

Effect of Polyvinylpyrrolidone Molecular Weights on Morphology, Oil/Water Separation, Mechanical and Thermal Properties of Polyetherimide/Polyvinylpyrrolidone Hollow Fiber Membranes

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ABSTRACT: We prepared polyetherimide (PEI) hollow fiber membranes using polyvinylpyrrolidones (PVP) with different molecular weights (PVP 10,000, PVP 40,000, and PVP 1,300,000) as additives for oil/water separation. Asymmetric hollow fiber membranes were fabricated by wet phase inversion technique from 25 wt % or 30 wt % solids of 20 : 5 : 75 or 20 : 10 : 70 (weight ratio) PEI/PVP/*N*-methyl-2-pyrrolidone (NMP) solutions and a 95 : 5 NMP/water solution was used as bore fluid to eliminate resistance on the internal surface. Effects of PVP molecular weights on morphology, oil-surfactant-water separation characteristics, mechanical, and thermal properties of PEI/PVP hollow fiber membranes were investigated. It was found that an increase in PVP molecular weight and percentage in PEI/PVP dope solution resulted in the membrane morphology change from the finger-like structure to the spongy structure. Without sodium hypochlorite posttreatment, hollow fiber membranes with higher PVP molecular weights had a higher rejection but with a lower water flux. For oil-surfactant-water emulsion systems (1600 ppm surfactant of sodium dodecylbenzenesulfonate and 2500 ppm oil of *n*-decane), experimental results illustrated that the rejection rates for surfactant, total organic carbon, and oil were 76.1 \approx 79.8%, 91.0 \approx 93.0%, and more than 99%, respectively. Based on the glass transition temperature values, PVP existed in hollow fiber membranes and resulted in the hydrophilicity of membranes. In addition, using NaOCl as a posttreatment agent for membranes showed a significant improvement in membrane permeability for PVP with a molecular weight of 1300 K, whereas the elongation at break of the treated hollow fiber membranes decreased significantly. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2220–2233, 1999

Key words: asymmetric hollow fiber membrane; skinless internal layer; oil-surfactant-water emulsion; polyetherimide; polyvinylpyrrolidone

INTRODUCTION

Oily water wastes constitute a major environmental problem in many industries.^{1–8} Especially in

the field of rare metal ion extraction, the use of surfactants can pose many difficulties for phase separation. Treatment of contaminated effluents and ground waters associated with the hydrocarbon and edible oil industries frequently involves the removal of free and emulsified oils. Metal-working operations use water to remove dirt and grease before painting. Oil/water emulsions are used for cooling and lubrication of tools and dyes during metal machining operations.⁵ These oily

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wastes can be grouped into three broad categories: free-floating oil, unstable oil/water emulsions, and highly stable oil/water emulsions.^{1,2} Free oil can be readily removed by mechanical separation devices, which use gravitational forces as the driving force. Unstable oil/water emulsions can be mechanically or chemically broken and then gravity separated. However, stable emulsions require more sophisticated treatment to meet the effluent standards before the development of membrane technology. These emulsions consist of water, surfactant, and oil. Typically, oil-surfactant-water emulsion contains 0.1 \approx 10% oil.⁹ It can be divided into two types of emulsions: micro-emulsions and macro-emulsions. The former contain oil droplets with sizes ranging from 10 to 150 nm in the water whereas the latter contain oil droplets having diameters from 0.2 to 10 μm .¹⁰

Except chemical methods, various physical methods including microfiltration (MF), ultrafiltration (UF), nanofiltration, gravity settling, centrifugation, air flotation, and fibrous or packed beds coalescence have been applied in oil-surfactant-water separation.¹⁻⁸ Among these physical methods, membrane technology is by far used most extensively. However, the basis for selecting membranes and membrane-operating conditions to achieve adequate rejection of oil and emulsified material while maintaining permeate flux remains largely empirical. Many studies have reported the application of the treatment of macro-emulsions using commercial UF and MF membranes.^{1,2,8-17} For example, Lipp et al.⁸ studied the fundamental basis of oil-water separation using UF membranes with Amicon YM5, YM30 and PM30, polyamide CJT 35, and polyacrylic IRIS 3038. Bodzek and Konieczny⁹ reported the suitability of polyacrylonitrile and poly(vinyl chloride) UF membranes for spent emulsion wastewater separation. The flux drop depended on the kind of emulsifying oil, oil rejection was 95 \approx 99%, and chemical oxygen demand was 91 \approx 98%. Daiminger et al.¹¹ proposed two methods of oil/water separations using commercial membranes (produced by Satorius and Millipore); in both methods, wetting was found to play an important role. Hlavacek¹² also reported the use of a commercial MF membrane (Polypropylene) for separating the two phases of an industrial emulsion from the aluminum industry. In that case, the membrane acted as a coalescer. Belkacem et al.¹³ obtained new results in metalworking wastewater using the commercial polyacrylonitrile UF membrane. The permeation fluxes were increased by the addition of a reactive salt at a very low

concentration in the feed solution. Using commercial Ceramesh and poly(vinylidene fluoride) MF membranes, Field et al.¹⁵ studied the influence of different types of surfactants. The surfactants were an anionic (sodium lauryl sulphate) and two nonionic surfactants [poly(ethylene glycol) 2025 (PEG 2025) and polyoxyethylene sorbitan monooleate (Tween 80)]. The flux reductions were found to be more pronounced with hydrophobic poly(vinylidene fluoride) membrane. Koltuniewicz and Field¹⁶ focused further on the problem of the process factors that affect the permeation fluxes in the separation of oil-in-water emulsion. Nazzal and Wiesner⁷ reported effects of transmembrane pressure and membrane pore on the microfiltration of oil-in-water emulsion. Generally, oil drops in oil-surfactant-water emulsion are deformable, the transmembrane pressure relative to the membrane pore size and size distribution of oil drops in the feed solution is likely to be a critical operation variable as membrane composition and solution chemistry.⁷

In an effort to improve fouling resistance, hydrophilic and low surface charge membranes were developed because hydrophilic materials are less sensitive to adsorption than hydrophobic ones.^{1,2,17,26,27} Using polyetherimide (PEI) as the membrane material and polybenzimidazole and poly(ethylene glycol) (PEG 600) as the additives, Xu and coworkers¹⁷ prepared hydrophilic hollow fiber membranes for oil-surfactant-water separation. Experimental results also illustrated that the rejection rates for surfactant, total organic carbon, and oil were 51.4 \approx 79.1%, 83.1 \approx 92.7%, and more than 99%, respectively.

In this study, PEI and polyvinylpyrrolidone (PVP) were used for the preparation of hydrophilic hollow fiber membranes for the oil-surfactant-water separation. PEI is relatively hydrophobic whereas PVP is a water-soluble polymer like poly(ethylene glycol) (PEG) and has been used as an additive of membranes.¹⁷⁻²⁵ Both PEI and PVP are good membrane materials because they form the miscible blend.²⁵ The investigation is focused on the effect of different PVP molecular weights on membrane formation, membrane performance for oil-surfactant-water separation, thermal properties, and mechanical properties.

