Preparation of Polyvinylidene Fluoride Membrane Via a Thermally Induced Phase Separation Using a Mixed Diluent

Xiaolong Lu, Xianfeng Li

Key Laboratory of Hollow Fiber Membrane Materials and Membrane Process of Ministry of Education, Tianjin Polytechnic University, 300160, China

Received 19 February 2008; accepted 3 February 2009
DOI 10.1002/app.30184
Published online 17 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyvinylidene fluoride (PVDF) membranes were prepared via a thermally induced phase separation method with a mixed diluent (dibutylphthalate/dioctyl phthalate). The effects of PVDF concentration and cooling bath temperature (CBT) on the structure and properties of the membranes were investigated. Scanning electron microscopy photos showed that the cross-section of all the membranes, regardless of PVDF concentration and CBT, presented a bi-continuous structure with the spherulitic pattern; moreover, the spherulitic patterns became clear gradually from the top surface to the bottom surface, and the top surface was denser than the bottom surface. As a result, all the membranes exhibited an asymmetric structure. The membrane property measurement indicated that, as PVDF concentration increased from 25 to 35 wt %, the pure water flux (PWF) decreased from 342 to 80 L $m^{-2} h^{-1}$, and the porosity decreased slightly, whereas the minimum bubble point pressure (BPP) increased, which indicates maximum pore size decreased. In addition, with the increase in CBT, the PWF increased, but, the minimum BPP and porosity decreased. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1213–1219, 2009

Key words: polyvinylidene fluoride; membrane; thermally induced phase separation (TIPS); property; structure

INTRODUCTION

More studies are focusing on preparing polyvinylidene fluoride (PVDF) membrane via a thermally induced phase separation (TIPS) due to the excellent physical and chemical properties of PVDF and the various advantages of TIPS method.[1–13] However, these jobs, other than some patents, are still in the earlier stage of membrane preparation and have not touched on the membrane properties. It is very difficult to prepare PVDF membrane with good properties by using the TIPS method because few kinds of solvents in industrial products can be selected as the diluent. In our previous work,[9] bi-continuous morphology was obtained by using a kind of mixed diluent (MD)—dibutyl phthalate (DBP) and dioctyl phthalate (DOP); however, the practical properties were not presented because of the membrane samples were too small.

In this article, the proper membrane samples were cast by employing a kind of MD under an elevated temperature environment. The structure and properties of the membranes were characterized by scanning electron microscopy, pure water flux (PWF), minimum bubble point pressure (BPP), and porosity.

MATERIALS AND METHODS

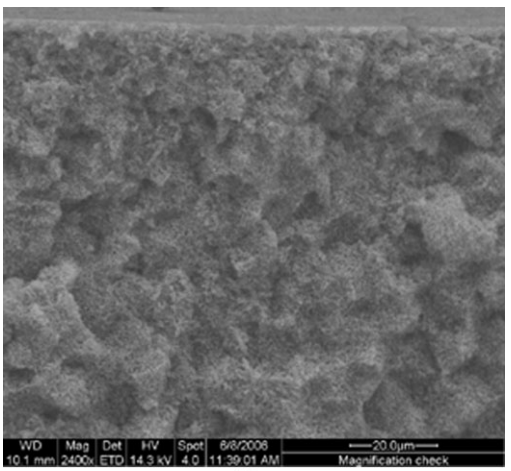
Materials

PVDF (solef1010, melt flow index 2 at 2.16 kg) was supplied by Solvay (Tavaux, France). Both DBP (density, 1.046 g/cm^3; boiling point, 340°C) and DOP (density, 0.985 g/cm^3; boiling point, 370°C) are analytical grade (Tianjin Yongda Chemical Reagent, Tianjin, China). Ethanol is industrial product.

