Effects of Solvent Sort, PES and PVP Concentration on the Properties and Morphology of PVDF/PES Blend Hollow Fiber Membranes

Lishun Wu,[1,2] Junfen Sun,[3] Chunju He[3]

[1]*Department of Chemistry and Chemical Engineering, Heze University, Heze, Shandong Province 274015, People's Republic of China*
[2]*Key Laboratory of Science and Technology of Eco-Textile, Donghua University/Jiangnan University, Ministry of Education, Songjiang, Shanghai 201620, People's Republic of China*
[3]*State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Songjiang, Shanghai 201620, People's Republic of China*

Received 4 September 2008; accepted 3 September 2009
DOI 10.1002/app.31573
Published online 5 January 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly (vinylidene fluoride) (PVDF)/polyethersulfone (PES) hollow-fiber membranes were spun by dry–wet spinning setup. PVDF and PES were employed as base polymers. Four different solvents including dimethyl sulphoxide, dimethyl formamide, 1-methyl-2-pyrrolidone, and dimethyl acetamide (DMAc) were used as the solvents. Polyvinylpyrrolidone (PVP) was used as pore-forming additive. The preparation variables in this work are sort of solvents, content ratio of PVDF/PES, and concentration of PVP. The membranes prepared by phase inversion were characterized by using scanning electron microscopy. Membrane performance was evaluated by shrinkage ratio, pure water flux and retention to bovine serum albumin (BSA). The shrinkage ratio of PVDF/PES blend hollow fiber membrane decreases when DMAc was used as a solvent. The pure water flux of blend membranes reaches the maximum and the retention to BSA reaches the minimum when the casting solution contains 1.5 wt % PES. The pure water flux reaches the maximum when the concentration of PVP is 5 wt %. The retention to BSA decreases and the shrinkage ratio increases with PVP concentration increasing. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1566–1573, 2010

Key words: poly (vinylidene fluoride); polyethersulfone; blend; hollow-fiber membrane; shrinkage ratio

INTRODUCTION

High chemical resistance to many acids, alkalis and oxidents as well as good biology and blood compatibility make poly (vinylidene fluoride) (PVDF) as an excellent membrane material.[1–3] PVDF can be fabricated into asymmetric hollow fiber membrane by dry–wet technique with high flux and low resistance. The interaction between nonsolvent and polymer is weak because of the low surface tension of PVDF,[4] which results in a low coagulation rate and formation rate of the membrane. However, coagulation rate and formation rate of the membrane can be accelerated by adding hydrophilic additive into the casting solution. On the other hand, shrinkages appear during drying process and lead to a decrease of mean pore size, porosity, and flux of membrane.[4,5] Many studies were carried out in fabrication, property and structure of PVDF flat sheet membrane.[1,6] But few studies relate to PVDF hollow fiber membrane and PVDF blend hollow fiber membrane.[7,8] There are many differences between the preparation method of PVDF flat sheet membrane and that of hollow fiber membrane. First of all, a flat sheet membrane can be prepared from polymer dope with its viscosity as low as a few hundred cP, on the other hand a minimum dope viscosity required to spin hollow fibers is a few thousand cP.[9] Secondly, the phase inversion process starts from the top surface of flat sheet membrane, whereas in the case of hollow fiber membrane with dry–wet spinning technique employed, the phase inversion conditions of inner face and outer face are not same when casting solutions are just extruded out of the spinneret. The phase inversion medium of the inner face is bore liquid and the medium of the outer face is air. Then the nascent hollow fiber membrane comes into external coagulation bath. The phase inversion media of inner face and outer face could be same or different by choosing same or different components for bore liquid and external coagulation bath. Polyethersulfone (PES) has excellent thermal, dimensional stability, good chemical resistance and blood compatibility. PVDF/PES flat sheet membrane was investigated in our previous study.[10] However,

Correspondence to: J. Sun (junfensun@sohu.com).

little information is available for PVDF/PES blend hollow fiber membrane. In this article, PVDF hollow fiber membranes with low shrinkage were prepared by blending PVDF and PES. We investigated shrinkage ratio, pure water flux and retention to bovine serum albumin (BSA) of PVDF/PES blend hollow fiber membrane. The shrinkage ratio of blend membrane decreases and the pure water flux increases sharply, which may offer the blend membrane a prospective biology application as a microfiltration membrane.

EXPERIMENTAL

Materials

PVDF (FR904) has an intrinsic viscosity 1.67 [tested at 30°C and dimethyl acetamide (DMAc) was used as solvent] and was obtained from Shanghai Institute of Organic Fluoric Materials (China). Polyether sulfone (PES) and polyvinylpyrrolidone (PVP powder with an average molecular weight of 36,000 Da) were supplied by BASF Shanghai Co. (China). DMAc (analysis grade), dimethyl formamide (DMF, analysis grade), dimethyl sulphoxide (DMSO, analysis grade), 1-methyl-2-pyrrolidone (NMP, analysis grade) were used as solvent. All these solvents and BSA (M_w = 67,000) were bought from Shanghai Chemical Reagent Company (China).