EXPERIMENTAL

Materials

An aromatic PEI (Ultem 1010) was obtained from GE Plastics (New York) whereas PVPs with dif-

ferent molecular weights (10 K, 40 K, and 1300 K, i.e., PVP 10,000, PVP 40,000, and PVP 1,300 000) was supplied by Aldrich Chemical Company. *N*-methyl-2-pyrrolidone (NMP) (MERCOR-Schuchardt), polyethylene glycol (PEG 35,000) (from Fluka Chemie AG, Switzerland), and sodium dodecylbenzenesulfonate (Fluka Chemie AG), *n*-dodecane (99%) as oil (Nacalai Tesque Inc., Japan) were used as received.

Preparations of Hollow Fiber Membranes and Modules

Wet-spinning technique, described elsewhere, was used to fabricate hollow fibers.^{26,27} The spinneret has an outer diameter of 850 μm and an inner diameter of 450 μm . Tables I and II summarize the spinning conditions and outer diameter/inner diameter dimensions of the fabricated hollow fibers. Here, all ratios of dope solution rates and bore fluid rates were constant (1.83) in all spinning processes. All nascent fibers were not drawn (hence no extension), which means that the take-up velocity of the hollow fiber membrane was nearly the same as the free falling velocity in the coagulation bath. After the formation of hollow fibers, the fibers were stored in the water bath for at least 1 day, and then immersed in a tank containing 10 wt % glycerol for at least 1 day to prevent the collapse of porous structures. Subsequently, hollow fibers were dried for a day before the fabrication of modules. For the fibers treated with sodium hypochlorite (NaOCl) solutions, they were also subsequently immersed into a tank containing 10% glycerol for at least 1 day and the same procedure was followed for module fabrication.^{17,23,24}

To test quantitatively the hollow fiber separation performance in terms of permeation flux and rejection, permeation modules were prepared. Each module consisted of 10 \approx 12 fibers with a length of 25 cm as listed in Table III. The shell sides of the two ends of the bundles were glued onto two stainless steel union crosses using a normal-setting epoxy resin (Eposet). These modules were left overnight for curing before tested. To eliminate the effect of the residual glycerol on module performance, each module was immersed in water for 1 day, and then run in the test system for 1/2 h before any sample collection.

Measurements of Surfactant Concentration and Total Organic Carbon (TOC)

Surfactant concentration was determined based on absorbance in UV-spectrophotometer (Shi-

Table I Dope Compositions and Spinning Conditions of Wet-Spun PEI/PVP Hollow Fiber Membranes

Solution No.	Dope Polymer Concentration (%)	PEI/PVP Ratio	Viscosity ^a cp	Bore Fluid Solution	Dope Rate (g/min)	Bore Fluid Rate (ml/min)		Take-Up Rate (cm/s)	
						Dope Rate	Take-Up Rate		
1	25.0	20 : 5 PEI : PVP 10,000	2830	95 : 5 NMP : water	0.550	0.300	1.83	3.09	
2	25.0	20 : 5 PEI : PVP 40,000	3460	95 : 5 NMP : water	0.416	0.226	1.83	2.64	
3	25.0	20 : 5 PEI : PVP 1,300,000	12,400	95 : 5 NMP : water	0.488	0.266	1.83	2.06	
4	30.0	20 : 5 : 5 PEI : PVP 40,000 : PVP 1,300,000	14,900	95 : 5 NMP : water	0.865	0.471	1.83	2.38	
5	30.0	20 : 10 PEI : PVP 1,300,000	33,600	95 : 5 NMP : water	0.290	0.158	1.83	1.19	

^a Measurement at shear rate = 10 S⁻¹ and 25.0°C.

Table II Dimensional Change of Wet-Spun PEI/PVP Hollow Fibers

Solution No.	OD (μm)	ID (μm)	OD/ID Ratio	Cross-Section Area Change Ratio ^a
1	750	480	1.56	0.64
2	780	580	1.34	0.52
3	900	680	1.32	0.67
4	1080	850	1.27	0.85
5	950	780	1.22	0.57

^a Ratio of a fiber cross-section area to a spinneret (850 μm /450 μm) cross-section area for fiber spinning.

madzu UV-Visible Spectrophotometer, UV-1601) at 1-cm path length and 224-nm wavelength. At the wavelength of 224 nm, the relationship of ABS and surfactant concentration is linear. Deionized water was used as reference. Samples were collected for each separation test, and deionized water was used to dilute the sample accordingly.

A Total Organic Carbon Analyzer (TOC-5000A) from Shimadzu (Japan) was used to determine the organic carbon content in the samples. Standard solutions supplied by the manufacturer were used to calibrate the machine. Calibrations for the total carbon and inorganic carbon were performed in triplicates. The machine was used to determine total carbon content and total inor-

ganic carbon content. TOC was obtained from the following equation,

$$\text{Total Organic Carbon (TOC)} = \text{Total Carbon (TC)} - \text{Total Inorganic Carbon (IC)} \quad (1)$$

Samples were collected for each separation test and necessarily diluted with deionized water.

Oil-Surfactant-Water Emulsion Separation Experiments

The emulsion was prepared as follows: an appropriate amount of surfactant (sodium dodecylbenzenesulfonate) was first added to deionized water and dissolved completely. *N*-dodecane as oil was then added to the solution. Agitation and circulation rates were adjusted to ensure that an emulsion was formed. An average diameter of oil droplets was $2.5 \pm 1.0 \mu\text{m}$ (Fig. 1). This was determined based on the observation of oil droplets using an Olympus BX 50 Microscope.

Figure 2 shows a schematic of oil-surfactant-water separation membrane unit. At a transmembrane pressure of 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 experimental data of hollow fiber membrane modules. Pure wa-

Table III Experimental Data of PEI/PVP Hollow Fiber Membrane Modules

Membrane No.	PEI/PVP Ratio	Posttreatment of Membranes	No. of Hollow Fiber Membrane	Module Membrane Area (cm^2)	Cross Flow Velocity (cm/s)
1	20 : 5 PEI : PVP 10,000	50.0°C for 1 day in water	12	56.5	20.1
2	20 : 5 PEI : PVP 10,000	50.0°C for 1 day in water and 4000 ppm NaOCl for 2 days	12	56.5	20.1
3	20 : 5 PEI : PVP 40,000	50.0°C for 1 day in water	12	58.5	23.3
4	20 : 5 PEI : PVP 40,000	50.0°C for 1 day in water and 4000 ppm NaOCl for 2 days	12	58.5	23.3
5	20 : 5 PEI : PVP 1,300,000	50.0°C for 1 day in water	12	56.5	24.3
6	20 : 5 PEI : PVP 1,300,000	50.0°C for 1 day in water and 4000 ppm NaOCl for 2 days	12	56.5	24.3
7	20 : 5 : 5 PEI : PVP 40,000 : PVP 1,300,000	50.0°C for 1 day in water	10	47.8	19.4
8	20 : 5 : 5 PEI : PVP 40,000 : PVP 1,300,000	50.0°C for 1 day in water and 4000 ppm NaOCl for 2 days	10	47.8	19.4
9	20 : 10 PEI : PVP 1,300,000	50.0°C for 1 day in water	10	47.5	20.9
10	20 : 10 PEI : PVP 1,300,000	50.0°C for 1 day in water and 4000 ppm NaOCl for 2 days	10	47.5	20.9

