Effect of Polyethylene Glycol Molecular Weights and Concentrations on Polyethersulfone Hollow Fiber Ultrafiltration Membranes

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ABSTRACT: Polyethersulfone (PES) hollow-fiber membranes were fabricated using poly(ethyleneglycol) (PEG) with different molecular weights (MW = PEG200, PEG600, PEG2000, PEG6000, and PEG10000) and poly(vinyl pyrrolidone) PVP40000 as additives and *N*-methyl-2-pyrrolidone (NMP) as a solvent. Asymmetric hollow-fiber membranes were spun by a wet phase-inversion method from 25 wt % solids of 20 : 5 : 75 (weight ratio) PES/PEG/NMP or 18 : 7 : 75 of PES/(PEG600 + PVP40000)/NMP solutions, whereas both the bore fluid and the external coagulant were water. Effects of PEG molecular weights and PEG600 concentrations in the dope solution on separation properties, morphology, and mechanical properties of PES hollow-fiber membranes were investigated. The membrane structures of PES hollow-fiber membranes including cross section, external surface, and internal surface were characterized by scanning electron microscopy and the mechanical properties of PES hollow-fiber membranes were discussed. Bovine serum albumin (BSA, MW 67,000), chicken egg albumin (CEA, MW 45,000), and lysozyme (MW 14,400) were used for the measurement of rejection. It was found that with an increase of PEG molecular weights from 200 to 10,000 in the dope solution, membrane structures were changed from double-layer fingerlike structure to voids in the shape of spheres or ellipsoids; moreover, there were crack phenomena on the internal surfaces and external surfaces of PES hollow-fiber membranes, pure water permeation fluxes increased from 22.0 to 64.0 L m^{-2} h^{-1} bar^{-1}, rejections of three protein for PES/PEG hollow-fiber membranes were not significant, and changes in mechanical properties were decreased. Besides, with a decrease of PEG600 concentrations in the dope solution, permeation flux and elongation at break decreased, whereas the addition of PVP40000 in the dope solution resulted in more smooth surfaces (internal or external) of PES/(PEG600 + PVP40000) hollow-fiber membranes than those of PES/PEG hollow-fiber membranes. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3398–3407, 2004

Key words: hollow-fiber membranes; polyether sulfones; additives; polyethylene glycol; polyvinylpyrrolidone

INTRODUCTION

One important aim in membrane technology is to control membrane structure and membrane performance. This objective is not easy to achieve because membrane structure and performance depend on different factors such as polymer choice, solvent and nonsolvent choice, composition and temperature of coagulant, and casting solution, for example. Furthermore, by changing one or many of these variables, which are dependent on each other, membrane structure may be affected quite significantly. The addition of organic or inorganic components as a third component to a casting solution has been one of the important techniques used in membrane preparation. However, the role of organic and inorganic additives such as, for example, methylcellulose, glycerine, poly(vinyl pyrrolidone) (PVP), polyethylene glycol (PEG), water, LiCl, and $ZnCl_2$ in casting solutions has been reported as a pore-forming agent enhancing permeation properties. This behavior was explained in terms of their water-soluble characteristics.[1–3]

Several authors reported that adding a second polymer, such as PVP, to solutions of polysulfone (PSF) and polyethersulfone (PES) produces membranes with higher porosity, well interconnected pores, and surface properties that were different from the properties of the pure membrane-forming polymer.[4,5] Wood et al.[6] studied the effect of polymer concentration in a membrane casting solution on the performance of resultant flat and hollow-fiber membrane products. Polyvinyl pyrrolidone (PVP) was included in the film-casting solution to ensure that membranes can be made over wide variations in the PES polymer concentration. Besides, Kim and Lee[7] investigated the effect of PEG additive as a pore-former on the structure formation of membranes and their permeation of thermodynamic and kinetic properties in a phase-inversion process. Torrestiana-Sanchez et al.[8] studied

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TABLE I
Composition and Spinning Conditions of PES Hollow-Fiber Membranes

Solution no.	Polymer concentration (%)	PES/additives/NMP ratio	Bore fluid solution
1	25	20 : 5 : 75 PES : PEG 200 : NMP	Water
2	25	20 : 5 : 75 PES : PEG 600 : NMP	Water
3	25	20 : 5 : 75 PES : PEG 2000 : NM	Water
4	25	20 : 5 : 75 PES : PEG 6000 : NMP	Water
5	25	20 : 5 : 75 PES : PEG 10000 : NMP	Water
6	25	18 : 7 : 0 : 75 PES : PEG 600 : PVP 40000 : NMP	Water
7	25	18 : 6 : 1 : 75 PES : PEG 600 : PVP 40000 : NMP	Water
8	25	18 : 4 : 3 : 75 PES : PEG 600 : PVP 40000 : NMP	Water
9	25	18 : 2 : 5 : 75 PES : PEG 600 : PVP 40000 : NMP	Water
10	25	18 : 0 : 7 : 75 PES : PEG 600 : PVP 40000 : NMP	Water

the relationship among the presence of nonsolvent additive, the rheological behavior of spinning solutions, and properties of hollow-fiber membranes. The additives were water, polyvinylpyrrolidone (PVP), and polyethylene glycol (PEG), whereas the basic mixture was polyethersulfone/*N*-methyl-2-pyrrolidone (PES/NMP). In addition the effect of combining water and PVP or PEG was also studied. Among the investigations of hollow-fiber membrane formation by the phase-inversion method, Chaturvedi et al.[9] studied the effect of the nature of additive, solvent, ambient humidity during membrane casting, and the gelling medium on membrane-performance behavior of PES ultrafiltration (UF) membranes.

