Preparation of Poly(ether sulfone) Hollow Fiber UF Membrane for Removal of NOM

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ABSTRACT: In this study, a high performance poly(ether sulfone) (PES) hollow fiber ultrafiltration (UF) membrane has been prepared for removal of natural organic matter (NOM). The membrane was spun from a dope solution containing PES/poly (vinyl pyrrolidone) (PVP 40K)/*N*-methyl-2-pyrrolidone (NMP) by using a wet-spinning process. Characterization of the membrane in terms of pure water flux, molecule weight cut-off (MWCO), and retention for a model humic acid (HA) were conducted, and the fouling resistance was analyzed. The experimental results showed that the membrane had a pure water permeability of 20×10^{-5} L m^{-2} h^{-1} Pa^{-1} and a nominal MWCO of 6000 Da. The results also showed that the membrane retention for humic acid was over 97% and both productivity and selectivity for HA increased with increasing feed velocity. The PES membrane in this study exhibited a much lower fouling tendency than the commercial polysulfone membrane. SEM images revealed that the membrane had an outer dense skin and a porous inner surface. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 430–435, 2006

Key words: fibers; membranes; natural organic matter; poly(ether sulfones); ultrafiltration

INTRODUCTION

In surface water treatment for drinking purposes, removal of natural organic matter (NOM) has emerged as a critical issue[1–3] due to the facts that NOM can result in the formation of disinfection byproducts (trihalomethanes) that are harmful to humans[2] and also NOM can cause microbial regrowth in the distribution system and impede the removal of iron and manganese from the water. Although nanofiltration (NF) or reverse osmosis (RO) in spiral-wound module can be used to remove NOM efficiently,[3,4] the current commercial NF or RO membranes have low water permeability in a range of 3–7 $\times$ 10^{-5} L h^{-1} m^{-2} Pa^{-1}. Moreover, in NF and RO processes, NOM can attach to the membrane surface and cause serious fouling. Currently hollow fiber UF membrane has been widely applied in water treatment as it possesses the following advantages compared to the configurations of spiral-wound or flat-sheet membrane modules: 1) it provides an optimum in packing density and offers the lowest cost per unit membrane area; 2) it is self-supporting and thus can be backwashed to recover the membrane flux; and 3) it has good flexibility in operation. Thus, it is essential to develop a hollow fiber UF membrane with high permeation flux and low fouling tendency that is suitable for NOM removal.

PES UF membranes are well known for their excellent chemical resistance, good thermal stability, and mechanical properties.[5–8] To increase the hydrophilicity of the resultant membrane, a hydrophilic polymer PVP is often blended with hydrophobic PES as its membrane is fabricated.[9–15] This study explores a high performance hollow fiber UF membrane having high flux and low fouling suitable for NOM removal, made from a dope solution containing PES/PVP (40K)/NMP by using a wet-spinning process.

EXPERIMENTAL

Materials

The polymeric membrane material, PES (A-200), was purchased from Amoco Performance Products Inc. (Ohio, USA). The blend polymer, PVP (40K) (average MW 40,000 Da), was supplied by Fluka (Milwaukee, USA). The solvent, NMP (>99%), was supplied by Merck (Darmstadt, Germany). Four types of polyethylenglycol (PEG 1K, 4K, 6K, and 8K, respectively) purchased from Merck were applied to characterize the separation performance of a hollow fiber membrane.

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In addition, a commercially available polysulfone (PSU) hollow fiber UF membrane purchased from Mo Tian Membrane Eng Co. China, which had an outer skin with MWCO 6000 Da, was tested to compare its performance with the membrane prepared in the study. Humic acid (MW > 2000 Da) supplied by Sigma Aldrich (Steinheim, Germany) was used as a model to test the efficiency of the hollow fiber membranes for removal of NOM.

Fabrication of hollow fiber UF membranes

A spinning dope of PES/PVP (40K)/NMP was prepared by the following procedure: PVP (40K) was dried in a vacuum oven at 60°C for 24 h, and PES was dried in an oven at 150°C for 5 h to remove the moisture content. NMP and PVP were mixed in a container. The dried PES was then added and the mixture was blended with a stirrer at room temperature until the solution became homogeneous. Finally, the formulated dope in a solution tank and the bore fluid in a metal canister were degassed before spinning to remove any gas bubbles.