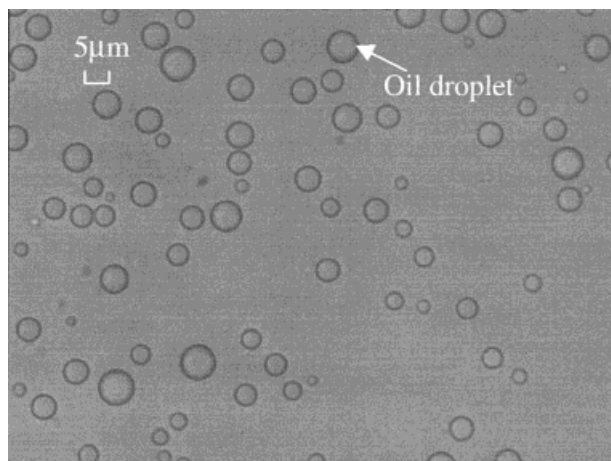


Figure 1 A typical microscope picture of oil droplets in oil-surfactant-water emulsion (average diameter: $2.5 \pm 1.0 \mu\text{m}$).

ter permeation fluxes (PWP, J_w), PEG 35,000-water permeation fluxes (J_{PEG}), surfactant-water permeation fluxes (J_s), and oil-surfactant-water permeation fluxes (J_e) of membranes were obtained as follows:

$$J_i = \frac{Q_i}{\Delta P \times A} \quad (2)$$

where J_i = permeation flux of membrane for solution i ($\text{L}/\text{m}^2 \cdot \text{h} \cdot \text{bar}$); Q_i = volumetric flow rate of solution i (L/h); ΔP = transmembrane pressure drop (bar); A = membrane outer surface area (m^2).

The rejection (R) for each component in the separation of surfactant-water or oil-surfactant-water was given by:

$$R = 1 -$$

$$\frac{\text{Surfactant or oil concentration in permeate}}{\text{Surfactant or oil concentration in feed}}$$

(3)

Scanning Electron Microscope (SEM)

Membrane samples for SEM were first immersed in liquid nitrogen, fractured, and then sputtered with gold using a Jeol JFC-1100E Ion Sputtering Device. We used a Hitachi S-4100 field emission SEM to investigate the morphology of hollow fiber membranes.

Measurements of Thermal Properties and Mechanical Properties of Hollow Fiber Membranes

After vacuum drying at 120°C for at least 24 h, the glass transition temperature (T_g) of hollow

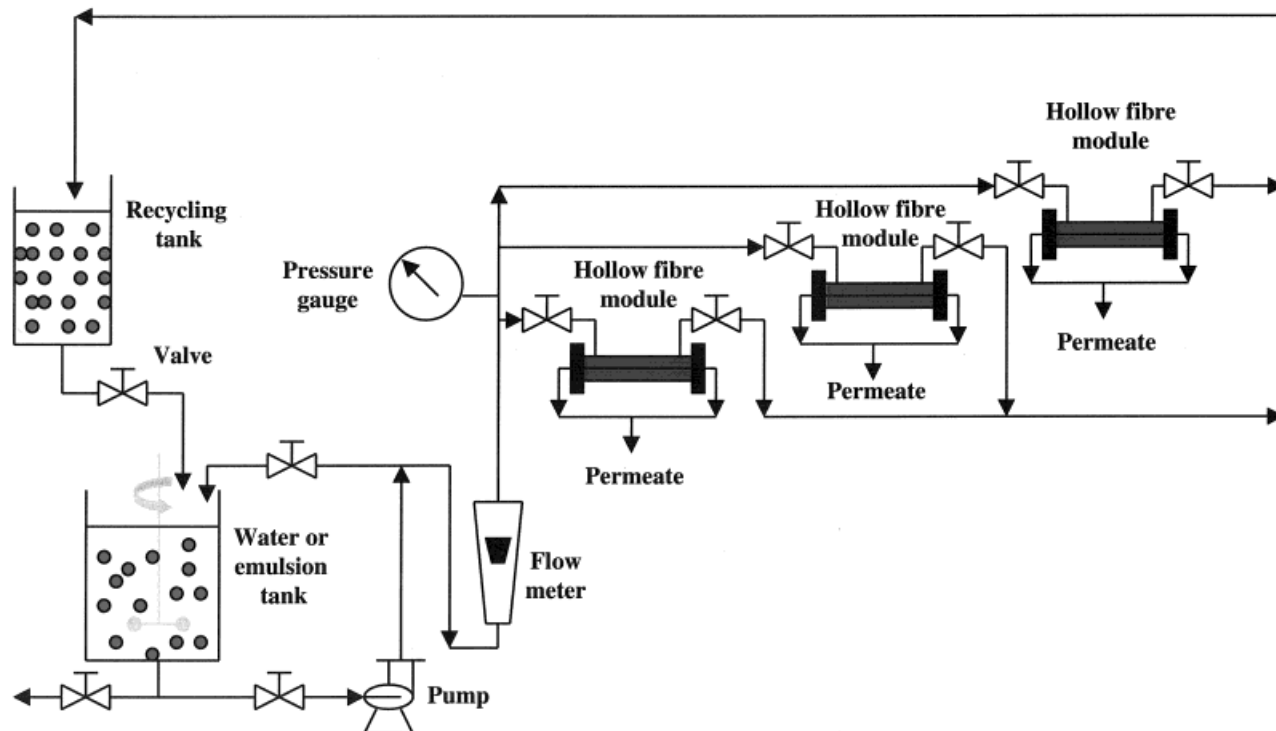


Figure 2 Schematic diagram of oil-surfactant-water membrane separation.