Many researchers focused on the effect of type of additives, dope solutions, and procedures in the preparation of hollow-fiber UF membranes on membrane performance characteristics and spinning conditions. In this study, polyethersulfone (PES), poly(ethylene glycol) (PEG) with different molecular weights, and polyvinylpyrrolidone (PVP) were used for the preparation of hollow-fiber membranes by a wet phase-inversion method. PES is relatively hydrophobic, whereas PVP and PEG are water-soluble polymers used as additives in membranes.[1,8,10,11] Both PES and additives (PVP and PEG) are good membrane materials because they form miscible blends.[11] This investigation focused on the effect of different PEG molecular weights and PEG600 concentrations on separation properties, morphology, and mechanical properties of PES hollow-fiber UF membranes.

EXPERIMENTAL

Materials

Polyethersulfone (PES) in powder form, obtained from Jida High Performance Materials Co. (China), was used as membrane material. Reagent-grade *N*-methyl-2-pyrrolidone (NMP $\gg$ 98%), used as solvent, the polymeric additive PEG with various molecular weights (MW = PEG200, PEG 600, PEG 2000, PEG 6000, and PEG 10,000), and PVP40000 (MW 40,000) were obtained from Shanghai Chemical Agent Company (China). Deionized water was used as the internal coagulant as well as the nonsolvent from the coagulation bath. For UF experiments, bovine serum albumin (BSA; MW 67,000), chicken egg albumin (CEA; MW 45,000), and lysozyme (MW 14,400) were purchased from Bio Life Science and Technology Co. (Shanghai, China).

Preparation of hollow-fiber membranes and modules

First, PES was dried in an oven for about 24 h at 80°C to remove its moisture content under vacuum. Then, PEG with different molecular weights and PVP40000 were mixed with NMP in glass bottles. After that, the dried PES was added to the bottled mixtures. Finally, each solution was mixed until it became homogeneous.

PES hollow-fiber membranes were prepared using a dry/wet-spinning method, described elsewhere.[10,12–14] The spinneret had an outer diameter of 900 μm and an inner diameter of 500 μm. Tables I and II summarize dope composition, spinning conditions, and outer diameter/inner diameter dimensions of PES hollow-fiber

TABLE II
Dimensional Change of PES Hollow-Fiber Membranes

Membrane no.	OD (μm)	ID (μm)	ID/OD Ratio	Thickness (μm)
1	870	470	0.54	200
2	920	500	0.54	210
3	960	560	0.58	200
4	870	570	0.66	150
5	820	580	0.71	120
6	960	430	0.45	265
7	920	430	0.47	245
8	880	510	0.58	185
9	1020	500	0.49	260
10	840	430	0.51	205

TABLE III
Permeation Fluxes of Pure Water and Lysozyme–Water and Rejection of Proteins for PES Hollow-Fiber Membranes

Membrane no.	J_W[a] ($L/m^{-2}\ h^{-1}\ bar^{-1}$)	J_L[b] ($L/m^{-2}\ h^{-1}\ bar^{-1}$)	BSA rejection (%)	CEA rejection (%)	Lysozyme rejection (%)
1	22.0 ± 0.6	—	100 ± 0.0	99 ± 0.0	98 ± 0.07
2	27.7 ± 0.5	—	99 ± 0.08	98 ± 0.36	97 ± 0.2
3	54.0 ± 0.8	—	99 ± 0.07	98 ± 0.11	96 ± 0.41
4	59.5 ± 1.1	—	99 ± 0.2	97 ± 0.19	95 ± 0.22
5	64.0 ± 2.0	—	99 ± 0.23	96 ± 0.3	95 ± 0.6
6	81.0 ± 3.0	30.4 ± 2.4	99 ± 0.11	98 ± 0.6	95 ± 0.8
7	76.7 ± 4.4	56.2 ± 3.5	98 ± 1.0	98 ± 0.4	60 ± 2.6
8	38.0 ± 0.6	34.7 ± 2.3	96 ± 0.0	94 ± 0.0	79 ± 1.8
9	27.5 ± 1.8	21.3 ± 0.7	95 ± 0.56	90 ± 0.36	45 ± 5.5
10	28.0 ± 1.5	26.0 ± 4.0	96 ± 0.42	93 ± 0.35	87 ± 3.0

[a] Pure water permeation flux.
[b] Permeation flux of 0.05 wt % protein solution (lysozyme with molecular weight MW 14,400).

membranes. Also, the pressure applied on the spinning solution was about 0.15 MPa and the bore fluid flow rate was kept at about 0.4 mL/min in all spinning processes. All nascent fibers were not drawn (no extension), which means that the take-up velocity of the hollow-fiber membrane was nearly the same as the falling velocity in the coagulation bath. All the experiments were conducted at room temperature. The coagulation bath and bore fluid were maintained at room temperature.

The fabricated hollow fibers were stored in the water bath for 24 h to remove the residual NMP. After this period, the fibers were posttreated by two methods: (1) they were kept in a 50 wt % glycerol aqueous solution for 48 h, to prevent the collapse of porous structures; and (2) they were dried in air at room temperature for making test modules.

To test quantitatively the hollow-fiber separation performance in terms of permeation flux and rejection, permeation modules were prepared. Each module consisted of five fibers with a length of 24 cm. The shell sides of the two ends of the bundles were glued into two stainless-steel tees using a normal-setting epoxy resin. These modules were left overnight for curing before testing. To eliminate the effect of the residual glycerol on module performance, each module was immersed in water for 1 day, and run in the test system for 1.5 h before any sample collection.

