Effects of Pluronic F127 on the Polymorphism and Thermoresponsive Properties of PVDF Blend Membranes via Immersion Precipitation Process

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ABSTRACT: Amphiphilic copolymer Pluronic F127 was used as macromolecular additive to investigate the polymorphism and thermoresponsive properties of poly(vinylidene fluoride) (PVDF) membranes. Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were conducted to characterize the polymorphism and morphology of PVDF/F127 blend membranes. FTIR results indicated that F127 existed stably in the blend membranes, and lower F127 concentration in the cast solution was in favor of the formation of α-crystal phase, but higher F127 concentration could promote the formation of β- and γ-crystal phase in PVDF membranes. The results of XRD also confirmed these phenomena. With the increase of F127 in the cast solutions, a more sponge-like structure appeared at the bottom surface of the membranes as investigated by SEM. PVDF/F127 blend membranes also exhibited good thermoresponsive properties. The water flux of the membranes increased distinctly with the increase of the experimental temperature, decreased with the decrease of the temperature, and the increasing and decreasing curves were almost overlapped. Contact angle measurement and permeation experiment indicated that the blend membranes had good hydrophilicity and fouling resistance. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 124: E330–E337, 2012

Key words: PVDF; membranes; Pluronic F127; thermal properties; polymorphism

INTRODUCTION

Pluronic® F-127 (F127) is a kind of commercially available nonionic macromolecular surface-active agents, which is water-soluble triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) and often denoted as PEO-PPO-PEO or $(EO)_x(PO)y(EO)_x$. F127 is an important class of surfactants and has found widespread industrial applications in detergency, dispersion stabilization, foaming, emulsification, lubrication, etc.[1] As an amphiphilic copolymers, F127 has become a good candidate for the template agent in preparing the mesoporous materials.[2,3] For the good hydrophilic and antifouling properties of PEO segment, F127 has been widely investigated in biomedical applications and membrane separation fields.[4–6]

As a good hydrophilic modifier and template agent, F127 has been used widely in the preparation of polyethersulfone (PES) and polysulfone(PSF) membranes. Raslan et al.[7] used Pluronic F127 to prepare the antifouling polysulfone ultrafiltration mem-

brane and found that F127 was useful to improve the hydrophilicity of the blend membranes. Wang et al.[8] prepared the ultrafiltration membranes by blending F127 and polyethersulfone (PES) via immersion precipitation process, and found that F127 could exist stably in blend membranes, and the addition of F127 exerted minor effect on the mechanical properties of blend membranes. Other studies[9,10] also found that during the preparation process of PES/F127 blend membranes, F127 acted as the dual roles of surface modifier and pore-forming agent, and further study found that PES/F127 blend membranes were very effective to separate the oil/water emulsion, which might be due to the good hydrophilicity and antifouling properties of the membranes.

In membrane preparation process, blending the PEO-containing block copolymers or other amphiphilic copolymers into the hydrophobic polymers are the most popular and simple methods. The main problem is that the hydrophobic segment in the copolymer should have good compatibility with hydrophobic polymer matrix. As for the modifier, Wang et al. suggested that F127 is a suitable candidate because PPO segments are miscible with PVDF.[11] Moreover, F127 could also tune the porous structure of membranes, Cui et al.[12] prepared PVDF/F127

blend membranes via thermally induced phase separation (TIPS) process and they found that F127 could control the structure of the membranes and increased both the electrolyte uptake of blend membranes and the ionic conductivity of corresponding polymer electrolytes.

Meanwhile, F127 is also a kind of thermal responsive polymer, its aqueous solutions of 20–30 wt % have the interesting characteristic of reverse thermal gelation, i.e., they are liquid at refrigerated temperatures (4–5°C), but gel upon warming to a body temperature (37°C).[13] The thermal properties of F127 have attracted more and more attention, e.g., the reverse thermal gelation and low toxicity have been the basis of research into the use of F127 as a possible drug delivery system in man.[14] But the reports on the thermal-sensitive properties of F127 in membranes were quite limited.

PEO segment in F127 is a typical crystalline polymer segment which can affect the polymorphism and properties of semicrystalline polymer membrane. PVDF is a polymorphic semicrystalline polymer, which has at least four different crystalline including α, β, γ, and δ forms, and the crystal phase can transform from one to the other under certain conditions, e.g., stretching can promote the transformation of α-phase to β-phase of PVDF fibers made by melt spinning process.[15] Zhang et al.[16] also studied the polymorphism of porous PVDF membranes formed via immersion precipitation process, and found that the crystal structure of PVDF membranes can be affected by PVDF concentration in casting solution and precipitation temperature. So it is necessary to study the effects of F127 on the crystal structure of PVDF membranes. To the best of the authors' knowledge, the details of the polymorphism in porous PVDF membrane, its dependence on F127 casting solution, and the thermal sensitivity of the blend membranes have not been reported.