Hollow fiber UF membranes were spun using the wet-spinning process.[7,8,13] The experimental parameters used in the spinning of UF hollow fiber membranes are summarized in Table I. The as-spun fibers were rinsed in flowing water at room temperature for 48 h. After rinsing, the fibers were placed into a 50 wt % aqueous glycerol solution for 48 h and then air dried at room temperature for making UF test modules.

TABLE I
Experimental Parameters of Spinning Hollow Fiber UF Membranes

Parameter	Value
Dope solution composition (wt %)	PES/NMP/PVP 40K (25 : 65 : 10)
Dope viscosity (Pa · s)	2.45 ± 0.1 at 22°C
Solution extrusion pressure (MPa)	0.34
Dope flow rate (cm^3/min)	3
Bore fluid composition (wt %)	NMP/H_2O (80 : 20)
Bore fluid flow rate (cm^3/min)	8
Air gap distance (mm)	0
External coagulant	water
Take-up speed (m/min)	3.43
Coagulant temperature (°C)	26 ± 0.5
Water flow rate in coagulation bath (L/h)	120
Dimensions of spinneret (mm)	0.60/1.23 (ID/OD)
Spinneret temperature (°C)	22 ± 0.5
Room relative humidity (%)	58 ± 2

Characterization of prepared hollow fiber UF membranes

Flux and separation performance measurements of the UF membranes were carried out in a cross-flow filtration set-up at room temperature of 25 ± 1°C, as shown in a previous article.[15] As the hollow fibers have an outer dense skin, the feed was pumped into the shell side of the module and the permeate was collected at the lumen side of the fibers. Eight 27-cm-long fibers were assembled into a test module. The effective membrane area was 113 cm^2. The space between hollow fibers or the water flow channel was 1.3×10^{-5} m^2. Three modules were freshly prepared and tested for each membrane sample, and the average of their performance was reported.

In the tests, ultrapure water was first used to characterize the pure water flux of a fresh membrane. The membranes were flushed with ultrapure water in a single pass mode (both permeate and retentate streams were drained) during the first 10 min, followed in a partial re-circulation mode (the permeate was drained but the retentate was re-circulated to the feed tank) over 3 h before the pure water flux measurements were conducted for 3 min. A 5-L feed solution containing 100 mg/L of the different solutes tested in ultrapure water was then used to test the separation performance of the membrane. Sampling for analysis was conducted after 60 min of conditioning time to stabilize the filtration in a full re-circulation mode (both permeate and concentrate were re-circulated except sampling). The average transmembrane pressure ΔP was 100 kPa, and the feed cross flow velocity was 0.6 m/s. The solute concentration in the feed or permeate was determined using a TOC-V Analyser (Shimadzu). This method has previously been used in characterization of membranes.[3,11,15,16] The permeability and percentage retention of the hollow fiber UF membranes were calculated by using eqs. (1) and (2), respectively.

$$\text{Permeability} = Q/(A \times \Delta P) = Q/(N\pi d_o \ell \times \Delta P) \quad (1)$$

where Q is the volume flow rate of the permeate (L/h), A is the effective membrane area (m^2), ΔP is the transmembrane pressure (Pa), N is the number of fibers, d_o is the outer diameter of the fiber (m), and ℓ is the effective fiber length (m).