Measurement of permeation flux and protein rejection

The separation membrane unit for the measurement of permeation flux and protein rejection is described elsewhere.[10,12–14] At a transmembrane pressure (1 bar) and room temperature, all experiments were performed in hollow-fiber modules. Three modules were prepared for each hollow-fiber sample. Table III shows the experimental data of hollow-fiber membrane modules. Pure water permeation fluxes (PWP, J_W) and lysozyme–water permeation fluxes (J_L) of membranes were obtained as follows:

$$J_i = \frac{Q_i}{\Delta P \times A} \tag{1}$$

where J_i is the permeation flux of membrane for solution i ($L\ m^{-2}\ h^{-1}\ bar^{-1}$), Q_i is the volumetric flow rate of solution i (L/h), ΔP is the transmembrane pressure drop (bar), and A is the membrane surface area (m^2).

A protein solution (0.05 wt %) in deionized water was used for the measurement of protein rejection of each hollow-fiber module. To realize the separation efficiency for different molecular weights, three kinds of proteins [bovine serum albumin (MW 67,000), chicken egg albumin (MW 45,000), and lysozyme (MW 14,400)] were applied, respectively. The membrane rejection (R) is defined as

$$R = 1 - \frac{C_p}{C_f} \tag{2}$$

where C_f and C_p are the protein concentration in the feed solution and permeate solution, respectively. The concentration of protein was determined based on absorbency in a UV-spectrophotometer (Shimadzu-UV 3000, Kyoto, Japan) at a wavelength of 280 nm.

Fiber characterization

Inner and outer diameters of hollow fibers were measured by means of an optical microscope. Membrane morphology was examined by using a scanning electron microscope (SEM; JEOL Model JSM-6360 LV, Tokyo, Japan). The surface and cross section of hollow fibers for the SEM were prepared after breaking the membranes in liquid nitrogen to avoid destroying the structure of the cross sections of hollow fibers.

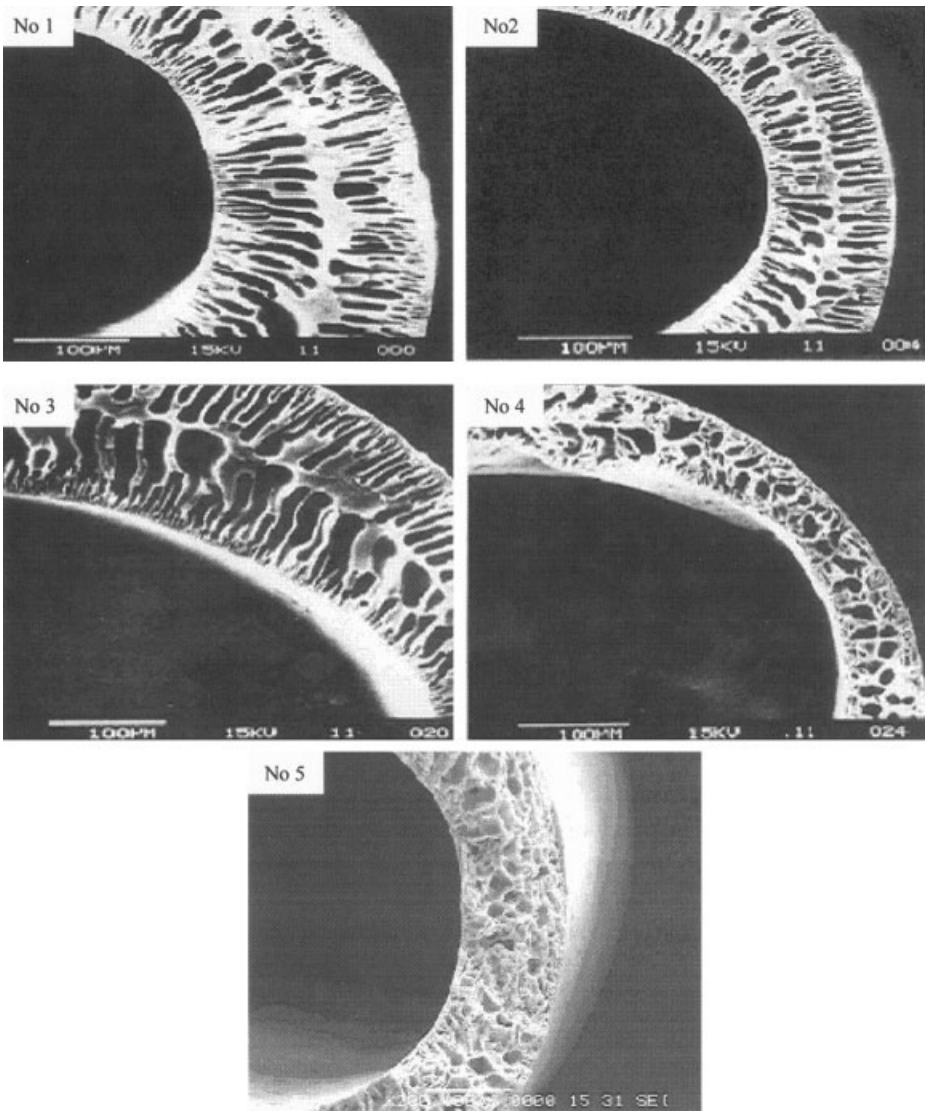

Figure 1 Scanning electron micrographs of the cross sections of PES hollow-fiber membranes spun from dope solutions 1–5 (original magnification ×200).

