

Fabrication of Polysulfone Asymmetric Hollow-Fiber Membranes by Coextrusion Through a Triple-Orifice Spinneret

Yufeng Zhang,¹ Qiyun Du,² Yun Wu,¹ Peng Wang,¹ Jinghang Wu¹

¹School of Materials and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, China

²Tianjin Motian Membrane Engineering and Technology Company Ltd., Tianjin 300160, China

Received 26 August 2003; accepted 15 March 2004

DOI 10.1002/app.20886

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polysulfone (PSf) asymmetric hollow-fiber membranes, which have a dense outer layer but a loose inner layer, were tentatively fabricated by coextrusion through a triple-orifice spinneret and a dry/wet-phase inversion process. Two simple polymer dopes were tailored, respectively, for the dense outer layer and the porous inner layer according to the principles of the phase-inversion process. By adjusting the ratio of the inner/outer extrusion rate, the hollow-fiber membranes with various thicknesses of

outer layers were achieved. The morphology of the hollow-fiber membranes was exhibited and the processing conditions and the water permeability of the membrane were investigated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 259–266, 2004

Key words: polysulfone; membranes; coextrusion; triple-orifice spinneret; morphology

INTRODUCTION

Large-scale membrane applications remained limited until Loeb and Sourirajan¹ developed the first asymmetric skinned membrane. Asymmetric membranes commonly have a thin, dense skin layer supported by a thick, porous sublayer. It is well known that such membranes have advantages over symmetric ones because of their lower mass transfer resistance and longer life span.^{2–5} The dry/wet-phase inversion process is widely used in spinning asymmetric hollow-fiber membranes, which involves essentially the following five steps: (1) formulating the polymer solution, (2) spinning of nascent hollow fibers, (3) coagulating of the nascent hollow fibers, (4) washing and drying, and (5) posttreatment. During the whole process of making asymmetric membranes, there are many interrelating factors that not only can affect the structure and performance of the final membranes but are also extremely difficult to evaluate their individual effects quantitatively. Furthermore, conditions for the formation of a dense skin layer are quite different from, or even contradictory to, those for the formation of a porous sublayer. The formation of a dense skin layer has been shown to be the result of the higher

polymer concentration in the surface layer compared with that in the supporting sublayer and the coalescence and deformation of the polymer aggregates at the air solution interface attributed to capillary force.^{6,7} For a polymer/solvent binary solution system; three fundamentally different concepts may cause the local polymer concentration at the surface to increase: (1) solvent removal by evaporation during the dry process; (2) rapid solvent outflow relative to the coagulant inflow in the wet-phase inversion process; and (3) higher surface tension of the solvent compared to that of the polymer. These aspects have been extensively reviewed by several authors.^{6–11}

The formation of the sublayer of an asymmetric membrane is very complicated and is usually featured by macrovoids, close and open cell types of structure. In general, the sublayer structures may be broadly divided into two types: sponge-type structure and fingerlike structure.⁹ Many different mechanisms on the sublayer formation of asymmetric membranes have been proposed and reviewed in detail by Smolders et al.¹² and Paulsen et al.¹³ Unfortunately, there is no a single mechanism that can well describe the structures of the membranes prepared under different membrane making conditions. However, adding a nonsolvent additive (NSA) in solution system can contribute to the formation of macrovoids during the phase-inversion process.^{12,13} It is believed that for a ternary polymer/solvent/NSA solution system, the solution properties determined by the interactions of components, coagulation kinetics determined by the

Correspondence to: Y. Zhang (zyf9182@tjpu.edu.cn).

Contract grant sponsor: Tianjin Municipal Education Commission, China; contract grant number: 20010506.

coagulant tolerance of the polymer solution and the diffusion rates of solvent and NSA away from the membrane, and diffusion rate of coagulant into the membrane, together control the cross-sectional structure of the membrane.^{12,13}

The addition of a NSA in a polymer solution may also affect the formation of the dense skin layer. In some cases, the effect is positive, but in other cases, it is negative. For example, during the dry process in a dry/wet-phase inversion process, solvent and/or NSA evaporate from the surface layer of the nascent membrane, which results in increasing the local polymer concentration. If the boiling point of solvent is higher than that of the NSA, rapid vaporization of the NSA will increase the local solvent power. As a result, the solution composition of nascent membrane at the surface shifts away from the point of phase separation. This tends to form a membrane with a dense, thick skin layer. Conversely, a faster loss of solvent molecules from the membrane surface tends to form a thin, porous skin layer.

