300 rpm).

The 0.4 wt% solution of the following mixture in the 0.05 M phosphate buffer (pH 7.4) was used in the experiment: tryptophan (M_w 204 Da), vitamin B12 (M_w 1340 Da), cytochrome C (M_w 12.5 kDa), chymotrypsinogen (M_w 24 kDa), ovalbumin (M_w 44.5 kDa), bovine serum albumin (M_w 67 kDa), γ-globulin (M_w 160 kDa) (all Sigma-Aldrich Inc). Static sorption of proteins was performed by dipping membrane into the hermetically closed cell containing 4 ml of protein mixture solution. These solutions were periodically stirred. The solute concentration was controlled periodically by determination the optical density of the solutions at λ = 280 nm and λ = 415 nm. Optical density was measured using the spectrophotometer (Specord M-40, Carl Zeiss, Jena, Germany). Equilibrium concentration was reached in 4 hours. The total duration of the experiment was 20 hours. Each experiment was repeated three times and the average result was reported.

3. Results and discussion

PA/C_{60} composites with different C_{60} content (up to 10 wt%) were prepared by solid-phase method. Mechanical destruction of particles increases their surface area and, correspondingly, the surface energy. Contacts between the polymer and carbon nanoadditives occur in the solid phase. The excess of the surface energy enhances activity and solubility of fine particles, thus providing formation of a material with the properties different from those of the pristine polymer. Figure 1 shows SEM images of (A) C_{60}, (B) PA, and (C) PA/C_{60}(10%) powders (the last sample - after thorough mixing). The comparison of images confirms that the surface interaction between PA and C_{60} powders takes place already at the solid-phase mixing stage.

As stated in the Introduction, fullerene molecule possesses the unique π-electron structure. Several authors used spectroscopy data to prove the existence of donor-acceptor interactions between polymer and fullerene in PS/C_{60} [4] and PVP/C_{60} [37] complexes. The authors of review [38] analyzed the data concerning changes of polymers properties in fullerene-doped polymer systems and suggested that the interaction between 'aromatic' C_{60} and phenylene rings of polymers takes place. Poly(phenylene isophtalamide) chain also contains phenylene rings. The possibility of donor-acceptor interaction of fullerene C_{60} with several active centers of a single PA molecule as well as with neighbor macromolecules in the pervaporation membrane matrix was discussed elsewhere [30].

The occurrence of fullerene – PA interaction will be taken into account in the analysis of our results

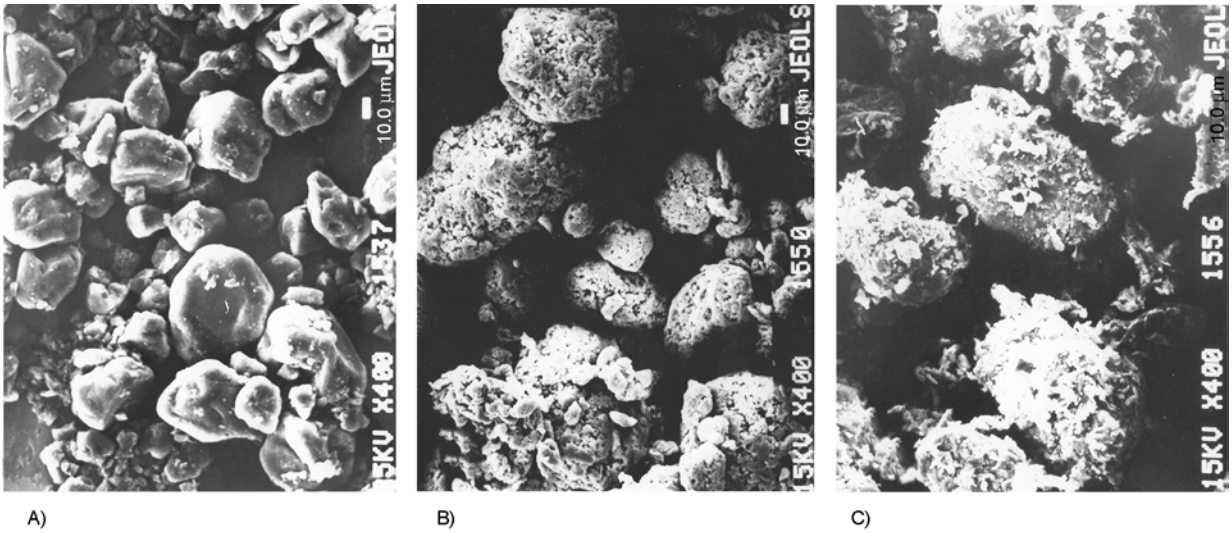

Figure 1. SEM images of powders: (A) C_{60}, (B) PA, and (C) PA/C_{60}(10%)

obtained during the study of properties of PA/C_{60} solutions and membranes.