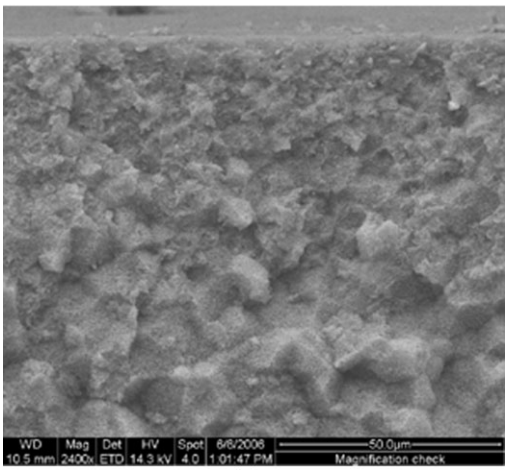
Membrane preparation

PVDF/MD mixtures were shaken in flasks at 220°C under nitrogen until forming a homogeneous solution, kept still 2–4 h to degas, and then transferred to a stainless steel trough to form film by drawknife in an elevated temperature environment. The film was solidified by quenching in the water bath at a specific temperature and then put into the industrial grade ethanol bath to extract MD. The ethanol bath was changed three times once every 12 h and then

Correspondence to: X. Li (xianfengli022@yahoo.com.cn).
Contract grant sponsor: Open Program of Key Laboratory of Hollow Fiber Membrane Materials and Membrane Processes of Ministry of Education; contract grant number: 060518.
Contract grant sponsor: Science Council of Tian Jin.



(a)



(b)

Figure 1 Asymmetric structure of membrane cross-section (a, 25%; b, 35%; 20°C cooling temperature).

the membrane samples were prepared and kept in ethanol bath for further characterization. The ratio of DBP/DOP in MD is 5/5. Both PVDF concentrations and diluent composition are presented in weight percentage (wt %).

Membrane characterization

Structure

Membranes were taken out from ethanol, dried naturally at room temperature, fractured in liquid nitrogen, and coated with gold. The surface and cross-sectional morphologies were observed by using a scanning electron microscopy (Quanta 200, Netherlands FEI).

Pure water flux

The pre-wet membranes were prepared by putting ethanol-saturated membrane into pure water enough times (over 24 h). The PWF of the pre-wet membrane was measured with a stainless cell (effective area, 11.9 cm^2) at a transmembrane pressure of 0.1 MPa and a constant feed flow rate. After running 15 min, the flux was calculated according to the time of collecting 10 mL water.

Minimum bubble point pressure

The minimum BPP was used for characterizing the maximum pore size, which was measured by using pure ethanol by nitrogen pressure (minimum BPP is inversely responded to maximum pore size). By slowly increasing nitrogen pressure, the pressure of the first bubble was recorded for minimum BPP.

Porosity

The membrane porosity (ε) is defined as the pores volume divided by the total volume of the porous membrane. It can be determined by gravimetric method:

$$\varepsilon = \frac{(W_w - W_d)/\rho_W}{(W_w - W_d)/\rho_W + W_d/\rho_P} \times 100\% \qquad (1)$$

where W_w and W_d are the weights of the wet and dry membranes, respectively. ρ_W is the water density, and ρ_P is the polymer density (1.78 g/cm^3) that comes from PVDF material density. The wet membrane is the water-saturated membrane, and the dry membrane originates from the wet membrane, which is fully dried.

Differential scanning calorimetry

About 10 mg samples were measured by DSC (Perkin-Elmer, DSC-7, Wellesley, MA) from room temperature to 200°C at 10°C/min heat rate. Crystallization heat ΔH_c was determined from the exothermic peak area. The degree of crystallinity was evaluated by

$$\Phi_{\mathrm{DSC}} = \Delta H_m / \Delta H_{100}$$

$\Delta H_{100} = 104.7$ J/g is the melting enthalpy for a 100% crystalline sample of PVDF.[14]

RESULTS AND DISCUSSION

Effect of concentration on the structure and properties

The structure of membranes is shown in Figures 1–3. It can be seen from Figures 1 and 2 that the membranes present an asymmetric structure. Specifically, the cross-sections of the membranes (Fig. 3) exhibit a bi-continuous structure with spherulitic pattern for all the PVDF concentrations. Furthermore, the