Preparation of blend solutions for spinning

The blend solutions based on PVDF and PES polymers were prepared by dissolving both of polymers in different compositions in the presence of additive, PVP, in different solvents including DMSO, DMF, NMP, and DMAc. PES concentration was changed from 0 to 3 wt % and PVP concentration was changed from 0 to 10 wt %.

The mixture was put into a dissolving container at 40°C under constant mechanical stirring for 0.5 h to make the polymers swell. Then the temperature of dissolving container rose up to 80°C for another 8 h to make the polymers dissolve completely. Then, the solution was filtrated across a 20 μm filter and put into a storing container. The homogeneous solution was allowed to stand for at least 8 h at 40°C in the storing container at vacuum condition to get rid of air bubbles.

Preparation of hollow fiber membrane

Hollow fiber membranes were spun on the spinning apparatus. The schematic representation of spinning line is shown in Figure 1. The casting solution at 40°C was extruded through a hollow fiber spinneret. The nascent membrane was introduced into the coagulation bath after a 18 cm air gap [25°C, room humidity (RH) 65%]. Water at room temperature was selected as both the inner and outer coagulation media and the pressure of inner coagulation water was adjusted to 0.25×10^{-4} MPa. The hollow fiber membrane was set to pass through three distilled water tankers and was rolled up on a roller. The membranes were washed thoroughly with distilled water and were immersed into glycerin aqueous solution (40%, v/v) for 4 h. Then the membranes were dried at 45°C.

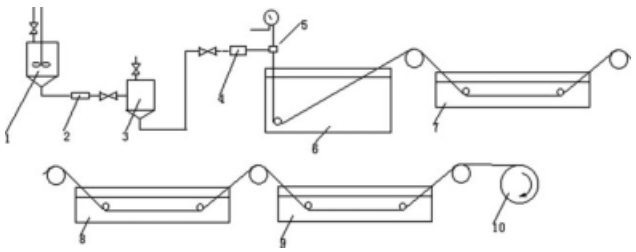

Figure 1 Spinning line for hollow fiber membrane preparation. (1) Dissolving container, (2) filter, (3) storing container, (4) gear pump, (5) spinneret, (6) outer coagulation bath, (7) first water tanker, (8) second water tanker, (9) third water tanker, and (10) roller.

Some hollow fiber membranes were placed in the tubes made from polycarbonate with 25 cm in length and 2 cm in diameter. Two ends of the tube were sealed with polyurethane adhesive on a rotary apparatus and the properties of blend membranes including pure water flux and retention to BSA were tested.

Membrane characterization

Pure water flux

Hollow fiber membranes after compaction, were subjected to pure water flux estimation at a transmembrane pressure of 0.1 MPa under cross-flow filtration. The permeability was measured under steady-state flow. Pure water flux was calculated as follows:

$$J_w = \frac{Q}{A\,\Delta t}$$

where Q is the quantity of permeate collected (in m^3), J_w is pure water flux ($m^{-2}\ h^{-1}$), Δt is the sampling time (hour), and A is the membrane area (m^2).

Retention to BSA

The retention ratio of membranes was tested with 0.5 mg/L BSA solution. The absorbance of original liquids and permeated liquids was determined with a UV/VIS spectrophotometer (Shanghai Techcomp 7500) at the wavelength of 280 nm. The retention ratio was derived as follows:

TABLE I
Solubility Parameters and Polarity Parameters of Four Different Solvents. Shrinkage Ratios of PVDF/PES Blend Hollow Fiber Membrane Prepared with Four Different Solvents

Solvent	DMAc	NMP	DMF	DMSO
Solubility parameter ($MPa^{1/2}$)	22.7	22.9	24.8	26.7
Polarity parameter ($MPa^{1/2}$)	11.5	12.3	13.7	16.4
Shrinkage ratio (%)	6.6	6.9	7.9	21

The casting solution contains 13.5 wt % PVDF, 1.5 wt % PES and 5 wt % PVP.
PVDF, poly (vinylidene fluoride); PES, polyethersulfone; DMAc, dimethyl acetamide; NMP, 1-methyl-2-pyrrolidone; DMF, dimethyl formamide; DMSO, dimethyl sulphoxide.

$$\text{Retention ratio } (\%) = \left(1 - \frac{2 \times c_2}{c_0 + c_1}\right) \times 100\%$$

where c_0 is the original concentration of feeding solutions and c_0 becomes c_1 after filtration. c_2 is the concentration of permeation solutions.