Measurement of mechanical properties of PES hollow-fiber membranes

Tensile properties of PES hollow-fiber membranes were measured at 50-mm gauge length using an Instron test unit (model 4442; Instron, Canton, MA). The test method was based on ASTM measurements. At least five samples were tested for each experimental result.

RESULTS AND DISCUSSION

Effect of PEG molecular weights and PEG600 concentration in the dope solution on membrane morphology of PES hollow-fiber UF membranes

When a spun-polymer dope solution is immersed directly in a nonsolvent bath (dry/wet-spun), an asymmetric membrane is formed with a dense skin supported by a porous substructure. In the case of a UF membrane, a skin with 1- to 50-nm pore size is present. In this study, hollow-fiber UF membranes were dry/wet-spun from a dope solution, which contains polyethersulfone (PES) and additives (PEG and PVP).

SEM images of the cross sections of PES/PEG hollow-fiber membranes spun from 20 : 5 PES/PEG (PEG200, PEG600, PEG2000, PEG6000, and PEG10,000) solutions in Table I (solutions 1–5) are shown in Figure 1. As can be seen, membranes 1–3 had double-layer fingerlike structures. For PES, water is a strong nonsolvent, which means that coagulation occurs rapidly when the polymer solution is brought into contact with water. The cross sections of membranes 4–5 have voids in the shape

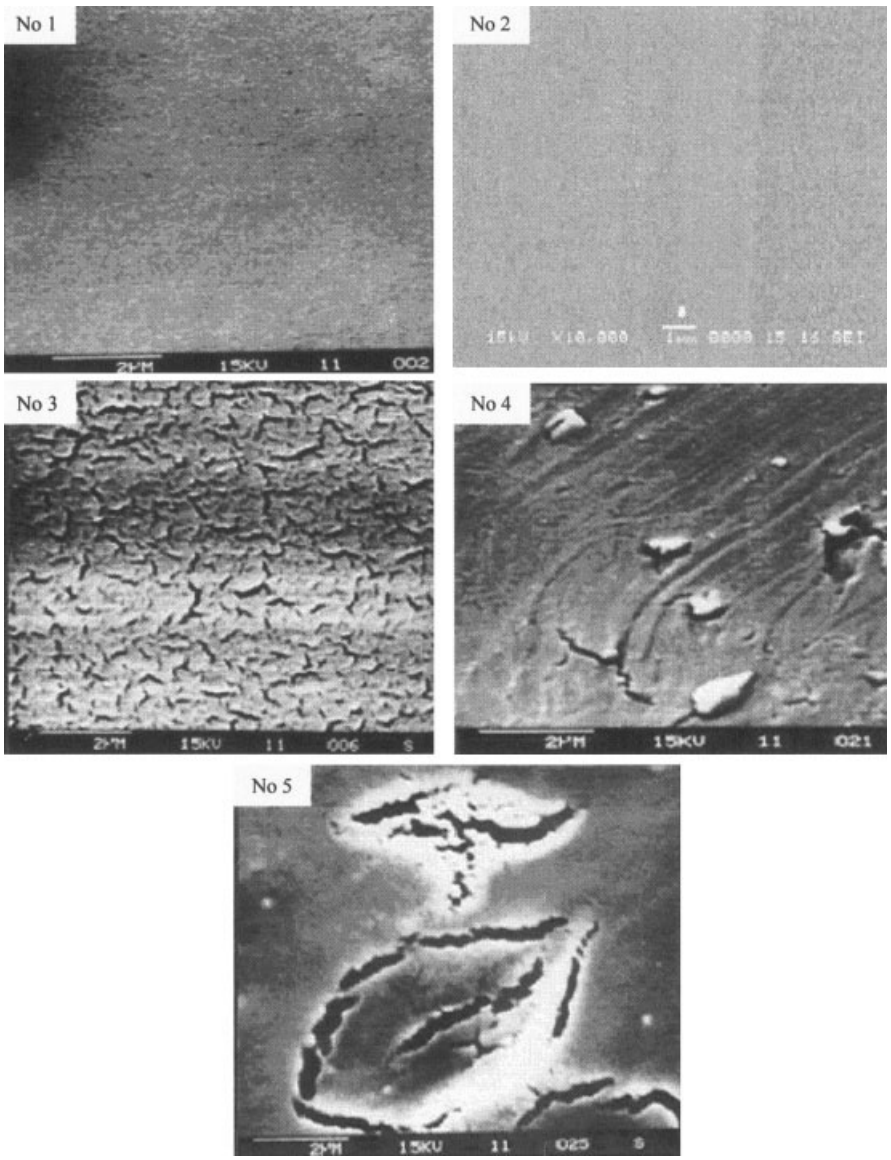

Figure 2 Scanning electron micrographs of the internal surface of PES hollow-fiber membranes spun from dope solutions 1–5 (original magnification ×10,000).

of spheres or ellipsoids in Figure 1. As reported by Kesting,[1] large fingerlike macrovoids is generally formed when the coagulation process is fast, whereas the slow coagulation rate results in a porous spongelike structure. This explanation is consistent with the experimental results in Figure 1. Therefore, membrane morphology changed from a double-layer fingerlike structure (membranes 1–3) to the voids in the shape of spheres or ellipsoids (membranes 4 and 5) with an increase of PEG molecular weight in the dope solution.