In this work, the effect of F127 on the polymorphism of porous PVDF/F127 blend membranes prepared via immersion precipitation process was studied in some detail. The thermal sensitivity of the membranes was also studied. Emphasis was placed upon the effects of precipitation temperature and F127 concentration in the casting solution on the structure and properties of the blend membranes.

EXPERIMENTAL

Materials

PVDF (SOLEF 1015) with a melt flow index of 0.2 (230°C, 5 kg) was purchased from Solvay Solexis Co. (Brussels, Belgium). Pluronic F127 (mole ratio of EO/PO/EO = 100/65/100, M_n = 12,600) was purchased from Sigma-Aldrich. Polyethylene glycol

TABLE I
The Composition of Casting Solution and Coagulation Temperature for Preparing PVDF/F127 Blend Membranes

Membrane type	Composition of casting solution				Coagulation temperature (°C)
	PVDF (g)	F127 (g)	PEG2000 (g)	DMAc (g)	
M1	9.0	0	9.0	42.0	30
M2	9.0	1.8	—	49.2	30
M3	9.0	3.6	—	47.4	10,20,30,40,50
M4	9.0	5.4	—	45.6	30
M5	9.0	7.2	—	43.8	30
M6	9.0	9.0	—	42.0	30

2000 (PEG2000) was purchased from Aladdin Chemical Reagent Co. (Shanghai, China). Bovine serum albumin (BSA, M_w = 67 kDa) were purchased from Sino-American Biotechnology Co. Phosphate-buffered saline (PBS, 0.01M) was prepared by dissolving preweighed quantities of potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$) in deionized water. Commercially available N,N-dimethyl acetamide (DMAc), supplied by Shanghai Jingwei Chemical Plant (Shanghai, China), served as solvent and were used without further purification.

Membrane preparation

PVDF/F127 porous membranes were prepared by phase inversion method. The formulations of casting solutions and the coagulation temperature are exhibited in Table I. PVDF and F127 with different weight ratios were dissolved in DMAc solution and stirred at 60°C for about 12 h to ensure the homogeneous mixing. After filtered and degassed, the solution was cast onto a horizontal glass plate at room temperature using a glass blade. After exposed in air for 20 s, the nascent membrane was immersed into different temperature deionized water bath for gelation. The resulting membrane was stored in de-ionized water for at least 2 days before characterization.

Membrane characterization

Surface and interior morphologies of the membranes were examined by a scanning electron microscope (SEM, JSM-5610, JEOL, Japan). For this purpose, samples were fractured in liquid nitrogen to obtain tidy cross sections and sputter-coated with gold layer before SEM observation. The surface chemical composition and crystal structure was characterized by infrared spectroscopy (FT-IR) (Bruker, vector 22) at a 1 cm^{-1} resolution and in the 400–4000 cm^{-1} wave number range. The crystal phase structure was also characterized by X-ray diffraction (XRD)

measurements performed on an X-ray Diffractometer (Rigaku D/max-RA) with Cu Kα radiation (λ = 0.154 nm), and a scanning rate of 4°/min.

The top surface hydrophilicity of membranes was characterized on the basis of a water contact angle system (OCA20, Dataphysics, Germany) equipped with video capture at room temperature. To minimize experimental error, the contact angles were measured five times for each sample and then averaged.

Filtration experiments were conducted on an ultrafiltration instrument (SF-SA, Hangzhou Saifei Co., China) with three membrane cells and the membrane diameter is about 54 mm. Each membrane was initially pressurized at 0.15 MPa for 30 min, and then the pressure was lowered to the operating pressure of 0.1 MPa. The water flux J_w (L/(m² h)) was calculated by the following equation:

$$J_w = \frac{V}{A\Delta t} \qquad (1)$$

where J_w is the pure water flux (L/(m² h)), V is the permeate volume (L), A is the membrane area (m²), and Δt is the time (h).

After that, a 1 g/L BSA phosphate-buffered saline solution was forced to permeate through membrane at the pressure of 0.1 MPa for 30 min, and the flux was recorded as J_p. After filtration of BSA solution, these membranes were washed by pure water for 30 min at 25°C and then the pure water fluxes (J_R) were measured again. By comparing the value of J_w, J_p, and J_R, the water flux recovery and the cleaning property of the fouled membranes were investigated. The filtration experiments were measured three times and then averaged.