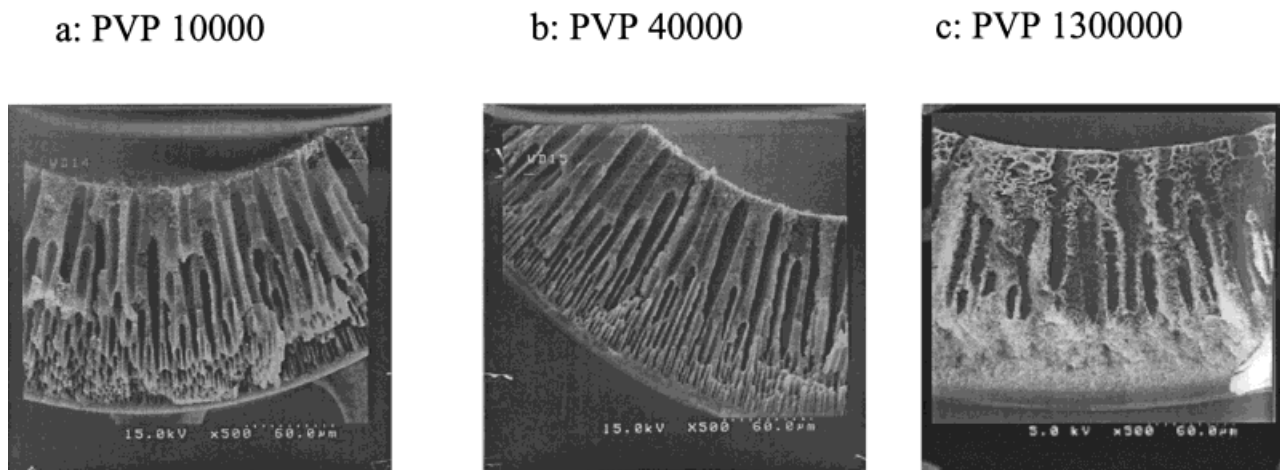


Figure 3 Effect of PVP molecular weights on the cross-section structures of hollow fiber membranes wet-spun from 25 wt % solids of 20 : 5 PEI/PVP solution (original magnification, $\times 500$).

fibers was measured using a Thermal Mechanical Analyzer (TMA 2940, Waters Corporation) at a heating rate of $5^{\circ}\text{C}/\text{min}$ and a force of 0.05N from room temperature to 250°C . Hollow fiber samples were cut into the length of approximately 35 mm and then loaded on a TMA 2940 instrument. The onset temperature was obtained as an indication of the T_g in these measurements.

Tensile properties of hollow fiber membranes were measured at 50-mm gauge length with a speed of 50 mm/min using an Instron test unit (model: INSTRON 5542). The test method was based on ASTM measurements. At least five samples were tested for each datum.

RESULTS AND DISCUSSION

Membrane Morphology of PEI/PVP Hollow Fiber Membranes

When a spun polymer dope solution is immersed directly in a nonsolvent bath, an asymmetric membrane is formed with a dense skin supported by a porous substructure.^{19,25} For reverse osmosis, gas separation, and pervaporation, this skin is necessary and essential for the separation process, which is based on differences in solubility and diffusion rates of the components in the dense skin. In the case of ultrafiltration membrane, a skin with $1 \approx 50\text{ nm}$ pore is present.^{1,2,19,25} Here, hollow fiber ultrafiltration membranes are wet-spun from a dope solution containing PEI and PVP. During the membrane formation, the PEI/PVP/NMP dope solution separates into two

phases based on a liquid-liquid demixing process.^{22,24} One phase is a PEI rich phase whereas another is a PVP rich phase.

Figure 3 shows SEM images of the cross sections of the hollow fiber membranes wet-spun from 25 wt % solids of 20:5 PEI/PVP (PVP 10 K or PVP 40 K or PVP 1300 K) solutions listed in Table I (solution nos.1–3). As can be seen with a 95:5 NMP/water solution as bore fluid, PEI/PVP hollow fiber membrane (membrane nos.1, 3, and 5) had a “three-layer structures” in the cross section. The “three-layer structures” consisted of an internal finger-like layer, an external sponge layer, and an external skin layer. With an increase of PVP molecular weight in the dope solution, the thickness of an external sponge layer of hollow fiber membranes became larger in Figure 3 whereas the external skin layer became denser. The results suggest that the higher PVP molecular weight in the polymer dope solution may result in hollow fiber membranes with a denser external skin and smaller pore sizes in the external surface. This membrane (membrane no. 5) presented lower permeation flux and higher separation characteristics, which will be confirmed by later results.

In an effort to reduce hydrodynamic resistance to water on the internal layer, a 95:5 NMP/water solution was used as bore fluid. In all experiments, it was found that delayed demixing for the internal layer resulted in the formation of fully porous internal surfaces of the hollow fiber membranes. The reasons were high solvent concentration in the bore fluid and the diffusion of the

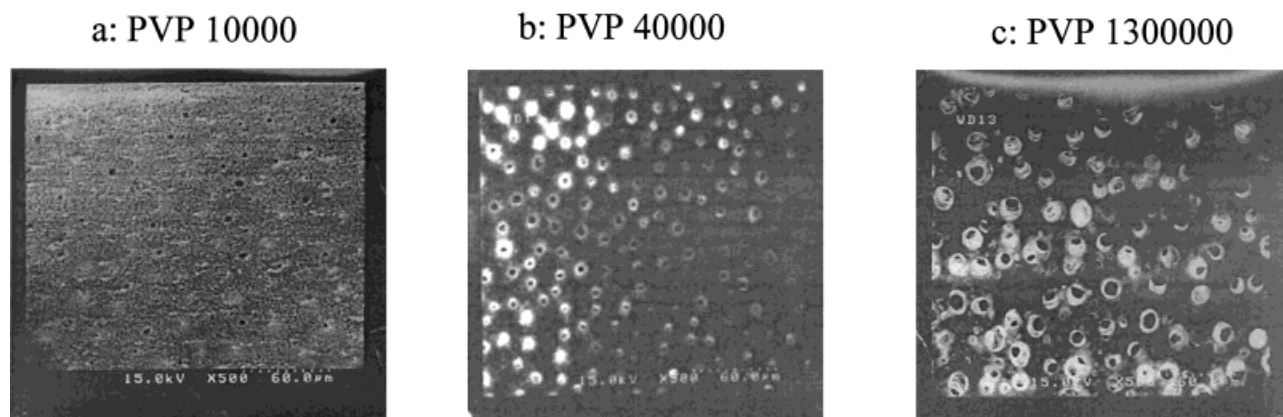


Figure 4 Effect of PVP molecular weights on the internal structures of hollow fiber membranes wet-spun from 25 wt % solids of 20 : 5 PEI/PVP solution (original magnification, $\times 500$).

water-soluble PVP from the dope solution to the bore fluid. Figure 4 clearly illustrates that all internal surfaces were porous due to delay liquid-liquid demixing. In the meanwhile, the pores of the internal surfaces of membrane nos. 1, 3, and 5 were different and roughly $4 \approx 12 \mu\text{m}$ in Figure 4. This result concluded that the higher the PVP molecular weight is, the bigger the pore is. However, it can be observed that the external surfaces at a higher magnification for hollow fiber membranes with different PVP molecular weights were dense due to instantaneous liquid-liquid demixing process as shown in Figure 5. In comparison with double skin layers (internal and external), that were marketed by Asahi Chemical Industry (Japan) and Pall Corporation (USA),¹ the morphology of this single external skin layer reduced significantly hydrodynamic resistance to water.