3.1 Properties of PA/C_{60} solutions

Properties of PA/C_{60} complexes in DMAc solution were studied both by static (light scattering) and dynamic (viscometry and rheological study) methods. The supramolecular structure of polymer solutions was studied by static light scattering. Asymmetric indicatrixes of isotropic light scattering were obtained for dilute PA and PA/C_{60} solutions in DMAc at concentrations ranging from 0.01 to 0.1 wt%. The M_w of PA does not exceed 100 kDa, and the size of macromolecule is substantially less than the light wavelength. Therefore, the contribution of individual macromolecules to the light scattering asymmetry is negligibly small [39, 40]. We can conclude that clusters were already present in dilute PA/C_{60} solutions. Table 1 shows that the dimensions of clusters (a_v) in unperturbed dilute DMAc solutions increase with increasing C_{60} content. It should be mentioned that similar results were obtained in the study of water-soluble complexes of PVP with C_{60} or C_{70} [5, 7, 8]. Optical heterogeneity of solutions ($<v^2>$) also tends to rise with increasing C_{60} content. DMAc (ε = 37.8) is a polar solvent, as well as water, and the presence of soluble supramolecular structures is in agreement with the results reported in [16]. Intrinsic viscosities of solutions of various polymers and their complexes with fullerene are compared in Table 2 where both original and published data are given. It was found that the intrinsic viscosity of PA/C_{60} decreases with increasing C_{60} content. The decrease in [η] values of the polymer-fullerene complexes was observed for polymers of different chemical nature, M_w, various fullerene content, and in different solvents [7, 13, 14, 34]. The higher the polymer M_w, the more substantial decrease in the inherent size of polymer-fullerene complex takes place. For PVP with M_w = 12 kDa the [η]

Table 1. Sizes of intermolecular associates and optical heterogeneity parameters in DMAc solutions

Sample	PA	PA/C_{60}(2%)	PA/C_{60}(5%)
a_v [nm]	31	49	57
$< v^2> \cdot 10^{10}$	6.7	6.8	6.9

Table 2. Intrinsic viscosity of polymers and their complexes with fullerene (cited and original data)

Polymer – solvent	Pristine polymer M_W [kg/mol]	C_{60} content [wt%]	[η] of composite [dl/g]	[η] of pristine polymer [dl/g]	Ref.
PA – DMAc	100	2.0 5.0 10.0	2.86 2.70 2.52	2.93	[34]
Poly(α-methyl styrene) – chloroform	500	6.1	0.76	0.87	
PVP – chloroform	360	0.4	0.90	1.32	
PVP – water	12	0.2	0.102	0.102	[7]
PPO – benzene	30 140	0.5 0.5	0.47 0.86	0.59 0.99	[13]
PS – benzene	1130	6.2	1.90	2.40	[14]

value of its fullerene-containing complexes remains virtually constant (Table 2) [7]. These results are in good agreement with the model of polymer-fullerene interaction suggested in [4]. It should be emphasized that for polydisperse compositions the [η] value is an integral parameter that allows rather comparing macromolecular sizes than determining them precisely.

Rheological behavior of PA/C_{60}(10%) casting solutions used for membrane preparation shows that the increase in fullerene C_{60} content leads to a slight increase in the dynamic viscosity of casting solution. This characteristic indicates the interaction between polymer molecules, polymer-fullerene and polymer-solvent interaction. On the contrary, carbon black as inert additive had virtually no influence on the dynamic viscosity of 10 wt% casting solutions. Figure 2 shows the dependences of dynamic viscosities of fresh casting solutions on velocity gradient. The differences in dynamic viscosities of PA solutions and PA solutions containing from 2 to 10 wt% C_{60} were more pronounced at minimal hydrodynamic action. With increasing velocity gradient, the values of dynamic viscosity descend and approach each other. The casting solutions of polysulfone with porous ZrO_2 nanoparticles also revealed shear thinning under rheological experiments [25]. In both cases a polymer-particle network was broken by the applied force. It would seem that the rheological behavior of PA/C_{60} solutions with different C_{60} content and the values of their intrinsic viscosity are in conflict. However, here the value of velocity gradient (γ) should be taken into account. In rheological experiments, it