The thermoresponsive experiment was also conducted on the ultrafiltration instrument (SF-SA, Hangzhou Saifei Co., China). The temperature of the feed pure water was controlled by a thermostatic water bath. Before each measurement, the membrane should be operated at 0.1 MPa under the measured temperature water for at least 30 min to ensure a consistent temperature between the water and the membranes. Then the water flux of the membranes under different temperatures was measured and calculated by the eq. (1) as shown in the filtration experiment.

RESULTS AND DISCUSSION

Polymorphism of PVDF blend membranes

FT-IR was often used to investigate the chemical composition and polymorphism behavior of PVDF blend membranes, as shown in Figure 1. The results indicated that the typical adsorption peak of C–O–C
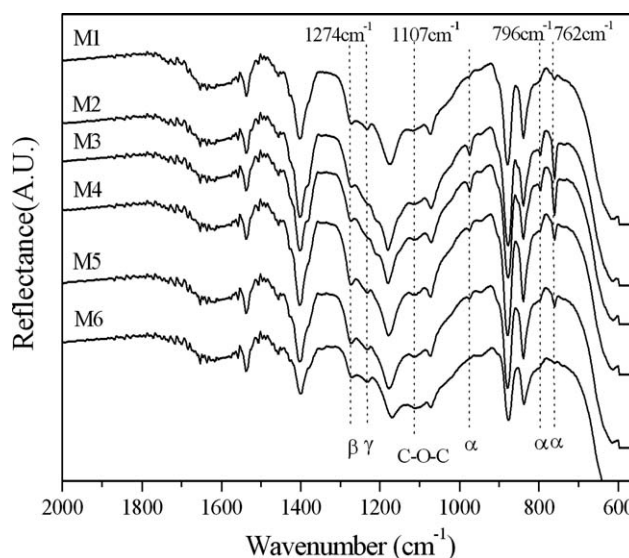

Figure 1 FT-IR spectra of PVDF blend membranes from M1 to M6, the coagulation temperature is 30°C.

of F127 appeared in 1107 cm^{-16} and the adsorption intensity increased with the increase of F127 in PVDF membranes. These phenomena indicated that F127 could migrate onto the surface of the membranes by surface segregation during the inversion precipitation process.

The crystal structure of the blend membrane was also affected by the addition of F127 in the blend membranes. As for PVDF/F127 blend membranes, lower F127 concentration in the cast solution could favor the formation of α-crystal phase. For M1, M2, and M3 membranes, three obvious IR adsorption peaks of α-crystal phase appeared at 762, 796, and 974 cm^{-1}, and only a weak β-crystal phase adsorption appeared at 1274 cm^{-1} exhibited in Figure 1. With the increase of F127 in the cast solution, the intensity of α-crystal phase decreased, and a new γ-crystal phase adsorption appeared at 1232 cm^{-1} as shown in the adsorption curves of M4, M5, and M6 blend membranes.[17] For M6 membrane, only γ- and β-crystal phase existed in the membranes, and no α-crystal phase was found. Compared with M6 membrane, there was obvious α-crystal phase adsorption in M1 membranes, which suggested that PEG was more helpful to the formation of α-crystal phase than F127 in the blend membranes.

To further explain the crystal behavior, XRD instrument was used to investigate the crystal structures of the membranes, the results were shown in Figure 2. It was indicated that the crystal peaks of α(020) and α(110) appeared at 2θ = 18.4° and 19.9° in the blend membranes from M1 to M4.[18] As for M5 and M6 membranes, the intensity of the diffraction peaks at 2θ = 18.4° decreased, and the peaks at 2θ = 19.9° disappeared with the increase of F127 in the blend membranes, and several new crystal peaks
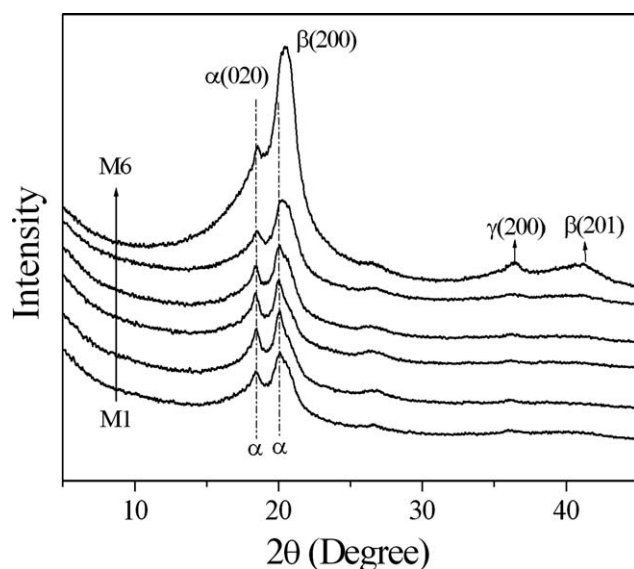
Figure 2 XRD curves of PVDF/F127 blend membranes.

