

# Supercritical Carbon Dioxide Extraction in Membrane Formation by Thermally Induced Phase Separation

Chun-Fang Zhang, Bao-Ku Zhu, Gen-Liang Ji, You-Yi Xu

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Received 12 December 2005; accepted 17 March 2006

DOI 10.1002/app.24620

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

**ABSTRACT:** In this study, a novel and environmentally friendly extracting method, supercritical carbon dioxide (SC-CO<sub>2</sub>) extraction, was investigated in the thermally induced phase separation (TIPS) process for making microporous membranes. In the SC-CO<sub>2</sub> extraction, the effects of extraction time, pressure, and temperature on the extraction fraction, membrane morphology, and membrane performance were investigated. It was concluded that with extraction conditions of 18 MPa, 35°C and 2 h, the porous membrane had the highest extraction fraction. There was a close relationship between membrane performance and the

extraction conditions of SC-CO<sub>2</sub>, and it is possible to tailor membrane performance through the choice of extraction conditions. Compared with traditional solvent extraction, a dry membrane treated by SC-CO<sub>2</sub> extraction has much less shrinkage and greater water permeability, whereas the degree of crystallization of a membrane extracted by SC-CO<sub>2</sub> is slightly greater than that extracted by ethanol. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1632–1639, 2007

**Key words:** extraction; membranes; polyethylene; supercritical carbon dioxide; phase separation

## INTRODUCTION

Recently, the thermally induced phase separation (TIPS) technique is one of the most effective ways to prepare microporous membranes.<sup>1,2</sup> In contrast to other conventional membrane preparation methods such as solvent casting, stretching, track etching, and so on, the TIPS technique has been reported to be applicable to a wide variety of polymers and to allow greater flexibility, higher reproducibility, and effective control of the final pore size of membrane.<sup>3</sup> The TIPS process begins by dissolving a polymer in a diluent at high temperature. The solution is then cast or extruded into the desired shape (flat sheet, hollow fiber, etc.) and cooled to induce phase separation and polymer solidification (crystallization or glass transition). The diluent that remains in the membrane is extracted by solvent exchange, and the extractant is usually evaporated to yield a microporous structure.<sup>4–12</sup>

Many previous studies indicated that replacing diluent with extractant could cause the membrane to either swell or contract, and the evaporation of the extractant would result in contraction of the membrane from surface tension.<sup>13,14</sup> Surface tension at liquid–gas interfaces is responsible for the pressure

decrease at the pore wall of the membrane during the evaporation, which can be understood by the Laplace equation.<sup>15</sup> Furthermore, large amounts of expensive, harmful, and partly flammable extractants used in TIPS process have to be recycled because of cost and environmental laws. Hence, an expensive closed cycle of the process stream is required. In addition to these disadvantages, the extraction efficiency of the traditional solvent extraction method may be limited by the speed of diffusion between the diluent and the extractant.

Compared with the traditional solvent extraction, the extraction process with SC-CO<sub>2</sub> has the following advantages. On the one hand, SC-CO<sub>2</sub> can dry the polymer membrane rapidly without collapsing the structure because of the absence of a liquid–vapor interface. This advantage is very important for keeping the primal morphology of the membrane.<sup>16</sup> On the other hand, diluent dissolved in the SC-CO<sub>2</sub> can be easily recycled from the gaseous CO<sub>2</sub> after the pressure is diminished. The nontoxicity, nonflammability, and inexpensiveness of CO<sub>2</sub> are also advantages of this process and favor its industrial use.<sup>17</sup> The use of SC-CO<sub>2</sub> fluid in extraction was widely studied in the early 1980s, and SC-CO<sub>2</sub> fluid was commercialized for use in several industries, for example, coffee and tea decaffeination, natural product extraction, and chromatography.<sup>18–21</sup> But there is very little in the literature about the application of SC-CO<sub>2</sub> to membrane extraction in the TIPS process.

In the present study, ultrahigh-molecular-weight polyethylene/liquid paraffin (UHMWPE/LP) films

Correspondence to: You-Yi Xu (opl-yyxu@zju.edu.cn).

Contract grant sponsor: National 973 Foundation of China; contract grant number: 2003.CB615705.

were extracted using two methods: ethanol extraction and SC-CO<sub>2</sub> extraction. We investigated the influence of the extraction conditions of SC-CO<sub>2</sub> on the extraction fraction of LP. The porous structure and performance of the membranes in different conditions as well as the effects of two different extracting methods on membrane shrinkage and porous structure were also studied.

## EXPERIMENTAL

### Materials

UHMWPE was kindly supplied by the Beijing No. 2 Auxiliary Agent Factory (China). The viscosity average molecular weight was  $2.5 \times 10^6$ . LP obtained from Hangzhou Chemical Reagent Co., Ltd. (China), was used as the diluent without further purification. Ethanol and CO<sub>2</sub>, which were used as the extractant for wet UHMWPE/LP films, were purchased from Shanghai Chemical Reagent Factory and Hangzhou Jingong Specialty Gases Co., Ltd. (China), respectively.

### Membrane preparation

A homogeneous polymer–diluent sample with a polymer concentration of 10 wt % was prepared in the mixing chamber of the rheometer (HAAKE HBI System 90). Then the solid sample was chopped into small pieces and placed between two pieces of aluminum foil. To prevent loss of diluent by evaporation during the TIPS process, Teflon film with a thickness of 130 μm and a square opening in the center was inserted between the pieces of aluminum foil. After being heated on a hot stage (self-made) at 473.5 K for 5 min, each sample was cooled to room temperature in the air. Then the diluent in the membrane was extracted by SC-CO<sub>2</sub> or ethanol.