Studies were also conducted to evaluate the effect of PVP compositions on the hollow fiber membranes fabricated according to the conditions listed in Table I (solutions 4 and 5). Membrane no. 7 was wet-spun from 30 wt % solids of 20:5:5 PEI/PVP 40K/PVP 1300 K dope solution (solution 4) whereas membrane no. 9 from 30 wt % solids of 20:10 PEI/PVP 1300 K dope solution (solution 5). As shown in Figure 6, the cross section of the PEI/PVP hollow fiber membranes (membrane nos. 7 and 9) consisted of only two layers (a sponge substructure layer and an external skin layer) vs. three layers (one additional finger-like voids) for membranes nos. 1, 3, and 5. Membrane nos. 7 and 9 also show a rather uniform sponge layer throughout the cross section of the membrane in Figure 6. In comparison with the hollow fiber membranes wet-spun from 25 wt % solids of solutions nos. 1–3 (Figs. 4 and 5), the internal sur-

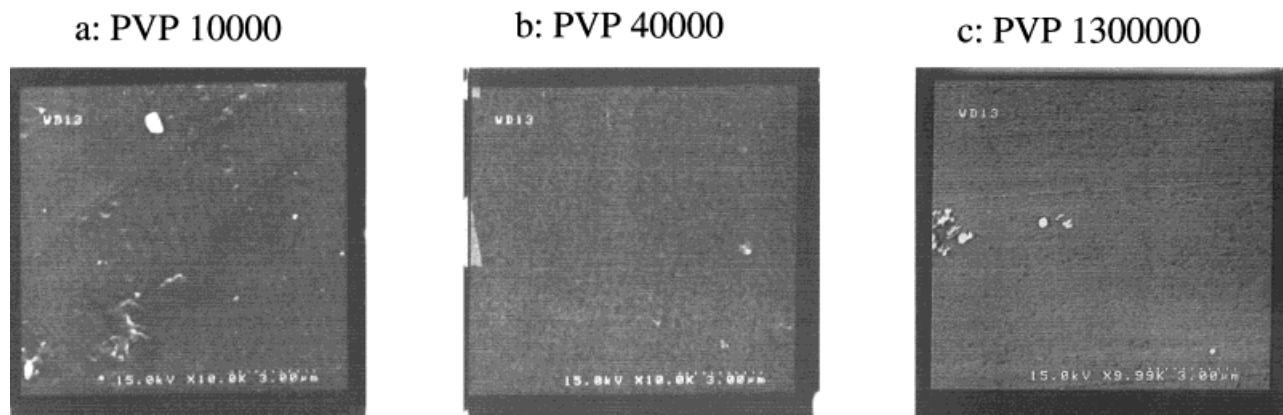


Figure 5 Effect of PVP molecular weights on the external structures of hollow fiber membranes wet-spun from 25 wt % solids of 20 : 5 PEI/PVP solution (original magnification, $\times 10,000$).

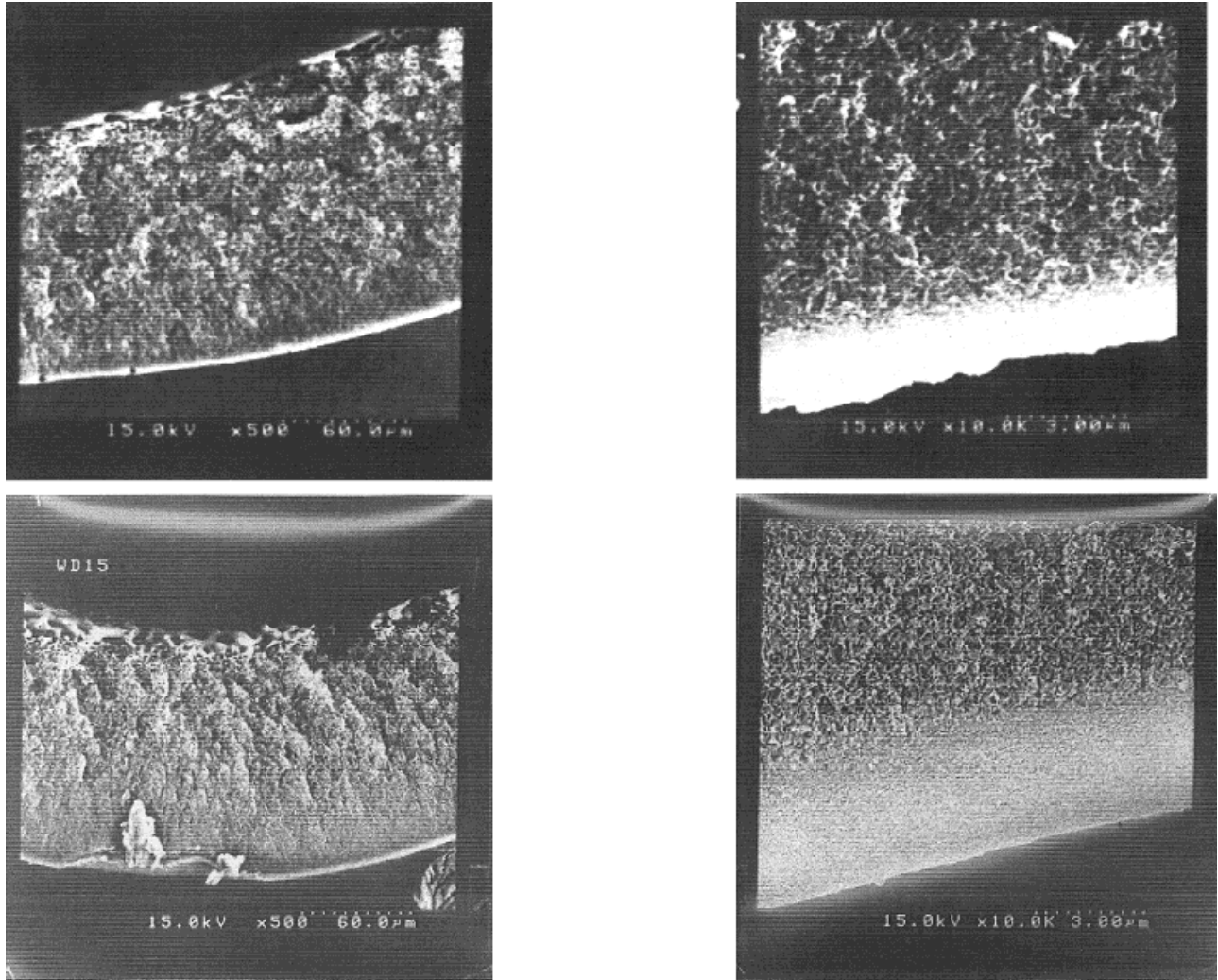


Figure 6 Effect of PVP compositions on the cross-section structures of hollow fiber membranes wet-spun from 30 wt % solids of PEI/PVP dope solutions. Top: PEI/PVP ratio—20 : 5 : 5 PEI/PVP 40,000/PVP 1,300,000; left—original magnification, $\times 500$; right—original magnification, $\times 10,000$; bottom: PEI/PVP ratio—20 : 10 PEI/PVP 1,300,000; left—original magnification, $\times 500$; right—original magnification, $\times 10,000$.

faces of hollow fiber membranes wet-spun from 30 wt % solids of solutions 4 and 5 were more porous and tortuous whereas the external surfaces were denser as evident from Figures 7 and 8. Conventionally, a high solid content dope yields a denser structure. However, in the present case, the percentage of PVP seemed to be the determining factor on the porosity rather than the total solid content.