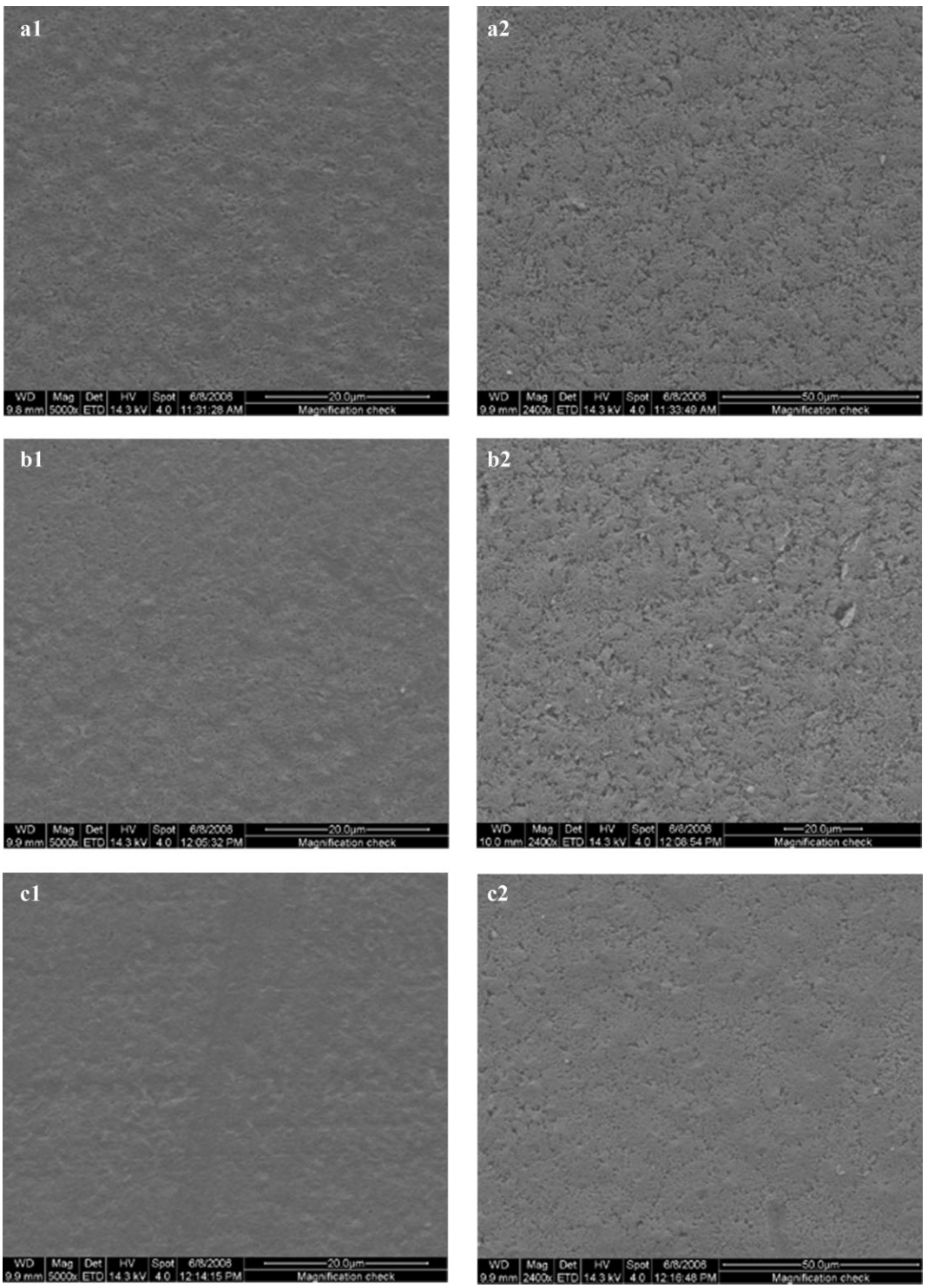
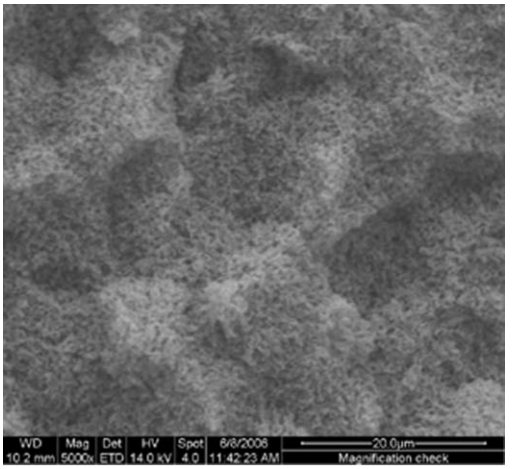


