

Effect of Posttreatment on Morphology and Properties of Poly(ethylene-co-vinyl alcohol) Microporous Hollow Fiber via Thermally Induced Phase Separation

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Received 24 January 2006; accepted 22 October 2006

DOI 10.1002/app.25685

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

ABSTRACT: Poly(ethylene-co-vinyl alcohol) (EVOH) hollow fiber membranes were prepared by thermally induced phase separation (TIPS) process. Water, methanol, and acetone were used to extract the diluents in the fibers, respectively. Bigger shrinkage of fibers during extractant evaporation was observed when water or methanol was used. Their interaction parameters with EVOH were calculated via Hansen solubility, respectively. The mechanism of hollow fiber volume shrinkage was discussed. It was found that affinity of the extractant with polymer was the critical factor except for the surface tension of extractant. Through the X-ray diffraction analysis during extraction and

evaporation, the crystallization behavior of the polymer was studied. From the SEM photos, it was observed that the volume shrinkage was derived from the collapse of porous structure. The fiber sample extracted by acetone had similar morphology with the sample freeze-dried. The gas and water permeability were also measured and the results were coincident with the morphology of fibers and shrinkage data. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 4106–4112, 2007

Key words: thermally induced phase separation; poly(ethylene-co-vinyl alcohol); extractant; posttreatment

INTRODUCTION

Poly(ethylene-co-vinyl alcohol) (EVOH) is a semicrystalline random copolymer with very low gas permeability, excellent chemical resistance, and mechanical properties.¹ As gas-barrier films it has been widely used as packing material for food, cosmetic, and chemical products.² Recently, EVOH membranes have also attracted plenty of research interests in the water treatment application, since hydrophilic EVOH copolymer has many superior properties over other hydrophobic polymers for the prevention of membrane fouling.³ Porous EVOH membrane can be conveniently prepared by thermally induced phase separation (TIPS).^{3–6}

TIPS has been extensively used to form porous membranes and gained great interest for the advantages of convenient membrane structure control and various polymers applicable. In TIPS process, a homogeneous solution of polymer is prepared at an elevated temperature by blending the polymer with a diluent of high-boiling point, then the solution is cooled to

induce phase separation, and finally a microporous structure is formed after the diluent is extracted by a volatile solvent. Recently, it was found that the diluent extraction and drying process also had a great effect on membrane morphology.^{7–10} Matsuyama et al.⁷ used 10 different extractants to remove mineral oil from polyethylene films prepared via TIPS and investigated the effect of the solubility parameters, surface tension, and the boiling point of the extractant on membrane morphology. Other researchers who focused on cellulose acetate (CA) membrane prepared by immersion-precipitation method have used this way to get the membrane with different properties. Gantzel and Merten⁸ used quick-freezing and vacuum-sublimation treatment to dry CA membrane; Lui et al.⁹ applied different solvent exchange methods to get CA membrane; Jie et al.¹⁰ proposed drying mechanism of cellulose hollow fiber membrane. However, to our best knowledge, the hydrophilic material membrane prepared by TIPS has not been studied in this area.

In this article, EVOH hollow fiber was fabricated via TIPS process. Water, methanol, and acetone were used to extract the diluent. According to the interaction parameters of extractant and polymer, the reason of fiber shrinkage was discussed. From the results of the X-ray diffractograms, the behavior of polymer crystallization was analyzed during extraction. Two kinds of drying processes were applied and their influence on volume shrinkage and morphology was

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Contract grant sponsor: Fundamental Study on Design and Preparation of Application-Oriented Membrane Materials; contract grant number: 2003CB615700.

investigated. Finally, the gas and water permeability of fibers treated in different way was compared.

EXPERIMENTAL

Materials

EVOH containing ca. 38 mol % ethylene (EVOH-38) with degree of polymerization of 960 was purchased from Kuraray (Japan). 1,4-Butanediol and poly(ethylene glycol) 400 (PEG400) were used as diluents; acetone and methanol were used as extractants. These reagents were purchased from Shanghai Chemical Reagent (Shanghai, China) and used without further purification.