Shrinkage ratio of the membrane

A number of wet hollow fiber membranes immersed in the glycerin solution were cut into L_0 mm in length and dried at 45°C for 3 h, then the lengths of the membrane became L_1 mm. The shrinkage ratio was calculated by using the formula as follows:

$$\text{Shrinkage ratio} = \left(\frac{L_0 - L_1}{L_0}\right) \times 100\%$$

Morphological study

A scanning electron microscope (SEM) (JEOL Model JSM-5600LV) was used to examine the cross section of the hollow-fiber membranes. The membranes were cut into segments of various sizes and mopped with filter paper. These segments were immersed in liquid nitrogen for 20–30 s and were frozen. Frozen bits of the membranes were broken and kept in a desiccator. These dry samples were gold sputtered for producing electric conductivity, and photomicrographs were taken in very high vacuum conditions at 10 KV. Various SEM images were taken at some magnification for cross section views of the polymeric membranes.

RESULTS AND DISCUSSION

Effects of solvents on shrinkage ratio

Table I shows the shrinkage ratios of PVDF/PES blend hollow fiber membranes prepared from the casting solutions with four different solvents. The casting solution based on PVDF and PES polymers contains 13.5 wt % PVDF, 1.5 wt % PES, and 5 wt % PVP. The membrane prepared from the casting solution with DMSO as solvent has the highest shrinkage ratio, 21%. However, above 20% of shrinkage will bring many negative effects on porosity and mean pore sizes of membranes. While the membrane prepared from the casting solution with DMAc as solvent has the lowest shrinkage ratio, 6.6%, as shown in Table I. The effect on the shrinkage ratio of blend hollow fiber membranes was also found in the preparation of PVDF/PES blend flat sheet membrane.[10]

Generally speaking, membrane casting solutions belong to polymer concentrated solutions. In polymer concentrated solutions, there are many entanglements existing among macromolecules because of the interactions of molecular chains, which lead to the formation of network. Flow of the solution tends to align the sections of chains between coupling points. So, elastic energy stores in the sections of entangled chains. The energy is released after a time τ when the flow stops. The casting solution extruded out of the spinneret is solidified and becomes membrane so rapidly that stress is fixed between the entanglements of macromolecules in the nascent membranes. The stress will be released when temperature rises during drying process. The solubility parameter (δ_{sp}) and polarity parameter (δ_{pp}) of solvents[11] are shown in Table I. PVDF and PES belong to polarity polymers, the solubility parameter and polarity parameter of PVDF[12] and PES[13] are 23.2 $MPa^{1/2}$, 12.5 $MPa^{1/2}$, and 22.7 $MPa^{1/2}$, 10.3 $MPa^{1/2}$, respectively. Among the solubility parameters (δ_{sp}) of polymers and solvents, the δ_{sp} of NMP (22.9 $MPa^{1/2}$) is the closest to that of PVDF (23.2 $MPa^{1/2}$), but the δ_{sp} of DMAc (22.7 $MPa^{1/2}$) is equal to that of PES (22.7 $MPa^{1/2}$). PES is in a good dissolution state and macromolecules of PES in the blend solution spread most sufficiently when DMAc is used as solvent. The length of PES chain segment is longer and the anti-shrinkage function of PES is performed most completely because of the rigidity of PES molecules. So, the shrinkage ratio of blend membrane is

TABLE II
Pure Water Flux and Retention to BSA of PVDF/PES Blend Hollow Fiber Membranes Prepared with Four Different Solvents

Solvent	DMAc	NMP	DMF	DMSO
Pure water flux [$m^3 \times 10^{-3}/(m^2\ h)$]	498.5	460	230	8.5
Retention to BSA (%)	40.2	49.1	63	98

The casting solution contains 13.5 wt % PVDF, 1.5 wt % PES and 5 wt % PVP.
BSA, bovine serum albumin; PVDF, poly (vinylidene fluoride); PES, polyethersulfone; DMAc, dimethyl acetamide; NMP, 1-methyl-2-pyrrolidone; DMF, dimethyl formamide; DMSO, dimethyl sulphoxide.

the lowest when DMAc is selected as solvent. Among the polarity parameters (δ_{pp}) of polymers and solvents, the δ_{pp} of PVDF (12.5 $MPa^{1/2}$) is higher than that of PES (10.3 $MPa^{1/2}$), and the δ_{pp} of DMSO (16.4 $MPa^{1/2}$) is the highest among four different solvents. Macromolecules of PVDF are more extended and more entanglements form on one molecular chain when DMSO is used as solvent because of the strong interaction between molecules of PVDF and solvent. So more stress is fixed among entanglements in the membranes prepared from the casting solution with DMSO as solvent and more shrinkage appears during drying process, as shown in Table I.