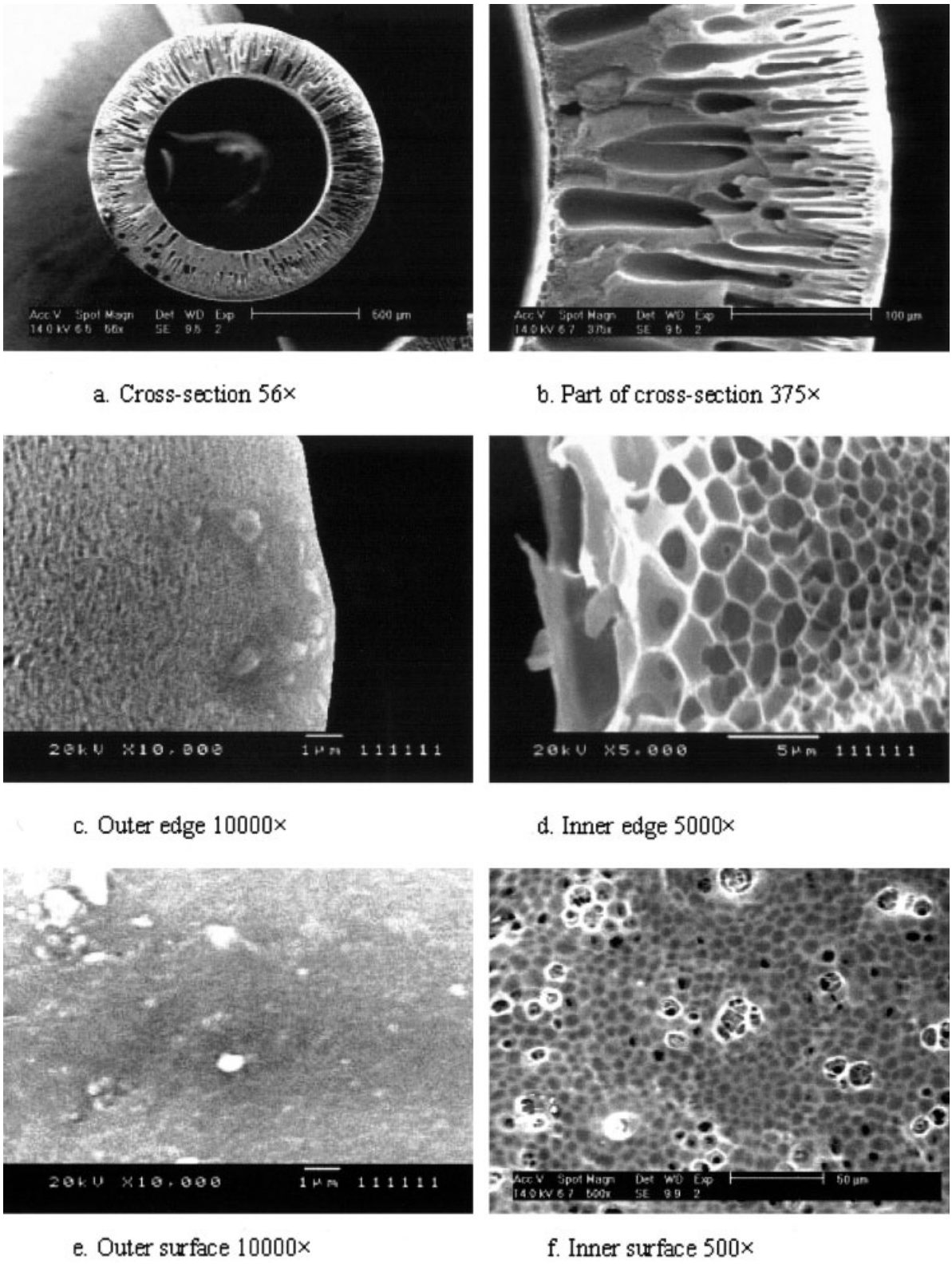

Figure 1 SEM images of PES hollow fiber membrane with an outer skin: (a) Cross section, × 56; (b) Part of cross section, × 375; (c) Outer edge, × 10,000; (d) Inner edge, × 5000; (e) Outer surface, × 10,000; (f) Inner surface, × 500.

TABLE II
Measurements of Pure Water Permeability and Separation Performances of the Membrane

Pure water permeability ($\times 10^{-5}$ L m^{-2} h^{-1} Pa^{-1})	Retention (%)			
	PEG 1K	PEG 4K	PEG 6K	PEG 8K
20	23	80	90	95

$$\text{Retention} = (1 - C_p/C_f) \times 100\% \quad (2)$$

in which C_f (mg/L) and C_p (mg/L) represent the solute concentrations in the feed and permeate, respectively.

The structure and morphology of the fibers were studied using a JEOL® JSM 5310 LV SEM, as described in a previous article.[10]

Study of fouling tendency of the hollow fiber UF membrane

The pure water flux through a fresh membrane, the HA solution flux, and the pure water flux through a fouled membrane were measured as J_{vw}, J_v, and J_{va}, respectively. In the tests, the same procedure of membrane characterization as described above was followed. In addition, the solution flux measurements were conducted during sampling for analysis after 60 min of conditioning time. Finally, the fouled membrane was flushed with ultrapure water in a single pass mode, and the pure water flux of the fouled membrane was measured again.