Preparation of hollow fiber

EVOH hollow fibers were prepared by the apparatus showed in Figure 1. The mixture of 1,4-butanediol and PEG400 was used as diluent and mixed with EVOH38 in the mixing vessel at 150°C for 2 h under a nitrogen atmosphere. The homogeneous solution was held at this temperature for 0.5 h to eliminate gas bubbles. The solution was extruded from the spinneret and then entered a cooling bath of water. The bore liquid was introduced into the inner orifice of the spinneret to make the lumen of the hollow fiber. Table I lists the experimental parameters for the spinning of hollow fibers.

Measurement of hollow fiber shrinkage

The nascent and dried hollow fibers were observed and measured by optical microscope. The shrinkage

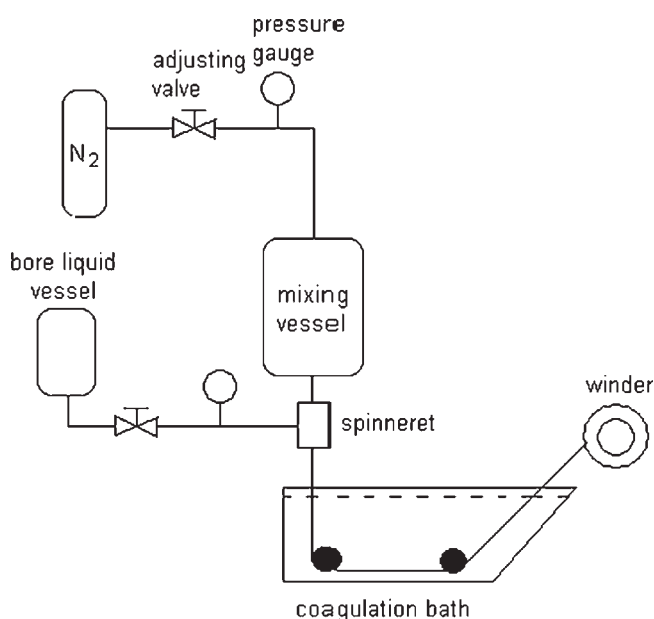


Figure 1 Schematic diagram of the spinning apparatus for hollow fiber.

TABLE I
Experimental Parameters for the Spinning Hollow Fiber

Parameters	Values
Solution composition (wt %)	EVOH38/1,4-butanediol/PEG400 = 40 : 18 : 42
Bore liquid composition (wt %)	1,4-butanediol/PEG400 = 3 : 7
Spinneret, ID/OD (mm)	1.2/3
Air gap (mm)	5
Temperature in mixing vessel (°C)	150
N ₂ pressure in mixing vessel (MPa)	0.05
Bore liquid temperature (°C)	130
N ₂ pressure in bore liquid vessel (MPa)	0.35
Spinneret temperature (°C)	135
Cooling liquid temperature (°C)	50

of length (LS), thickness (TS), outer diameter (ODS), and volume (VS) was defined as following equations, respectively.

$$LS (\%) = \left(1 - \frac{L}{L_0}\right) \times 100 \quad (1)$$

$$TS (\%) = \left(1 - \frac{T}{T_0}\right) \times 100 \quad (2)$$

$$ODS (\%) = \left(1 - \frac{OD}{OD_0}\right) \times 100 \quad (3)$$

$$VS (\%) = \left[1 - \frac{OD^2 - (OD - T)^2}{OD_0^2 - (OD_0 - T_0)^2}\right] \times 100 \quad (4)$$

Measurement of crystallinity

X-ray diffraction measurements of hollow fiber during extraction and after drying were carried out by X' Pert PRO (PANalytical) diffractometer at room temperature. In the measurement of hollow fiber during extraction, the background of corresponding extractant was deducted because its existence would interfere the diffractograms. The diffraction profiles were obtained at 40 kV and 40 mA, with a scanning rate of 1°/s.

SEM observation

The samples were fractured in liquid nitrogen and coated with gold-palladium, and then observed by a scanning electron microscope (JSM-5610LV).

Permeability of gas and water

The gas permeability of hollow fiber was measured by soap bubble flow-meter. The water permeability

TABLE II
Shrinkage of Natural Drying Hollow Fibers Treated with Different Extractants

	LS (%)	TS (%)	ODS (%)	VS (%)
Acetone	0.06	0.13	0.05	0.22
Water	0.12	0.24	0.21	0.46
Methanol	0.12	0.23	0.24	0.47

was determined according to the procedure described previously.¹¹ During the measurement, N₂ or pure water was forced to permeate from the inside to the outside of the hollow fiber membrane. The water permeability was calculated on the basis of the outer surface area of the hollow fiber membrane.