To sum up, it is desired to control different compositions of membrane-forming solution systems for dense skin layer and sublayer, respectively. By using coextrusion, one can make a variety of matches, which can construct asymmetric hollow-fiber membranes. The asymmetric includes not only morphology but also material. That is, half the thickness is one kind of polymer materials system and the other half thickness is another. In this study, morphologically asymmetric hollow-fiber membranes were tentatively prepared by coextrusion through a triple-orifice spinneret and dry/wet-phase inversion process. Triple-orifice spinnerets were previously used elsewhere^{14,15} for different aims. Two polymer solution systems, dope I and dope II, tailored to the formation of the dense skin layer and the porous sublayer, respectively, were presently formulated. By adjusting the ratio of the inner/outer extrusion rate, fibers with various thicknesses of outer layers were achieved. The morphology of the hollow-fiber membranes was exhibited and the membrane-forming conditions and the water permeability of the membrane were investigated. The results show that a dense outer layer of the hollow-fiber membrane can be obtained with an outer layer dope characterized by high polymer concentration and low NSA content and the NSA is preferably volatile and miscible with water and the solvent. On the other hand, the inner layer of the membrane is macroporous, without dense skin at the inner surface, which can be achieved by using a dope with low polymer concentration and high NSA content, in that the solution is close to the point of phase separation and a low precipitation rate at the inner surface of the membrane. The thickness of the outer layer can be easily adjusted by verifying the ratio of the inner/outer extrusion rates, and the water permeability of the membrane was thus changed.

EXPERIMENTAL

Materials

PSf used was the products from Dalian Plastic Plant No. 1 (Liaoning, China), with $[\eta] = 0.57$; the solvent is *N,N*-dimethyl acetamide (DMAc; Shanghai Chemicals, Shanghai, China); the nonsolvent additives (NSAs) include polyvinylpyrrolidone K30 (PVP; $M_n = 30,000$) and ethanol absolute (EOH, 99.7%; Tianjin Chemicals, Tianjin, China).

Preparation of asymmetric hollow fibers

The asymmetric hollow fibers were prepared by a dry/wet-phase inversion method with a triple-orifice spinneret in a self-made mini-spinning apparatus. The schematic diagram of the spinneret is shown in Figure 1 where the dimensions of the inner and outer orifices and the inner tube are given in the inset.

Two preformulated polymer dopes, the inner layer dope and the outer layer dope, are poured into two solution tanks, respectively. The compositions of the two dopes are slightly different. The inner dope is of low polymer concentration (PSf/DMAc = 20/80 by weight) and high PVP content (PVP/PSf = 40/60 by weight); the outer layer dope is high polymer concentration (PSf/DMAc = 30/70 by weight) but low PVP content (PVP/PSf = 10/60 by weight) with or without a proper amount of EOH. During the spinning operation, the dopes are fed under nitrogen pressure and/or the gear pump through the spinneret. The inner layer dope is fed into the inner orifice; the outer layer dope, into the outer orifice; and the internal coagulant is introduced into the inner tube of the spinneret. The extrusion rates of both spinning dopes are properly controlled so as to obtain membranes with various thickness of both inner and outer layers. In this study, the inner extrusion was controlled to be constant, about 1.1 mL/min, but the outer extrusion rate was adjusted in the range of 0.1 to 1.2 mL/min to make outer layers of different thicknesses. Tap water at room temperature was used as an external coagulant. The internal coagulant was tap water or mixtures of water and the solvent DMAc, with a ratio of solvent to water being no more than 20:80. The internal coagulant injection was controlled in the range of 0.8–1.2 mL/min. The nascent hollow fiber passes through an air gap of 10–15 cm and then into the coagulation bath at ambient conditions ($25 \pm 1^\circ\text{C}$ and $\text{RH} = 60\text{--}65\%$). The take-up velocity is about 2 m/min. The spinneret is arranged such that the nascent fiber is extruded vertically downward into the coagulation bath. After coagulation, the fiber is guided through the wash bath and then coiled into the storing tank. The hollow fiber is kept in a storing tank for at least 3 days to stabilize the structure.

