Preparation and Characterization of PVDF-HFP Membrane

Jianhua Cao[a]; Baoku Zhu[b]; Youyi Xu[b]; Jiding Li[a]; Cuixian Chen[a]

[a] Department of Chemical Engineering, Tsinghua University, Beijing, China [b] Institute of Polymer Science, Zhejiang University, Hangzhou, China

Online publication date: 04 January 2011

PLEASE SCROLL DOWN FOR ARTICLE

Preparation and Characterization of PVDF-HFP Membrane

JIANHUA CAO,[1] BAOKU ZHU,[2] YOUYI XU,[2] JIDING LI,[1] and CUIXIAN CHEN[1]

[1]Department of Chemical Engineering, Tsinghua University, Beijing, China
[2]Institute of Polymer Science, Zhejiang University, Hangzhou, China

Poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) microporous membrane was prepared by supercritical CO_2 extraction of dibutyl phthalate (DBP) template from PVDF-HFP/DBP film. The effects of extraction conditions such as pressure, temperature, and extraction time on extraction efficiency and the porosity of membrane were studied. The extraction efficiency of DBP and size stability of polymer membrane during extraction was compared with those of solvent extraction process. The structure of the resulting membrane was characterized by scanning electron microphotograph (SEM), X-ray diffraction (XRD) and differential scanning calorimeter (DSC). With increasing the extraction temperature, pressure and time, the extraction efficiency and the porosity increased. Maximum extraction efficiency is obtained at extraction pressure and temperature higher than 18 MPa and 75°C, respectively. The porosity of membranes depended on the extraction efficiency and shrinkage ratio of membranes. Compared with solvent extraction, supercritical CO_2 extraction of the film generated the membrane with more uniform structure and higher porosity.

Keywords: poly(vinylidene fluoride-co-hexafluoropropylene); dibutyl phthalate; supercritical CO_2; extraction; porous membrane

1 Introduction

Porous polymeric materials with interconnected microchannels are currently of major interest in the fields of food packaging, controlled release systems, and membranes for separation etc. Porous membrane materials are mainly prepared by phase inversion of polymer solutions (1). The demixing process, which stops at the vitrification point of polymer-rich phase, can be initiated either by the temperature change (thermal induced phase separation, TIPS) or by diffusive solvent-nonsolvent exchange (immersion precipitation) of binary, ternary, or multicomponent mixtures. Recently, another method was reported (2, 3) where the high boiling additive was introduced in polymer solution and then the volatile solvent evaporated. After removal of the additive by solvent extraction, the position of the additive in polymer matrix was converted into pores. In this process, the porous structures were formed at the extraction stage. Therefore, the extraction condition greatly affected the porous structure (4, 5). In Matsuyama's report (4), ten different extractants were used to remove the diluent used in the

TIPS process for making polyethylene membranes. The porosity increased from 0.059 for *p*-xylene to 0.53 for pentane. Therefore, the porosity of porous polymer membrane could be manipulated by the type of extractants.

As previously reported, polymer additives were usually extracted by liquid extraction (6). However, liquid extractions have drawbacks including long extraction time (e.g., several hours or even days), difficulty in separating additives from extractant, and toxicity of liquid solvent.

Supercritical fluid extraction (SFE) is attracting growing attention for its relatively low viscosity and high diffusivity, high selectivity and easy recycling. It is regarded as a promising alternative to conventional solvent extraction methods. The solvation ability of the supercritical fluid can be manipulated by changing pressure and/or temperature. Higher diffusivities and lower viscosities give a more rapid mass transfer of solutes and hence, reduce extraction time. Supercritical CO_2 is a most remarkable candidate for supercritical fluid extraction. Vaporizing by releasing to the lower pressure atmosphere, the extracted solutes can be easily isolated for further recycling. The application of supercritical CO_2 has been found in large-scale industrial processing in the analysis of coal tars (7), foods and drugs and soils (8, 9). In the field of polymeric materials, supercritical CO_2 has been used in extraction of monomers from poly(ethylene terephthalate) (10), aromatic amines in poly rubber (11), additives in polystyrene (12), plasticizers in polyvinyl chloride

Address correspondence to: Jianhua Cao, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China. Tel.: +86-10-62782432; Fax: +86-10-62770304; E-mail: caojh@mem.tsinghua.edu.cn