Effects of solvents on pure water flux, retention to BSA and morphology

Pure water flux and retention to BSA of membranes prepared from the casting solution with four different solvents are also shown in Table II. The casting solution based on PVDF and PES polymers contains 13.5 wt % PVDF, 1.5 wt % PES and 5 wt % PVP. By using DMAc as solvent, the membrane has a higher pure water flux and a lower retention to BSA. The membrane prepared from the casting solution with DMSO has a lower pure water flux and protein macromolecules hardly pass through it. As shown in Figure 2(A), the finger-like pores forming from the

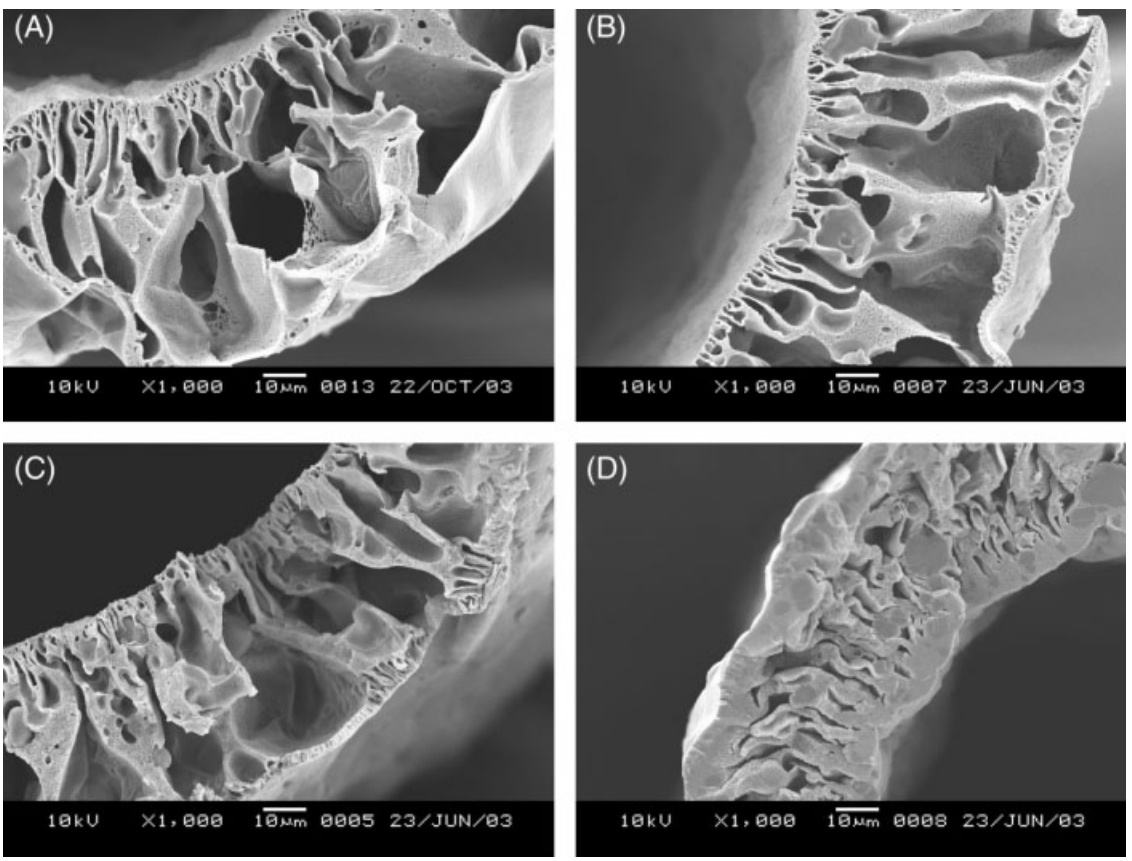

Figure 2 SEM photographs of PVDF/PES blend hollow fiber membranes prepared from casting solutions with four different solvents (The casting solution contains 13.5 wt % PVDF, 1.5 wt % PES, and 5 wt % PVP). (A) DMAc, (B) NMP, (C) DMF, and (D) DMSO.