### SC-CO<sub>2</sub> extraction procedures

A schematic diagram of the supercritical fluid extractor used in this study was previously described in detail.<sup>22</sup> The wet films were placed in the extraction cell. CO<sub>2</sub> was delivered from the CO<sub>2</sub> cylinder at a pressure of about 5.3 MPa to the extraction cell and compressed to the predetermined extraction pressure by the syringe pump. Simultaneously, CO<sub>2</sub> was heated to reach the predetermined extraction temperature. After extraction was finished, SC-CO<sub>2</sub> fluid was directed to the separation cell, where CO<sub>2</sub> and LP were separated because of the decrease in pressure.

The extraction fraction of SC-CO<sub>2</sub> was calculated from the ratio of the amount of extracted diluent to the initial diluent in the membrane. To determine the initial concentration of LP in the wet membrane, a known mass of wet membrane was wrapped in

filter paper and immersed in agitated ethanol for 48 h to extract the LP diluent. The sample was then dried for 24 h in a vacuum oven. Because a 100 wt % UHMWPE sample showed negligible weight loss, the difference in the weight of the sample before and after immersion was the amount of LP in the original membrane.<sup>23</sup> The amount of extracted diluent was determined by the following equation:

$$W_{\text{ed}} = W_{\text{wet}} - W_{\text{dry}} \quad (1)$$

where  $W_{\text{ed}}$  is the amount of extracted diluent and  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the membrane before and after extraction.

### Characteristics of membranes

DSC measurements were conducted on a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating rate of 10°C/min. The specimens were weighed in the range of 3–5 mg. During measurement, dried N<sub>2</sub> gas was purged at a constant flow rate. The degree of crystallinity ( $X_{\text{DSC}}$ ) was determined according to

$$X_{(\text{DSC})} = \frac{\Delta H_f}{\Delta H_f^0} \quad (2)$$

where  $\Delta H_f$  and  $\Delta H_f^0$  are the melting enthalpies of the UHMWPE membrane and 100% crystallized PE, respectively, and  $\Delta H_f^0$  is 273 J/g.<sup>24</sup>  $\Delta H_f$  was acquired through the integral area of a DSC heating curve.

Wide-angle X-ray diffraction (WAXD) patterns were recorded with an X-ray diffractometer (XD-98, Philips X light pipe). The crystalline diffraction and the amorphous component were separated with a fitting program that allowed the crystallinity of the sample to be estimated.

The dry membranes for scanning electron microscopy (SEM) were cryogenically fractured in liquid nitrogen and then sputtered with gold to a thickness of 200–300 Å using a Jeol JFC-1100E Ion Sputtering Device. A Hitachi<sup>®</sup> S-520 field emission scanning electron microscope was employed to view the morphology in cross section and the surface of the membrane.

### Membrane shrinkage test

The wet UHMWPE/LP membranes were cut into samples 2 × 2 cm in size, which were then measured. In the ethanol extraction, three samples were immersed in a bottle that contained approximately 200 mL of ethanol. The membranes were soaked overnight to allow LP–ethanol exchange and then air-dried at room temperature. Membrane size was then measured again. In the SC-CO<sub>2</sub> extraction, three

membranes were placed in the extraction cell, and the final dimensions were measured when extraction was finished. The length and width of the membranes were measured with a ruler (accurate to 0.05 cm), and membrane thickness was measured with a micrometer. The relative dimensions reported below are the final dimensions divided by the initial dimensions.

### Membrane porosity

The porosity ( $P$ ) was calculated from the density of the membrane ( $\rho_m$ ) and the density of pure UHMWPE ( $\rho_p = 0.935 \text{ g/cm}^3$ ):

$$P = 1 - \frac{\rho_m}{\rho_p} \quad (3)$$

Membrane density was determined by exact measurement of the volume and weight of the membrane.<sup>25,26</sup>

### Water permeability

Water flux was performed with an ultrafiltration cell with an effective membrane area of  $32.15 \text{ cm}^2$  (SCM-300, China). The experiments were conducted using compressed distilled water as the permeate. The membranes were initially pressurized with distilled water at 0.15 MPa for 0.5 h in order to compact the membranes to get a constant flux. And then the steady-state water flux was measured at 0.1 MPa.