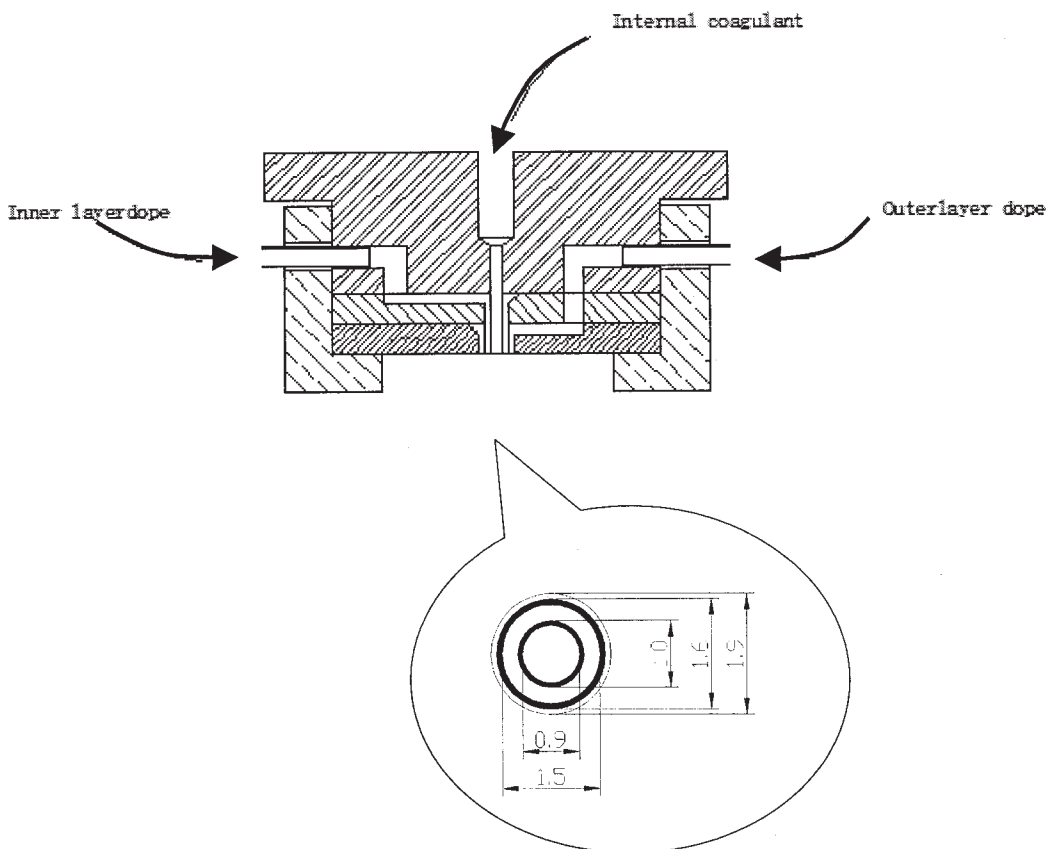


Figure 1 Schematic diagram of the triple-orifice spinneret.

Morphology examination

After being gold-coated, the structure of membrane cross sections were investigated by a Stereoscan 200 scanning electron microscope (Cambridge Instruments, Oxford, UK).

Membrane performance

The membrane performances (water permeate flux and egg white retention) were determined at 20°C, 0.2 MPa operating pressure, and 5 m/s recirculation rate. The apparatus and the method used are common, such as described in Bottino et al.¹⁶ and Majewska-Nowak.¹⁷ Pure water or a 1 wt % egg white aqueous solution was used.

RESULTS AND DISCUSSION

Figure 2 represents the morphology of a hollow-fiber membrane prepared by coextrusion through the triple-orifice spinneret with the outer dope of 30% and the inner dope of 20% PSf/DMAc. The ratio of the inner/outer extrusion rates (extrusion ratio) is 1. Furthermore, the outer dope is of lower NSA content to reach dense and smaller porous morphology but the inner dope is of higher NSA content, close to the point

of phase separation, to acquire larger porous morphology, usually fingerlike. The morphological structure of the cross section of the fiber membrane can be identified as two stages: the spongelike porous layer forming the outer layer and the fingerlike porous substrate layer forming the inner layer. The size of the spongelike porous gradually becomes smaller and denser from the inner to the outer. It is generally believed that there exists a thin but dense skin layer at the outermost region, although it cannot be distinctly unfolded by the presently available instruments. The formation of a dense skin layer has been shown to be the result of the coalescence and deformation of the polymer aggregates at the air-solution interface attributed to capillary force and higher polymer concentration in the surface layer compared with that in the supporting sublayer.^{6,7} It is well recognized that the performances of the membranes are mainly determined by their outer layers, exactly by their skin layers. On the one hand, the thickness of the outer dense layer is believed to be one of the main factors affecting the membrane resistance to the permeate flux. By increasing the extrusion ratio, the thickness of the dense outer layer can be properly reduced. Figure 3 is the SEM photograph of the morphology of the hollow fiber spun under extrusion ratio of 9. Compared to Figure 2, under an