such as β(200), β(201), and γ(110) appeared at 2θ = 20.4°, 41.22°, and 36.43° in M6 membrane exhibited in Figure 2, which indicated that the α-crystal phase in the blend membranes was transformed into the β- and γ-crystal phase with the increase of F127 in the membranes, which was in accordance with the results of FTIR.

FTIR results of M3 blend membrane under different coagulation temperature were also investigated as shown in Figure 3. It was indicated that mainly α-phase existed in the membranes when the coagulation temperature was above 30°C, and then with the decreasing of the coagulation temperature, the intensity of β-crystal phase became stronger and the intensity of α-crystal phase decreased exhibited in Figure 3. When the coagulation temperature decreased to 20°C, a new γ-crystal phase appeared, at this time there were three types of crystal structure existed in the membranes. These phenomena suggested that lower temperature was in favor of the formation of β-and γ-crystal phase.[17]

Studies about the crystal structure were very important to the separation properties of PVDF membranes, and many researchers have reported them, for example, PVDF membranes with mainly β- or γ-crystal phases were in favor of the pervaporation separation of EtAc/water mixture.[19] In this study, the polymorphism of PVDF blend membranes was controlled by the casting solution and the precipitation temperature during the membrane formation process.

Morphology of the membranes

The SEM images of the blend membranes were given in Figure 4. All the membranes exhibited mac-

rovoid formation in the cross sections, and with the increase of F127 in the casting solutions, the macrovoids were changed from irregular finger-like structure (M2 and M3 membranes) to regular finger-like structure (M4 and M5 membranes), and a more sponge-like structure appeared at the bottom surface of the membranes (M5 and M6 membranes). These results might be expected based on ternary diffusion models, which related pore formation to instantaneous or delayed liquid–liquid de-mixing during coagulation process.[20]

Since F127 is an amphiphilic copolymer, the presence of amphiphilic F127 component in the casting solutions might be expected to increase the affinity of the casting solution and precipitant, and lower the solvent–nonsolvent exchange. When F127 content in the casting solution was low, the phase inversion was mainly the instantaneous de-mixing which associated with macrovoid formation. But with more F127 addition, the affinity between solvent and nonsolvent became weaker which accelerated the in-diffusion rate of nonsolvent during phase inversion process. Therefore, a sponge-like structure of sublayer was obtained for M5 and M6 blend membranes.

Hydrophilic properties of the membranes

Surface hydrophilicity is one of the most important factors to the filtration membrane, and much attention has been paid to it.[21,22] Usually, the most convenient way to obtain the relative hydrophilicity of a polymer membrane surface is the contact angle measurement.

The dynamic contact angles of PVDF blend membranes were shown in Figure 5. It indicated that the
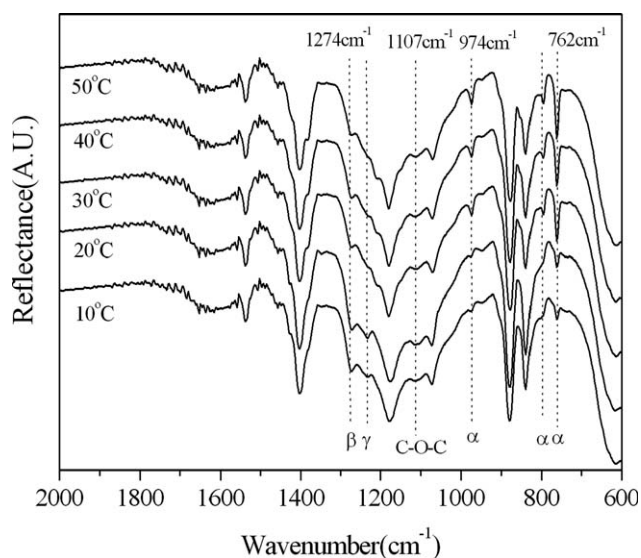