(13–15) etc. As far as preparation of porous polymer membrane is concerned, the supercritical CO_2 could be used as non-solvent to induce the phase separation of polymer solution. Kim (16) has investigated the fact that the polyethylene glycol (PEG) was extracted in supercritical CO_2 and prepared polycarbonate (PC) membranes with high tearing stress and porosity. In Matsuyama's works (17, 18), porous cellulose acetate and polystyrene membranes were prepared by phase separation with supercritical CO_2 as a non-solvent. Effects of the CO_2 pressure, the polymer concentration, the kinds of solvents and the temperature on the average pore size and membrane porosity were investigated. However, there was very little literature mentioned about the formation of porous membrane by extracting the template additives from polymer-template formers.

In this paper, extracting DBP from PVDF-HFP/DBP former films using supercritical CO_2 was investigated in the preparation of PVDF-HFP porous membranes. The effects of extraction time, extraction temperature and pressure on the extraction efficiency and the porosity of membrane were studied. The extraction efficiency of supercritical CO_2 ($SCCO_2$) extraction is compared with those of the classic solvent extraction process.

2 Experimental

2.1 Materials

The PVDF-HFP copolymer with 15 mol%HFP (Aldrich reagent, $M_w = 30, 8000$) was dried at $50°C$ in vacuum for two days before use. Dibutyl phthalate (DBP) and acetone (analytic grade) were used as template additives and solvent, respectively. Ethanol, trichloroethylene were used as extractants in the conventional extraction method. High purity carbon dioxide (99.99%) was obtained from Specialty Gas Station of Hangzhou.

2.2 Preparation of PVDF-HFP/DBP Former Films

PVDF-HFP pellets and DBP were dissolved in acetone with mechanical stirring at $50°C$ to form a homogenous solution with a composition of PVDF-HFP/DBP/acetone in 15:15:70 by volume. The viscous solution was cast at room temperature into liquid films, 200 μm thick, on a glass plate using a doctor blade. After drying in a vacuum oven at $50°C$ for 4 h, the flexible, transparent film of former composite PVDF-HFP/DBP was obtained.

2.3 Extraction of DBP from PVDF-HFP/DBP Former Films

The supercritical CO_2 extraction apparatus was shown in Figure 1. The $SCCO_2$ extraction experiments were operated in a static mode and in a 1 L tubular extractor, which was placed in a temperature controllable bath. The
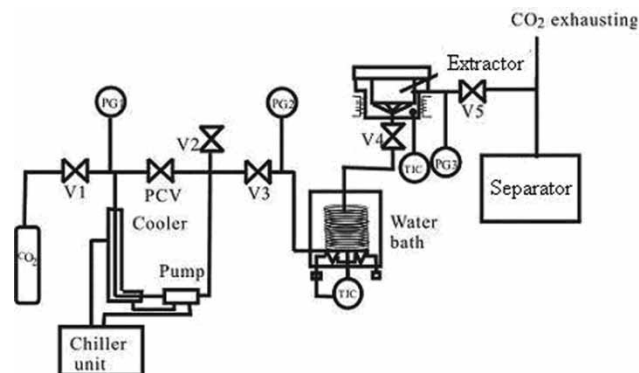

Fig. 1. The schematic diagram of SFE device V, valve; PG, pressure gauge; PCV, pressure control valve; TIC, temperature indicator and controller.

former film with known weight and size was placed in an extractor. After being compressed and heated, the supercritical CO_2 was introduced into the extractor by opening valve 4. The system was maintained at the specific pressure and temperature for a given time. Valve 5 was then opened and the system was slowly depressurized for about 2 h at the experimental temperature. The CO_2 was released in air and the DBP was collected in a separator. As the depressurization process was completed, the white, opaque membrane in the extractor was obtained. Weight and size of the membrane was measured for further characterization.

With the purpose of comparing the extraction results after $SCCO_2$ extraction and conversional solvent extraction, the PVDF-HFP/DBP former film with known weight and size was immersed in a large excess of extractants for 24 h to extract the DBP at $25°C$. After extraction, the film was further dried in air at $25°C$. The membrane was weighed and the size of membrane was measured to calculate the extraction efficiency and the size variation of membrane before and after extraction.