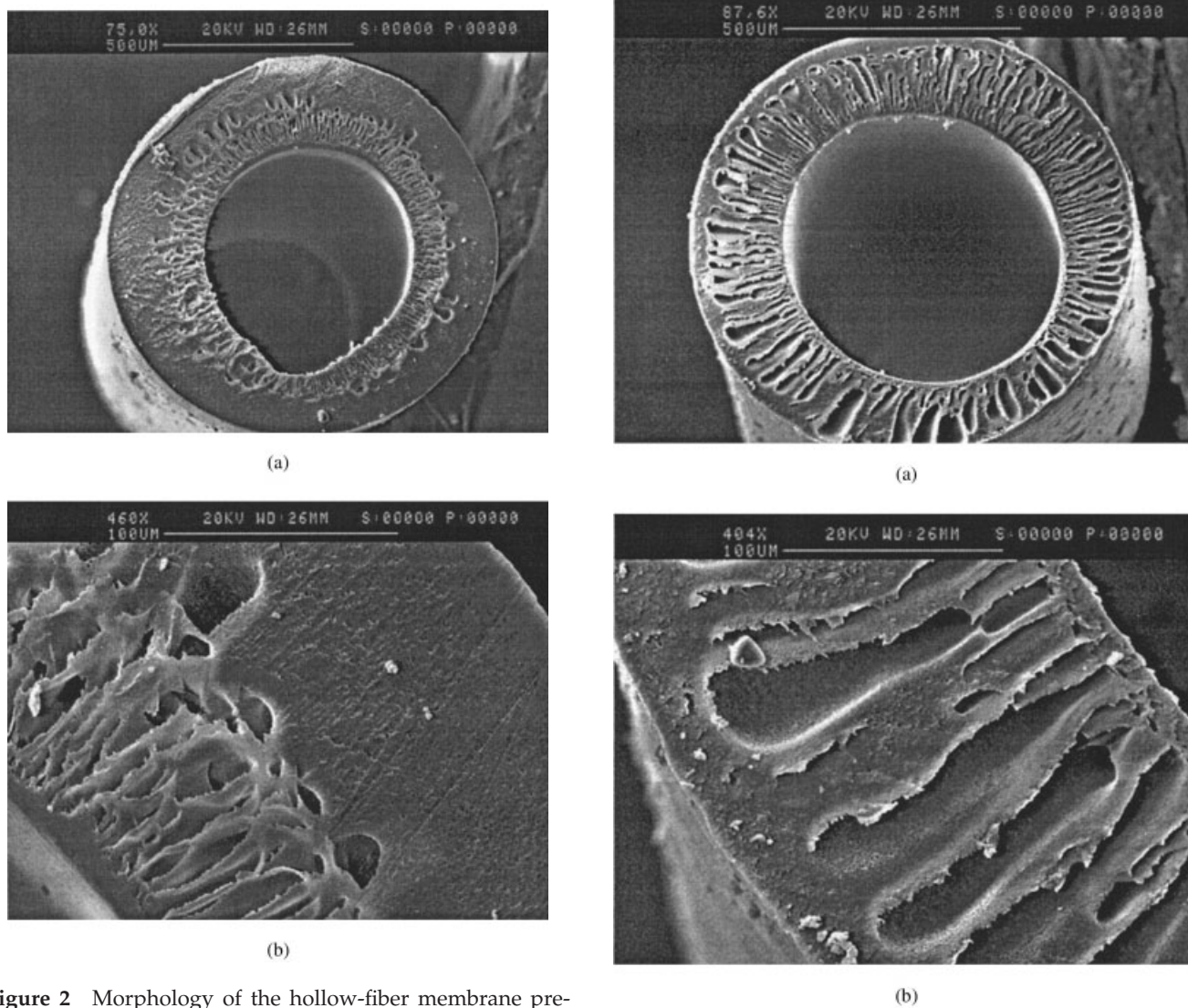


Figure 2 Morphology of the hollow-fiber membrane prepared by coextrusion through the triple-orifice spinneret with the outer dope of 30% and the inner dope of 20% PSf/DMAc. The extrusion ratio is 1.

extrusion ratio of 1, it has a much thinner outer layer. It is noticed that the thickness of the outer layer is not completely homogeneous, one side being thinner than the other, as shown in Figure 3(b) and (c). In this case, the outer layer seems to be disintegrated as shown in Figure 3(c). This problem used to occur when the extrusion ratio was above 7 and the reasons were probably that there was a substantial difference between the flow abilities of the two dopes, and the width of the annular orifice of the spinneret used did not match the extrusion rates. A well-designed and precisely manufactured spinneret may probably compensate for, or even solve, this problem. In addition, with the increase of the extrusion rate, the thickness of the outer layer decreases, and thus the membrane resistance decreases. Figure 4 shows the hydraulic permeate flux, representing the membrane resistance,