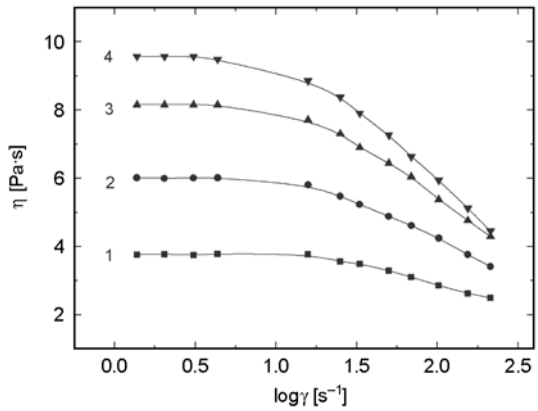

Figure 2. Viscosity vs. velocity gradient for casting solutions of (1) PA and PA/C_{60} with various C_{60} content: (2) 2%; (3) 5%; (4) 10%

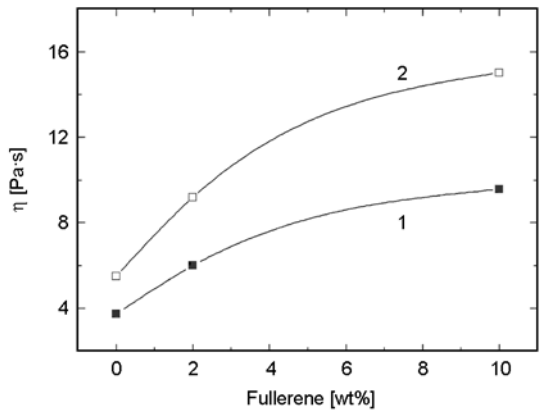

Figure 3. Viscosity vs. C_{60} content in 10% casting solution of PA/C_{60}. (1) pristine solutions and (2) kept 20 days casting solutions.

did not exceed 220 s^{-1}, whereas in intrinsic viscosity measurements the γ value reached 700 s^{-1} [7]. Apparently, clusters having dimensions proportional to fullerene content (in the absence of hydrodynamic action) dissociate at these velocity gradients; therefore, the [η] values characterize the individual molecules.

Rheological data characterizing the instability of casting solutions are shown in Figure 3. After 20 days the dynamic viscosity of PA casting solutions increased to a lesser extent than that of fullerene–containing solutions. The initial values of dynamic viscosity were reached after ultrasonic treatment of these solutions. This observation can serve as another proof of the lability of clusters formed in polymer solutions. It should be added that precipitation of PVP/C_{60} complex from chloroform solution as well as precipitation of poly(α-methyl styrene)/C_{60} complex from benzene – tetrahydrofuran mixture was also observed after storage for several days. The structure-forming ability of complexes can be crucial in technological applications; and, consequently, the long-term storage of solutions should be avoided.

3.2. Structural properties of membranes

The discussion about correspondence between the properties of complex solution and composite membrane characteristics will be based on the results given in this paper and on the data published before [33, 34].

The properties of casting solution determine structural and functional characteristics of the membrane obtained. To support this proposition, we will use

the data shown in Figures 4–7 as well as the results published earlier (Table 1 [33]).

All studied membranes were prepared by phase inversion method. The porous structure of membranes was formed during the immersion of polymer solution layer into precipitating water bath. The slower the membrane precipitation, the higher the density of the obtained membrane [41, 42]. The rate of water diffusion primarily depends on the viscosity of polymer solution. Casting solutions with higher C_{60} content were more viscous (Figure 2), leading to the formation of asymmetric membranes with lower overall porosity. The density of nonporous films prepared from the same solutions by evaporation also increased with increasing C_{60} content. (The data about membrane porosity and films density were provided in Table 1 [33]). These data are in agreement with published results [25].

