
MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Composite Materials Prepared by Phase Inversion Deposition of Polyacrylonitrile onto Porous Polyethylene Films

A. S. Olifirenko^{a,b}, E. Yu. Rosova^a, N. N. Saprykina^a, A. F. Mitilineos^b, and G. K. Elyashevich^a

^a*Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia*

^b*Aquafor Limited Liability Company, St. Petersburg, Russia*

Received March 12, 2009

Abstract—Composite ultrafiltration membranes were prepared by deposition of polyacrylonitrile onto a porous polyethylene support by the phase inversion procedure. The supports were hydrophilized by treatment in a barrier discharge argon plasma. Methods were suggested for controlling the pore size in the polyacrylonitrile layer. The filtration characteristics of the membranes and their mechanical properties were determined.

DOI: 10.1134/S1070427209080242

Polyacrylonitrile (PAN) and its copolymers are widely used for preparing membranes for dialysis, micro- and ultrafiltration, and pervaporation, and also for modifying and immobilizing membrane materials. Ultrafiltration is commonly used in water treatment and biotechnology for regenerating cell broth, for isolating cell cultures, and for purifying, concentrating, and separating proteins [1].

The most widely used procedure for preparing ultrafiltration membranes is the phase inversion procedure. In the course of wet phase inversion forming, a polymer solution is applied onto a support and immersed in a coagulation bath with a precipitant. Mutual diffusion of the solvent and precipitant results in gelatinization characterized by a definite cloud point. Further diffusion leads to the membrane densification and pore structure formation. The pore structure type depends on parameters of the component interaction. On the whole, the phase segregation as applied to preparation of membranes has been fairly well studied [2, 3]. The phase diagrams for ternary systems of polyacrylonitrile (PAN) with various solvents and precipitants have been constructed [4], and the effect exerted on properties of PAN membranes by additives introduced into the polymer solution or coagulation bath (salts, surfactants, low-molecular-weight organics [3]) and by the post-treatment has been examined. The annealing and extension of membranes, performed in a liquid that acts as plasticizer, are accompanied by recrystallization of the polymer and significant changes in the pore size distribution [5].

Filtration characteristics of membranes are determined by passing through them solutions of various polymers such as uncharged polyethylene glycol and polyethylene oxide [5–7], positively charged dextran [8, 9], and negatively charged proteins [1, 4] of known molecular weights.

Protein molecules are ampholytes, i.e., they contain both acid (carboxy) and base (amino) groups. Therefore, they can be sorbed on a charged surface irrespective of the sign of its charge. Furthermore, if the surface contains both acid and base groups simultaneously, the sorption will be virtually irreversible [10]. Interaction of proteins with a hydrophobic surface results in their “turning inside out”: hydrophobic groups of amino acids, hidden inside a globule in an aqueous solution, become located on the surface and interact with a hydrophobic surface. In the process, the tertiary structure of the protein is distorted [11]. At the same time, at the physiological pH value, the ionic strength (up to 4 M NaCl), temperature (4–37°C), and protein concentration in the solution do not appreciably affect the sorption [12]. Thus, the hydrophilicity and charge of the surface strongly affect the filtration characteristics of membranes.

The mechanical properties of planar PAN membranes taken alone are unsatisfactory: They are brittle, and they should be stored in the impregnated state, because they fail on drying. The problem can be solved by depositing a PAN layer onto a support, i.e., by preparing a composite

membrane. The use of thin polyethylene (PE) films as supports allows the thickness of composite membranes to be considerably decreased. Furthermore, in so doing, the filtration characteristics are somewhat improved owing to a decrease in the thickness of the barrier layer of the membrane.

Polyethylene as a commercial polymer has a number of important advantages: ease of processing, chemical stability, availability, and cheapness. The process developed for membrane preparation, based on extrusion of a polymer melt, is highly efficient, waste-free, and environmentally safe, because it does not involve the use of organic solvents and other toxic substances [13]. This procedure allows preparation of highly permeable microfiltration membranes which have small thickness (10–15 μm) and exhibit higher mechanical characteristics than all the known microporous materials [13, 14]. The rough surface and porous structure of these films ensure their high adhesion to any polymeric and nonpolymeric coatings, which allows their use as strong and elastic supports for preparing composite materials [15–17]. However, the hydrophobicity of PE membranes makes their water permeability low, which restricts their application. Various surface treatment procedures are used to impart to them hydrophilic properties.