The membrane fouling tendency was analyzed using the osmotic-pressure-adsorption model,[17] in which it was assumed that the flux decline would be due to two main mechanisms: (i) reduction in hydrodynamic driving force by osmotic pressure ($\sigma\Delta\Pi$), and (ii) increase in fouling resistance (R_a) from surface adsorption and pore plugging. The detailed description on study of the fouling tendency of hollow fiber membranes has been introduced elsewhere.[15]

RESULTS AND DISCUSSION

Morphology of the hollow fiber UF membrane

Figure 1 shows the SEM images of a PES hollow fiber membrane prepared in this study. The inner and outer diameters of the hollow fiber were 1.06 and 1.55 mm, respectively. Figures 1(a) and 1(b) show that the cross section of the as-spun fiber had a finger-like structure that started from the outer edge of the fiber and went through the whole cross section. Figure 1(c) indicates that the outer edge of the fiber with a thickness of above 1 μm had no visible pores at magnification of 10,000; but Figure 1(d) shows that the inner edge was fully microporous with a network of pores of 1–4 μm, which suggests that the hollow fiber membrane had an outer skin. Furthermore, it was revealed that the outer surface was dense at magnification of 10,000, as shown in Figure 1(e), and the inner surface was uniformly microporous at magnification of 500, as shown in Figure 1(f), which confirmed the above conclusion. The as-spun fiber with an outer dense skin and inner porous surface was formed due to the fact that an instantaneous phase separation started from the outer surface of the nascent fiber immediately after the spinning dope exited from the spinneret, while there was a delayed phase separation at the inner surface as a bore liquid with a high concentration of solvent was used.[11,13] The demixing of the dope solution continued towards the inner surface when the fiber went through the outer coagulation water bath. Finally, the outer coagulant completed the formation of the membrane structure.

Characterization of prepared hollow fiber UF membranes

Measurements of the flux and separation performance of the membrane are summarized in Table II. The pure water permeability of the membrane is 20 $\times$ 10^{-5} L m^{-2} h^{-1} Pa^{-1}. The retention of the membrane for PEG 6K reaches 90%. Thus, the nominal MWCO of this membrane may be estimated as 6000 Da.

Figure 2 illustrates the membrane retention of PEG solutes of varying molecular mass. As the retention curve for solutes with different molecular mass reflects the membrane pore size distribution, data presented in Figure 2 imply that the pore size distribution of the membrane was narrow. This membrane with narrow pore size distribution is favorable for the removal of NOM from water as shown by the latter results.

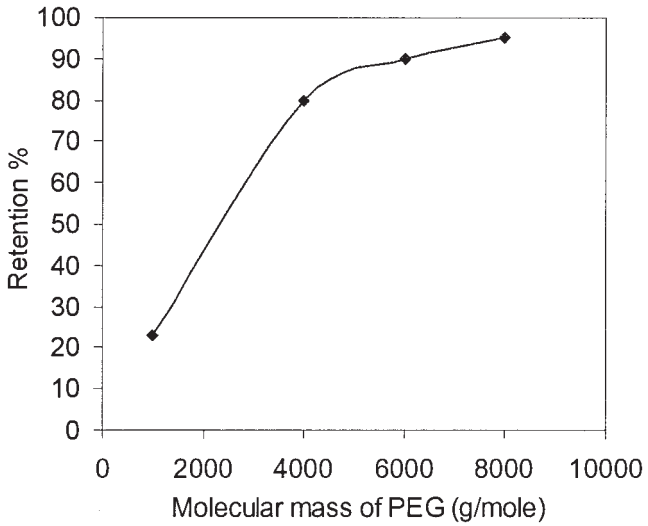

Figure 2 Retention of outer skin PES UF membrane versus molecular mass of the tested solutes.

TABLE III
Effect of Feed Velocity on Permeability of HA Solution and Retention of HA

Membrane type	Feed velocity (m s^{-1})	Solution permeability ($\times 10^{-5}$ L m^{-2} h^{-1} Pa^{-1})	Retention of HA (%)
PES	0.3	15.4	97.1
(this work)	0.6	16.5	97.4
	1.2	16.7	97.9
PSU[a]	0.6	8.3	93.7

[a] The polysulfone hollow fiber UF membrane with MWCO 6000 was purchased from Mo Tian Membrane Eng Co., China.