Permeation Fluxes of PEI/PVP Hollow Fiber Membranes

Table IV tabulates pure water fluxes (J_w) of different hollow fiber membrane fabricated accord-

ing to the listed conditions and posttreatment (Tables I–III). Water fluxes of hollow fiber membranes with PVP 1300 K (membranes nos. 5, 7, and 9) were found to be lower than that of other hollow fiber membranes with PVP 10 K and PVP 40 K (membrane nos. 1 and 3) without NaOCl posttreatment. These results were consistent and supported by the respective morphologies because the hollow fiber membrane spun from the dopes containing PVP 1300 K had smaller pore sizes and denser skin which resulted in a higher resistance for water permeation and a greater rejection for PEG 35 K solution. Besides, the water fluxes were small since PVP 1300 K in the membrane matrix swelled considerably in contact with

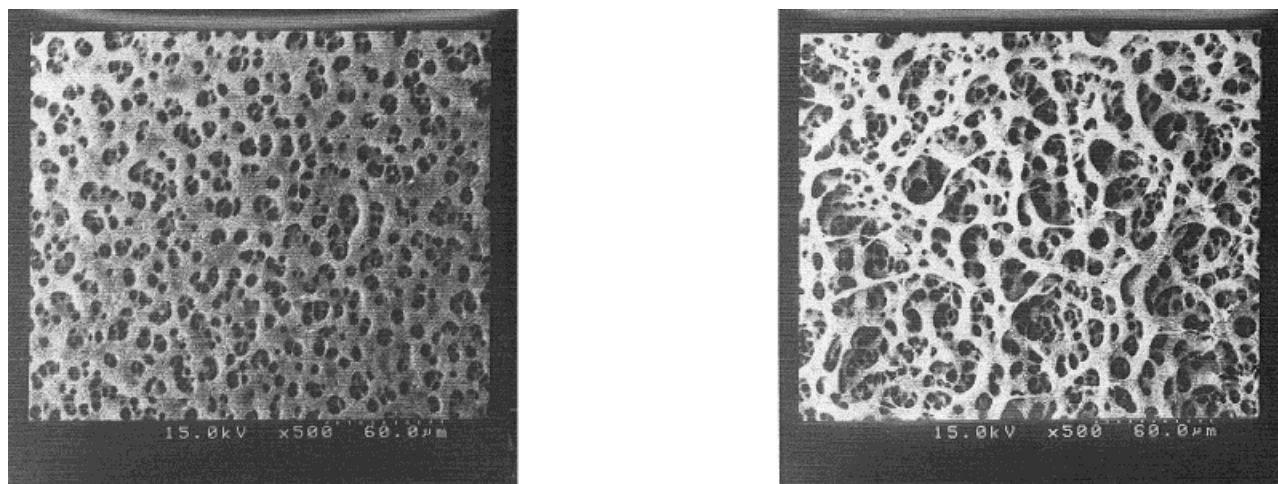


Figure 7 Effect of PVP compositions on the internal structures of hollow fiber membranes wet-spun from 30 wt % solids of PEI/PVP dope solutions (original magnification, $\times 500$). Right: PEI/PVP ratio—20 : 5 : 5 PEI/PVP 40,000/PVP 1,300,000; left: PEI/PVP ratio—20 : 10 PEI/PVP 1,300,000.

water. In an effort to increase the permeation fluxes of hollow fiber membranes with higher PVP molecular weights, NaOCl posttreatment on the fabricated membranes was applied. Commercially, NaOCl is widely used as a bleaching chemical for textile fibers and a posttreatment agent for membranes.^{1,23,24,28} The effects of hypochlorite on the performance of cellulose fibers and PEI/PVP (PVP molecular weight: 360,000) and PES/PVP (PVP molecular weight: 360,000) membranes have been studied extensively.^{1,23,24,28} In

the investigations of PEI/PVP and PES/PVP membranes, posttreatment with NaOCl has increased the permeability of membranes.^{23,24} Generally, the PVP in the membrane matrix is most likely located at the outer surface of pore walls because of its hydrophilic character. The reason is that the PEI/PVP/NMP dope solution during the membrane formation tends to separate into two phases (PEI rich phase and PVP rich phase) based on a liquid-liquid demixing process^{22,24} and these two heterogeneously distribute within the

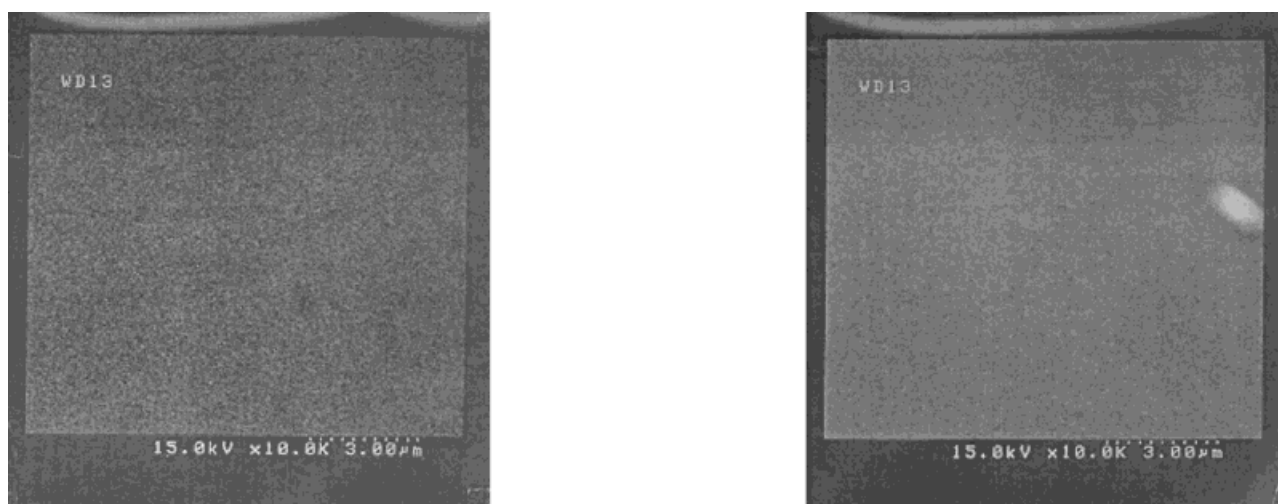


Figure 8 Effect of PVP compositions on the external structures of hollow fiber membranes wet-spun from 30 wt % solids of PEI/PVP dope solutions (original magnification, $\times 10,000$). Right: PEI/PVP ratio—20 : 5 : 5 PEI/PVP 40,000/PVP 1,300,000; left: PEI/PVP ratio—20 : 10 PEI/PVP 1,300,000.