The SEM images of PA/C_{60} membranes show homogeneous surfaces. The membrane morphology does not change with increasing fullerene amount in composite. The surface pore size of ultrafiltration membrane can be evaluated using calibration curve obtained in a previous study (Figure 4 [34]). The inclusion of carbon additives into membranes did not influence the shape of calibration curve and retained the molecular weight cut-off (MWCO) in the range of 40–50 kDa. (The value of MWCO is equal to M_w of protein rejected by 90%). Taking into account the size of rejected globular proteins, the surface pore size was estimated using a method described elsewhere [43]. The pore size was about 17 nm. SEM resolution used in our experiments (magnification up to 40 000) did not allow to see the distinctions in active layers of membranes having different composition. The tendency towards increasing active layer density (Figure 4) was observed for membrane containing 5 wt% C_{60} as compared with the pure PA membrane. During preparation of SEM samples, the fullerene-containing membranes exhibited higher strength and ability to preserve their internal structure. It should be noted that SEM does not allow observing all changes in membrane structure. For example, while gas separation membranes based on polysulfone with different carbon additives were of similar morphology they demonstrated different transport properties [44].

3.3. Functional properties of membranes

The effect of fullerene C_{60} present in PA membranes on their main functional characteristics (flux and protein sorption) was studied. Figure 5 (curve 1) shows water flux through membranes with different fullerene C_{60} content. The data given in Table 1 [33]

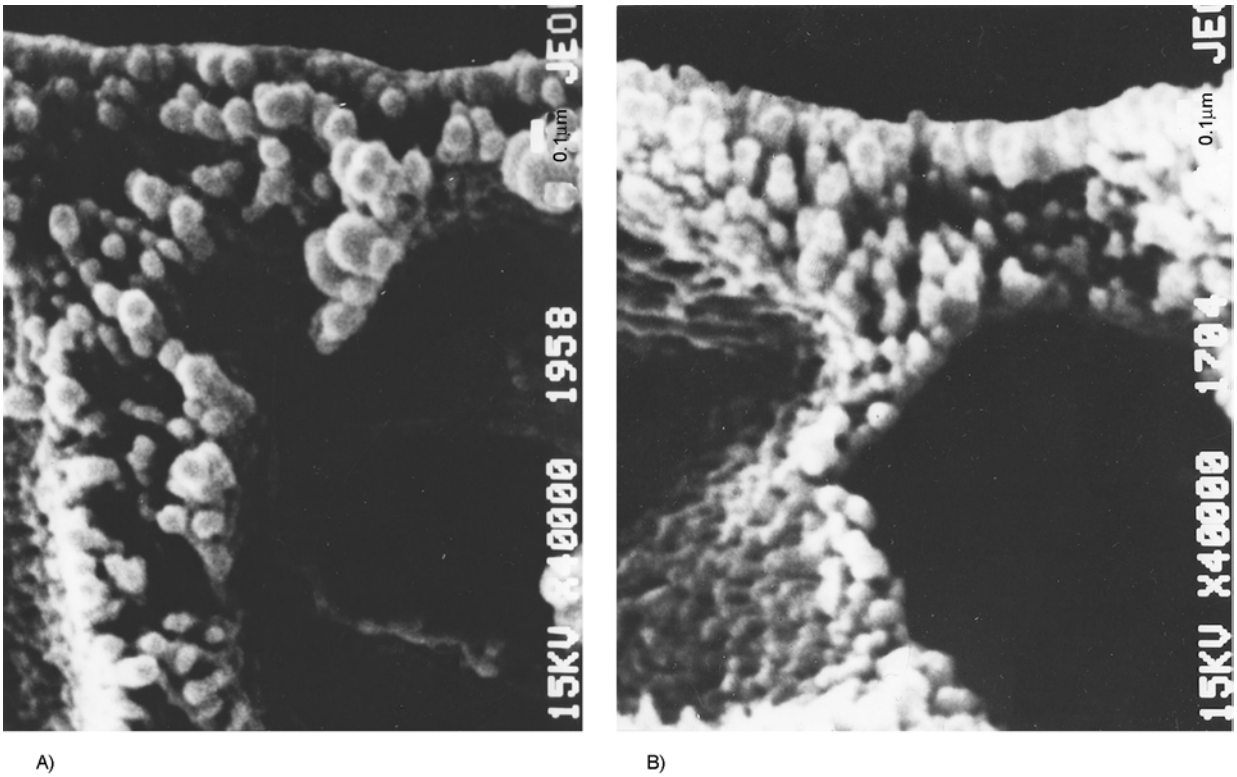

Figure 4. SEM images of (A) PA and (B) PA/C_{60}(5%) membranes active layer cross-section