In all experiments, instantaneous demixing occurred. The reasons were that water was used as the bore fluid. Figure 2 shows the SEM images of the internal surfaces of hollow-fiber membranes spun from solutions 1–5. In Figure 2, the internal surface structure of PES membranes (membranes 1 and 2) from PEG200 and PEG600 as additives in the dope solution was dense and smooth, whereas membranes 3–5 have some cracks. Besides, there are cracks on the external surfaces of membranes 1–5 in Figure 3. At the same time, the cracks of the external surfaces of membranes 1–5 become larger with an increase of PEG molecular weight. The crack formation on the internal and external membrane surfaces, especially the latter (Figs. 2 and 3), appeared during membrane drying in air at room temperature, attributed to the effect of surface tension force, which depends on the forces of attraction among the particles of water itself and with the particles of hollow fibers with which it comes in contact.

Studies were also conducted to evaluate the effect of PEG600 concentration on the morphology of PES/

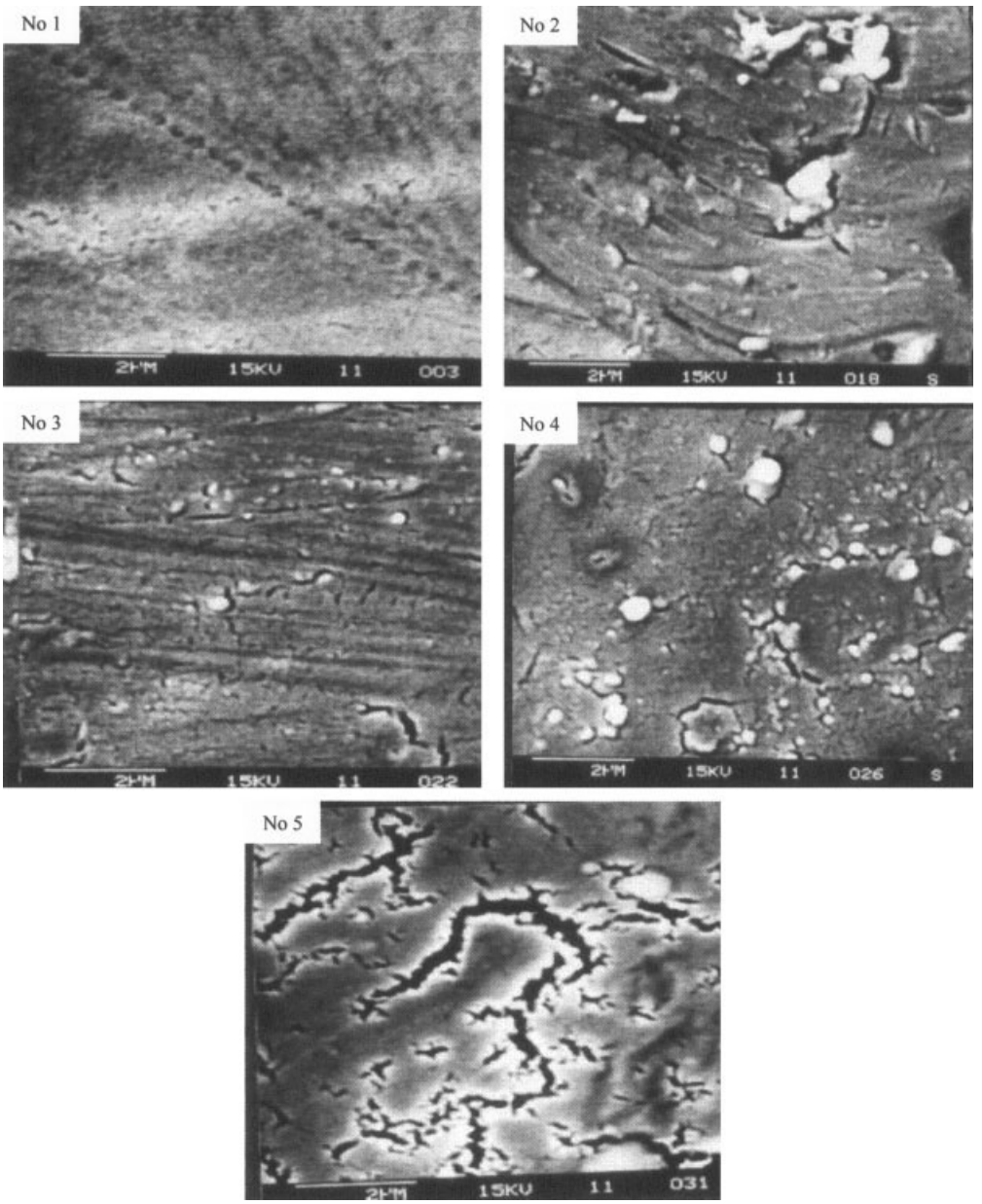

Figure 3 Scanning electron micrographs of the external surface of PES hollow-fiber membranes spun from dope solutions 1–5 (original magnification ×10,000).

(PEG + PVP40000) hollow-fiber membranes fabricated according to the conditions listed in Table I (solutions 7, 8, and 10). As shown in Figure 4 and Figure 5, the internal surfaces and external surfaces of membranes 7, 8, and 10 were dense and smooth. From the description above, it was found that the addition of PVP40000 results in hollow-fiber membranes with smoother surfaces than those formed by the addition of only PEG in the dope solution; for this reason, PVP40000 was used as additive with PEG600. This suggests that the addition of PEG with different molecular weights and the change of PEG/PVP ratio in the dope solution might be used to prepare the desired UF membranes.