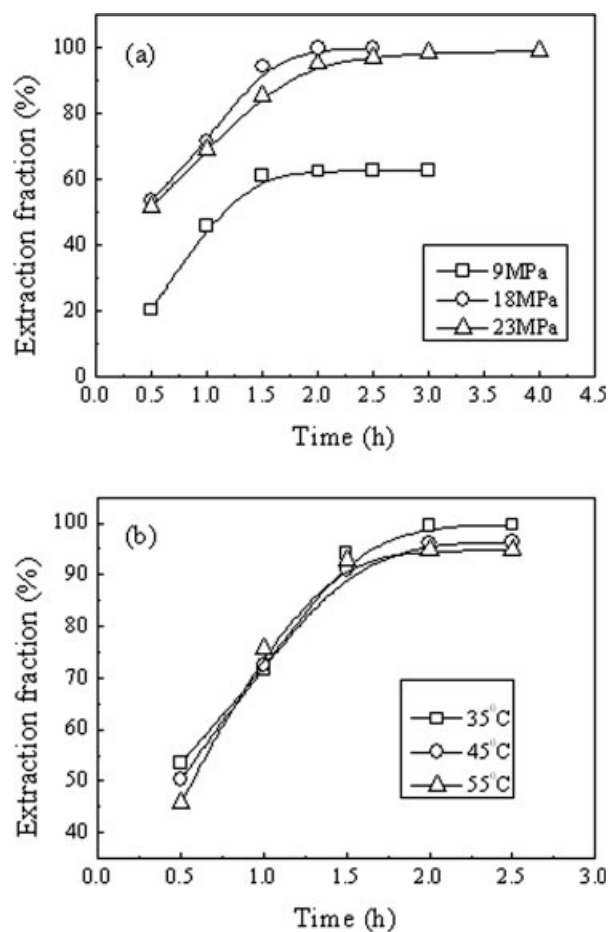
## RESULTS AND DISCUSSION

### Effects of SC-CO<sub>2</sub> extraction conditions on membranes

The main advantage of a supercritical fluid over the conventional extracting liquid is that its properties, that is, its density, solvating power, viscosity, and solute diffusivity, can be controlled by varying the applied pressure and temperature.<sup>27</sup> This leads to greater selectivity, rapid mass transfer, and higher flow rates compared with those in liquids. Therefore, SC-CO<sub>2</sub> can be used as an extractant in the membrane formation process via TIPS. A systematic study was conducted to optimize the extraction conditions—time, pressure, and temperature—of SC-CO<sub>2</sub>. When one variable was changed to study its effect, all other variables were kept constant.

#### Extraction time of SC-CO<sub>2</sub>

Figure 1 shows the relationship between extraction time and the extraction fraction of LP with different SC-CO<sub>2</sub> pressures and temperatures, where the ini-

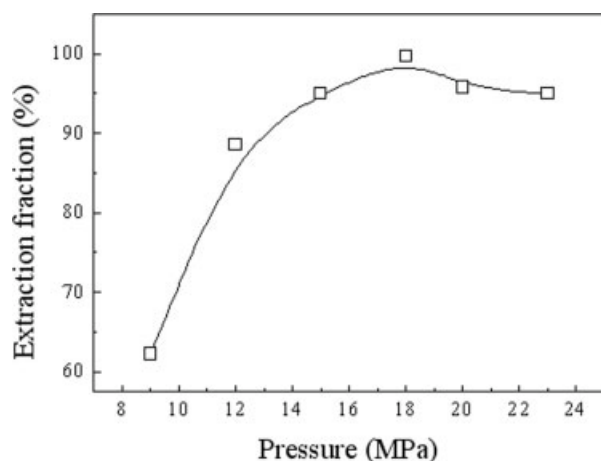


**Figure 1** Effect of extraction time on the extraction fraction of LP at different (a) pressures and (b) temperatures.

tial LP concentration was 90 wt %. It can be seen from Figure 1(a,b) that the extraction fraction of LP first increased with increasing extraction time and then remained nearly constant for all systems. This means the system reached the extraction equilibrium. The time required to achieve the extraction equilibrium varied with extraction pressure and temperature. The trend of diffusion with pressure was  $9 \text{ MPa} > 18 \text{ MPa} > 23 \text{ MPa}$  [Fig. 1(a)], and the trend of diffusion with temperature was  $55^\circ\text{C} > 45^\circ\text{C} > 35^\circ\text{C}$  [Fig. 1(b)]. This can be explained by the low diffusion rate of LP in SC-CO<sub>2</sub> at high pressure or low temperature.

#### Pressure of SC-CO<sub>2</sub>

Pressure is one of the most important physical parameters and has both theoretical and practical implications in SC-CO<sub>2</sub> extraction. A series of experiments were performed to determine the effect of pressure on the extraction fraction of LP at  $35^\circ\text{C}$  in the pressure range from 9 to 23 MPa (see Fig. 2).



**Figure 2** Effects of pressure on the extraction fraction of LP (temperature: 35°C; time: 2 h).

The original concentration of LP and was 90 wt %, and the original extraction time was 2 h.

The extraction fraction of LP increased with increasing pressure when the pressure was less than 18 MPa and decreased slightly when the pressure was more than 18 MPa. The extraction fraction was 99.6% at 18 MPa and was higher than that at any other pressure. This can be explained qualitatively as follows. Together with temperature, pressure defines the density of a supercritical fluid, which is directly correlated to a solute's equilibrium solubility.<sup>22,28</sup> It is correct to say that the maximum equilibrium solubility of a solute is achieved at the highest density of a supercritical fluid at a given temperature.<sup>29</sup> The density of CO<sub>2</sub> sharply increases in a range of about 7.0–18.0 MPa in the supercritical region at 35°C. Over this range, the effect of pressure on the density of CO<sub>2</sub> obviously decreases.<sup>30</sup> But the higher pressure, the higher is the viscosity of a supercritical fluid. The higher viscosity is unfavorable to the diffusion of LP in an SC-CO<sub>2</sub> fluid. The results shown in Figure 1(a) could clarify the impact of equilibrium solubility versus viscosity at different pressures. The time-dependent extraction fraction at 9 MPa was considerably lower than at 18 MPa and required less time to reach the extraction equilibrium. At 23 MPa, the time needed to achieve the highest extraction fraction was much longer than at 18 MPa because of the lower diffusion rate, which resulted from the high viscosity. Therefore, the effect of the equilibrium solubility of LP in SC-CO<sub>2</sub> was dominant at lower pressures, but at higher pressures viscosity was dominant. Consequently, the extraction fraction of LP increased in the range of 9–18 MPa and slightly decreased over this region with the same extraction time and temperature.