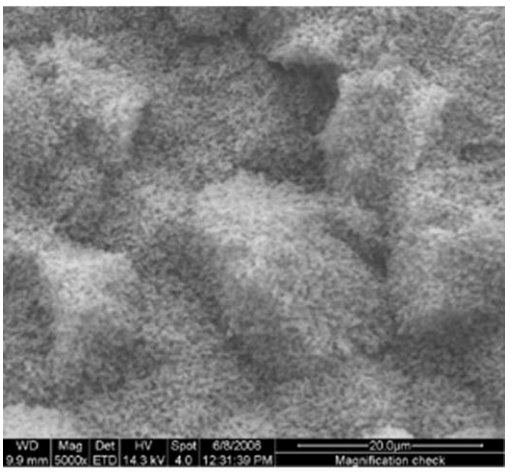
Figure 2 Effect of concentration on the top- and bottom-surface structure (a, 25%; b, 30%; c, 35%, 1, top surface; 2, bottom surface; 20°C cooling temperature).

spherulitic patterns are hardly discernible near the top surface of membrane but gradually become more prominent and larger near the bottom surface. Because there is no clear boundaries among spherulites, but there are still some faint patterns of spherulites, especially near the bottom surface, the membranes are considered bi-continuous structures with a spherulitic pattern.

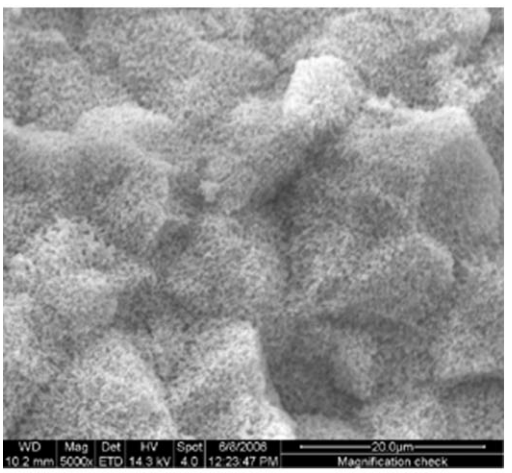
Comparing the top surface and bottom surface of the same membrane reveals significant differences in the structure. The bottom surface presents a porous, lacy structure, and the top surface is denser and



(a)



(b)



(c)

Figure 3 Effect of concentration on the cross-section structure (a, 25%; b, 30%; c, 35%; 20°C cooling temperature).