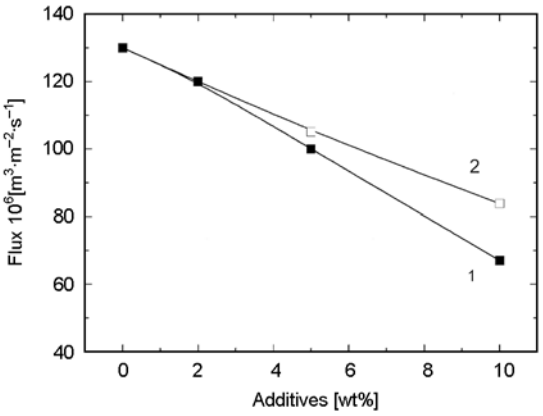

Figure 5. Water flux through composite membranes vs. carbon additives content. (1) fullerene, (2) carbon black.

show that the polymer-fullerene interaction slightly affects the membrane porosity and structure. Membranes with higher C_{60} content have lower porosity and demonstrate lower flux. To reveal the specific character of C_{60} influence on the functional properties of the membranes, the comparative study was carried out using similar membranes modified by carbon black. Figure 5 (curve 2) shows that the water flux through membranes containing carbon black additives is higher than that in the case of fullerene-containing membranes. Carbon black is an inert filler that causes mechanical obstructions against the liquid flow through porous structure of the membrane. If fullerene molecule were also inert with respect to polymer, the obstructions against flow would be similar in both cases. The presence of donor-acceptor interactions (for example, between fullerene and PA phenylene groups) leads to arising intermolecular attraction inside membrane matrix. These interactions cause lowering water flux through fullerene-containing membrane as compared with membrane containing inert carbon black.

Stability of membrane flux during filtration is one of the important technological characteristics of membrane process. Principal sources of decreasing the flux through the ultrafiltration membrane are concentration polarization, cake layer deposition on membrane surface, and adsorptive fouling [45, 46]. In the final stages of technological processes the flux characteristics are determined mainly by cake layer deposition, its degree depending on the composition of filtered mixture. The adsorptive fouling is an important cause of decreasing the protein flux [47, 48] especially on the initial stages of ultrafiltration [49]. In our work, the membrane fouling was studied under similar conditions (filtrate volume did not exceed 0.9 of initial proteins solution volume). We assumed that the adsorption of proteins on the membrane surface and pores caused decrease in flux, and this assumption was confirmed by determination of phosphate buffer flux reduced recovery (FRR). FRR was estimated after the contact between membrane and protein solution in ultrafiltration process and in static sorption tests, when membranes were held in protein solution for 20 hours. Both types of tests included measurements of phosphate buffer flux before (Q_0) and after (Q_1) contact between membranes and protein solution. Flux reduced recovery was calculated using Equation (1):

$$FRR = \frac{Q_1}{Q_0} \cdot 100 \tag{1}$$

Figure 6 shows the phosphate buffer flux reduced recovery for membranes which contacted with protein solution in ultrafiltration and static sorption tests. Evidently, the curves obtained in ultrafiltration experiments lie below the ones obtained in sorption tests. The mass transfer conditions are different in both tests. Under pressure gradient during ultrafiltration the greater part of protein molecules flows into the pores, as opposed to static sorption experiments. Internal membrane fouling is generally irreversible [45]. In our experiment the adsorptive fouling of membranes of different composition was influenced mainly by the chemical nature of

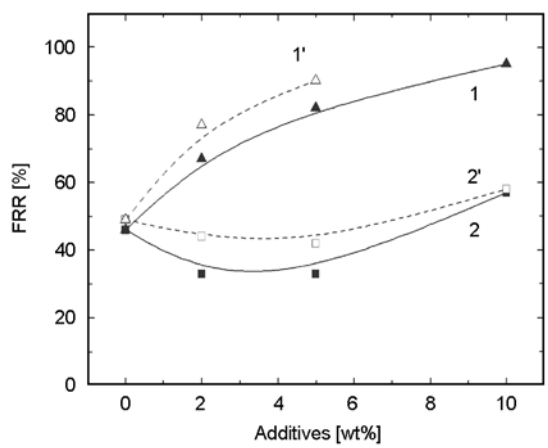

Figure 6. Flux reduced recovery of (1, 1′) PA/C_{60} and (2, 2′) PA/carbon black membranes vs. carbon additives content in (1, 2) ultrafiltration and (1′, 2′) static sorption

constituents, other factors (surface pore size, pressure, stirring rate, pH, ionic strength) being equal.