inner skin layer in the membranes prepared from the casting solution with DMAc extend to the outer skin layer and the thickness of the both skin layers are thin. It indicates that the finger-like pores forming from the inner skin layer develop to the outer skin before the outer face comes into the coagulation bath. The function of the external coagulation is to accelerate the solidification of the outer skin layer of membrane. The lowest shrinkage ratio, the thinner skin layer and thinner walls of finger-like pores make the membrane prepared from the casting solution with DMAc as solvent have a higher pure water flux and a lower retention to BSA. Compared to membrane prepared from the casting solution with DMAc as solvent, membranes prepared from the casting solution with NMP and DMF as solvents have a thicker outer layer [as shown in Fig. 2(B,C)] which make two membranes have a lower pure water flux and a higher retention to BSA. As the polymer solution is extruded out of the spinneret, the inner surface of the solution contacts the inner coagulant immediately and the inner skin forms. Under the inner skin layer, the growing points of finger-like pores develop toward the outer layer. The outer surface of the casting solution passed through a length of air gap and then was introduced into the external coagulation bath. In the external coagulation bath, the outer skin forms, at the same time, the growing points of finger-like pores develop under the outer skin layer. Two kinds of finger-like pores grow reversely, which results in a common bottom layer in the membrane. The shared bottom layer acts as a barrier in the membrane and membrane prepared from the casting solution with DMF as solvent has a small quantity of finger-like pores and the walls of finger-like pores are also thicker [as shown in Fig. 2(C)]. Finger-like pores with less volume generate in the membrane prepared from the casting solution with DMSO as solvent, and the inner skin layer and outer layer are thicker, as shown in Figure 2(D). The finger-like pores with less volume, thicker skin layers and large shrinkage ratio of membrane result in lower pure water flux and higher retention to BSA of the membrane prepared from the casting solution with DMSO as solvent.

It is concluded from above research that the membrane prepared from the casting solution with DMAc as solvent has the highest pure water flux and the lowest retention to BSA, which is consistent with the study of Yeow et al.[14] Moreover, the shrinkage ratio of the membrane prepared from the casting solution with DMAc as solvent is the lowest, compared to that of other membranes prepared from the casting solutions with other three solvents, as shown in Table I. So, DMAc was chosen as the solvent in the rest investigation.

TABLE III
Pure Water Flux, Retention to BSA, and Shrinkage Ratio of PVDF/PES Blend Hollow Fiber Membranes Prepared from the Casing Solutions with Different PES Concentration

PES concentration (%)	Pure water flux [$m^3 \times 10^{-3}/(m^2\ h)$]	Retention to BSA (%)	Shrinkage ratio (%)
0	37	81.7	15.6
0.75	339.4	55.3	8.7
1.5	498.5	40.2	6.6
2.25	305	62.6	6.36
3	16.5	96	6.2

The total PVDF and PES concentration is 15 wt % and 5 wt % PVP is added into the casting solution. PES concentration is changed from 0 to 3 wt % and PVDF concentration is changed from 15 to 12 wt % accordingly.

BSA, bovine serum albumin; PVDF, poly (vinylidene fluoride); PES, polyethersulfone.

Effect of PES concentration on shrinkage ratio, pure water flux, retention to BSA and morphology

Table III shows the shrinkage ratio, the pure water flux and the retention to BSA of PVDF/PES blend hollow fiber membranes with different PES concentration. The total PVDF and PES concentration is 15 wt % and 5 wt % PVP is added into the casting solution. PES concentration is changed from 0 to 3 wt % and PVDF concentration is changed from 15 to 12 wt % accordingly. As shown in Table III, membrane prepared from the casing solution with no PES shows high shrinkage ratio, low water pure water flux and high retention to BSA when the total polymer concentration and the concentration of PVP are stable. When the concentration of PES is 1.5 wt %, the shrinkage ratio of blend hollow fiber membrane decreases greatly, the pure water flux reaches the maximum ($498.5 \times 10^{-3}\ m^3\ m^{-2}\ h^{-1}$) and the retention to BSA reaches the minimum (40.2%). When more PES is added into the casting solution and the concentration of PES reaches 3 wt %, the shrinkage ratio of blend hollow fiber membrane slightly decrease, the pure water flux rapidly decreases and the retention to BSA sharply increases.

The macromolecule chains of PES are less flexible and the glass transition temperatures (T_g) of PES and PVDF are 235°C and −30°C, respectively. PES is under glass state and PES chain segments could not change their position freely at room temperature. So, PES acts as reinforcement in the blend membranes, which prevents the blend membranes from shrinking.