TABLE I
Effect of Concentration on the Minimum BPP (MPa)

PVDF concentration (wt %)	25	30	35
Minimum BPP (MPa)	0.31	0.40	>0.50

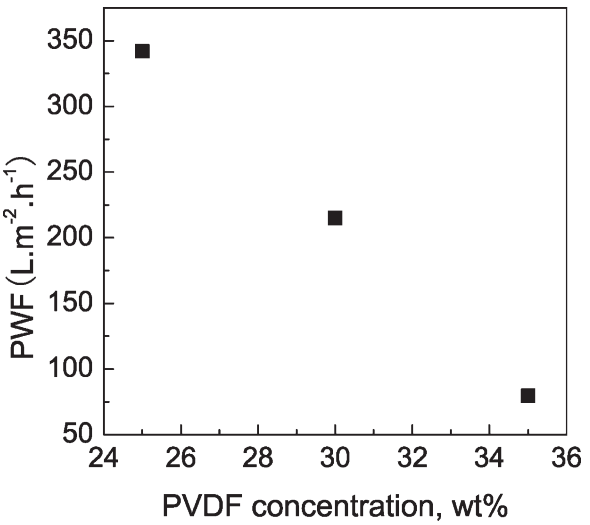


Figure 4 Effect of concentration on PWF.

smoother. Moreover, with the increase of concentration, the porosity of the whole membrane decreases. By contrast, the membrane in our previous work[9] presented an isotropic structure. This results from the different membrane casting processes. In the previous study,[9] the membrane was formed between two glass slices clipped by two alloyed plates, and thus, the diluent was not easy to evaporate; moreover, the cooling conditions of the top and bottom surface were the same. As a result, the whole body of membrane presented a symmetric morphology. In this study, however, the top surface is nakedly exposed to an elevated temperature environment in the casting process. This is favorable to the MD evaporation, which tends to result in a denser surface. Still, the difference of cooling rates between the top and bottom surface (the cooling rate of the top

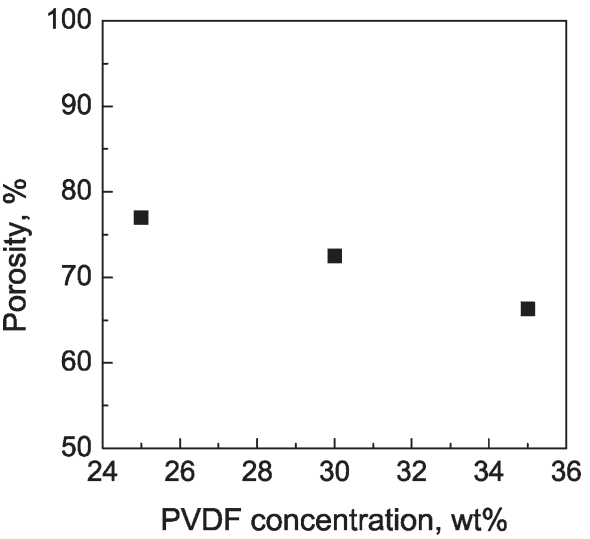


Figure 5 Effect of concentration on the porosity.