It is known that PE is highly resistant to the majority of oxidants. Modification of PE is started with activation of its surface using chemical and physical methods such as treatment with strong oxidants (chromic acid, nitric acid, potassium permanganate) [18, 19] and with high- and medium-energy radiations [20]. As a rule, the activation is followed by modification using polymer-analogous reactions or graft polymerization [21]. However, after chemical activation porous PE films lose mechanical properties owing to the polymer oxidation and degradation [20], because intercrystallite chains ensuring mechanical strength of films are oxidized first. The sample fails earlier than a noticeable degree of surface modification is attained. At the same time, treatment of the PE surface with a cold plasma involves only a thin surface layer approximately 25 nm thick and does not alter the bulk structure of the sample [22]. Furthermore, treatment with a plasma-forming gas of appropriate composition leads to formation on the polymer surface of various functional groups [20] which can be used for performing polymer-analogous transformations. Modification of porous PE films is a complex problem, but its solution can considerably expand the possible applications of porous

PE films and composites based on them.

The goal of this study was to prepare composite membranes based on polyacrylonitrile and porous PE films, hydrophilized with a barrier discharge plasma, and to determine their filtration and mechanical characteristics.

EXPERIMENTAL

As a support we used porous PE films prepared by the procedure based on melt extrusion followed by annealing, extension, and thermofixation [13, 23]. The film thickness was 12–15 μm , and the total porosity, 45%. The films contained a large amount of through pores with the mean size of 220 and maximal size of 800 nm.

The porous PE supports were modified by treatment with a barrier discharge plasma under dynamic conditions in an argon atmosphere at a normal pressure, discharge power of 160 W, and treatment time of 30 s. The cell consisted of two electrodes separated by a plate of aluminum oxide and placed under an evacuable bell jar. The cell space volume was 0.063 m³. The upper electrode was a set of plates 1 mm wide and 80 mm long, with the distance between the plates of 3 mm. The sample fixed on a glass table was moved at a constant rate at a height of 1 mm over the discharge electrodes [24].

Ultrafiltration PAN membranes were prepared by the phase inversion procedure. Solutions (10 and 15 wt %) of PAN ($M_w = 4.85 \times 10^5$) in dimethylformamide (DMF) were prepared at 25°C. The PAN solution was cast onto a glass plate (25 \times 30 cm) and leveled until the layer thickness $h = 120$ or 240 μm was attained. After keeping for 1 min, the sample was placed in a coagulation bath with deionized water for 2 h, after which the membrane was separated from the glass and washed with a large amount of water to remove DMF.

Ultrafiltration PE/PAN composite membranes were also prepared by the phase inversion procedure. A polyethylene film was fixed on a glass plate (25 \times 30 cm), and a PAN solution was cast onto the film and leveled to the required layer thickness which was varied from 30 to 240 μm . The subsequent procedure was the same as for PAN membranes (see above). After completion of the phase inversion process, the composite membrane was taken off from the glass, washed, and dried at room temperature to constant weight. Thus, PAN layer was formed only on one side of the PE support.

The permeability to ethanol and water and the size

distribution of through pores were determined by filtration porosimetry using a 30 : 70 ethanol–water mixture which does not wet polyethylene [2, 13, 14].

The contact angle was determined by the sessile drop technique [2, 24]. The total porosity P of films was determined by the density measurements and calculated by the formula $P = (\rho - \rho_p)/\rho$, where ρ_p is the porous film density (kg m^{-3}) determined by weighing the samples and ρ is the polyethylene density (950 kg m^{-3}).

The filtration characteristics of composite membranes were determined by the rejection of a bovine serum albumin (BSA, $M_w = 67000$) solution. BSA is used as a model protein and has the shape of a negatively charged ellipsoid with the dimensions of $40 \times 140 \text{ nm}$. Its isoelectric point is at pH 4.8 [25]. In our experiments we used a 1 g l^{-1} BSA solution in a phosphate buffer solution acidified to pH 7 with sulfuric acid [26]. Samples were taken after passing of the first 10 ml of the permeate. Experiments were performed at various pressures (0.5–5.0 atm) on a filtration cell of 8 cm^2 area. The BSA concentration in the initial protein solution and in the permeate was determined on an SF-46 spectrophotometer at a wavelength of 190 nm. The rejection R (%) was calculated by the formula $R = [(c_0 - c_p)/c_0] \times 100$, where c_0 is the initial BSA concentration (mg l^{-1}) and c_p is the BSA concentration in the permeate (mg l^{-1}).

The mechanical and adhesion properties of PE supports, PAN membranes, and PE/PAN composite membranes were determined with an R-5 tensile-testing machine (Ivanovo, Russia). The tensile strength and breaking elongation at uniaxial extension were determined. In deformation of composite membranes, we determined the elongation at which the PAN layer is broken and detached from the PE support (exfoliation).

The strength of adhesion of a PAN layer to a PE support was determined by the shear technique, with the acting force directed tangentially to the coating/support contact surface. To a composite membrane, we glued metal plates from two sides with an epoxy adhesive. The ends of the plates were fixed in the tensile-testing machine, and the detachment force was determined. The adhesion strength P_s (N mm^{-2}) was calculated by the formula $P_s = F_s/s$, where F_s is the detachment force (N) and s is the adhesion joint area (mm^2).