SEM photographs of blend hollow fiber membranes prepared from the casting solution with different PES concentrations are shown in Figure 3. The casting solutions are based on PVDF and PES

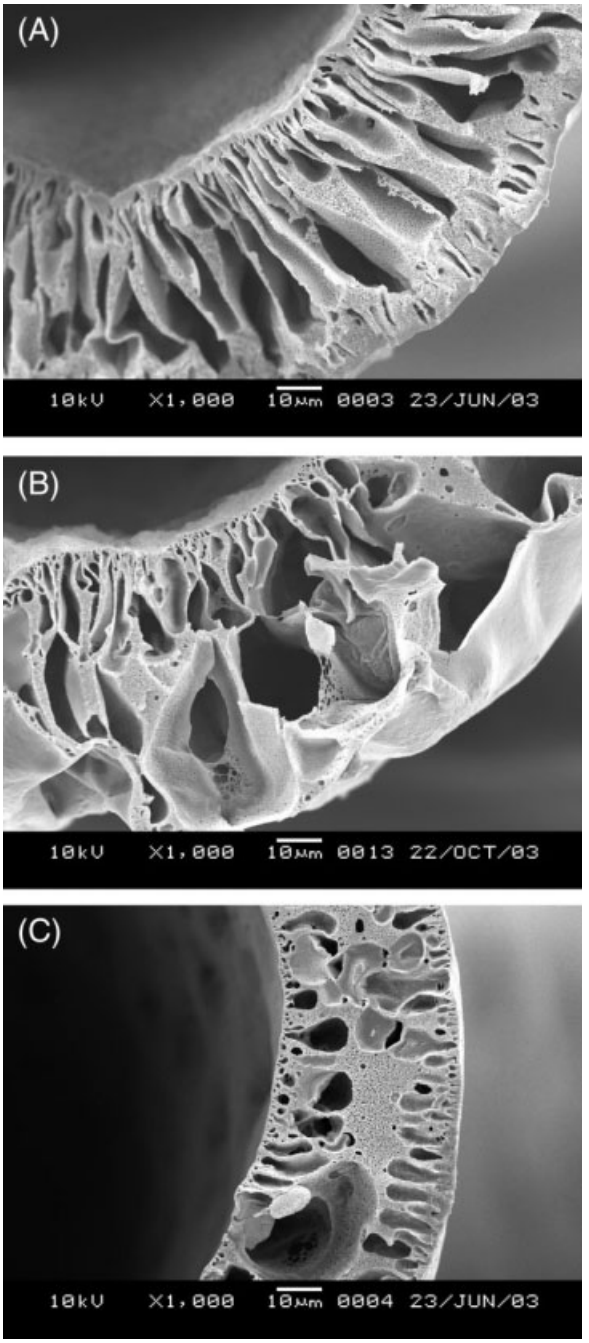

Figure 3 SEM photographs of PVDF/PES blend hollow fiber membranes prepared from the casting solutions with different PES concentration (The total PVDF and PES concentration is 15 wt % and 5 wt % PVP is added into the casting solution). PES concentration: (A) 0, (B) 1.5 wt %, and (C) 3 wt %.

polymers. The total concentration of PVDF and PES is 15 wt % and 5 wt % PVP is added into the casting solution. As shown in Figure 3(A), for pure PVDF membrane, the finger-like pores forming from inner skin layer do not extend completely to the outer skin layer. Short finger-like pores with less volume are formed under the outer skin layer and the membrane has a thicker inner and outer skin layer. The finger-like pores thoroughly extend from inner skin layer to the outer skin layer when the concentration of PES reaches 1.5 wt % [Fig. 3(B)]. The volume of finger-like pores is bigger and thin inner and outer skin layer formed. It indicates that the finger-like pores forming from the inner skin layer develop to the outer skin before the outer face of hollow fiber comes into the external coagulation bath. The function of the external coagulation bath is to accelerate the solidification of the outer skin. The thinner skin layers and finger-like pores crossing the inner and outer skin layer make the blend hollow fiber membrane have a higher pure water flux and a lower retention to BSA. When PES concentration gradually increases and reaches 3 wt %, few finger-like pores with less volume form under inner and outer skin layer, as shown in Figure 3(C). As the casting solution is extruded from the spinneret, double diffusion occurs simultaneously between the casting solution and the inner coagulation liquid, and the inner skin layer forms. Under the inner skin layer, the polymer pure phase forms and develops finger-like pores. Perhaps because the excessive content of PES slows down the double diffusion rate, there are few pure polymer phases growing up to finger-like pores and the growing rate of these pores is slow. The finger-like pores do not extend to the middle part of the nascent membrane when the membrane enters into the external coagulation bath. At that time, the outer skin layer appears and finger-like pores under the outer skin layer grow in the opposite direction. Because of the low diffusion rate of solvent and coagulant liquid, few finger-like pores with less volume form under both the inner and outer skin layer, and a sponge-like structure exists in the middle of the membrane. Membranes with this structure possess low penetration property, which leads to a lower water flux and a higher retention.