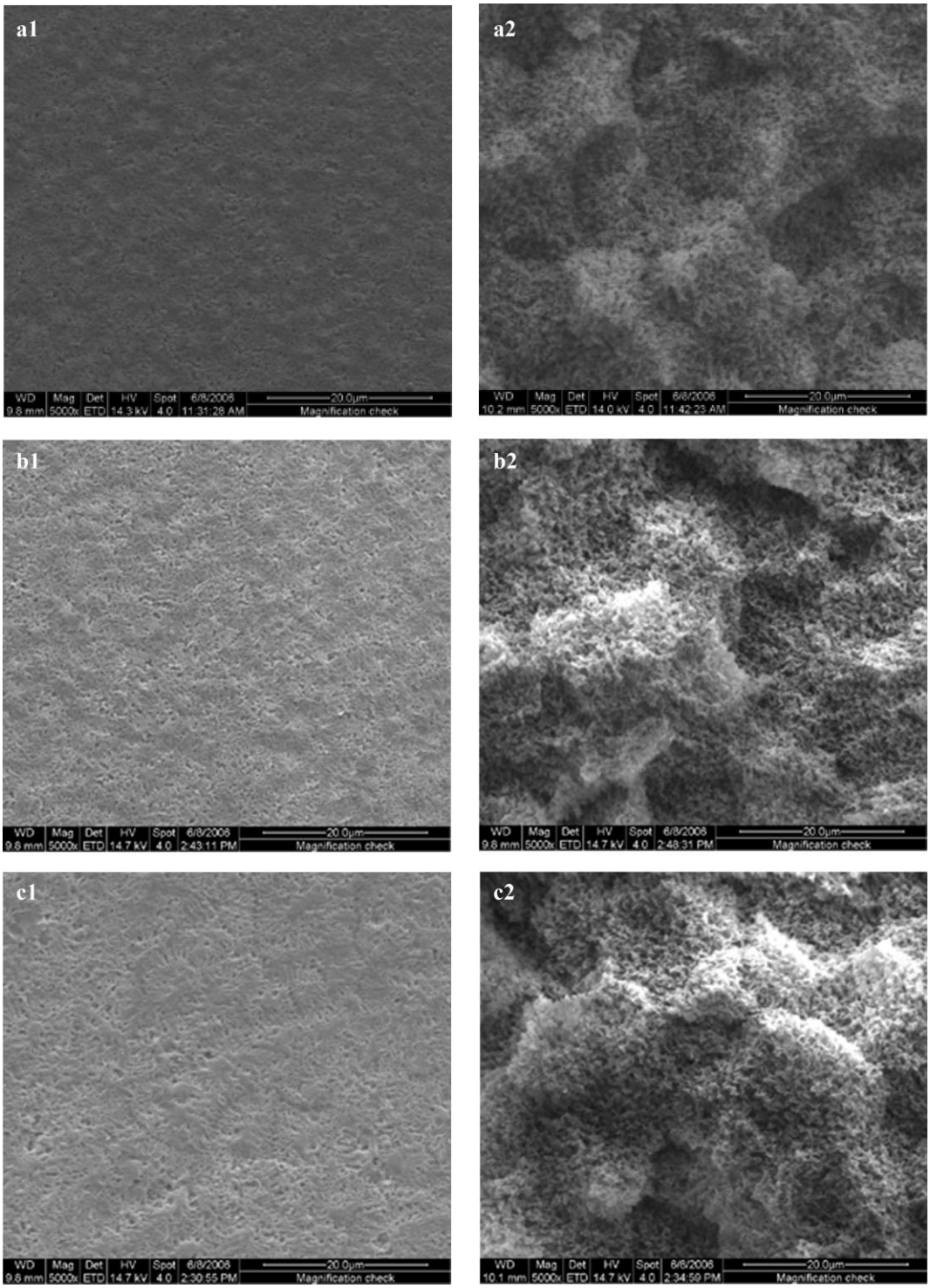


Figure 6 Effect of CBT on the structure (a, 20°C; b, 30°C; c, 50°C; 1, top surface; 2, cross-section).

surface is higher than that of the bottom surface) is another reason of an asymmetric structure.

As shown in Figure 3, with the concentration increasing, the change of spherulitic pattern is slight. It displays that the effect of the concentration on the cross-section structure is insignificant.

The minimum BPP, PWF, and porosity of the membrane are shown in Table I and Figures 4 and 5, respectively. The PWF of the membrane decreases from 342 to 80 L m^{-2} h^{-1} as PVDF concentration increases from 25 to 35%, and the porosity also decreases correspondingly, whereas the minimum BPP increases (the maximum pore size decreases).

This development trend with the concentration is a normal phenomenon, because the membrane pore mainly comes from the space occupied by the

TABLE II
Effect of CBT on the Minimum BPP (MPa)

CBT (°C)	20	30	50
Minimum BPP (MPa)	0.40	0.30	0.27

diluent, while the content of diluent decreases with the increase of PVDF concentration, and then the porosity and PWF decrease.

Effect of cooling bath temperature on the structure and properties

Figure 6 indicates the surface and cross-section morphology of membrane in the case of 30% PVDF concentration. Bi-continuous structure with a spherulitic pattern still characterizes the body of membrane and had no clear change when CBT enhanced.