The strength of adhesion of a PAN layer to a PE support was determined by the peel technique at an angle of 90° [27]. A test sample of a PE/PAN membrane was fixed from the PAN side on a standard adhesive

polyacrylate band 3M610 (3M enterprise, Russia) which was, in turn, fixed on a freely rotating wheel, and the PE support end cleaned to remove PAN was fixed in the upper clamp of the tensile-testing machine. The PE film width was 20 mm, and the adhesion joint length, 100 mm. We measured the force of detachment of the porous PE film from the polyacrylate film at an angle of 90° and a constant peel rate of 2.5 mm min^{-1} . The adhesion strength P_n (N mm^{-1}) was calculated by the formula $P_n = F_n/d$, where F_n is the detachment force (N) and d is the adhesion joint width (mm).

Effect of Plasma Treatment on Properties of PE Supports

As supports for ultrafiltration membranes we used porous PE films and PE films hydrophilized in cold plasma [24]. We examined changes in the surface characteristics and transport properties of hydrophilized PE supports compared to the initial porous films.

The effect exerted by treatment of the surface of PE films by cold plasma was evaluated from the contact angle of the films with water. Treatment with 160-W plasma in an argon atmosphere led to a dramatic decrease in the contact angle from 96° to 52° . In the process, the porous support became not only wettable with water but also permeable to water. The surface energy calculated from the contact angles [24] increased from 37.5 to 43.5 mJ m^{-2} . After 165-day storage of the samples in air, the contact angle somewhat increased to 56.1° , but the surface preserved the hydrophilic properties acquired after the plasma treatment, i.e., the modification effect was quite persistent and no aging was observed.

Changes in the chemical structure of the surface of PE films after their plasma treatment were examined by IR spectroscopy and ESCA [28]. In the IR spectra recorded in the MATIR mode, the following absorption bands appeared: carbonyl bands at 1700–1750 (weak) and 1632 cm^{-1} and the band at 1275 cm^{-1} , corresponding to C–O–C vibrations in the carboxy group.

ESCA examination also reveals significant changes in the surface composition. In addition to the C1s and Auger peaks of carbon, the O1s photoelectron peak, oxygen KVV Auger peaks, and a small N1s peak appear, suggesting considerable oxidation and weak incorporation of nitrogen. Quantitative estimation gives the following composition, at. %: 79 C, 20 O, and 1 N. The O1s peak is symmetrical and can be assigned to oxygen in C–O bonds. By resolution of the C1s ESCA peak into components, the following relative content (at. %) of various kinds of

carbon surroundings was determined: C–O groups 14, C=O and/or O–C–O groups 10, and, correspondingly, C–H groups 76. Thus, treatment of porous PE films with barrier discharge plasma results in incorporation of oxygen and nitrogen atoms with the formation of hydrophilic groups on the surface, making the sample wettable with water.

The transport properties of PE supports that had not been hydrophilized by plasma treatment were characterized by permeability to ethanol, and those of the hydrophilized supports, by the permeability to ethanol and water. The permeability of the hydrophilized films to ethanol differed from that of the initial films insignificantly (within the measurement error) (Table 1). After the hydrophilization, the PE films became permeable to water. As seen from Table 1, the water permeability appeared to be similar to the ethanol permeability.

The effective diameter of membrane pores can be judged from the rejection of particles of a known size. For the untreated PE films, the BSA rejection was 37%. Upon plasma treatment, the rejection decreased to 28%. This fact suggests an increase in the pore size. The permeability, however, remained unchanged (Table 1), i.e., the rejection is more sensitive to the treatment than the permeability. A change in the rejection is due to an appreciable decrease in the protein sorption on the treated PE films as a result of changes in the PE surface properties upon modification.

Transport properties of PAN/PE composite membranes. We prepared composite PAN/PE ultrafiltration membranes by phase inversion deposition of PAN onto a hydrophilized porous PE support. The properties of the composite membranes were compared with those of PE support and of unsupported PE membranes.

Composite membranes based on hydrophilized PE support have somewhat lower permeability to both ethanol and water than the support itself (Table 1). The decrease in the permeability is due to a decrease in the pore size in the support as a result of deposition of a PAN layer on pore walls. The difference, however, is not very significant.