2.4 Calculation of Membrane Shrinkage and Extraction Efficiency

The PVDF-HFP/DBP former film was cut into 4.0 cm casting direction (LD) × 3.0 cm perpendicular to LD direction (WD) rectangular sample and the dimensions of each sample were measured. The sample was immersed in each bottle, which contained 150 ml of extractant, and the bottle was sealed. After soaking 24 h to allow additive-extractant exchange, the membrane was taken out and air-dried at room temperature to a constant mass. The length and width of dry membranes were measured with a ruler and the membrane thickness was measured with a micrometer. The relative measurements reported below represent the final dimensions divided by the initial dimensions. The extraction efficiencies were calculated as indicated in

Equations (1) and (2).

$$\text{Efficiency}\,(\%) = \frac{\text{Relative mass loss}\,(\%)}{\text{Total plasticizer content}\,(\%)} \times 100 \quad (1)$$

$$\text{Relative mass loss}\,(\%) = \frac{\text{Initial mass} - \text{Final mass}}{\text{Initial mass}} \times 100 \quad (2)$$

2.5 Characterization of PVDF-HFP Membranes

The structure of the surface and cross-section fractured in liquid nitrogen of the obtained PVDF-HFP membrane was observed on a scanning electron microscope (JEOL, JSM-5510LV, Japan) with an accelerating voltage of 5 kV. X-ray diffraction patterns of PVDF-HFP and membranes were obtained using an X-ray diffractometer (XD-98, Philips X light pipe) using Cu Kα as a source (40 kV and 80 mA) with 2θ at $10-50°C$. The thermal properties of PVDF-HFP membranes were studied using a Perkin-Elmer differential scanning calorimeter (DSC) at a rate of $10°C/min$ in N_2 with a flow rate of $20\,ml/min$. The porosity *(P)* of the membrane was calculated from the density of the membrane (ρ_m, $g \cdot cm^{-3}$) and the density of pure PVDF-HFP ($\rho_p = 1.77\,g \cdot cm^{-3}$) (19, 20):

$$P(v\%) = \frac{1 - \rho_m}{\rho_p} \times 100\%$$

The membrane density was determined by measuring the volume and weight of the membrane.

3 Results and Discussion

3.1 Effects of Extraction Conditions of SCCO$_2$ on Extraction Efficiency and the Porosity of the Membranes

The extraction process is governed by the solubility of additives in the supercritical fluid or by their diffusion rate through the polymer matrix. The extraction efficiency depends on the applied pressure and temperature. In Marin et al. (21), the phthalate plasticizers in poly(vinyl chloride) had been effectively extracted by supercritical CO_2 extraction. Therefore, under these experimental conditions, it can be expected that the DBP would be sufficiently soluble in the supercritical CO_2 to permit efficient extraction DBP from the PVDF-HFP matrix.

3.1.1 Extraction Time

Figure 2 shows the effects of extraction time on the extraction efficiency and porosity of membrane at $75°C$ and 18 MPa. As shown in Figure 2, it is possible to distinguish three stages in the extraction behavior of DBP when the extraction time elapsed at a fixed pressure and temperature. The first stage (times lower than 0.5 h) shows a quick increase in the extraction rate due to the fast solution of the DBP in the supercritical CO_2. When SCCO$_2$ is brought into the extractor and contact
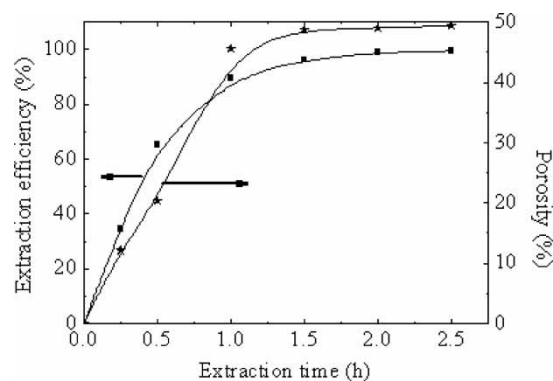

Fig. 2. Extraction efficiency of DBP and the porosity of membrane as a function of extraction time, 18 Mpa, $75°C$.

with the film surface, the DBP, at or close to the film surface, are rapidly extracted. As was proposed by Taylor (22), it can be considered that quasi-equilibrium conditions govern the solute partition in the dense fluid phase. As surface extraction is exhausted, the extraction rate becomes slower and the process is a transition to diffusion-controlled kinetics during the second stage (from 0.5 to 1 h). This phenomenon is consistent with the increased distances across which the remaining DBP have to migrate before being carried away in the bulk CO_2 flow. Finally, the process is completely diffusion-controlled from 1 to 2.5 h, and the extraction rate is even lower. Therefore, the extraction efficiency of DBP was nearly 100% in 2.5 h at the 18 MPa and $75°C$.