Effects of PVP concentration on shrinkage ratio, pure water flux, retention to BSA and morphology

Table IV shows the shrinkage ratio, the pure water flux and the retention to BSA of PVDF/PES blend hollow fiber membranes with different PVP concentration. The casting solution contains 13.5 wt % PVDF and 1.5 wt % PES. The concentration of PVP is changed from 0 to 10 wt %. As shown in Table IV, the shrinkage ratio increases slightly with increasing PVP concentration. Casting solutions belong to polymer concentrated solutions, and macromolecules orient when the casting solution is extruded through the spinneret. Part of the orientation is fixed in the membrane due to the quick precipitation of membrane. The relaxation of the oriented macromolecules causes shrinkage of membrane during drying process.

TABLE IV
Shrinkage Ratio, Pure Water Flux, and Retention to BSA of PVDF/PES Blend Hollow Fiber Membranes Prepared from the Casting Solutions with Different PVP Concentration

PVP concentration (%)	Pure water flux [$m^3 \times 10^{-3}/(m^2\ h)$]	Retention (%)	Shrinkage ratio (%)
0	198	48.1	5.3
2.5	392	43.2	6
5	498.5	40.2	6.6
7.5	341	37.4	7.5
10	165	34.7	8

The casting solution contains 13.5 wt % PVDF and 1.5 wt % PES.

BSA, bovine serum albumin; PVDF, poly (vinylidene fluoride); PES, polyethersulfone; PVP, polyvinylpyrrolidone.

The viscosity of casting solutions increases with increasing PVP concentration. So the macromolecular orientation increases accordingly. At the same time, PVP, a water soluble polymer, could be washed out in the later process. All these two reasons lead to the shrinkage ratio increasing with increasing PVP concentration.

Pure water flux reaches a maximum when the PVP concentration is 5 wt %, and the retention to BSA decreases over all the PVP concentration. Figure 4 shows SEM photographs of membranes prepared from the casting solution with different PVP concentration. As shown in Figure 4(A), a few shorter finger-like pores form in both the inner and outer parts of the membrane prepared from the casting solution without PVP. The length of the finger-like pores doesn't reach half of the membrane thickness and sponge-like structures form in the middle part of the membranes. Membrane with this structure often has a lower pure water flux and a higher retention. As shown in Figure 4(B), when PVP concentration reaches 5 wt %, the support layer becomes finger-like pores which grow from the inner skin layer to the end of the outer skin layer, and thin inner and outer skin layers form too. This structure results in a high pure water flux and a low retention of the membrane. Many investigators found that water flux increases and retention decreases with increasing PVP or polyethylene glycol (PEG) content when the pore former additives is at a lower concentration.[15,16] As shown in Figure 4(C), a few short finger-like pores and thick inner and outer skin layer form when PVP concentration reaches 10 wt %, which results in higher shrinkage ratio and lower pure water flux.

There are three reasons that account for the formation of these membranes: firstly, PVP is immiscible with PVDF and PES, and three domains may form in the casting solution. The number of microcell pores increases because PVP microcells exist in the skin layer and PVP may be partially washed out. Secondly, the double diffusion rate of solvent and precipitate is accelerated because of the hydrophilicity of PVP,[16,17] which results in bigger cavities. Thirdly, the concentration of casting solution increases when PVP is added into the casting solution. Membranes prepared from the casting solution with higher concentration result in smaller mean pore sizes. When PVP concentration is lower than