The membranes modified by fullerenes demonstrated high value of *FRR* equal to 70–90% (curves 1 and 1′). At the same time, *FRR* was close to 30–50% for the membranes of pure PA and modified by carbon black (curves 2 and 2′). Low *FRR* values indicate that membranes of pure PA and those modified by carbon black adsorb proteins strongly, and thus, their phosphate buffer flux decreased by a factor of 2 or 3. It should be noted that the similar behavior is common to the majority of known polymer membranes [48–50]. Membranes modified by fullerene adsorb proteins much less effectively than pure PA. We suppose that this phenomenon is caused by 'interlocking' fullerene sorption centers in PA which should adsorb proteins. On the surface of polyamide membrane both hydrophobic (phenylene) and hydrophilic (amide) groups are present. Fullerene interacts with phenylene group and changes surface profile, thus hindering adsorption of protein functional groups.

High *FRR* value of PA/C_{60} membranes is a very important operating characteristic that could facilitate process of membrane regeneration and promote decrease of target product losses. The resistance of the porous structure of the membranes to different solvents was estimated by filtration of various solvents through the membranes. The viscosities (η, 10^{-3} Pa·s) of the liquids used in this experiment were the following: 1.0 (water), 1.13 (ethanol), and 2.43 (*iso*-propanol). It should be noted that these solvents are often used in processes including ultrafiltration membranes for concentration, purification, and separation of proteins and similar compounds. In the previous paper [33] we reported that only negligible swelling of PA membranes with 5% of nanoadditives takes place in the liquids used. Here we estimated the stability of membrane structure by comparing the values of viscosity-normalized flux dispersion for the membranes with different composition. The viscosity-normalized flux (Q_n) is the product of the liquid viscosity and its flux through the membrane. The values of viscosity were adjusted to 22°C. Figure 7 shows the relative dispersions of viscosity-normalized flux (δQ_n). It was calculated by standard formula for root-mean square deviation. The mean value of normalized flux for definite membrane composition in these calculations was determined by averaging all normalized flux values for all solvents and all membranes used in the experiment. It is clear that relative dispersion of viscosity-normalized flux for PA and fullerene-containing membranes does not exceed 10% and decreases with increasing fullerene content. For membranes modified by carbon black, the relative dispersion does not correlate with the carbon black concentration and averages out 18%. Therefore, the modification by fullerene improves characteristics of membranes by increasing their resistance to different solvents.

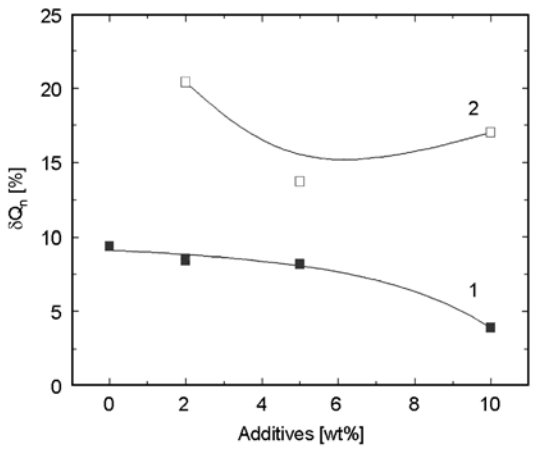

Figure 7. Relative dispersion of viscosity-normalized flux vs. carbon additives content. (1) fullerene, (2) carbon black

4. Conclusions

Asymmetric ultrafiltration membranes based on PA/fullerene C_{60} composites were prepared. The relationship between properties of casting solutions and the structure and characteristics of resulting asymmetric membranes was confirmed. It was established that increase in C_{60} content in the composite leads to the formation of rigid membranes and increases membrane resistance to organic solvents. Ultrafiltration of aqueous protein solutions, as well as static sorption experiments, showed that increase in C_{60} content in membrane causes decrease in protein adsorption on the membrane surface and inside pores. Therefore, the obtained membranes modified by fullerene demonstrate improved antifouling properties as compared with the membranes made from pure PA and those modified by carbon black. Hence, modification by fullerene improved technological parameters of membranes.

Acknowledgements

The authors are grateful to Dr. I.G. Silinskaya for performing light scattering experiments, Dr. N. N. Saprykina for providing SEM images and Ministry of Education and Science of Russian Federation (grant № 2011-1.3.1-207-008-058) for partial support of this work.

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