Table IV Permeation Fluxes of Pure Water, PEG-Water, Surfactant-Water, and Oil-Surfactant-Water Solutions for PEI/PVP Hollow Fiber Membranes

Membrane No.	J_w^a , L/m ² · h · bar	J_{PEG}^b , L/m ² · h · bar	J_s^c , L/m ² · h · bar	J_e^d , L/m ² · h · bar
1	102.0	53.0	34.7	32.6
2	104.0	38.0	35.0	33.1
3	94.5	44.3	34.3	33.3
4	101.0	38.2	35.2	34.1
5	28.1	18.9	13.4	10.2
6	121.0	43.0	42.3	40.9
7	19.6	18.0	14.0	14.1
8	115.0	66.5	58.7	59.4
9	11.0	10.2	5.9	6.1
10	117.0	58.2	46.7	49.1

^a Pure water permeation flux.

^b Permeation flux of 1000 ppm PEG 35,000 solution.

^c Permeation flux of surfactant-water solution (1600 ppm surfactant).

^d Permeation flux of oil-surfactant-water emulsion [1600 ppm surfactant; 2500 ppm oil (C₁₂H₂₆)].

membrane. Because PVP is water soluble and it may diffuse from the dope solution into water coagulation bath and bore fluid stream. However, this PVP diffusion process is low in comparison with the liquid-liquid demixing process. There may be some remaining PVP present in the membrane matrix. After a NaOCl posttreatment, most PVP could be removed from the polymeric membrane matrix. Membranes nos. 6, 8, and 10 with PVP 1300 K in Table IV clearly illustrate that water fluxes are markedly higher than that of hollow fiber membranes without NaOCl posttreatment (membrane nos. 5, 7, and 9) (115.0 ≈ 121.0 vs. 11.0 ≈ 28.1 L/m² · h · bar). However, these membranes were still wettable by water because of the fact that a certain amount of the PVP was still present in the membranes. This result will be confirmed by later T_g results.

To evaluate the permeation fluxes of the fabricated hollow fiber membranes for oily wastewater, surfactant-water and oil-surfactant-water solutions were tested because industrial oily wastewater contains oil and surfactant, which form the emulsion. As seen in Table IV, there was a significant decrease in surfactant-water permeation fluxes (J_s) and oil-surfactant-water permeation fluxes (J_e) of membranes (from J_w to J_s or J_e) when surfactant was added into water. Flux decline was caused by phenomena-like concentration polarization, gel layer formation, pore blocking, adsorption, etc. and it was one of the most limiting factors in the application of membrane separation processes like UF and MF.^{5,8,16,17,19} Generally, the adsorption of proteins, surfactants, and lipids on membrane surfaces is a key element

in membrane fouling.^{1,2,24} In this case, surfactant molecules formed micelles when surfactant was added at the critical micelle concentration. Critical micelle concentration was 1.20×10^{-3} mol/L (420 ppm) for sodium dodecylbenzenesulfonate.^{29,30} In our case, the surfactant concentration was 1600 ppm in the surfactant-water solution and is greater than the critical micelle concentration. As a result, micelles and surfactants acted as barriers for water filtration and the surfactant-water permeation flux dropped drastically for the hollow fiber membranes, as shown in Table IV. Similar to the case of surfactant-water solution, there was a drop in the oil-surfactant-water permeation flux as can be seen from Table IV due to micelle effect or membrane fouling.^{5,8,16,17,19} However, this drop was not so significant compared with the surfactant-water solution cases in Table IV. This was due to the fact that the surfactant molecules surrounded oil molecules and the molecules obstructing the passage of the water flowing across the membranes remained approximately the same as that in a surfactant-water system.

Rejection of PEG 35,000, Surfactant, and Oil in the Solutions

Table V shows the rejections of different hollow fiber membranes for 1000 ppm PEG 35,000 solution. Generally, PEG rejection represents an important property in membrane applications. PEG 35,000 rejection for hollow fiber membranes with PVP 1300 K (membrane nos. 5–10) was significantly greater than that for hollow fiber membranes with PVP 10 K and PVP 40 K (membrane

Table V Rejection of PEG-Water and Surfactant-Water Solutions for PEI/PVP Hollow Fiber Membranes

Membrane No.	PEG 35,000 Rejection ^a (%)	Surfactant Rejection ^b (%)
1	75.5	77.1
2	70.4	78.3
3	84.5	78.1
4	72.0	78.9
5	98.9	78.7
6	90.5	80.8
7	~ 100	77.4
8	99.0	75.9
9	~ 100	76.1
10	99.4	77.4

^a 1000 ppm PEG 35,000 solution.^b 1600 ppm surfactant surfactant-water solution.

nos. 1–4) regardless of with or without NaOCl posttreatment. However, PEG 35,000 rejection for hollow fiber membranes after NaOCl posttreatment was smaller than that without NaOCl posttreatment. This is due to the fact that the former may have bigger pore sizes because of the removal of PVP in the membrane matrix after NaOCl posttreatment. The effect of NaOCl posttreatment on PEG 35,000 rejection is much more enhanced for the cases of low M_w of PVP, such as PVP 10,000 and 40,000 because they removed easier than PVP 130,000. The NaOCl treated sample nos. 2 and 4 have much lower PEG 35,000 rejection rates than that of no. 6 (70.4%, 72.0% vs. 90.0%).