Separation performance of PES/PEG and PES/(PEG600 + PVP40000) hollow-fiber membranes

Table III tabulates pure water permeation flux (J_W) of different hollow-fiber membranes fabricated according to the conditions listed in Table I. Table III, Figure 6, and Figure 7 show that an increase of PEG molecular weights from 200 to 10,000 in the dope solution pure water permeation flux increases from 22.0 to 64.0 L m^{-2} h^{-1} bar^{-1}, thus achieving stability, whereas rejections of BSA, CEA, and lysozyme decrease. These results were supported by the respective morphologies because the hollow-fiber membrane spun from

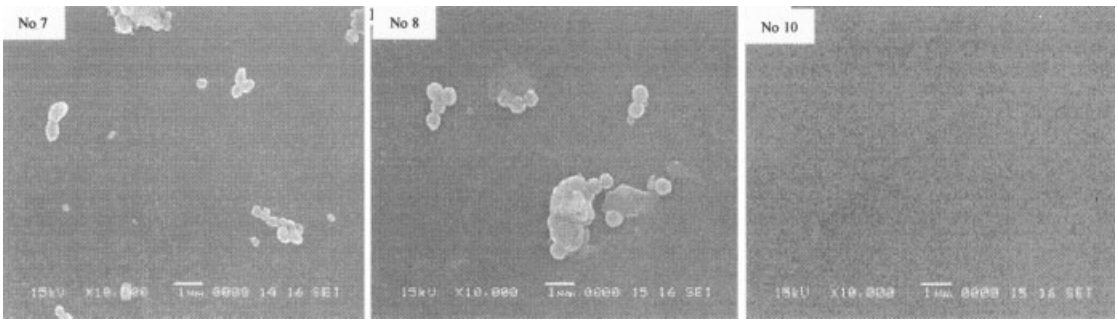

Figure 4 Scanning electron micrographs of the internal surface of PES hollow-fiber membranes spun from dope solutions 7, 8, and 10 (original magnification ×10,000).

the dope solution containing smaller molecular weight PEG had smaller pore size and denser skin, which resulted in lesser degrees of pure water permeation flux and greater protein rejection. However, with an increase of PEG molecular weight the pore size increases, the internal and external surfaces of the membrane became rough (as shown in Figs. 2 and 3), and the increase of pore size could be estimated from the roughness of the membrane surface. This agrees with the results reported by Kim and Lee.[7] At the same time, the cracks resulted in an increase of pure water flux with lower rejection, as shown in Figures 6 and 7. In addition, Table III also shows that the pure water permeation flux of 18 : 7 PES/PEG600 hollow-fiber membrane (membrane 6) was about three times that of 20 : 5 PES/PEG600 and 18 : 7 PES/PVP40000 hollow-fiber membranes (membranes 2 and 10). Otherwise, Table III, Figure 8, and Figure 9 show that PES/(PEG600 + PVP40000) hollow-fiber membranes (membranes 7–9) have higher pure water permeation flux values than that of membrane 10 (only PVP40000) and have lower pure water permeation flux values than that of membrane 6 (only PEG600). With a decrease of PEG600 concentration in the dope solution, a decrease of the permeation flux of PES/(PEG600 + PVP40000) hollow-fiber membrane could be correlated with the decrease of pore size of the membrane and also ascribed to the swelling of the hydrophilic PVP40000 present at the interface of the pore walls of nascent PES/(PEG600 + PVP40000) hollow-fiber membrane.

To evaluate separation performance of PES hollow-fiber membranes for protein–water solution, permeation flux and rejections of BSA (MW 67,000), CEA (MW 45,000), and lysozyme (MW 14,400) were measured. As seen in Table III, there is a significant decrease (from J_W to J_L) in protein–water permeation fluxes (J_L) of PES hollow-fiber membranes when protein (lysozyme) is added to water. In fact, the decrease of permeation flux was caused by a phenomenon-like concentration polarization attributed to accumulation of retained protein at the membrane surface in the first seconds of the run and fouling of the membrane surface. Fouling is a time-dependent phenomenon in which the adsorption of proteins at the membrane surface or pore blocking appear in less than 1 h and sometimes in a few minutes; a long-term fouling may occur in cases such as solute precipitation at high membrane surface concentration or protein denaturation under the processing conditions. It can be said that the concentration polarization and fouling phenomena are the most limiting factors in the application of UF and microfiltration (MF) membrane-separation processes. Generally, the adsorption of proteins, sur-

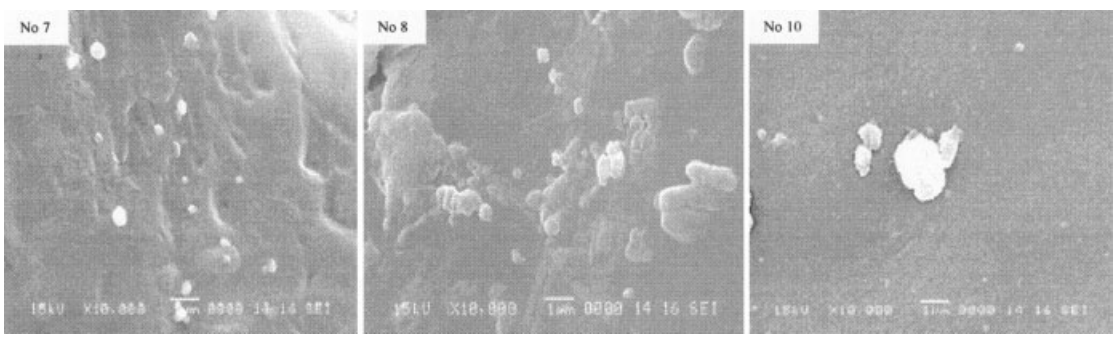

Figure 5 Scanning electron micrographs of the external surface of PES hollow-fiber membranes spun from dope solutions 7, 8, and 10 (original magnification ×10,000).