Efficiency and fouling tendency of the PES membrane for NOM removal

Effect of feed cross flow velocity

To study the effect of feed cross flow velocity on the performance of the prepared PES membrane, the permeability of the HA solution and retention of HA were measured over a range of feed velocity of 0.3–1.2 m/s. The results are summarized in Table III. It shows that the retention of HA remained above 97%. It also shows that both permeability of the HA solution and retention of HA increased with an increase in the feed velocity. The higher retention and flux at higher feed velocity could be attributed to the lower concentration-polarization at the membrane surface.[17] For comparison, a commercial PSU hollow fiber UF membrane with the same MWCO of 6000 Da as the PES membrane was tested at the feed velocity of 0.6 m/s, and the results are also listed in Table III. It can be seen that the PES hollow fiber UF membrane had better retention of HA and twice as high permeability than the commercial PSU membrane, indicating that the PES membrane developed in this study showed a better performance for NOM removal than the commercial PSU membrane tested.

Fouling tendencies of the UF membranes

Table IV shows experimental measurements of J_{vw}, J_v, and J_{va} of the PES and PSU membranes and the calculated values of R_m, R_a, $\sigma\Delta\Pi$, J_{ra}, J_{ro}, and J_{rt}, where: R_m is the membrane resistance; J_{ra} and J_{ro} are the relative flux reduction caused by the absorption R_a and the osmotic pressure ($\sigma\Delta\Pi$), respectively; $J_{ra} = (J_{vw} - J_{va})/J_{vw}$, $J_{ro} = (J_{va} - J_v)/J_{vw}$; and J_{rt} is the total relative flux reduction ($J_{rt} = J_{ra} + J_{ro}$). It can be seen that for the PES membrane, the hydraulic resistance of the absorbed layer (R_a) was 7.8% of the membrane (R_m), and the osmotic pressure ($\sigma\Delta\Pi$) was around 6.1% of the operating pressure ($\Delta P = 100$ kPa), that is, J_{ra} and J_{ro} were close, which indicated that the PES membrane fouling J_{rt} was caused by both the resistance of the absorbed layer R_a and the osmotic pressure $\sigma\Delta\Pi$. However, J_{ra} was 7.2 times larger than J_{ro} for the PSU membrane, which implied that the PSU membrane fouling J_{rt} was mainly contributed by the resistance of the absorbed layer R_a. Moreover, J_{ro} values were close for both PES and PSU membranes, but the J_{ra} value of the PES membrane was much smaller than that of PSU, which meant that the PSU membrane would show a much higher fouling than the PES membrane due to the high resistance of the absorbed layer R_a for the PSU membrane. This could be attributed to the relative hydrophobicity of the PSU membrane compared to the much-enhanced hydrophilicity of the PES membrane blended with residual PVP. As a consequence, the total relative flux reduction (J_{rt}) was 13 and 34% for the PES and PSU membranes, respectively. It may be concluded that the PES membrane in this study performed a much lower fouling tendency than the commercial PSU membrane when being used for NOM removal.

CONCLUSIONS

In this study, a hollow fiber UF membrane has been prepared from a dope solution containing PES/PVP 40K/NMP by using a wet-spinning process. The PES membrane had a pure water flux of 20×10^{-5} L m^{-2}

TABLE IV
Measurements of J_{vw}, J_v, and J_{va} of PES and PSU Membranes and the Calculated Values of R_m, R_a, $\sigma\Delta\Pi$, J_{ra}, J_{ro}, and J_{rt}

Membrane type	Flux ($\times 10^{-6}$ ms^{-1})			Resistance ($\times 10^{12}$ m^{-1})					
	J_{vw}	J_v	J_{va}	R_m	R_a	$\sigma\Delta\Pi$ (Pa)	J_{ra}	J_{ro}	J_{rt}
PES	5.24	4.57	4.86	21.4	1.67	6130	0.073	0.055	0.13
PSU	3.62	2.40	2.55	33.6	12.8	4510	0.296	0.041	0.34

h^{-1} Pa^{-1} and a nominal MWCO of 6000 Da. The membrane retention for Aldrich humic acid was over 97% in a range of feed velocity of 0.3–1.2 m/s and both the retention and specific flux for the humic acid solution increased with increasing feed velocity. The PES membrane in this study performed a much lower fouling tendency than the commercial PSU membrane. SEM images revealed that the membrane had an outer dense skin and a porous inner surface. A high performance PES hollow fiber UF membrane for removal of NOM has been developed.

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