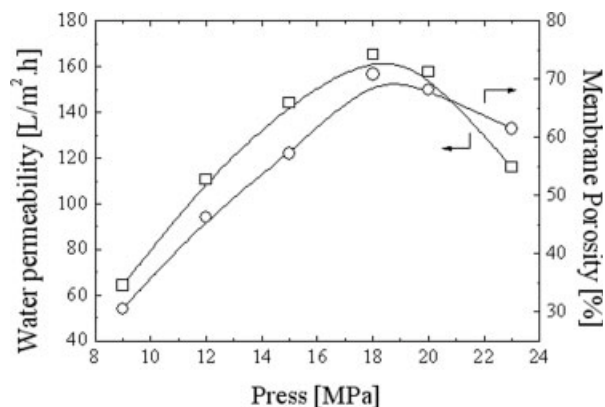
Figure 3 shows the data on membrane porosity and water permeability for membranes extracted at

pressures from 9 to 23 MPa. Water permeability and porosity followed the same variation trend with increasing SC-CO<sub>2</sub> pressure. At 18 MPa, both had their highest values. At a pressure below 18 MPa, the low water permeability and low porosity were mainly a result of the residual LP in the membrane. In this study, membrane porosity was defined using eq. (3). Because there was a fairly large residual concentration of LP in the membranes following extraction with CO<sub>2</sub> at low pressure, membrane weight would include the residual LP, which would result in low porosity. Above 18 MPa, the effect of residual LP on water permeability and membrane porosity was slight because 95% or more of the LP was extracted by SC-CO<sub>2</sub>. Therefore, the decreases in membrane porosity and water permeability were mainly a result of compression of the membrane because under higher pressures, the pores were more compressed by CO<sub>2</sub>.

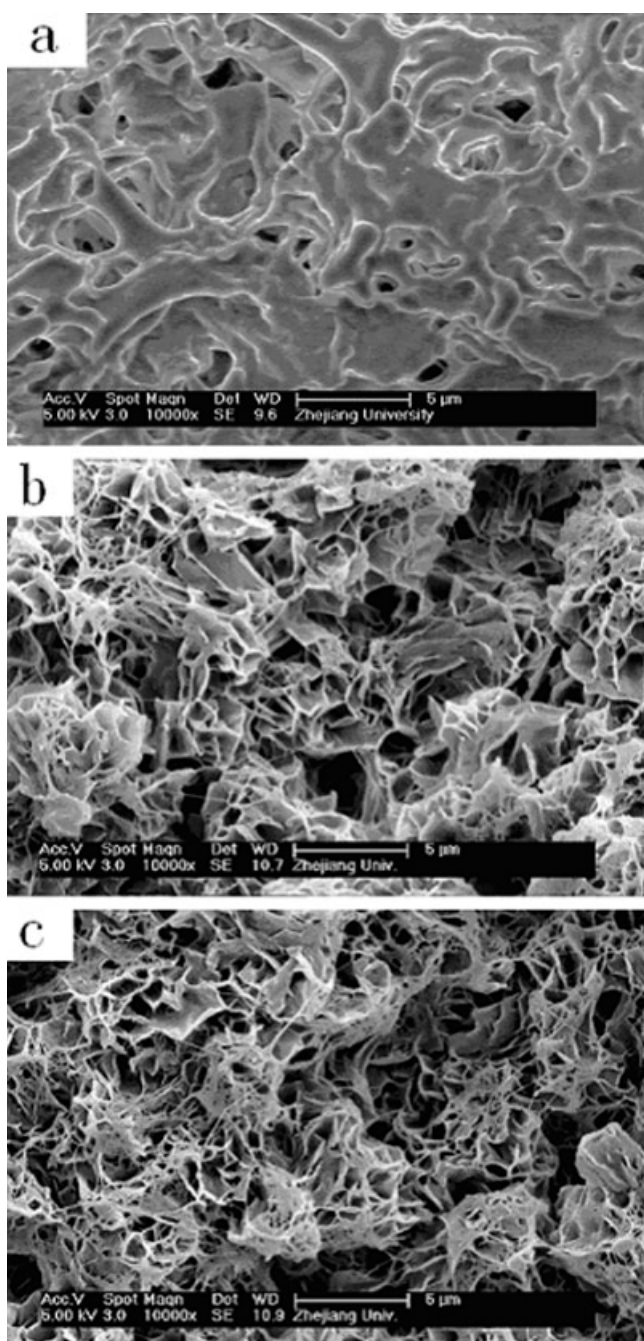
Figure 4 shows the cross sections of membranes extracted at three SC-CO<sub>2</sub> pressures: 9, 18, and 23 MPa. As can be seen in Figure 4, the morphology of the membrane extracted at 9 MPa was quite different from that extracted at 18 and 23 MPa. Most pores were blocked by residual LP and could not be seen. These results are consistent with those of lower porosity at 9 MPa, shown above. Although the porous structures were very similar at 18 and 23 MPa, the membrane extracted at 18 MPa still had a slightly larger pore size than that at 23 MPa. This was because the pores were more compressed by CO<sub>2</sub> fluid under higher pressure. This trend is consistent with the trends for membrane porosity and water permeability noted above.