Separation tests of hollow fiber membranes were also conducted to determine surfactant rejection and oil rejection for the surfactant-water and oil-surfactant-water solutions. Ideal surfac-

tant rejection is 73.8% [equal to (1600–420)/1600] if membranes remove all micelles completely in this study (surfactant concentration is 1600 ppm).^{29,30} As shown in Tables V and VI, all membranes had surfactant rejection rates higher than this value and no obvious difference. The membrane morphology and the micelle formation can explain these results. According to the SEM images of hollow fiber membranes in Figures 5 and 8, their membrane structure on the external surfaces seemed to be no significantly different. When oil was added into the solution in ppm level, an emulsion was formed, but the concentration of surfactant is almost invariant in the emulsion. Therefore, it can be noted in Tables V and VI that the trend in surfactant rejection from the oil-surfactant-water emulsion seemed to be the same as the surfactant-water solution. As can be seen in Table VI, the following results were ob-

Table VI Permeation Fluxes and Rejection of Oil-Surfactant-Water Emulsion for PEI/PVP Hollow Fiber Membranes

Membrane No.	J_e , L/m ² · h · bar	Surfactant Rejection (%)	TOC Rejection (%)	Oil Rejection (%)
1	32.6	78.0	92.5	99.8
2	33.1	79.8	93.0	99.6
3	33.3	78.3	92.3	99.4
4	34.1	79.3	92.7	99.6
5	10.2	77.6	92.3	99.6
6	40.9	79.6	92.9	99.5
7	14.1	78.1	91.5	99.6
8	59.4	76.1	91.0	99.2
9	6.1	76.9	91.1	99.2
10	49.1	77.0	91.3	99.5

Emulsion: 1600 ppm surfactant; 2500 ppm oil (C₁₂H₂₆).

Table VII Glass Transition Temperatures of PEI/PVP Hollow Fiber Membranes

Membrane No.	1	2	3	4	5	6	7	8	9	10
T_g^a (°C)	205.0	207.9	205.6	206.6	208.6	210.0	202.8	203.9	202.6	203.4

^a TMA T_g .

tained for oil-surfactant-water separation: oil rejection, >99%; TOC rejection, 91.0 \approx 93.0%; surfactant rejection, 76.1 \approx 79.8%.

Thermal Properties and Mechanical Properties of PEI/PVP Hollow Fiber Membranes

To evaluate the thermal and mechanical properties of membranes in the industrial applications, the T_g s and the values of tensile strength and elongation of hollow fiber membranes were determined, respectively.

Based on the TMA measurements, Table VII summarizes the T_g s of PEI/PVP hollow fiber membranes. All TMA curves of the hollow fiber membranes in this case only show one T_g . Clearly, PEI/PVP formed miscible blends. This result was not surprising because the blend miscibility of PVP is remarkably high and it has been reported that PVP is still capable of forming miscible blends with cellulose acetate, polyethersulfone, and polysulfone.^{19,23,31} The T_g s of PEI/PVP hollow fiber membranes with sponge structure (membrane nos. 7–10) were lower than that with finger-void structure (membrane nos. 1–6). Therefore, there was a greater PVP concentration in the former hollow fiber membrane than that in the latter hollow fiber membrane. Moreover, the T_g s of PEI/PVP hollow fibers with NaOCl post-

treatment (membrane nos. 2, 4, 6, 8, and 10) were a little greater than that without NaOCl post-treatment (membrane nos. 1, 3, 5, 7, and 9) because of the removal of PVP. Based on the experimental results, all T_g s of PEI/PVP hollow fiber membranes were less than neat PEI's T_g (217°C).²⁵ Besides, the T_g s of PVPs with different molecular weights were from 54 to 175°C.³² Thus, a small amount of PVP may exist in PEI/PVP hollow fiber membranes and result in the formation of hydrophilic membranes.

Table VIII shows the mechanical properties of all PEI/PVP hollow fibers. Within the experimental error, tensile strength at break and Young's modulus of hollow fibers with finger-void structures (membrane nos. 1–6) seemed to be independent of NaOCl posttreatment. Table VIII also illustrated that Young's modulus of hollow fibers with sponge structures (membrane nos. 7–10) seemed to be independent of NaOCl posttreatment. But, tensile strength at break of hollow fibers with sponge structures after NaOCl post-treatment (membrane nos. 8 and 10) were significantly lower than that without NaOCl posttreatment (membrane nos. 7 and 9). The elongation at break of PEI/PVP hollow fibers with NaOCl post-treatment (membrane nos. 2, 4, 6, 8, and 10) were significantly less than that without NaOCl posttreatment (membrane nos. 1, 3, 5, 7, and 9)

Table VIII Mechanical Properties of PEI/PVP Hollow Fiber Membranes

Membrane No.	Break Strength (MPa)	Elongation at Break (%)	Young's Modulus ^a (MPa)
1	4.06 \pm 0.15	22.1 \pm 2.4	166.3 \pm 2.2
2	3.72 \pm 0.27	9.7 \pm 1.5	172.2 \pm 6.7
3	3.89 \pm 0.33	31.3 \pm 1.3	156.2 \pm 4.4
4	3.95 \pm 0.20	21.4 \pm 2.8	160.7 \pm 3.9
5	4.94 \pm 0.11	41.7 \pm 1.8	147.8 \pm 2.4
6	4.58 \pm 0.10	27.8 \pm 2.3	154.9 \pm 3.1
7	4.50 \pm 0.20	49.4 \pm 3.4	121.8 \pm 6.5
8	3.7 \pm 0.22	21.1 \pm 2.4	117.0 \pm 2.9
9	6.31 \pm 0.17	56.8 \pm 2.6	156.1 \pm 3.8
10	4.87 \pm 0.35	22.9 \pm 3.1	146.6 \pm 5.0

^a Young's modulus calculated on the strain channel with a lower bound value of 0.5% and an upper bound value of 1.0%.

regardless of finger-void structures or sponge structures. However, the elongation at break in Table VIII clearly increased with an increase of PVP molecular weight. This phenomenon is due to that the fact that a higher PVP molecular weight tends to form a thicker sponge layer or denser skin layer as shown in Figures 3 and 6.

CONCLUSION

Using PEI as the membrane material and PVP with different molecular weights (PVP 10 K, PVP 40 K, and PVP 1300 K) as the additives, asymmetric hollow fiber membranes were wet-spun from 25 wt % or 30 wt % solids of 20:5:75 or 20:10:70 (weight ratio) PEI/PVP/NMP solutions. The investigation was conducted to evaluate the effect of different PVP molecular weights on morphology, oil-surfactant-water separation characteristics, mechanical, and thermal properties of PEI/PVP hollow fiber membranes. A 95:5 NMP/water solution was used as bore fluid to form hollow fiber membrane with skinless internal layer. SEM images illustrated that an increase of PVP in PEI/PVP dope solution resulted in the membrane morphology change from the finger-like structure to the spongy structure. Hollow fiber membranes with higher PVP molecular weights had a higher rejection, a thicker sponge layer, and a denser skin layer. For oil-surfactant-water emulsion systems (1600 ppm surfactant of sodium dodecylbenzenesulfonate and 2500 ppm oil of *n*-decane), experimental data illustrated that the rejection rates for surfactant, TOC, and oil were $76.1 \approx 79.8\%$, $91.0 \approx 93.0\%$, and more than 99%, respectively. Because all T_g data were less than that of a neat PEI, PVP existed in hollow fiber membranes and increased the hydrophilicity of membranes. NaOCl solution was used as a posttreatment agent to enhance membrane performance. The result illustrated a significant improvement in membrane permeability for PVP molecular weight 1,300,000, whereas the elongation at break of treated hollow fiber membranes decreased significantly.

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