When comparing PAN membranes and PAN/PE composites, it should be borne in mind that, in the course of preparation of PAN membranes, when a glass with the cast PAN solution is immersed in a coagulation bath, the phase separation occurs instantaneously, without induction period, which is characteristic of the chosen

Table 1. Permeability of PE supports, PAN membranes, and composite PAN/PE membranes.^a For PAN membranes and composites, the PAN solution concentration was 15%, and the coagulation bath temperature, 21°C

Membrane type	$G(\text{H}_2\text{O}) \times 10^5$	$G(\text{C}_2\text{H}_5\text{OH}) \times 10^5$
	$\text{m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ atm}^{-1}$	
PE film	—	1.8
PE film hydrophilized with plasma	1.4	1.9
PAN membrane (thickness 120 μm)	3.7	3.6
Composite PAN/PE membrane based on hydrophilized OE support	1.1	1.3

^a $G(\text{H}_2\text{O})$, permeability to water; $G(\text{C}_2\text{H}_5\text{OH})$, permeability to ethanol.

DMF–water system because of high mutual affinity of the components. The compositions described are beyond the binodal limits. As a result, membranes with a porous surface layer are formed. Such structure of the membranes provides high permeability and high protein rejection value. As seen from Table 1, the PAN membranes exhibit approximately equal permeability to water and ethanol. However, the composite membranes prepared under the same conditions are inferior to PAN membranes in filtration characteristics, because the permeability of PAN/PE membranes is limited by the pore density in PE support, which is lower compared to PAN membranes.

Morphology of Composite Membranes. Composite PAN/PE membranes were prepared by casting of a PAN solution onto a porous PE support fixed on a glass plate. Therefore, after detachment of the PAN/PE membrane from the glass, one side of the membrane is the surface of the PAN layer, and the other side is the surface of the PE support. The rough surface is the most characteristic feature of the porous PE support used. The oriented character of the support surface structure, formed as a result of deformations applied in the course of specimen preparation, is clearly seen in Fig. 1a. Large areas of the polymeric material 3 μm long and 0.5 μm wide, oriented perpendicularly to the extrusion direction [15], are seen in the electron micrograph. These formations

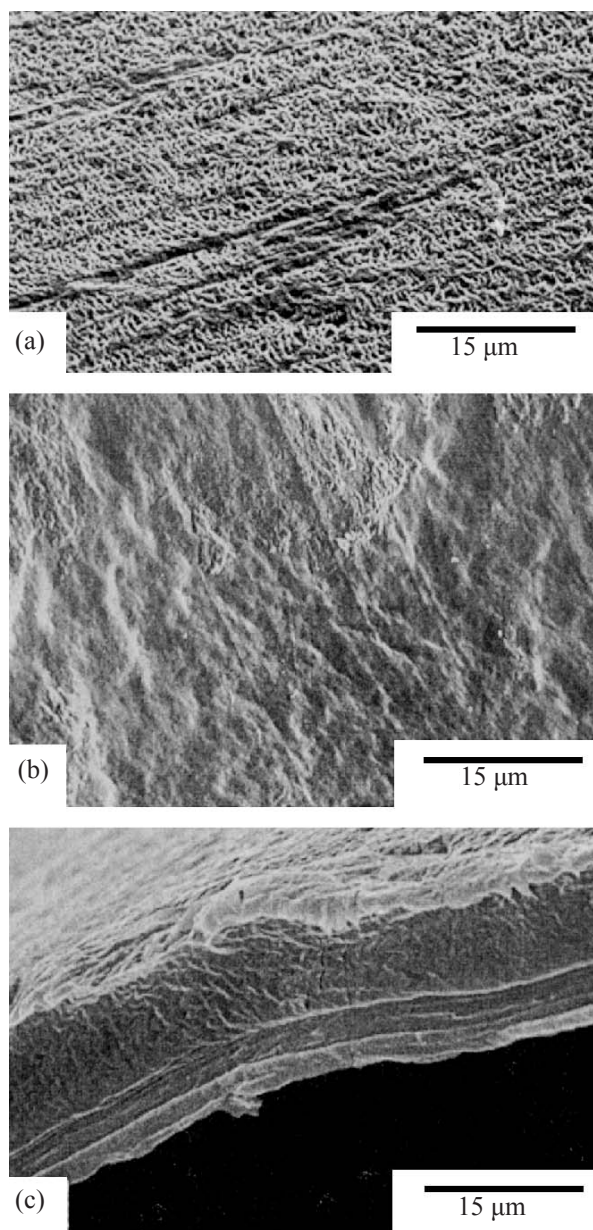


Fig. 1. SEM images of a cross section and surfaces of a composite membrane: (a) PE support surface, (b) PAN layer surface, and (c) cross section of a composite membrane.

are connected by strands $\sim 0.1 \mu\text{m}$ thick, arranged in the extrusion direction and providing mechanical strength of the specimens. The surface relief and porous structure ensure high adhesion of these porous films to coatings.

The surface of the PAN layer of the composite membrane (Fig. 1b) has a characteristic wavelike relief. It is uniform and flawless.