Figure 3 FTIR spectra of M3 blend membrane prepared at different coagulation temperature.
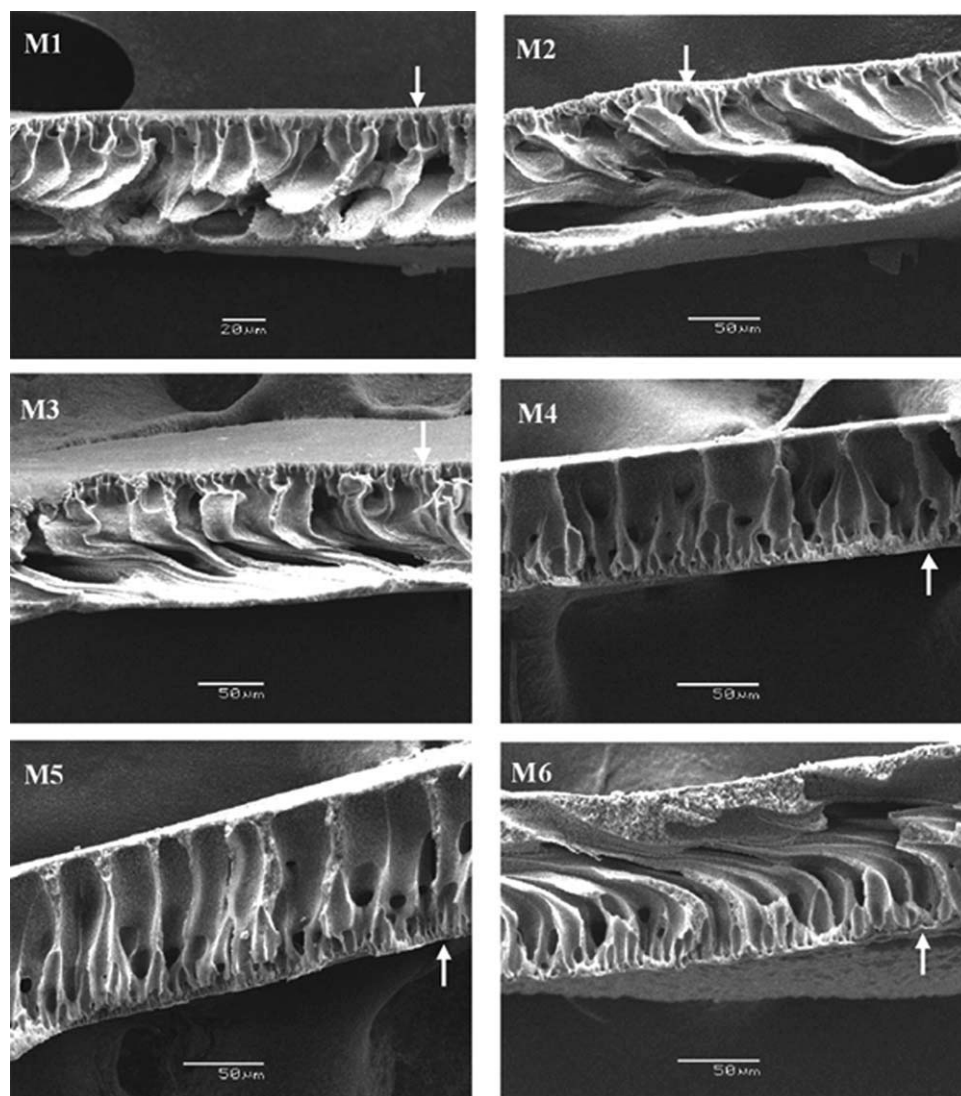
Figure 4 Cross-sectional SEM morphology of PVDF/F127 blend membranes (the arrow direction denotes the top surface of the membranes).

initial contact angles of blend PVDF membranes decreased greatly with the increase of F127 in the membranes. While PVDF membrane with PEG as the additives (M1) had an initial contact angle of 76°, and the value of contact angle had no dramatic changes during the measurement time. Compared with M1 membrane, the initial contact angle of M6 membrane decreased to 49°, which suggested that F127 was more helpful to improve the hydrophilicity of PVDF membranes than PEG. Further study also indicated that the contact angle value of the blend membrane decreased dramatically with the increase of F127 in PVDF/F127 blend membranes. As for M6 membrane, its contact angle value decreased from 49° to 34° within 40 s. So it could be inferred that F127 could increase not only the hydrophilicity of the membrane surface, but also the hydrophilicity of the internal pores of the membranes.