The variation trend of the membrane porosity after extraction is the same as that of extraction efficiency. With the extraction time elapsed, the porosity of membrane increased. The porosity of membrane is closely related to the efficiency of the extraction. In this study, the formation of the pore in the membrane comes from the position of DBP extracted. There was a large amount of DBP residual in the membrane in short extraction time. The weight of the membrane would include the DBP, which would result in low porosity according to the porosity equation. The membrane with a nearly complete absence of DBP showed the highest porosity (49.4%).

3.1.2 Extraction Pressure

If the rate-limiting factor is the solubility of the components in the supercritical fluids, an increase in pressure will increase the extraction rate. On the other hand, if the rate-limiting factor is the diffusion of the additives in the polymer matrix, the extraction pressure will have little or no effect on the extraction rate for SFE. Figure 3 indicates that the extraction efficiency and the porosity of membrane increased with increasing pressure. This increment is very fast in the $10-18$ MPa interval, reaching a plateau at pressures near 18 MPa. This can be due to the fact that when the pressure increases, the density of the supercritical fluid
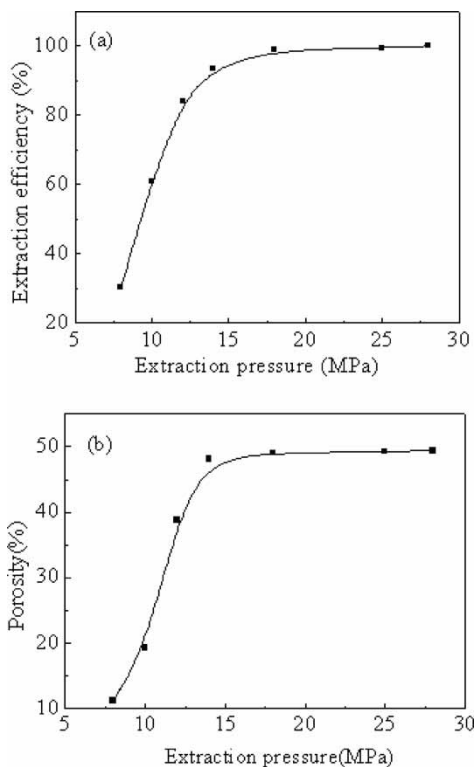
Fig. 3. The effect of extraction pressure on (a) the extraction efficiency of DBP and (b) the porosity of membrane, 75°C, 2 h.

Fig. 4. Influence of temperature on (a) the extraction efficiency of DBP and (b) the porosity of membrane, 18 MPa, 2 h.

increases and therefore, its solvent strength becomes higher. The ability of the supercritical fluid to diffuse through the polymer matrix could play an important role. Although, for dense gases, pressure is inversely proportional to diffusivity, polymer sorption of CO_2 has been found to be enhanced at a higher pressure. It is known that there is 14 wt.% sorption of CO_2 in PVDF at 676 bar and 130°C (23).

Moreover, at high pressure, swelling of the polymer by the supercritical fluid increases. Hence, an increase in pressure might increase the rate of diffusion of the DBP through the polymer matrix and results in higher extraction. So, both the higher solubility and faster diffusivity contributed to the increase of extraction efficiency. Moreover, the solubility of DBP in the $SCCO_2$ is the rate-limiting factor as described above under the extraction conditions performed in this work. The porosity of membrane increased with the extraction pressure rising. The pressure, from 8 to 28 MPa
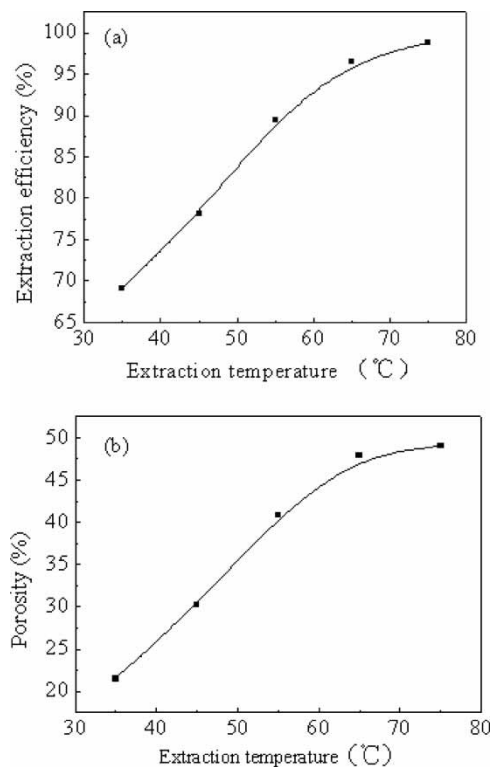
in the $SCCO_2$, enhanced the porosity of membrane from 11.2% to 49.2%.