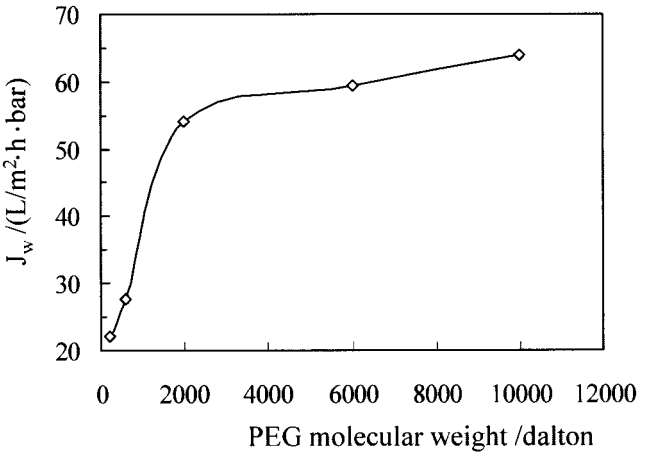

Figure 6 Effect of PEG molecular weights on J_W of PES hollow-fiber membranes.

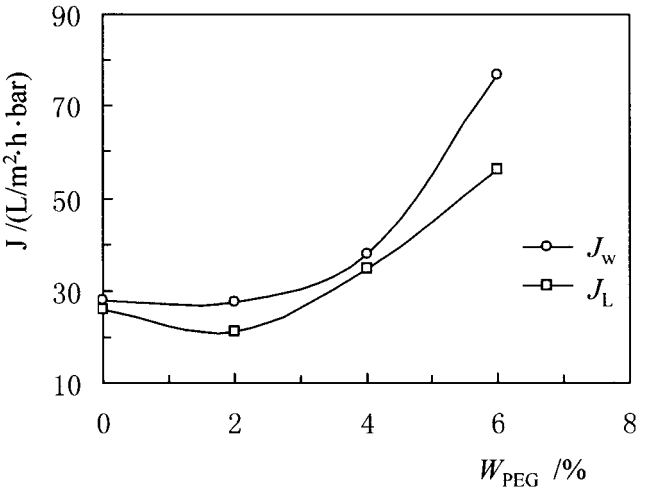

Figure 8 Effect of PEG and PVP concentration in the dope solution on J_W and J_L of PES hollow-fiber membranes.

factants, and lipids on membrane surfaces is a key element in membrane fouling.[16–18] The above pure water flux and protein–water flux changes seem to be related not only to differences on the surface porosity but also to variations in the pore size.

Generally, proteins rejection represents an important property in membrane applications. As shown in Table III and Figure 7, the rejections of PES/PEG hollow-fiber membranes for 0.05 wt % protein solution of BSA (MW 67,000), CEA (MW 45,000), and lysozyme (MW 14,400) are not significant changes with an increase of PEG molecular weights (membranes 1–5). In addition, protein rejections for PES/(PEG + PVP40000) hollow-fiber membranes are shown in Figure 9. It is found that BSA and CEA rejections are not obvious changes with a decrease of PEG600 concentration in the dope solution (membranes 7–10).

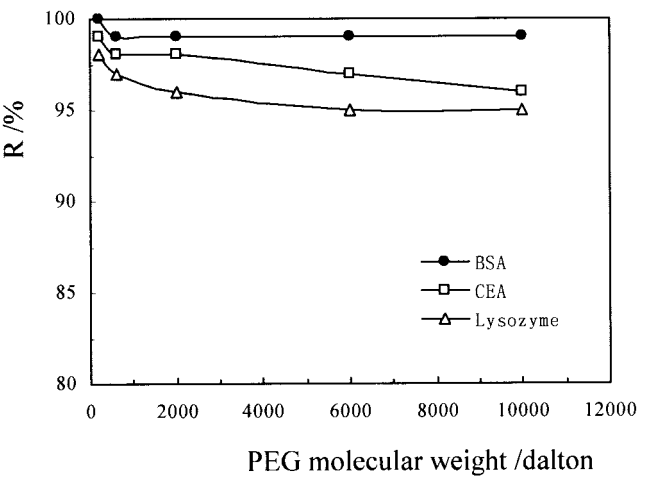

Figure 7 Effect of PEG molecular weights on protein rejection of PES hollow-fiber membranes.

As seen in Table III, the following results were obtained for protein–water separation: BSA rejection varies from 95 to 100%, CEA rejection varies from 90 to 99%, and lysozyme rejection varies from 45 to 98%. Besides, pure water permeation fluxes of membranes 1–5 are from 22.0 to 64.0 L m^{-2} h^{-1} bar^{-1}, whereas pure water permeation fluxes of membranes 6–10 are from 27.5 to 81.0 L m^{-2} h^{-1} bar^{-1}.