Figure 1c shows a cross section of a composite membrane (the slit thickness in membrane preparation

was $30 \mu\text{m}$; specimen drying was accompanied by its thickness shrinkage). In the upper part of the figure, one can see a porous PE support. Its thickness is $10\text{--}12 \mu\text{m}$. It can be seen that the thickness of the PAN layer seen in the lower part of the figure is approximately $4 \mu\text{m}$, i.e., this layer is considerably thinner than in PAN membranes (120 or $240 \mu\text{m}$). The PAN layer fulfilling the membrane-barrier functions is fairly uniform in thickness. There are no microvoids which are undesirable in membrane preparation because they act as structural defects and deteriorate the mechanical properties of PAN membranes.

Influence of Conditions of Preparing PAN Membranes and Composite Membranes on Their Filtration Characteristics

Coagulation bath temperature. We prepared a series of unsupported PAN membranes from a 10% solution of PAN in DMF (Fig. 2). The slit thickness was $240 \mu\text{m}$. The membranes prepared at a bath temperature of 23°C were permeable even at a low pressure differential ($10 \text{ cm H}_2\text{O}$). With a decrease in the coagulation bath temperature, the permeability decreased and BSA rejection increased, suggesting a decrease in the pore size. Thus, transport characteristics of the membrane can be controlled by varying the coagulation bath temperature.

Coagulation bath composition. We examined the effect of adding NaCl to the coagulation bath on filtration characteristics of composite PAN/PE membranes. We prepared two series of samples at different thicknesses of the forming slit (Fig. 3). The PAN layer was deposited onto a porous PE film ($15 \mu\text{m}$). The solution layer thickness was 120 and $240 \mu\text{m}$. Figure 3 shows that the thickness of thinner membranes increases with an increase in the

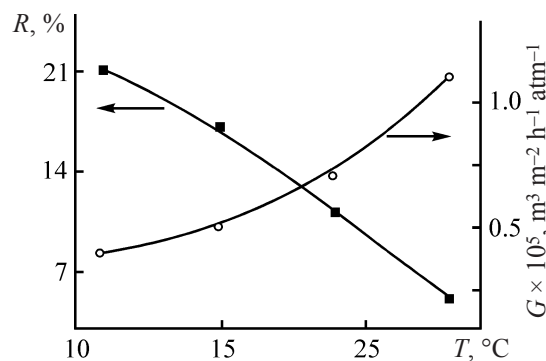


Fig. 2. Permeability of PAN membranes to water G and BSA rejection R as functions of the coagulation bath temperature T . The membranes were prepared from a 10% PAN solution, slit thickness $240 \mu\text{m}$.

NaCl concentration, whereas for the thicker membranes small additions of NaCl lead to a slight decrease in the membrane thickness and larger amounts of NaCl added do not noticeably affect the membrane thickness.

Comparison of Figs. 3 and 4 shows that the trends in variation of the membrane permeability with the NaCl concentration are opposite to those observed with the membrane thickness: An increase in the PAN layer thickness is accompanied by a decrease in the permeability, which is quite natural. For thicker membranes, the permeability increases with the membrane thickness remaining unchanged, that suggests changes in the membrane structure. Indeed, BSA rejection tends to decrease with increasing NaCl concentration for both types of PAN/PE membranes: As the NaCl concentration is increased from 4 to 16%, the BSA rejection decreases from 91 to 82% for thinner membranes and from 82 to 74% for thicker membranes. This means that the NaCl concentration affects the pore size in the PAN layer, which decreases with an increase in the salt concentration in the coagulation bath.

These data can be accounted for by the fact that surface pores are formed in the first step of phase inversion (their size depends on the coagulation bath temperature), whereas formation of the pore structure in the bulk of the membranes is governed by solvent diffusion through surface pores and depends on the salt content in the coagulation bath. The BSA rejection is determined by the size of surface pores, whereas the membrane permeability depends on the pore structure in the bulk of the PAN layer.

Thermostating. PAN membranes prepared by phase inversion at 23°C were thermostated in water at 30 to

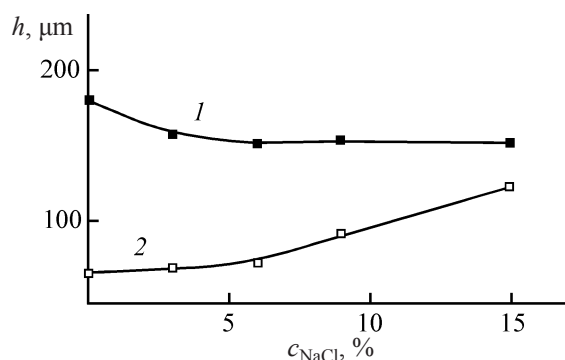


Fig. 3. Thickness h of PAN/PE composite membranes as a function of NaCl concentration in the coagulation bath c_{NaCl} at a slit thickness of (1) 240 and (2) 120 μm . PE support thickness 15 μm .