3.1.3 Extraction Temperature

The influences of temperature on the efficiency extraction of DBP were shown in Figure 4(a). As can be observed, temperature is one of most important factors in the extraction of DBP. There is a major increase in the efficiency when the temperature is raised from 35 to 75°C. Efficiency lower than 80% is observed at 35°C, while it is approximately 100% at 75°C. There was no apparent difference when temperatures were higher than 75°C. The variation in the extraction efficiency with temperature may be caused by the diffusion of the DBP, CO_2 density and solubility. With temperature increasing at constant pressures, the density of CO_2 decreases and the solubility decreases further. However, the rates of diffusion of the DBP through the PVDF-HFP and into CO_2 will increase with an increasing

Table 1. The extraction efficiency and size variation of films by different extraction procedures

Extractants	Extraction efficient (%)	LD	WD	Membrane thickness direction	Relative volume
Ethanol	93.1	0.89	0.86	0.92	0.70
Trichloroethylene	62.4	0.75	0.73	0.85	0.47
$SCCO_2^a$	98.5	0.99	0.98	0.99	0.96

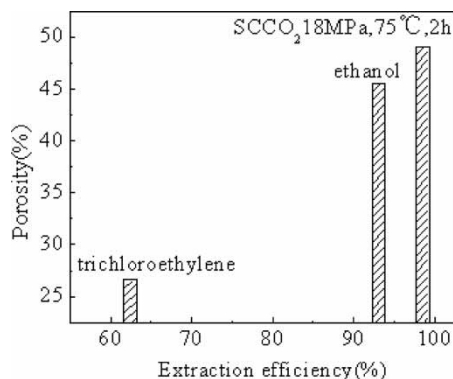[a]The extraction condition: 18 MPa, 75°C, 2 h.

Fig. 5. Extraction efficiency vs. porosity of membranes for different solvents extraction.

temperature. Marin's (18) study indicated that the efficiency of extraction of *o*-acetyl tri-*n*-butyl citrate in PVC decreased with the temperature increasing at low pressure, however, the temperature enhanced the efficiency at high pressure. In the present study, it is noted that the DBP diffusion in the film is the major factor in this temperature range at 18 MPa.

The glass transition temperature (Tg) and melt temperature (Tm) of the polymer should be taken into account. The extraction efficiency of a polymer is enhanced above its Tg and is increased still further above the polymer Tm. A temperature above the Tg results in enough molecular motion in the amorphous phase of the polymer so that the $SCCO_2$ can diffuse into the amorphous region easily. However, a temperature higher than the Tm is not practical because once the crystalline phase melts, clogging the extraction system and possibly ruining the extraction vessel may easily happen. The conclusions proposed by Kuppers (10) for a variation in the extraction

temperature, when it is closer to the glass transition temperature (Tg), are not valid in the present case. Tg in plasticized PVDF-HFP is below 0°C. Therefore, Tg is clearly lower than the working temperature and there is no influence on extraction efficiency.

The membrane porosity after extraction increased with the extraction temperature increasing, as shown in Figure 4(b). The higher the extraction temperature, the smaller the residual DBP in the membrane is. Therefore, the ratio of the volume of the pore and membrane becomes larger. In other words, the porosity of the membrane increased.