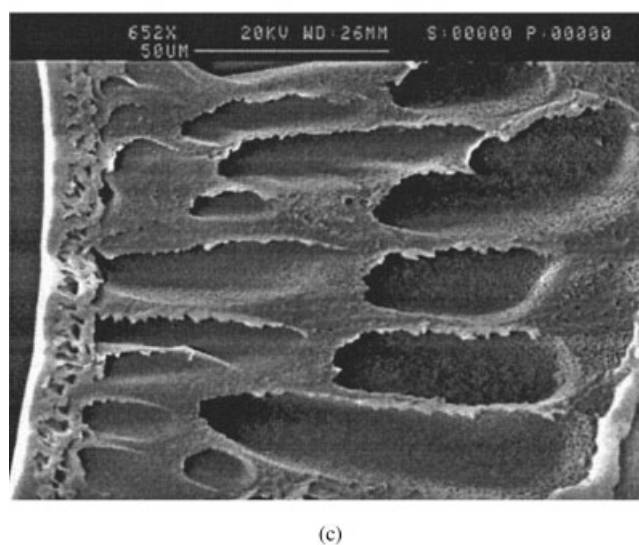


Figure 3 Morphology of the hollow-fiber membrane prepared by coextrusion through the triple-orifice spinneret with the outer dope of 30% and the inner dope of 20% PSf/DMAc. The extrusion ratio is 9.

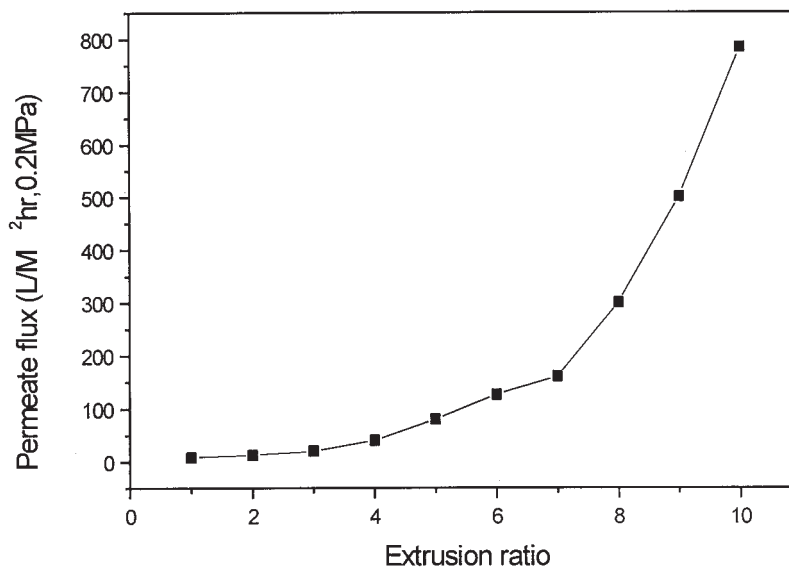


Figure 4 Hydraulic permeate flux of the membranes as a function of the extrusion ratio.

as a function of the extrusion ratio. It is obvious that the flux slowly increases with the extrusion ratio at the initial stage, but increases sharply when the ratio is above 7, which probably explains why the outer layer is disintegrated besides the decrease of its thickness, as shown in Figure 3.

On the other hand, the dense outer layer, especially the outer dense skin at the outermost region of the membrane, determines the separation characteristics of the membrane. The formation of the outer layer of the membrane can be controlled by the principles of the dry/wet-phase inversion process. The dry/wet-phase inversion processes constitute the exposure of the nascent membrane to air for a short duration (dry process) before entering a water bath for coagulation (wet process). The effect of the dry process on the dense skin layer formation of asymmetric membrane is important and also complicated.

For a polymer/solvent binary solution system, three fundamentally different concepts may cause the local polymer concentration at the surface to increase: (1) solvent removal by evaporation during the dry process; (2) rapid solvent outflow relative to the coagulant inflow in the wet-phase inversion process; and (3) higher surface tension of the solvent compared to that of the polymer. When NSA is added into the solution, during the dry process, solvent and/or NSA evaporate from the surface layer of the nascent membrane, which results in the increase of the local polymer concentration. The rates of evaporation depend on their volatilities as well as temperature of the polymer solution and the atmosphere. If the boiling point of solvent is higher than that of the NSA, the more rapid vaporization of the NSA will increase the local solvent power. As a result, the solution composition of nas-

cent membrane at the surface shifts away from the point of phase separation. This tends to form a membrane with a dense, thick skin layer. Conversely, a faster loss of solvent molecules from the membrane surface tends to form a thin but porous skin layer. Besides loss of the solvent and NSA, the solution in the outermost region of the membrane absorbs moisture simultaneously and this will further hasten the process of phase separation.