Thermal properties of the blend membranes

F127 is a typical thermal-sensitive copolymer besides being a good hydrophilic agent. During the membrane formation process, the coagulation temperature also has great effect on the water flux of the blend membranes, as shown in Figure 6. The results indicated that the pure water flux of the membranes decreased with the increase of the coagulation temperature. The highest water flux of the membranes reached to 94.6 L/m^2 h when the coagulation temperature was 10°C and then decreased to 62 L/m^2 h when the coagulation temperature increased to 50°C. These results indicated that the coagulation temperature could affect the surface segregation of F127 in coagulation process.

These phenomena might be explained by the hydrophilicity and thermal responsibility of F127. As a typical thermal-sensitive copolymer, F127 was more
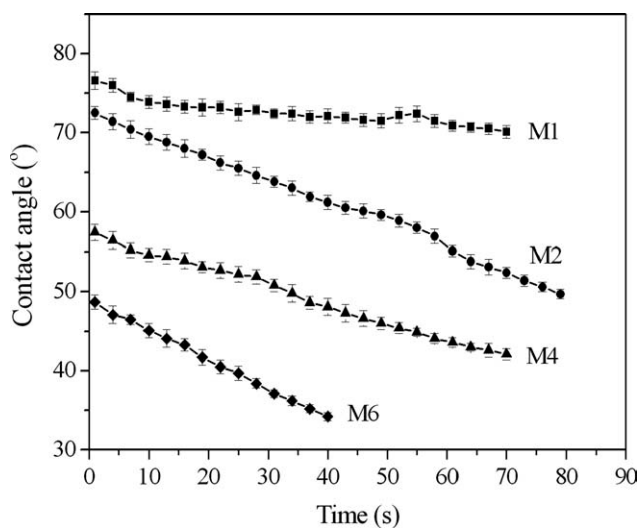
Figure 5 Time dependence of water contact angle on the membrane surfaces.

Figure 6 Effects of coagulation temperature on water flux of the blend membranes.

soluble in cold water than in hot water as a result of increased salvation and hydrogen bonding at lower temperatures.[23] The reason might be that at low temperatures in aqueous solutions, a hydration layer surrounded F127 molecules. However, when the temperature increased, the hydrophilic chains of the copolymer became desolvated as a result of the breakage of the hydrogen bonds that had been established between the solvent and these chains. So at lower temperature, the hydration layer surrounded the copolymer and made F127 migrate easily into the surface and the inner of the pores of the membrane during the phase inversion process, thus the membranes exhibited better hydrophilicity than that of the membranes prepared in higher temperature.

To study the thermal sensitivity of PVDF/F127 blend membranes, the water flux of the membranes at different temperatures was studied exhibited in Figure 7. The blend membranes (M4) with a bulk composition of 9 wt % F127 were used as the experiment system. It indicated that the water flux of the membrane increased distinctly with the increase of the temperature, while the water flux of the membrane without F127 had no obvious changes under the same condition. When the temperature decreased from 50 to 10°C, the water flux of the membrane decreased accordingly. Moreover, the increasing and decreasing curves were almost overlapped, and the transition temperature was about 25°C. These phenomena indicated that the blend membranes had the characteristic of thermal sensitivity, and the thermal sensitivity of the membranes was reversible. The reason might be explained by the molecular chain conformation of PEO and PPO segments in F127. When the temperature was below 25°C, an extended conformation of PEO chain was formed in the surface of the membrane which makes the pore size of the membrane reduced,
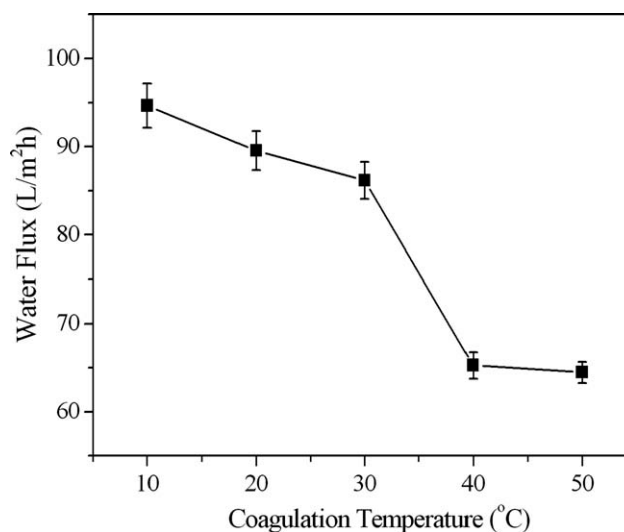
thus the water flux of the membrane was low. However, when the temperature was above 25°C, the chain conformation was changed, too. The whole chains entangled, and the chain size reduced, which would make the pore size on the surface of the membrane become larger, thus the membranes would have higher water flux. This explanation supported the mechanism of pore size control due to reversible conformational changes of surface-localized PEO chains.[9]