3.2 Comparison with Solvent Extraction

3.2.1 The Shrinkage of Membranes

The extraction efficiency, the shrinkage of films in LD, WD and thickness are summarized in Table 1. A much larger quantity of DBP was extracted from the film sample by $SCCO_2$ than those by the organic solvent. After 24 h of soaking the film in ethanol, DBP continued to be removed. This is in clear contrast to $SCCO_2$ where the DBP is completely removed in 2.5 h of static extraction. This could be due to greater diffusion CO_2 into the matrix at the higher temperature of the SFE, as opposed to the lower temperature liquid-solid extraction. The films can be sharply contracted when the organic solvent was applied as extractant. In general, the evaporation of the extractant would result in contraction of the membrane from surface tension. Surface tension at liquid−gas interfaces is responsible for the pressure decrease at the pore wall of the membrane during the evaporation. $SCCO_2$ has zero surface intension because of the absence of a liquid−vapor interface. $SCCO_2$ can dry the
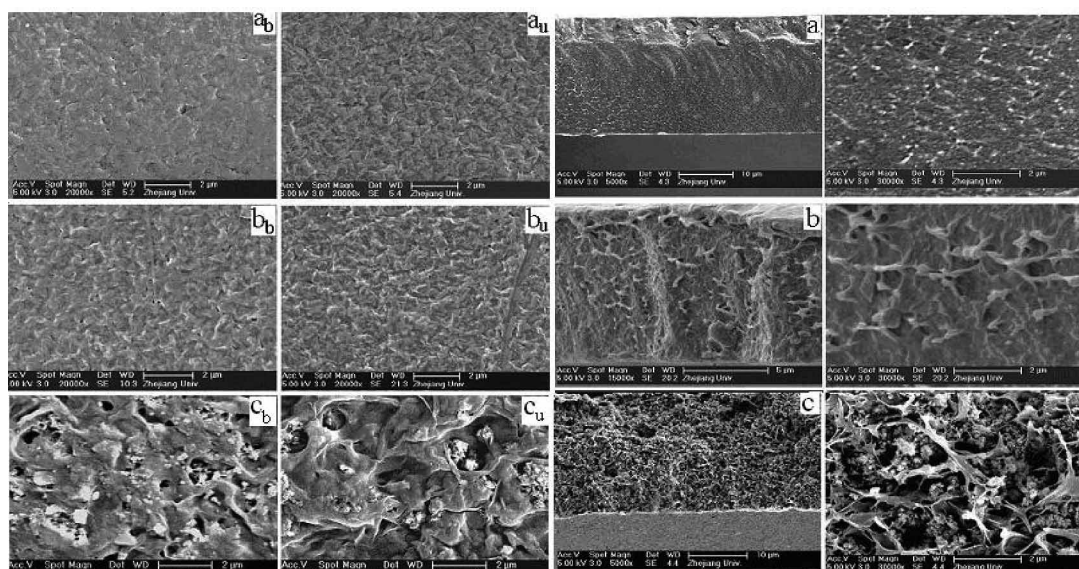

Fig. 6. The SEM images of membranes extracted by different extraxtants (first row, trichloroethylene; second row, ethanol; third row, $SCCO_2$; The subscript b and u are the surface facing the glass plate and air, respectively. The third column is the cross-section images and the fourth column is the magnification of cross-section).
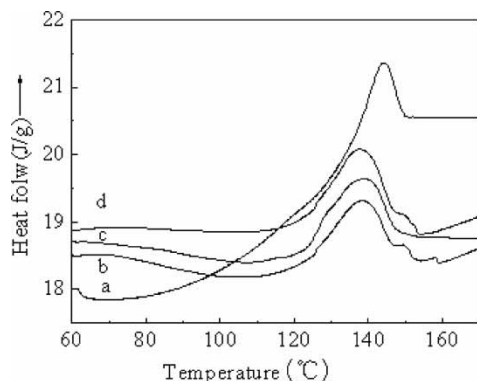
Fig. 7. The DSC curves of raw PVDF-HFP (a) and membrane obtained by different extractant, (b) SCCO$_2$ (18 MPa, 75°C, 2 h); (c) ethanol; (d) trichloroethylene.

polymer membrane rapidly without collapsing the structure. It is obvious that the films extracted by SCCO$_2$ leads to lower shrinkage than traditional solvent extraction.