EOH, which has good volatility and is completely miscible with water and DMAc, was used as a NSA added in the outer dope in this study. The aim is to fabricate membranes with different outer layer densities. Other similar additives, such as methanol, propanol, butanol, pentanol, ethylene glycol, diethylene glycol, and so forth, may have the same effects according to the above principles and were systematically investigated by a number of authors^{13,20,21} Figure 5 shows the hydraulic permeability and the egg white retention of the membranes as functions of the ratio of EOH to the solvent DMAc in the outer dope. The membranes were prepared under an extrusion ratio of 6 and using water as the internal coagulant. It is observed, on the one hand, that the hydraulic permeability decreases with the increase of EOH content when the EOH content of the outer dope is lower than 6%, but increases when above 6% and more sharply when above 10%. On the other hand, the retention is nearly constant, about 99%, when the EOH content is low, no more than 8%, but decreases dramatically when the EOH content is above 10%, corresponding to the change of hydraulic permeability of the membranes in this range of EOH content, indicating that a macroporous outer layer formed. It is clear that when the EOH concentration is low, the evaporations of

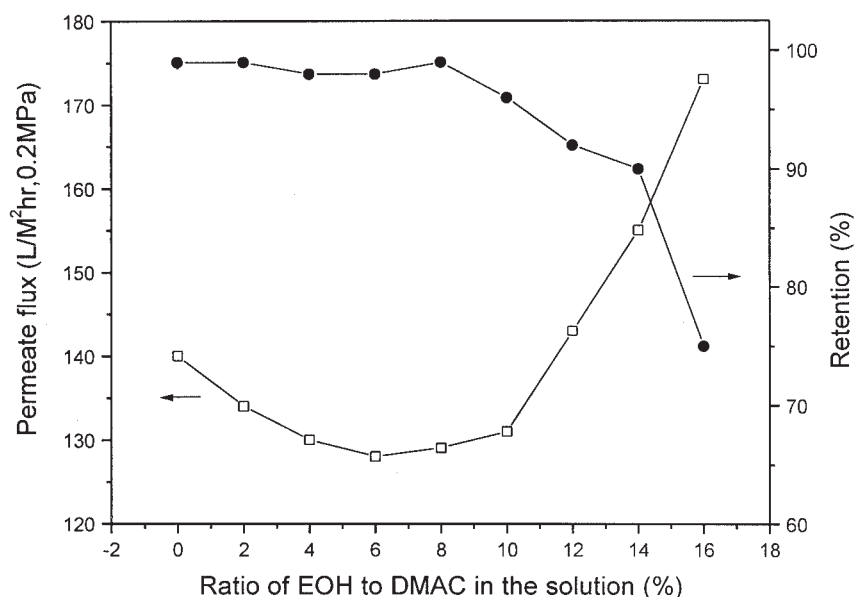


Figure 5 Hydraulic permeate flux and egg white retention of the membranes as functions of the ratio of EOH to DMAc in the outer dope. The membranes were prepared under an extrusion ratio of 6 and with water as the internal coagulant.

EOH and DMAc from the surface of the nascent membrane play a dominant role. Loss of the solvent and NSA leads to a relatively higher polymer concentration at the surface of the nascent membrane and eventually a dense skin layer. The higher the EOH content, the denser the skin layer and the lower the hydraulic permeability of the membrane. With the increase of the NSA content, the dissolving power of the solvent decreases and polymer-polymer interaction rises. In this case, the polymer chains may have a smaller excluded volume because of a more tightly coiled conformation, that is, polymer aggregates are formed in the polymer solution. On the other hand, a polymer lean phase also appears in the polymer solution. The polymer lean phase is responsible for the initiation of macrovoids.^{12,13} The size of polymer aggregates depends on the interaction strengths of the solvent-NSA-polymer system. When a sufficient amount of the EOH is added, interaction of solvent-EOH may be strong enough and interactions of solvent-polymer and NSA-polymer weak enough to lead to large polymer aggregates, resulting in the formation of big cavities. Figure 6 shows the morphology of the membrane spun from an outer dope with the ratio of EOH to DMAc of 14%. It is obvious that small fingerlike cavities and macrovoids appear at the outer layer because of the high EOH content. Thus, the hydraulic permeability of the membrane rises with a low retention (Fig. 2).

The inner layer solution mainly constructs the sub-layer that is usually featured by macrovoids, close and open cell types of structure without any skin formed. Such a morphological structure is believed to be not only of low membrane resistance but also of low pres-

sure endurance. Different from the formation process of the outer layer of the hollow-fiber membrane, the inner layer actually experiences a wet-phase inversion process, with the inner coagulant contacting the inner surface of the nascent hollow-fiber membrane at the very beginning of the extrusion of the inner dope. Until now, unfortunately, there has yet to be a single mechanism that can describe well the formation of the structures of membranes prepared under different conditions. It is clear, however, that a high NSA content in the polymer solution, usually close to the point of phase separation, is necessary to achieve such morphological structure of fingerlike macrovoids.^{12,13} Besides, a lower polymer concentration tends to form larger macrovoids. It is believed that for a ternary polymer/solvent/NSA solution system, the solution properties determined by the interactions of components, coagulation kinetics determined by the coagulant tolerance of the polymer solution, and the diffusion rates of solvent and NSA away from the membrane, and diffusion rate of coagulant into the membrane, together control the cross-sectional structure of the membrane.