The effects of CBT on the properties of PVDF membrane were studied in the case of 30% PVDF concentration. As shown in Table II, Figures 7 and 8, with CBT enhancing, PWF increases, and the minimum BPP and porosity decrease, which shows maximum pore size increases (Fig. 8). The above results were also presented in some literature.[15,16] The membrane structure is related to the coarsening process after liquid–liquid phase separation. The detailed discussion can refer to the literature.[17,18] In all cases, the coarsening often results in a reduction in the number of droplets and an increase in the droplet size. The coarsening process will be prolonged with the quenching temperature increasing, that is to say, there are more times for the development of droplet size. Therefore, maximum pore size and PWF increase with the increase of CBT.

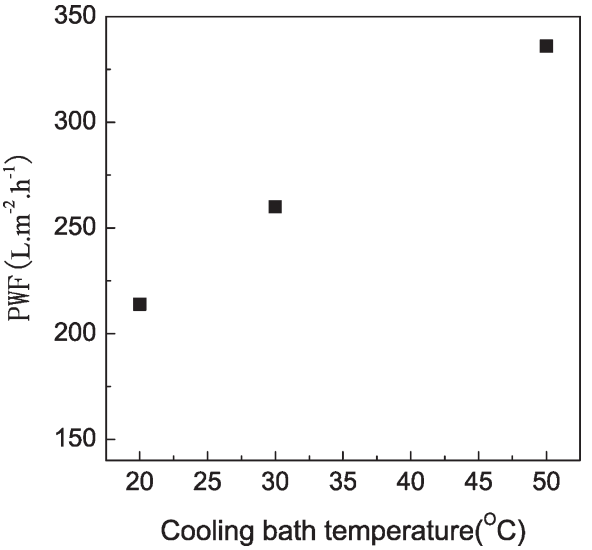


Figure 7 Effect of CBT on PWF.

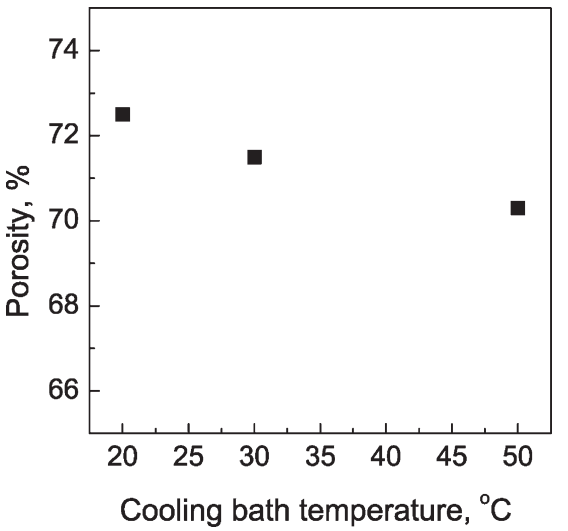


Figure 8 Effect of CBT on the porosity.

The crystallization of the membrane was investigated by DSC to find the reasons the porosity decreases with CBT increasing. As a result, it was found that the melt heat increased from 65.96 to 68.44 J/g with increasing the cooling bath temperature from 20 to 50°C, which shows crystallinity enhances slightly. It may be a reason influencing the porosity. It is well known that higher temperature is favorable to the crystallization of polymer. This would influence the microstructure of membrane, that is to say, more or bigger crystallites would push more diluent outside of membrane, thus decreasing the porosity of the membrane.

In contrast with the previous work,[9] DSC curves shown in Figure 9 still display the multiple melt peaks. However, there is no obvious change in peak temperature site and shape as CBT increases.