#### Temperature of SC-CO<sub>2</sub>

To determine the influence of temperature on the extraction fraction of LP, a series of experiments were run at 18 MPa with different temperature of



**Figure 3** Effect of pressure on water permeability and membrane porosity (temperature: 35°C; time: 2 h).



**Figure 4** SEM images of the UHMWPE membranes at different SC-CO<sub>2</sub> pressures: (a) 9 MPa; (b) 18 MPa; (c) 23 MPa.

SC-CO<sub>2</sub>, and the results are shown in Figure 5. Extraction time was 2 h. The extraction fraction of LP decreased with increasing temperature in the range studied. It is important to point out that the solubility of a substance in a supercritical fluid was affected by two factors, the volatility of the substance and the solvating effect (related to density) of the supercritical fluid.<sup>22,31</sup> Thus, on the one hand, raising the fluid temperature can greatly increase the solubility for compounds with significant vapor

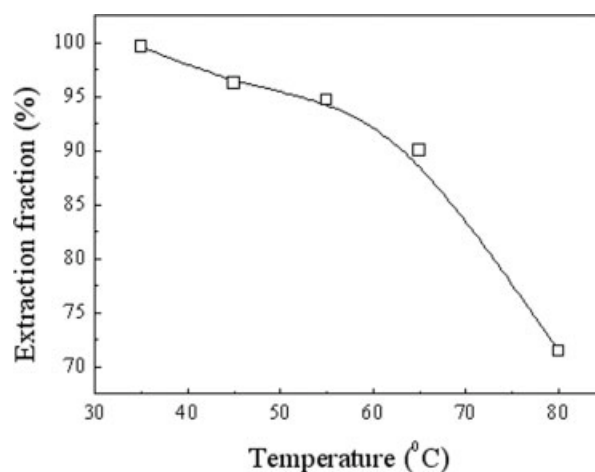
pressures. On the other hand, at a constant pressure, increasing the temperature will induce a decrease in the density of CO<sub>2</sub>, which is unfavorable to the solvating ability of the SC-CO<sub>2</sub> fluid. Because of not having significant vapor pressure at the range of temperatures studied, the volatility of LP changed slightly in SC-CO<sub>2</sub> with elevated temperature. So, the extraction fraction of LP decreased with an increase in the SC-CO<sub>2</sub> temperature because of the decreased density of CO<sub>2</sub>.

Figure 6 shows the SEM cross-section images of membranes extracted at two temperatures. A comparison of the two images in Figure 6 confirmed that temperature did not have a large influence on the structure and pore size of UHMWPE membranes, but both water permeability and the porosity decreased obviously with an increase in temperature (seen Fig. 7). This was probably because of the residual LP in the membrane. Further research is needed to clarify the relationship between SC-CO<sub>2</sub> temperature and membrane properties.

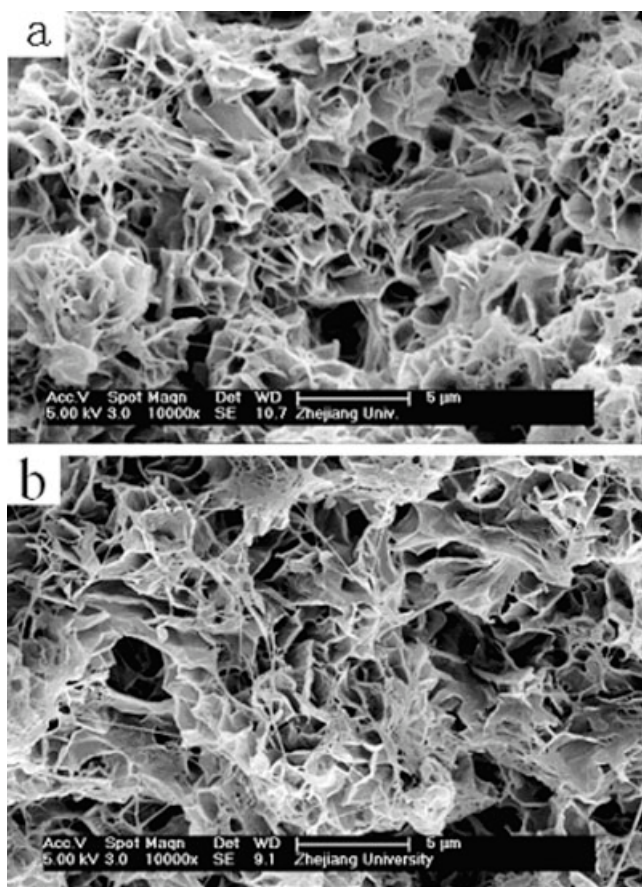
### Comparison with solvent extraction

#### Membrane shrinkage

In this study, ethanol was used as the extractant in solvent extraction. Table I lists the relative dimension of the membrane after extraction. Relative dimension was defined as the rate of change in dimensions after extraction over the initial dimensions. It can be seen that the membrane extracted by SC-CO<sub>2</sub> had less shrinkage in area and in thickness than that extracted by ethanol. Porosity of the membrane extracted with SC-CO<sub>2</sub> was 70.82%, much higher than the 31.02% of that extracted by ethanol. Meanwhile higher water permeability, 165.3 L m<sup>-2</sup> h<sup>-1</sup>, was obtained for the SC-CO<sub>2</sub>-extracted membrane.