When a NSA is added into a polymer-solvent solution, the interaction between the nonsolvent and solvent molecules leads to a reduction of the dissolving power of the solvent, which further enhances the polymer-polymer interaction. In this case, the polymer chains may have a smaller excluded volume because of a more tightly coiled conformation. The polymer aggregates are formed in the polymer solution. Thus, an initially homogeneous solution may become microscopically heterogeneous. If a sufficient amount of the NSA is added, a polymer lean phase may exist in the

polymer solution. The polymer lean phase is responsible for the initiation of macrovoids.^{12,13} The size of polymer aggregates depends on the interaction strengths of the solvent–NSA–polymer system. Strong interaction of solvent–NSA and weak interactions of solvent–polymer and NSA–polymer tend to form large, or even superpolymer aggregates, resulting in the formation of big cavities and fingerlike structure. The kinetics of phase separation during the wet coagulation process plays a major role in the control of membrane morphology. The accelerated rate of phase separation resulting from the addition of a NSA may restrict the rearrangement of polymer aggregates, further resulting in the formation of a membrane with small macrovoids. If the diffusion of the solvent molecules is faster than that of the NSA, the rapid outflow of solvent molecules will further enhance the polymer–polymer interaction before the membrane is so-

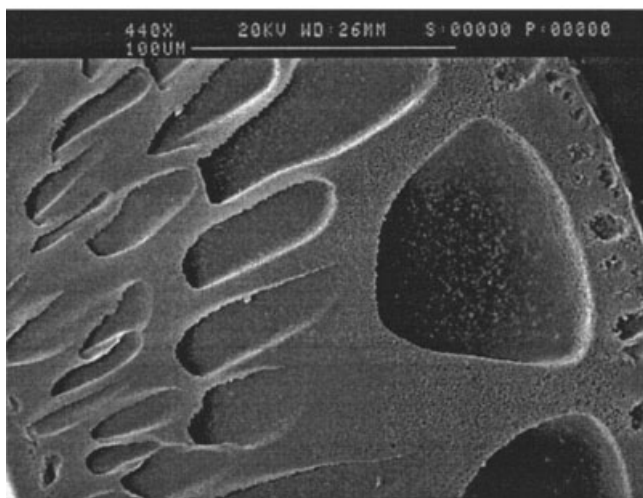
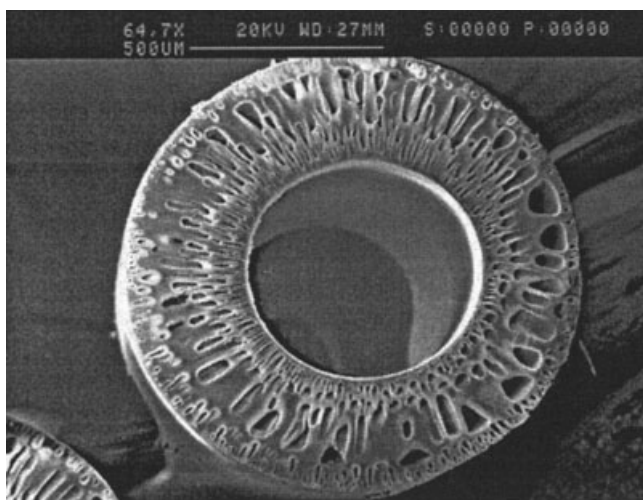


Figure 6 Morphology of the membrane spun from an outer dope with the ratio of EOH to DMAc of 14%. The extrusion ratio is 6.

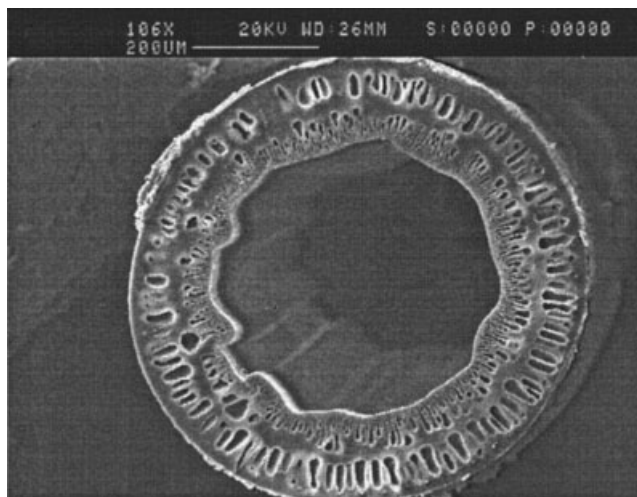


Figure 7 Morphology of the hollow fiber with a noncircular lumen cross section using the mixture of water/DMAc 70/30 as the internal coagulant.

lidified. This is likely to intensify the formation of superaggregates with the creation of big macrovoids. In this study, PVP was used as the NSA with much lower diffusion rate than that of DMAc because of its macromolecular weight.