Filtration performance

To investigate the fouling resistance of the prepared membranes, the pure water flux and protein solution permeation process were conducted in this study, and BSA was used as a model protein. After that, the membranes were cleaned, and the pure water
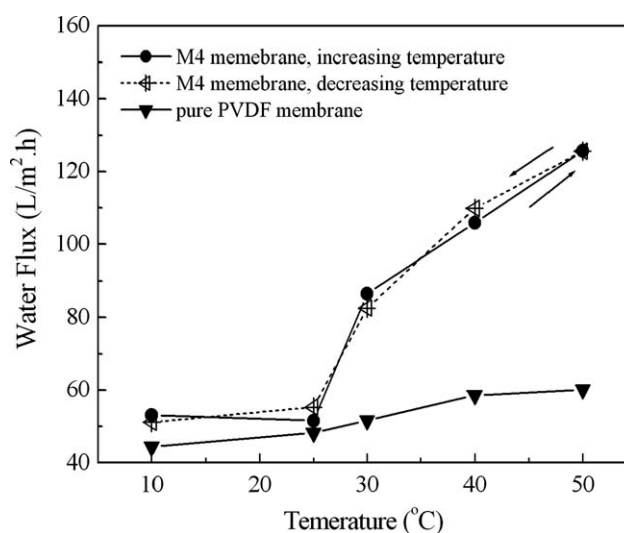

Figure 7 Water flux of M4 blend membrane and pure PVDF membrane at different experimental temperature.
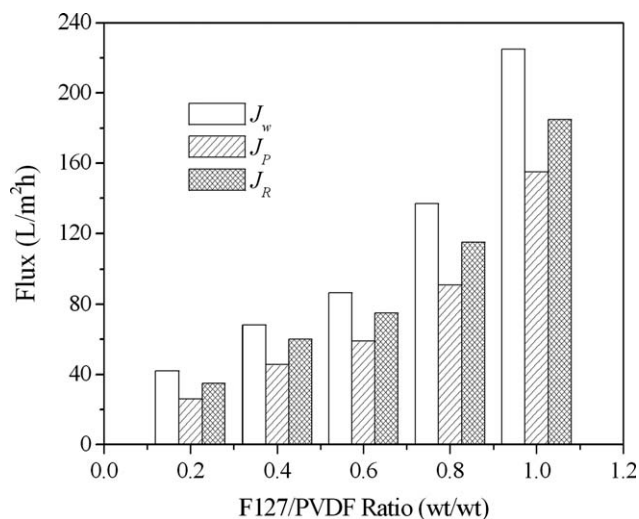
Figure 8 Pure water and BSA solution flux of the blend membranes.

flux was measured again, the results were listed in Figure 8.

In this study, F127 was added as a surface modifier and pore-forming agent during the membrane preparing process.[9] When the content of F127 was lower, the limited number of pores on the surface of the membranes would be formed, which would result in the lower flux of water and BSA solution. With the increase of F127 in the membranes, the flux of water and BSA solution of the blend membrane increased dramatically, and the highest water flux value reached to 225 L/m^2 h. These results might be ascribed to the increase of pore size and hydrophilic properties on the surface of PVDF/F127 blend membranes. As for the J_R, it could be seen that the water flux of the membranes was mostly recovered after the membranes were cleaned by deionized water, and the value of J_R increased with the increase of F127 in blend membranes. Many researches had revealed that if the water state on the surface was similar to an aqueous solution or the free water fraction was high, the protein irreversible adsorption could be reduced effectively.[21] In this study, the enrichment of the amphiphilic polymer F127 might be expected to increase the free water content on membrane surface. Thus, protein molecules had little or no conformational change when they approached the membrane surface. Therefore, irreversible protein adsorption or deposition was decreased greatly, and the water flux could be sufficiently recovered after water washing. As a result, the F127 increased the permeation and antifouling properties of PVDF membrane greatly.