**Figure 5** Effect of temperature on the extraction fraction of LP (pressure: 18 MPa; time: 2 h).

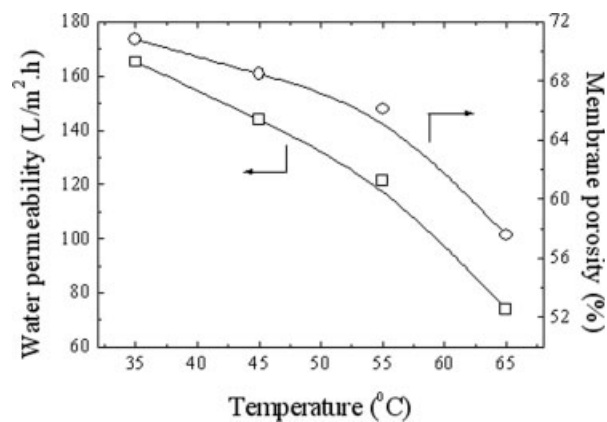


**Figure 6** SEM images of the UHMWPE membranes at different extraction temperatures: (a) 35°C; (b) 55°C.

For the sample extracted with ethanol, evaporation of the extractant was the major cause of contraction of the membrane. This contraction can be attributed to a combination of two kinds of physical phenomena: densification of the amorphous regions of the membrane and capillary force due to surface tension.<sup>13</sup> But because the polymer under study had high crystallinity (62%), the impact of densification of the amorphous regions on membrane contraction was probably much less significant than the capillary force. SC-CO<sub>2</sub> fluid does not have surface tension because of the absence of a liquid–vapor interface. It can dry the polymer membrane rapidly and avoid collapse of the pore structure of the membrane.

#### Membrane structure

To illustrate the structural significance of the sample contraction, surface and cross-section micrographs were taken of the dry membranes. Figure 8 shows the surface and cross-section micrographs of two membranes that were extracted by the two different methods described above (all micrographs are at the same magnification). For two membranes, there was no skin layer at the surface, and its porous structure was simi-



**Figure 7** Effect of temperature on water permeability and membrane porosity (pressure: 18 MPa; time: 2 h).

lar to that in the cross section. Based on the data in Table I and Figure 8, the sample extracted with ethanol underwent a more serious contraction than that extracted by SC-CO<sub>2</sub>. Therefore, compared with traditional solvent extraction, SC-CO<sub>2</sub> is a better method for keeping the primal morphology of the membrane.

#### DSC and WAXD

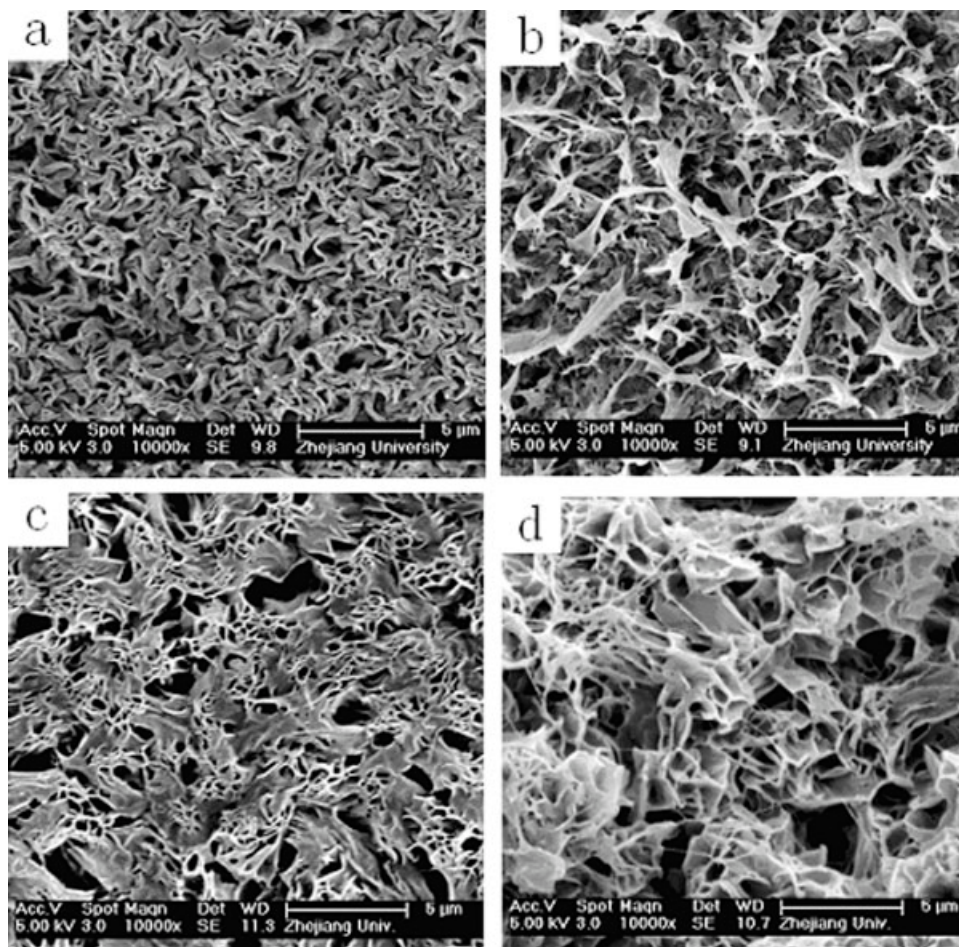
Figure 9 shows a DSC thermogram of the UHMWPE. The wide melt peaks with a little shoulder peak are displayed in the DSC curves of UHMWPE materials and the ethanol-extracted membrane. The shoulder peak of the ethanol-extracted membrane can be attributed to the imperfect crystallization structure. But there was only a single melt peak for the SC-CO<sub>2</sub> extracted membrane. The results of crystallinity are given in Table II. The discrepancy in the degree of crystallization was slight for the three samples, and the trend in variation was: UHMWPE materials < ethanol-extracted membrane < SC-CO<sub>2</sub> extracted membrane. We inferred that this result could be attributed to a combination of two physical effects: reorganization of imperfect crystals and SC-CO<sub>2</sub>-induced crystallization. During the SC-CO<sub>2</sub> extraction, CO<sub>2</sub> absorbed by the UHMWPE membranes was able to plasticize the polymer chain segment. Some of the defective crystals were destroyed to the more relatively perfect crystals.<sup>32</sup> Simultaneously,