Effect of PEG molecular weights and PEG600 concentration in the dope solution on mechanical properties of PES hollow-fiber membranes

In the industrial applications of membranes, the mechanical properties are very important for the membrane performance. Therefore, data of tensile strength

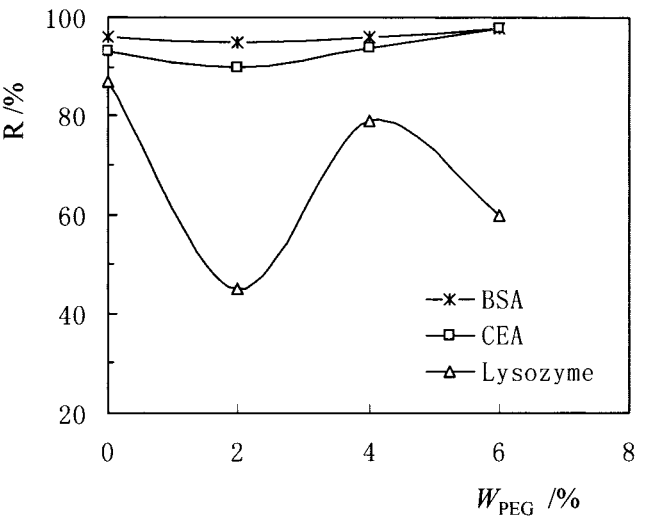

Figure 9 Effect of PEG and PVP concentration in the dope solution on protein rejection of PES hollow-fiber membranes.

TABLE IV
Mechanical Properties of PES Hollow-Fiber Membranes

Membrane no.	Break strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
1	5.7 ± 0.2	69.0 ± 0.9	173.2 ± 10.2
2	5.3 ± 0.9	67.0 ± 3.4	147.1 ± 5.5
3	3.9 ± 0.3	40.9 ± 2.0	147.0 ± 6.5
4	2.1 ± 0.0	9.2 ± 2.0	79.6 ± 13.5
5	2.0 ± 0.1	9.0 ± 3.1	77.8 ± 9.8
6	5.6 ± 0.1	46.9 ± 0.5	143.2 ± 4.4
7	6.3 ± 0.1	44.3 ± 1.0	156.6 ± 1.5
8	4.3 ± 0.1	42.3 ± 1.5	146.2 ± 1.7
9	3.7 ± 0.0	41.1 ± 1.9	94.1 ± 1.6
10	3.2 ± 0.2	17.1 ± 0.5	95.3 ± 4.9

and elongation of hollow-fiber membranes were determined. Table IV shows the mechanical properties of PES hollow-fiber membranes. Within experimental error, the tensile strength at break, elongation at break, and Young's modulus of PES/PEG hollow-fiber membranes seem to be dependent on PEG molecular weights (membranes 1–5). Membrane 4 (PEG6000) and membrane 5 (PEG10,000) have lower mechanical properties than those of membrane 1 (PEG200) and membrane 2 (PEG600), which have a slight difference in mechanical properties. This phenomenon is attributed to the fact that a smaller PEG molecular weight tends to form the denser external skin and internal skin (Figs. 2 and 3). Besides, Table IV shows that the mechanical properties of membrane 6 (only PEG600) are better than those of membrane 10 (only PVP40000), whereas the mechanical properties of membranes 7–9 increase with an increase of PEG600 concentration in the dope solution. This is attributed to the fact that a lower PVP tends to form a denser skin layer (Figs. 4 and 5). Because of using pure water as the bore fluid and external coagulation agent, higher mechanical properties were obtained, which is attributed to the fact that pure water is a powerful coagulation agent, which tends to form dense internal and external layers. It was mentioned here that an adequate hollow-fiber diameter ratio D_i/D_o close to 0.5 was optimal to obtain good mechanical properties.[6] Furthermore, it was previously reported that the D_i/D_o ratio is strongly affected by the type of additives used,[19] and it was suggested that the D_i/D_o ratio is dependent on the higher viscosity solutions, which are independent of the type of additives used.[8] In this study, experimental results in Table II suggest a D_i/D_o ratio close to 0.5 on the type of additive used and composition of membrane material (PES) also obtained good mechanical properties.

CONCLUSIONS

Using PES as the membrane material, PEG with different molecular weights (PEG200, PEG600, PEG2000, PEG6000, and PEG10000) and poly(vinyl pyrrolidone) PVP40000 as additives and *N*-methyl-2-pyrrolidone (NMP) as a solvent, asymmetric hollow-fiber membranes were spun by a wet phase-inversion method from 25 wt % solids of 20 : 5 : 75 (weight ratio) PES/PEG/NMP or 18 : 7 : 75 of PES/(PEG600 + PVP40000)/NMP solutions, whereas both the bore fluid and the external coagulant were water. The investigation was conducted to evaluate the effects of PEG molecular weights and PEG600 concentrations in the dope solution on separation properties, morphology, and mechanical properties of PES hollow-fiber membranes. The rejections of bovine serum albumin (BSA, MW 67,000), chicken egg albumin (CEA, MW 45,000), and lysozyme (MW 14,400) were measured for PES/PEG and PES/(PEG600 + PVP40000) hollow-fiber membranes. SEM images illustrated that membrane structures were changed from double-layer fingerlike structure to voids in the shape of spheres or ellipsoids and there were crack phenomena on the internal surfaces and external surfaces of PES hollow-fiber membranes with an increase of PEG molecular weights from 200 to 10,000 in the dope solution. Based on the experimental results, pure water permeation fluxes increased from 22.0 to 64.0 L m^{-2} h^{-1} bar^{-1}, rejections of three proteins for PES/PEG hollow-fiber membranes were not significant changes, and mechanical properties were decreased. With a decrease of PEG600 concentrations in the dope solution permeation flux and the elongation at break decreased, whereas the addition of PVP40000 in the dope solution resulted in more smooth surfaces (internal or external) of PES/(PEG600 + PVP40000) hollow-fiber membranes than those of PES/PEG hollow-fiber membranes.

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