CONCLUSIONS

As a multifunctional additive, Pluronic F127 was introduced into PVDF to improve the polymorphism

and properties of PVDF membranes. FTIR results showed the typical adsorption peak of C–O–C of F127 appeared in 1107 cm^{-1}, and its adsorption intensity increased with the increase of F127 in PVDF membranes, which indicated that F127 existed stably in the membranes, and some of them had migrated onto the surface of the membranes. Further study found that both F127 and coagulation temperature had great effects on the polymorphism of PVDF membranes, lower F127 concentration and higher coagulation temperature could favor the formation of α-crystal phase, but higher F127 concentration and lower coagulation temperature could promote the formation of β- and γ-crystal phase in the membranes. The results of XRD also confirmed these phenomena. SEM images showed that with the increase of F127 in the membranes, the pore structure of the membrane changed from irregular finger-like structure to regular finger-like structure, and a more sponge-like structure appeared at the bottom surface of the membranes. The water contact angle data indicated that the initial contact angles of membranes decreased from 76° to 49° with the increase of F127 in the membranes. Filtration experiment suggested that F127 could improve the permeation and antifouling properties of PVDF membrane greatly. PVDF/F127 blend membranes also had good thermoresponsive properties, and the water flux of the membrane increased distinctly with the increase of the temperature, decreased with the decrease of the temperature, and the increasing and decreasing curves were almost overlapped.

References

1. Alexandridis, P.; Hatton, T.A. Colloids Surfaces A: Physicochem Eng Aspects 1995, 96, 1.

2. Zhao, D. Y.; Feng, J. L.; Huo, Q. S.; Melosh, N.; Glenn H. Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. Science 1998, 279, 548.

3. Mohamed, A.; Ballem, J. M.; Córdoba, M. O. Micropor Mesopor Mater 2010, 129, 106.

4. Moore, T.; Croy, S.; Mallapragada, S.; Pandit, N. J. Control Rel 2000, 67, 191.

5. Wang, Y. Q.; Wang, T.; Su, Y. L.; Peng, F. B.; Wu, H.; Jiang, Z. Y. Langmuir 2005, 21, 11856.

6. Qiu, Y. R.; Rahman, N. A.; Matsuyama, H. Sep Purif Technol 2008, 61, 1.

7. Raslan, R.; Mohammad, A. W. J Appl Sci 2010, 10, 2628.

8. Wang, Y. Q.; Su, Y. L.; Sun, Q.; Ma, X. L.; Ma, X. C.; Jiang, Z. Y. J Membr Sci 2006, 28, 44.

9. Zhao, W.; Su, Y. L.; Li, C.; Shi, Q.; Ning, X.; Jiang, Z. Y. J Membr Sci 2008, 318, 405.

10. Chen, W. J.; Peng, J. M.; Su, Y. L.; Zheng, L. L.; Wang, L. J; Jiang, Z. Y. Sep Purif Technol 2009, 66, 591.
11. Wang, Y. J.; Kim, D. J Power Sources 2007, 166, 202.
12. Cui, Z. Y.; Xu, Y. Y.; Zhu, L. P.; Zhu, B. K. J Membr Sci 2008, 325, 957.
13. Escobar-Chávez, J.; López-Cervantes, M.; Naïk, A.; Kalia, Y. N. J Pharm Pharmaceut Sci 2006, 9, 339.
14. Kim, S. Y.; Ha, J. C.; Lee, Y. M. J Control Rel 2000, 65. 345–358.
15. Du, C. H.; Zhu, B. K.; Xu, Y. Y. J Appl Polym Sci 2007, 104, 2254.
16. Zhang, M.; Zhang, A. Q.; Zhu, B. K.; Xu, Y. Y. J Membr Sci 2008, 319, 169.
17. Du, C. H.; Zhu, B. K.; Xu, Y. Y. J Mater Sci 2006, 41, 417.
18. Hasegawa, R.; Takahashi, Y.; Chatani, Y. Polym J 3: 600 1972.
19. Tian, X. Z.; Jiang, X.; Zhu, B. K.; Xu, Y. Y. J Membr Sci 2006, 279, 479.
20. Li, J. H.; Xu, Y. Y.; Wang, J. H.; Du, C. H. Chin J Polym Sci 2009, 27(6):821.
21. Zhao, Y. H.; Zhu, B. K.; Kong, L.; Xu, Y. Y. Langmuir 2007, 23, 5779.
22. Mackay, M. E.; Carmezini, G. Chem Mater 2002, 14, 819.
23. Jorgensen, E.; Hvidt, S.; Brown, W.; Schillen, K. Macromolecules 1997, 30, 2355.