**TABLE I**  
Relative Dimensions After Extraction

Extractant	Area	Thickness	Porosity (%)	Water permeability (L m <sup>-2</sup> h <sup>-1</sup> )
Ethanol <sup>a</sup>	0.32	0.52	31.02	38.6
SC-CO <sub>2</sub> <sup>b</sup>	0.90	0.89	70.82	165.3

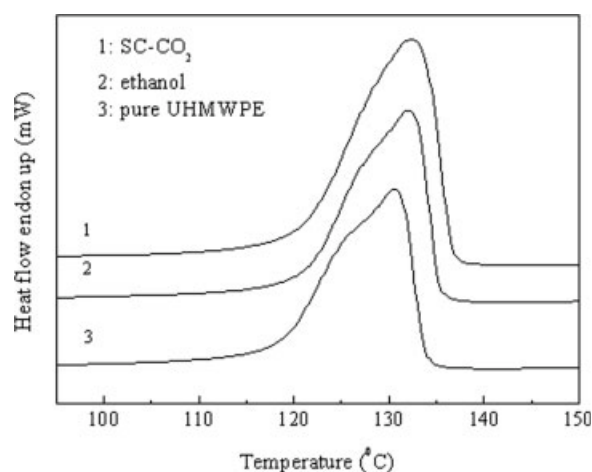
<sup>a</sup> Extraction time: 24 h.

<sup>b</sup> Extraction conditions: 18 MPa, 35°C, and 2 h.



**Figure 8** Membrane structure: (a) surface of membrane extracted by ethanol; (b) cross section of membrane extracted by ethanol; (c) surface of membrane extracted by SC-CO<sub>2</sub>; (d) cross section of membrane extracted by SC-CO<sub>2</sub> (pressure: 18 MPa; temperature: 35°C; time: 2 h).

SC-CO<sub>2</sub> readily induced crystallization in the membranes of amorphous UHMWPE.<sup>33</sup> Consequently, in the SC-CO<sub>2</sub>-extracted membrane, the shoulder peak attributed to the incomplete crystals disappeared, and the overall crystallinity raised. We think there is



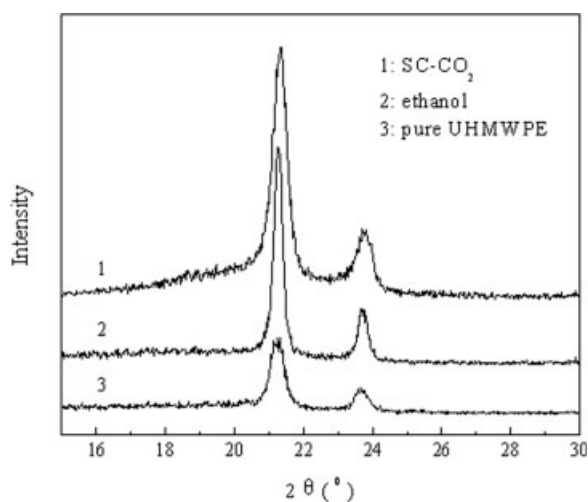
**Figure 9** DSC curves of UHMWPE membranes extracted by two methods.

a cumulative impact of these two effects on membrane crystallization. But additional detailed studies are required to distinguish accurately the magnitude of each of these effects.

The WAXD curves obtained for UHMWPE materials and membranes are compared in Figure 10. On the scattering curve two peaks of (100) and (110) reflection were observed at angles  $2\theta$  of about 21.2° and 23.7°, respectively. As shown on the intensity distribution curves for the three samples, no shift in the crystalline peaks was observed, but there were some differences in the intensity of the scattering. The calculated crystallinities of the pure UHMWPE

**TABLE II**  
Degree of Crystallization of Membranes

Samples	Degree of crystallization (%)	
	DSC	WAXD
UHMWPE materials	60.5	53.3
Ethanol-extracted membrane	65.4	58.5
SC-CO <sub>2</sub> -extracted membrane	67.3	63.1



**Figure 10** WAXD spectra of UHMWPE membranes extracted by two methods.

material and the two UHMWPE membranes were 53%, 58%, and 63%, respectively, as shown in Table II. Although the degree of crystallization values calculated by WAXD and DSC exhibited a trivial discrepancy, the variation trends of the degree of crystallization from both WAXD and DSC are the same.