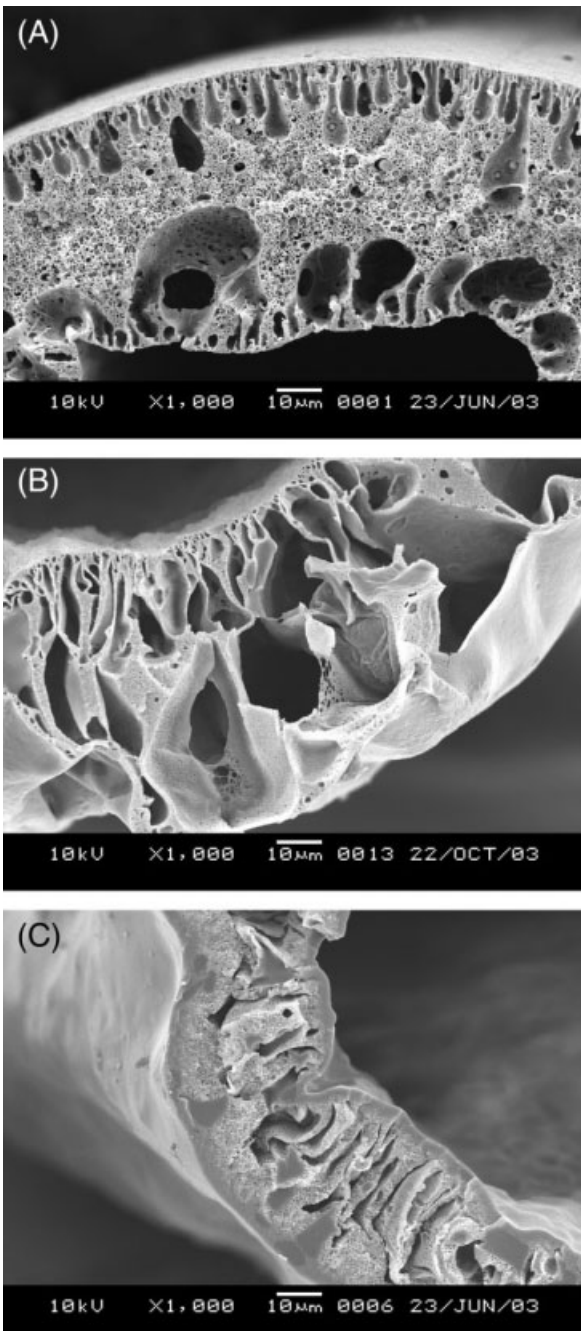

Figure 4 SEM photographs of PVDF/PES blend hollow fiber membranes prepared from the casting solutions with different PVP concentration (The casting solution contains 13.5 wt % PVDF and 1.5 wt % PES). PVP concentration: (A) 0, (B) 5 wt %, and (C) 10 wt %.

5 wt %, the first and the second reasons play the dominant roles in the formation of membranes. The pure water flux increases and the retention to BSA decreases with increasing PVP concentration. However, the third reason plays a leading role when PVP concentration surpasses 5 wt %, and smaller pores and thicker skin layer of the membranes result in a lower pure water flux. The retention of membrane is mainly completed by the skin layer. The bigger PVP microcells owing to the first reason cause the decrease of retention with increasing PVP concentration.

CONCLUSIONS

PVDF/PES blend hollow fiber membranes prepared from the casting solution with DMAc as solvent have the lowest shrinkage ratio, the highest pure water flux and the lowest retention to BSA, compared to the hollow fiber membranes prepared from the casting solution with DMSO, DMF, and NMP as solvents. Moreover, the shrinkage ratio of PVDF/PES blend hollow fiber membranes prepared from the casting solution with DMAc as solvent decreases. The pure water flux of PVDF/PES blend hollow fiber membranes reaches the maximum and the retention to BSA reaches the minimum when the casting solution contains 1.5 wt % PES. PVP concentration has a great influence on the properties and morphology of PVDF/PES blend hollow fiber membranes. Finger-like pores grow from the inner skin layer to the end of the outer skin layer and thin inner and outer skin layer form in the hollow fiber membrane prepared from the casting solution with 5 wt % PVP. At the same time, the pure water flux reaches the maximum when the casting solution contains 5 wt % PVP. The retention to BSA decreases over all the PVP concentration. The shrinkage ratio decreases with increasing concentration of PES and concentration of PVP.

References

1. Munari, S.; Bottino, A.; Capannelli, G. J Membr Sci 1983, 16, 181.
2. Lin, D. J.; Beltsios, K.; Young, T. H., Jeng, Y. S.; Cheng, L. P. J Membr Sci 2006, 274, 64.
3. Fontananova, E.; Johannes, J. C.; Cristiano, A., Curcio, E.; Drioli, E. Desalination 2006, 192, 190.
4. Wang, D. L.; Li, K.; Teo, W. K. J Membr Sci 2000, 178, 13.
5. Jian, K.; Pintauro, P. N. J Membr Sci 1997, 135, 41.
6. Duputell, D.; Staude, E. J Membr Sci 1993, 78, 45.
7. Yeow, M. L.; Liu, Y.; Li, K. J Membr Sci 2005, 258, 16.
8. Lang, W. Z.; Xu, Z. L.; Yang, H.; Tong, W. J Membr Sci 2007, 288, 123.
9. Deshmukh, P.; Li, K. J Membr Sci 1998, 150, 75.
10. Wu, L.; Sun, J.; Wang, Q. J Membr Sci 2006, 285, 290.
11. Bottino, A.; Camera-Roda, G.; Capannelli, G.; Munari, S. J Membr Sci 1991, 57, 1.
12. Bottino, A.; Capannelli, G.; Munari, S.; Turturro, A. J Polym Sci Part B: Polym Phys 1988, 26, 785.
13. Wang, D. L.; Li, K.; Teo, W. K. J Membr Sci 1996, 115, 85.
14. Yeow, M. L.; Liu, Y. T.; Li, K. J Appl Polym Sci 2004, 92, 1782.
15. Wang, D. L.; Li, K.; Teo, W. K. J Membr Sci 1999, 163, 211.
16. Kong, J. F.; Li, K. J Appl Polym Sci 2001, 81, 1643.
17. Munari, S.; Bottino, A.; Roda, G. C.; Capannelli, G. Desalination 1990, 77, 85.