65°C under the conditions preventing the length shrinkage of the specimen (Table 2). We found that, under these conditions, PAN membranes undergo thickness shrinkage in the course of thermostating. The process is accompanied by sample densification and, correspondingly, by a decrease in the permeability and an increase in the BSA rejection. For PAN membranes, the permeability decreased from 6.6×10^{-5} to $3.6 \times 10^{-5} \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ atm}^{-1}$, and the BSA rejection increased from 12 to 73%. As seen from Table 2, the effect is noticeable even at a low thermostating temperature (30°C) and becomes stronger as this temperature is increased. This is due to recrystallization processes that occur at elevated temperature in the presence of a plasticizer (water) and are accompanied by an increase in the crystallite size and in the degree of crystallinity of PAN [29]. Changes in the transport characteristics also indicate that thermostating is a tool for controlling the pore size.

The effect exerted by thermostating on composite PAN/PE membranes is similar to that exerted on PAN membranes (Table 2), because the filtration characteristics of the composites are determined by the structure of the PAN layer.

Mechanical Properties of Ultrafiltration Membranes.

The tensile characteristics of the PE support were determined in the uniaxial extension mode in the direction parallel and perpendicular to the orientation axis. The tensile strength appeared to be 98 and 9 MPa, and the breaking elongation, 110 and 13%, respectively. Large anisotropy of the mechanical properties is due to oriented structure of PE supports, resulting from the orienting effect on the film in the course of its preparation. The strength characteristics are relatively high for analogous materials of small thickness and low density (the porosity is 40–45%) [14].

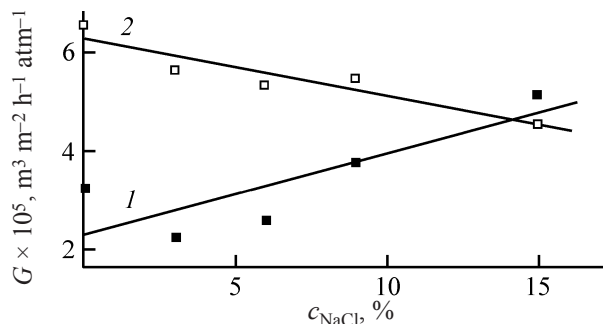


Fig. 4. Permeability of PAN/PE composite membranes to water G as a function of NaCl concentration in the coagulation bath c_{NaCl} at a slit thickness of (1) 240 and (2) 120 μm .

Table 2. Transport properties of thermostated PAN membranes and composite PAN/PE membranes.^a Thickness of initial PAN membranes 240 μm

Membrane type	T_b , °C	$G \times 10^{-5}$	$G_p \times 10^{-7}$	R , %
		$\text{m}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ atm}^{-1}$		
PAN ^b	30	3.6	5.2	73
	50	1.9	2.9	94
PAN/PE ^c	45	3.0	5.1	74
	65	1.1	4.6	88

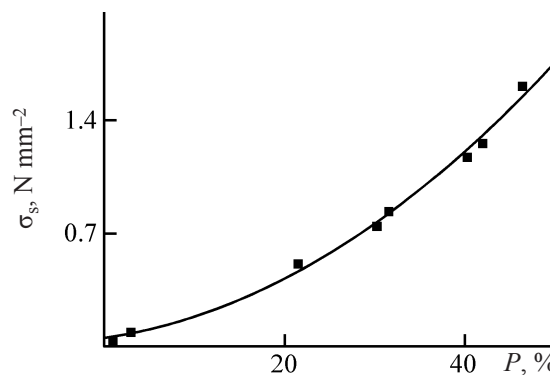
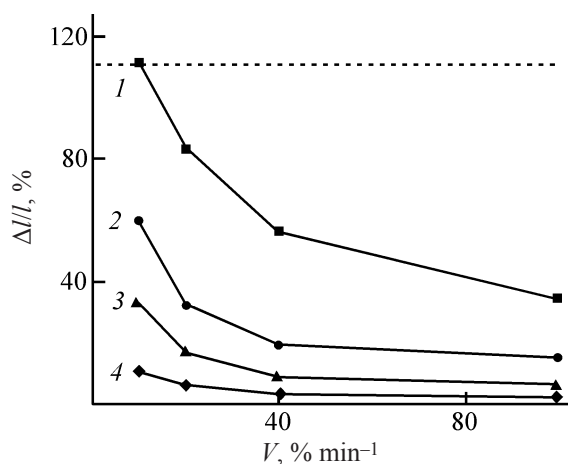
^a (T_i) Thermostating temperature, (G) water permeability, (G_p) permeability in protein filtration, and (R) BSA rejection.