### CONCLUSIONS

In SC-CO<sub>2</sub> extraction, the extraction time needed to reach the extraction equilibrium varied with extraction pressure and temperature because of the effect of diffusion rate. The extraction fraction increased with increasing pressure when the pressure was less than 18 MPa and decreased slightly with increasing pressure when the pressure was more than 18 MPa, with the extraction fraction higher at 18 MPa than at any other pressure. The water permeability and membrane porosity at different pressures were consistent with this trend. Water permeability and porosity were both highest at 18 MPa. Under different pressures, the higher the pressure, the smaller was the pore size. In the temperature range from 35°C to 65°C, the extraction fraction decreased with increasing temperature, as did water permeability and membrane porosity. Temperature had little influence on the structure and pore size of the membranes.

Comparing the effects of SC-CO<sub>2</sub> extraction and traditional ethanol extraction on the shrinkage and morphology of the membranes showed that the sample extracted with SC-CO<sub>2</sub> underwent considerably less contraction than that extracted by ethanol. Meanwhile,

higher water permeability and porosity were obtained for membranes extracted with SC-CO<sub>2</sub>. Therefore, SC-CO<sub>2</sub> extraction is obviously superior to the traditional solvent extraction in keeping the primal morphology of membranes. The degree of crystallization of membranes extracted by SC-CO<sub>2</sub> was slightly higher than that of those extracted by ethanol because of the reorganization of UHMWPE molecular chains.

### References

- Berghmans, H.; De Cooman, R.; Rudder, J. D.; Koningsveld, R. *Polymer* 1998, 39, 4621.
- Caneba, G. T.; Soong, D. S. *Macromolecules* 1985, 18, 2538.
- Tamaswamy, S.; Greenberg, A. R.; Krantz, W. B. *J Membr Sci* 2002, 210, 175.
- Hiatt, C.; Vitzthum, G. H.; Wagener, K. B.; Gerlach, K.; Josefiak, C. *Materials Science of Synthetic Membranes*; ACS Press: Washington, DC, 1985.
- Tsai, F. J.; Torkelson, J. M. *Prog Clin Biol Res* 1989, 61, 789.
- Lloyd, D. R.; Kinzer, K. E.; Tseng, H. S. *J Membr Sci* 1990, 52, 239.
- Lloyd, D. R.; Kim, S. S.; Kinzer, K. E. *J Membr Sci* 1991, 64, 1.
- Kim, S. S.; Lloyd, D. R. *J Membr Sci* 1991, 64, 13.
- Lim, G. B. A.; Kim, S. S.; Ye, Q.; Wang, Y. F.; Lloyd, D. R. *J Membr Sci* 1991, 64, 31.
- Matsuyama, H.; Iwatani, T.; Kitamura, Y.; Tearamoto, M.; Sugoh, N. *J Appl Polym Sci* 2001, 79, 2449.
- Atkinson, P. M.; Lloyd, D. R. *J Membr Sci* 2000, 171, 1.
- Kim, W. K.; Char, K.; Kim, C. K. *J Polym Sci, Part B: Polym Phys* 2000, 38, 3042.
- Matsuyama, H.; Kim, M.; Lloyd, D. R. *J Membr Sci* 2002, 204, 413.
- Song, S. W.; Torkelson, J. M. *Macromolecules* 1994, 27, 6389.
- Bikerman, J. J. *Surface Chemistry*; 2<sup>nd</sup> ed., Academic Press: New York, 1958.
- Luna-Bárceñas, G.; Kanakia, S. K.; Sanchez, I. C.; Johnston, K. P. *Polymer* 1995, 36, 3173.
- Li, D.; Han, B. X. *Ind Eng Chem Res* 2000, 39, 4506.
- McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction*; Butterworth-Heinemann: Boston, 1994.
- McNally, M. E. P.; Deardorff, C. M.; Fahmy, T. M. *Supercritical Fluid Technology*; ACS Press: Washington, DC, 1992.
- Janda, V. *J Chromatogr* 1993, 642, 283.
- Jeong, M. L.; David, J. C. *J Supercrit Fluid* 1999, 16, 33.
- Quan, C.; Li, S. F.; Tian, S. J.; Xu, H.; Lin, A. Q.; Gu, L. *J Supercrit Fluid* 2004, 31, 149.
- Lim, G. B. A.; Lloyd, D. R. *Polym Eng Sci* 1993, 33, 513.
- Gao, J. G.; Yu, M. S.; Li, Z. T. *Eur Polym J* 2004, 44, 1533.
- Kim, J. H.; Min, B. R.; Perk, H. C.; Won, J.; Kang, Y. S. *J Appl Polym Sci* 2001, 81, 3481.
- Reuvers, A. J.; Smolders, C. A. *J Membr Sci* 1987, 34, 67.
- Bodzek, M.; Bohdziexwicz, J. *J Membr Sci* 1991, 60, 25.
- Foster, N. R.; Gurdial, G. S.; Yun, J. S. L.; Liang, K. K.; Tilly, K. D.; Ting, S. S. T.; Singh, H.; Lee, J. H. *Ind Eng Chem Res* 1995, 30, 1955.
- Bowadt, S.; Hawthorne, S. B. *J Chromatogr A* 1995, 703, 549.
- Kim, M. S.; Lee, S. J. *J Supercrit Fluid* 2004, 31, 217.
- Langenfeld, J. J.; Hawthorne, S. B.; David, J. M.; Pawliszyn, J. *Anal Chem* 1993, 65, 338.
- Smole, M. S.; Zipper, P. *Mater Res Innovat* 2002, 6, 55.
- Beckman, E.; Porter, R. S. *J Polym Sci, Part B: Polym Phys* 1987, 25, 1511.