We do not expect a skin to exist on the inner surface of the hollow-fiber membrane. Decelerating the solidification rate of the fiber surface or accelerating the solidification rate inside the membrane can prevent the formation of skin. As mentioned above, the phase separation would easily happen with enhanced coagulation rate when adding a sufficiently high amount of NSA. In addition, adding a certain amount of solvent to the internal coagulant can decelerate the surface solidification rate, which prevents the formation of the dense skin at the inner surface of the membrane. It should be noted that if the solidification rate is too low, no good hollow-fiber morphology would be expected and a noncircular lumen cross section of the hollow fiber was formed, as shown in Figure 7. The internal coagulant is a mixture of water/DMAc 70/30.

CONCLUSIONS

To fabricate asymmetric hollow-fiber membrane, co-extrusion through a triple-orifice spinneret was used. The inner layer dope and the outer layer dope were specifically tailored. The outer layer dope for the dense outer layer is characterized by a high polymer concentration and low NSA content and the NSA is preferably volatile and miscible with water and the solvent used. On the other hand, the inner layer of the membrane is macroporous without a dense skin at the inner surface, which can be achieved by use of a dope with low polymer concentration and high NSA content, in that the polymer solution is close to the point

of phase separation and a low precipitation rate at the inner surface of the membrane. The thickness of the outer layer can be easily reduced by enhancing the ratio of the inner/outer extrusion rates, and the hydraulic permeability of the membranes can thus be enhanced.

In the end, it is desired that a great variety of membranes of both morphological and material asymmetry be developed for special aims.

The authors gratefully acknowledge the research development funds (20010506) provided by the Tianjin Municipal Education Commission.

References

1. Loeb, S.; Sourirajan, S. *Adv Chem Ser* 1962, 38, 117.
2. Panar, M.; Hoehn, H. H.; Hebert, R. R. *Macromolecules* 1973, 6, 777.
3. Tsay, C. S.; McHugh, A. J. *J Polym Sci Part B: Polym Phys* 1990, 28, 1327.
4. Li, K.; Kong, J. F.; Teo, W. K. *AIChE J* 1999, 45, 1211.
5. Li, K.; Wang, D.; Koe, C. C.; Toe, W. K. *Chem Eng Sci* 1998, 53, 1111.
6. Wijmans, J. G.; Smolders, C. A. In: *Synthetic Membranes: Science, Engineering and Applications*; Bungay, P. M.; Lonsdale, H. K.; de Pinho, M. N., Eds., Reidel: Dordrecht, The Netherlands, 1983; p. 39.
7. Wijmans, J. G.; Kant, J.; Mulder, M. H. V.; Smolders, C. A. *Polymer* 1985, 26, 1539.
8. Yong, T. H.; Chen, L. W. *J Membr Sci* 1991, 57, 69.
9. Strathmann, H. In: *Materials Science of Synthetic Membranes*; Lloyd, D. R., Ed.; America Chemical Society: Washington DC, 1985; p. 165.
10. Koros, W. J.; Fleming, G. K. *J Membr Sci* 1993, 83, 1.
11. Tanny, G. B. *J Appl Polym Sci* 1974, 18, 2149.
12. Smolders, C. A.; Reuvers, A. J. Boon, R. M.; Wienk, L. M. *J Membr Sci* 1992, 73, 259.
13. Paulsen, F. G.; Shojaie, S. S.; Krantz, W. B. *J Membr Sci* 1994, 91, 265.
14. Li, S.-G.; Koops, G. H.; Mulder, M. H. V.; Van den Boomgaard, T.; Smolders, C. A. *J Membr Sci* 1994, 94, 329.
15. Wang, D.; Li, K.; Teo, W. K. *J Membr Sci* 2000, 166, 31.
16. Bottino, A.; Capannelli, G.; Imperato, A.; Munari, S. *J Membr Sci* 1984, 21, 247.
17. Majewska-Nowak, K. *Desalination* 1989, 71, 83.
18. Kesting, R. E.; Fritzsche, A. K.; Murphy, M. K.; Handermann, A. C.; Cruse, C. A.; Malon, R. F. U.S. Pat. 4,871,494, 1989.
19. Wang, D.; Li, K.; Teo, W. K. *J Membr Sci* 1995, 98, 233.
20. Wang, D.; Li, K.; Teo, W. K. *J Membr Sci* 2000, 178, 13.
21. Wang, D.; Teo, W. K.; Li, K. *J Appl Polym Sci* 1999, 71, 1789.