3.2.2 The Morphology and Porosity of Membranes

The porosity in the membranes after extraction is closely related to the efficiency of the extraction. As illustrated in Figure 5, the higher the extraction efficiency, the higher the porosity of membranes is. The change of porosity with the extraction procedure can be explained in terms of the enhancement of the removal of template in the films. At this point, the use of SCCO$_2$ as solvent makes easier its access to the plasticizer-filled micropores located in the films in contrast with the case of ethanol molecules. Figure 5 indicates that it is possible to influence membrane porosity through the choice of extractant used in membrane production.

The morphology of membranes formed by the three representative extractants was shown in Figure 6. It is clear that the membrane appears as an asymmetric structure when trichloroethylene and ethanol were used. At the membrane surface, there was a dense skin layer. However, in the case of SCCO$_2$ extraction, the membrane did not have a skin layer
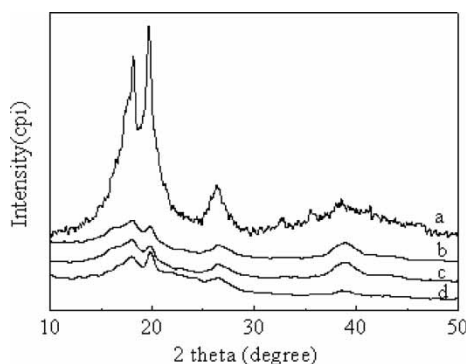

Fig. 8. The XRD patterns of raw PVDF-HFP (a) and membrane obtained by different extractants, (b) SCCO$_2$ (18 MPa, 75°C, 2 h); (c) ethanol; (d) trichloroethylene.

and shows nearly uniformity distribution. This uniformity is not achieved through conventional solvent extraction. In the surface, a porous structure formed similar to that in the cross-section although the porosity at the membrane surface was lower than that in the cross section. It is outstanding that the films extracted with CO$_2$ under supercritical conditions show a narrow pore size distribution similar to that reported by the Grieken et al. (24). The pore formation in the films may be related to the use of SCCO$_2$ for DBP extraction. The pore size and porosity of membranes increased in the order of trichloroethylene, ethanol and SCCO$_2$ as extractants. Due to the evaporated ethanol (trichloroethylene), capillary pressure action on the membrane decreased, the membrane shrank and the pore collapsed. The capillary pressure is in direct proportion to the surface intension of solvents. The order of the surface intension of the solvents is trichloroethylene (28.70 mN/m) > ethanol (21.97 mN/m) at 20°C. For SCCO$_2$, because of its zero surface intension, there was little contraction when SCCO$_2$ was used as extractant. Therefore, the membrane porosity is higher and the pore distribution is more uniform when the SCCO$_2$ was used as extractant.

3.2.3 The Thermal and Crystallinity Properties of Membranes

Because the DBP was nearly extracted in the PVDF-HFP films, thermal behavior of PVDF-HFP membranes formed with different extractants was expected to exhibit a similar trend. As shown in Figure 7, there was an endothermic peak in the DSC curves, which was ascribed to the PVDF-HFP melting process. The melting temperature was almost 143°C and was close to that of the pure PVDF-HFP.

XRD patterns of the raw PVDF-HFP and membranes were presented in Figure 8. From the diffraction patterns, three distinct Bragg diffraction peaks were observed at $2\theta = 18.2°$, 20°, 26° for all membranes. The crystalline peaks can be associated with the reflections (100) + (020), (110), and (021), respectively (25). By comparing the XRD characteristics with those of poly(vinylidene fluoride) (26, 27), the same diffraction peaks indicated the crystalline in these PVDF-HFP was generated from vinylidene fluoride (VDF) segments and typical for the orthorhombic cell of neat of PVDF in its crystalline form α.

4 Conclusions

Supercritical CO$_2$ extraction was used to remove the DBP used in porous PVDF-HFP membrane fabrication. The extraction efficiency was related to the temperature, pressure and extraction time. The extraction efficiency over 98% is obtained for extraction time of 2.5 h at temperature 75°C and at pressure about 18 MPa. Supercritical CO$_2$ extraction is a fast, high efficient alternative to liquid extraction. The membrane extracted by supercritical CO$_2$ does not have a skin layer and shows a nearly uniformity distribution.

The membrane pore size and porosity are larger than that of the membrane extracted by organic solvents. The thermal behavior and crystallinity of the membrane are unchanged during the extraction process. The membrane appears α crystal with excellent thermal stability.