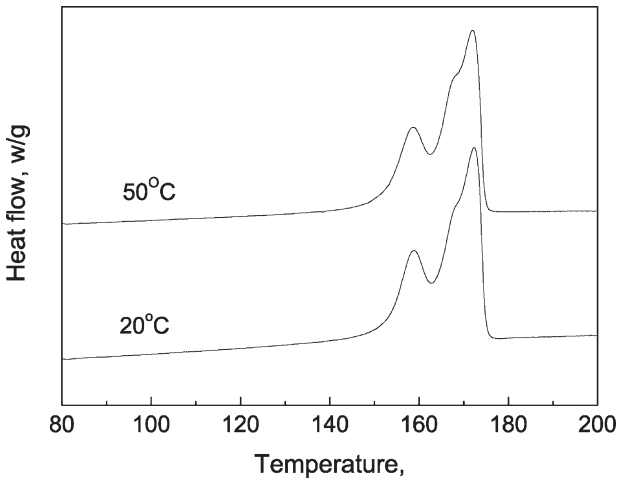


Figure 9 DSC curves of membrane from the different CBTs.

CONCLUSION

The cross-section of all the membranes exhibited a bi-continuous structure with the spherulitic pattern; moreover, the spherulitic pattern near the top surface was smaller (even illegible) than that near the bottom surface, and the skin of the top surface was denser than that of the bottom surface. Hence, the membranes presented an asymmetric structure. The properties of membrane were tested by PWF, minimum BPP, and porosity. As PVDF concentration increased, the PWF and porosity of membrane decreased, and the minimum BPP increased, which revealed that the maximum pore size decreased. When CBT increased, the porosity and minimum BPP decreased slightly, which led to the increase of PWF.

References

1. Lloyd, D. R.; Kinzer, K. E.; Tseng, H. S. J Membr Sci 1990, 52, 239.
2. Hamanaka, K.; Shimizu, T. Eur. Pat. Appl. 1,369,168 (2003).
3. Takamura, M.; Yoshida, H. U.S. Pat. 6,299,773 (2001).
4. Doi, Y.; Matsumura, H. U.S. Pat. 5,022,990 (1991).
5. Smith, S. D.; Shipman, G. H.; Floyd, R. M.; Freemyer, H. T.; Hamrock, S. J.; Yandrasits, M. A.; Walton, D. G. S. U.S. Pat. 2,005,058,821 (2005).
6. Gu, M. H.; Zhang, J.; Wang, X. L.; Ma, W. Z. J Appl Polym Sci 2006, 102, 3714.
7. Gu, M. H.; Zhang, J.; Wang, X. L.; Tao, H. J.; Ge, L. T. Desalination 2006, 192, 160.
8. Li, X. F.; Lu, X. L. J Appl Polym Sci 2006, 101, 2944.
9. Li, X. F.; Xu, G. Q.; Lu, X. L.; Xiao, C. F. J Appl Polym Sci 2008, 107, 3630.
10. Ji, G. L.; Du, C. H.; Zhu, B. K.; Xu, Y. Y. Polymer 2007, 48, 6415.
11. Ji, G. L.; Zhu, B. K.; Cui, Z. Y.; Zhang, C. F.; Xu, Y. Y. J Appl Polym Sci 2007, 105, 1496.
12. Su, Y.; Chen, C. X.; Li, Y. G.; Li, J. D. J Macromol Sci Pure Appl Chem 2007, 44, 305.
13. Cha, B. J.; Yang, J. M. J Membr Sci 2007, 291, 191.
14. Marega, C.; Marigo, A. Eur Polym J 2003, 39, 1713.
15. Matsuyama, H.; Okafuji, H.; Maki, T.; Teramoto, M.; Kubota, N. J Membr Sci 2003, 223, 119.
16. Shang, M. X.; Matsuyama, H.; Teramoto, M.; Lloyd, D. R.; Kubota, N. Polymer 2003, 44, 7441.
17. Kim, W. K.; Char, K.; Kim, C. K. J Polym Sci Part B: Polym Phys 2000, 38, 3042.
18. Song, S.-W.; Torkelson, J. M. Macromolecules 1994, 27, 6389.