^b PAN solution concentration 10%, coagulation bath temperature 11 $^\circ\text{C}$.

^c PAN solution concentration 15%, coagulation bath temperature 21 $^\circ\text{C}$.

The adhesion strength is a very important characteristic of a material in its use as support in composite systems. Pull-off tests showed that plasma treatment considerably enhances the adhesion strength of the porous PE film: from 78.2 to 182.9 N m^{-1} . This is due to formation of hydrophilic oxygen-containing groups on the surface of the porous PE film. Their presence leads to an increase in the surface energy and in the affinity for adhesives [24]. In application of a polyacrylate band, the adhesion contact occurs only on the surface of the PE support, and the porous structure does not contribute to the adhesion in this case.

Measurements of the adhesion strength of the PE support to the PAN layer by the shear technique showed that the adhesion strength is determined by the total porosity of the support (Fig. 5) and is independent of the time of its plasma treatment. Coating formation involves penetration of the material being deposited into the porous structure of the film, i.e., physical fixation of the forming layer on the film surface and on pore walls. Through pores play a particularly important role in the process, because the layer on their walls links together the coatings on both sides of the support. An increase in the total porosity is accompanied by an increase not only in the number and size of through channels, but also in the amount of surface pores capable to participate in fixation of the polyacrylonitrile layer. In this case, in the case of membrane break or exfoliation, the adhesion joint

**Fig. 5.** Adhesion strength of PAN/PE composite membranes σ_s , measured by the shear method, as a function of the total porosity of specimens P .**Fig. 6.** Elongation at exfoliation of PAN/PE composite membranes $\Delta l/l$ as a function of deformation rate V at a PAN layer thickness of (1) 24, (2) 84, (3) 139, and (4) 197 μm .

strength is determined by the strength of the material being deposited.

The adhesion strength of composite PAN/PE membranes measured by the peel technique at an angle of 90 $^\circ$ is 52 N mm^{-1} irrespective of the membrane thickness. This value is also independent of the support surface energy and is determined by the strength of the PAN material, because the tests involve break of the PAN layer. The elongation at exfoliation was determined for four series of composite PAN/PE membranes with different thicknesses of the PAN layer. As seen from Fig. 6, the elongation at exfoliation of the composite membranes decreases with an increase in the deformation rate and increases with a decrease in the PAN layer thickness. At small thickness (24 μm) and low deformation rates (10% min^{-1}) (Fig. 6, upper point in curve 1), PAN/PE membranes do not undergo exfoliation. They are

deformed as a single whole up to 110% elongation at which the PE support fails (dashed line). At the same time, deformation of all the membranes at higher rates and with larger thicknesses of the PAN layer results in exfoliation at elongations that are smaller than the breaking elongation of the support.

The stress–strain curves for composite PAN/PE membranes show that, for the composite with a thick PAN layer (197 μm), there is a maximum at 10% elongation corresponding to exfoliation. The membrane fails at elongation determined by the support strain (109%). The PAN layer takes up a part of the load at the moment of its break and exfoliation of the composite membrane, after which the stress decreases, and further strain is determined by the properties of the PE support. In deformation of a membrane with a thin PAN layer (24 μm), the process is not accompanied by exfoliation, the membrane undergoes deformation as a single whole, and the breaking elongation corresponds to that for the PE support.

The tensile strength of composite PAN/PE membranes is as high as that of porous PE supports (98 MPa). At the same time, the tensile strength of PAN membranes is poor (3.36 MPa), because they gave a porous structure with no reinforcing elements. In addition, PAN in the membrane occurs in the amorphous state, and the strength of the amorphous polymer is considerably lower than that of the crystalline polymer.

Thus, composite membranes compared to PAN membranes have considerably higher deformation-strength characteristics, with the level of transport and filtration properties preserved.

CONCLUSIONS

(1) Composite membranes consisting of a polyethylene support and a polyacrylonitrile layer deposited onto it were prepared by the phase inversion method. The composites are characterized by good adhesion of the polyacrylonitrile layer to the polyethylene support, which is provided by the porous structure and developed relief of its surface. The uniformity of the polyacrylonitrile layer and the absence of microvoids were demonstrated by scanning electron microscopy.

(2) The polyacrylonitrile–polyethylene composites well compete with polyacrylonitrile membranes in filtration properties but have a considerably smaller thickness of polyacrylonitrile layer. The mechanical

properties of the composite membranes are determined by high deformation-strength characteristics of the porous polyethylene support, which allows the thickness of the polyacrylonitrile layer to be considerably decreased and thus the membrane permeability to be increased.

(3) The influence of temperature and NaCl concentration in the coagulation bath on the pore structure of the composite membranes was examined. By varying these parameters, it is possible to control the transport properties of the membranes: permeability and BSA rejection.