5 Acknowledgments

6 References

1. Xu, Y.Y. and Xu, Z.K. *Polymer Membrane Materials*; Chinese Chemical Industry Press: Beijing, 83−95, Chapt. 2, 2005.
2. Gozdz, A.S., Tarascon, J.M. and Warren, P.C. (1995) Patent US 5418091.
3. Arascon, J.M., Gozdz, A.S., Schmutz, C.N., Shokooh, F. and Warren, P.C. (1996) *Solid State Ionics*, **49**, 86−88.
4. Matsuyama, H., Kim, M. and Lloyd, D.R. (2002) *J. Membr. Sci.*, **204**, 413−419.
5. Gozdz, A.S., Schmutz, C.N., Tarascon, J.M. and Warren, P.C. (1996) Patent US 5540741.
6. Song, J.Y., Cheng, C.L. and Wan, C.C. (2002) *J. Electrochem. Soc.*, **149**, A1230−1236.
7. Altwaiq, A.M., Wolf, M. and Eldik, R. (2003) *Analytica. Chimica. Acta.*, **491**, 111.
8. Morselli, L., Setti, L., Iannuccilli, A., Maly, S., Dinelli, G. and Quattroni, G. (1999) *J. Chromatography A*, **845**, 357−363.
9. Lehotay, S.J. (1997) *J. Chromatography A*, **785**, 289−312.
10. Kuppers, S. (1992) *Chromatographia.*, **33**, 434−440.
11. Reche, F., Garrigos, M.C., Marin, M.L., Canto, A. and Jimenez, A. (2002) *J. Chromatography A*, **963**, 419−426.
12. Bermudez, M.D. and Carrion-Vilches, F.J. (2002) *J. Supercritical Fluids*, **23**, 59−63.
13. Guerra, R.M., Maryn, M.L., Sanchez, A. and Jimenez, A. (2002) *J. Chromatography A*, **950**, 31−39.
14. Guerra, R.M., Marin, M.L., Sanchez, A. and Jimenez, A. (2002) *J. Supercritical Fluids*, **22**, 111−118.
15. Hunt, T.P., Dowle, C.J. and Greenway, G. (1991) *Analyst*, **116**, 1299−1304.
16. Kim, M.S. and Lee, S.J. (2004) *J. Supercrit. Fluids*, **31**, 217−225.
17. Matsuyama, H., Yamamoto, A., Yano, H., Maki, T., Teramoto, M., Mishima, K. and Matsuyama, K. (2002) *J. Membr. Sci.*, **204**, 81−87.
18. Matsuyama, H., Yano, H., Maki, T., Teramoto, M., Mishima, K. and Matsuyama, K. (2001) *J. Membr. Sci.*, **194**, 157−163.
19. Magistris, A., Mustarelli, P., Parazzoli, F., Quartarone, E., Piaggio, P. and Bottino, A. (2001) *J. Power Sources*, **97−98**, 657−660.
20. Min, H.S., Kang, D.W., Lee, D.Y. and Kim, D.W. (2002) *J. Polym. Sci., Part B Polym. Phys.*, **40**, 1496−1451.
21. Marin, M.L., Jimenez, A., Berenguer, V. and Lopez, J. (1998) *J. Supercritical Fluids*, **12**, 271−277.
22. Zhou, L.Y., Ashraf-Khorassani, M. and Taylor, L.T. (1999) *J. Chromatography A*, **858**, 209−218.
23. Shenoy, S.L., Fujiwara, T. and Wynne, K.J. (2003) *Macromolecules*, **36**, 3380−3385.
24. Grieken, R.V., Calleja, G., Stucky, G.D., Melero, J.A., Garcia, R.A. and Iglesias, J. (2003) *Langmuir*, **19**, 3966−3973.
25. Hasegawa, R., Takahashi, Y., Chatani, Y. and Tadokoro, H. (1972) *Polym. J.*, **3**, 600−610.
26. Abbrent, S., Tegenfeldt, J., Plestil, J., Hlavata, D., Lindgren, J. and Wendsjoc, A. (2001) *Polymer*, **42**, 1407−1416.
27. Giovanni, M., Puergiorgio, V., Mariano, P. and Francesco, C. (1996) *Polym. Int.*, **41**, 35−41.