(4) Membranes based on the polyacrylonitrile–polyethylene composite on a hydrophilized polyethylene support can be used for purification and separation of aqueous solutions.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 07-03-00177).

REFERENCES

1. Xu, Z.K., Kou, R.K., Liu, Z.M., et al., *Macromolecules*, 2003, vol. 36, pp. 2441–2447.
2. Kesting, R.E., *Synthetic Polymeric Membranes: a Structural Perspective*, New York: Wiley, 1985, 2nd ed.
3. Van de Witte, P., Dijkstra, P.J., Van den Berg, J.W.A., and Feijen, J., *J. Membrane Sci.*, 1996, vol. 117, pp. 1–31.
4. Phadke, M.A., Kulkarni, S.S., Karode, S.K., and Musale, D.A., *J. Polym. Sci., Part B: Polym. Phys.*, 2005, vol. 43, pp. 2074–2085.
5. Yang, M.C. and Chou, M.T., *J. Membrane Sci.*, 1996, vol. 116, pp. 279–291.
6. Kim, I.C., Yun, H.G., and Lee, K.H., *J. Membrane Sci.*, 2002, vol. 199, pp. 75–84.
7. Khayet, M., Feng, C.Y., Khulbe, K.C., and Matsuura, T., *Desalination*, 2002, vol. 148, pp. 321–327.
8. Nouzaki, K., Nagata, M., Arai, J., et al., *Desalination*, 2002, vol. 144, pp. 53–59.
9. Scharnagl, N. and Buschatz, H., *Desalination*, 2001, vol. 139, pp. 191–198.
10. Jescic, F., *React. Polym.*, 1989, vol. 11, pp. 253–260.
11. Han, W., Gregor, H.P., and Pearce, E.M., *J. Appl. Polym. Sci.*, 2000, vol. 77, pp. 1600–1606.
12. Brynda, E., Houska, M., Pokorna, Z., et al., *J. Bioeng.*, 1978, vol. 2, pp. 411–418.

13. El'yashevich, G.K., Bitskii, A.E., Kozlov, A.G., and Rozova, E.Yu., *Zh. Prikl. Khim.*, 1997, vol. 70, no. 7, pp. 1175–1179.
14. El'yashevich, G.K., Kozlov, A.G., and Rozova, E.Yu., *Vysokomol. Soedin., Ser. A*, 1998, vol. 40, no. 6, pp. 956–963.
15. Elyashevich, G.K., Kuryndin, I.S., and Rosova, E.Yu., *Polym. Adv. Technol.*, 2002, vol. 13, nos. 10–12, pp. 725–736.
16. Buyanov, A.L., Revel'skaya, L.G., Bobrova, N.V., and Elyashevich, G.K., *Vysokomol. Soedin., Ser. A*, 2006, vol. 48, no. 7, pp. 1135–1142.
17. Elyashevich, G.K., Rosova, E.Yu., and Kuryndin, I.S., *Desalination*, 2002, vol. 144, pp. 21–26.
18. Perena, J.M., Lorenzo, V., Zamfirova, G., and Dimitrova, A., *Polym. Test.*, 2000, vol. 19, pp. 231–236.
19. Favaro, S.L., Rubira, A.F., Muniz, E.C., and Radovanovic, E., *Polym. Degrad. Stab.*, 2007, vol. 92, no. 7, pp. 1219–1226.
20. Shrojal, M., Desai, R., and Singh, P., *Adv. Polym. Sci.*, 2004, vol. 169, pp. 231–293.
21. Wang, J., Yue, Z., Ince, J.S., and Economy, J., *J. Membr. Sci.*, 2006, vol. 286, pp. 333–341.
22. Svorcik, V., Kolarova, K., Slepicka, P., et al., *Polym. Degrad. Stab.*, 2006, vol. 91, pp. 1219–1225.
23. RF Patent ???Номер не указан.
24. Novak, I., Elyashevich, G.K., Chodak, I., et al., *Eur. Polym. J.*, 2008, vol. 44, pp. 2702–2707.
25. Nie, F.Q., Xu, Z.K., Wan, L.S., et al., *J. Membr. Sci.*, 2004, vol. 230, pp. 1–11.
26. Jung, B., *J. Membrane Sci.*, 2004, vol. 229, pp. 129–136.
27. Zimon, A.D., *Adgeziya plenok i pokrytii* (Adhesion of Films and Coatings), Moscow: Khimiya, 1977.
28. Olifirenko, A.S., Novak, I., Rozova, E.Yu., et al., *Vysokomol. Soedin., Ser. B*, 2009, vol. 51, no. 7, pp. 1233–1242.
29. Jung, B., Yoon, J.K., Kim, B., and Rhee, H.W., *J. Membrane Sci.*, 2005, vol. 246, pp. 67–76.