RESULTS AND DISCUSSION

Shrinkage of hollow fiber

Table II lists the value of dimension shrinkage of natural-drying hollow fibers after being treated with acetone, water, and methanol. It was found that using acetone as extractant, all the items were much smaller than others, which can be explained according to the interaction parameters of the extractants and polymer. Table III shows the value of each pair of interaction parameters calculated via Hansen solubility theory as follows:

$$\chi_{ij} = \frac{V_m}{RT} [(\delta_{di} - \delta_{dj})^2 + 0.25(\delta_{pi} - \delta_{pj})^2 + 0.25(\delta_{hi} - \delta_{hj})^2] \quad (5)$$

where V_m is the molar volume of extractant, δ_d , δ_p , and δ_h were solubility parameter components and could be directly obtained from the following equations, respectively.

$$\delta_d = \frac{\sum_i F_{d,i}}{V_m} \quad \delta_p = \frac{(\sum_i F_{p,i}^2)^{1/2}}{V_m} \quad \delta_h = \left(\frac{\sum_i E_{h,i}}{V_m} \right)^{1/2} \quad (6)$$

where i denoted the numbers of the structural groups, $F_{d,i}$ and $F_{p,i}$ were the group molar attractions, and $E_{h,i}$ was the cohesive energy contributed from hydrogen bonding.¹⁴ The T was taken as room temperature (298 K). From the Table III, it was found that the values of $\chi_{\text{EVOH38-water}}$ and $\chi_{\text{EVOH38-methanol}}$ were small, which indicated that the molecules of water and methanol had stronger interaction with polymer. The strong interaction was attributed to the generation of hydrogen bonding between polymer and extractant. Whereas, $\chi_{\text{EVOH38-acetone}}$ was much larger, which meant the affinity of them was weak. In general, during the process of extractant evaporation, the molecules of extractant will draw the polymer molecules around the pore structure because of the loss of volume, and this kind of draft force results in the shrinkage. Basically, the intensity of draft force was determined by the affinity of extractant with polymer and capillary force.⁷ The capillary force is proportional to the surface tension of extractant.⁷ Table III also listed the surface tension of each extractant, and it was found that acetone had similar value with methanol, but the volume shrinkage of methanol was as big as water, which indicated that when hydrogen bonding exists in system, the affinity of extractant with polymer was the decisive item beside the capillary force.

To reduce the shrinkage of hollow fiber, a modified drying process was carried out. The two ends of nascent fiber were fixed on a steel frame. During the drying, the frame would give a stretch force to prevent the fiber from shrinking in length direction. The data of shrinkage were shown in Table IV. Compared with Table II, it can be found that the volume shrinkage was smaller than those by the natural-drying process. Fixed-drying process could effectively reduce the fiber shrinkage. The following results were all based on this kind of drying method.

Crystallinity

Figure 2 shows the X-ray diffractograms of hollow fiber in extraction and dried state. Figure 2(b–d)

TABLE III
Solubility Parameters for EVOH38 and Extractant and the Interaction Parameters between Them

	δ (MPa) ^{0.5}	δ_d (MPa) ^{0.5}	δ_p (MPa) ^{0.5}	δ_h (MPa) ^{0.5}	χ (298K)	Surface tension, 298K (mN/m) ^a
EVOH38 ^b	26.8	16.3	9.2	29.2	–	–
Acetone ^c	20.1	15.5	10.4	7	3.685	25.63
Water ^c	47.9	15.5	16	42.4	0.405	72.75
Methanol ^c	29.7	15.1	12.3	22.3	0.260	22.07

^a Ref. 7.

^b Ref. 12.

^c Ref. 13.

TABLE IV
The Shrinkage of Hollow Fiber Using Fixed Ends Drying Process

	TS (%)	ODS (%)	VS (%)
Acetone	0.13	0.05	0.16
Water	0.24	0.20	0.39
Methanol	0.24	0.22	0.38

shows the diffractograms of hollow fiber in extraction and hollow fiber obtained after backgrounds of acetone, water, and methanol were deducted. Compared with Figure 2(a), it can be found that the sites of peaks in Figure 2(b–d) were all the same as the original polymer's, which means the crystal form did not change during extraction. However, the peak

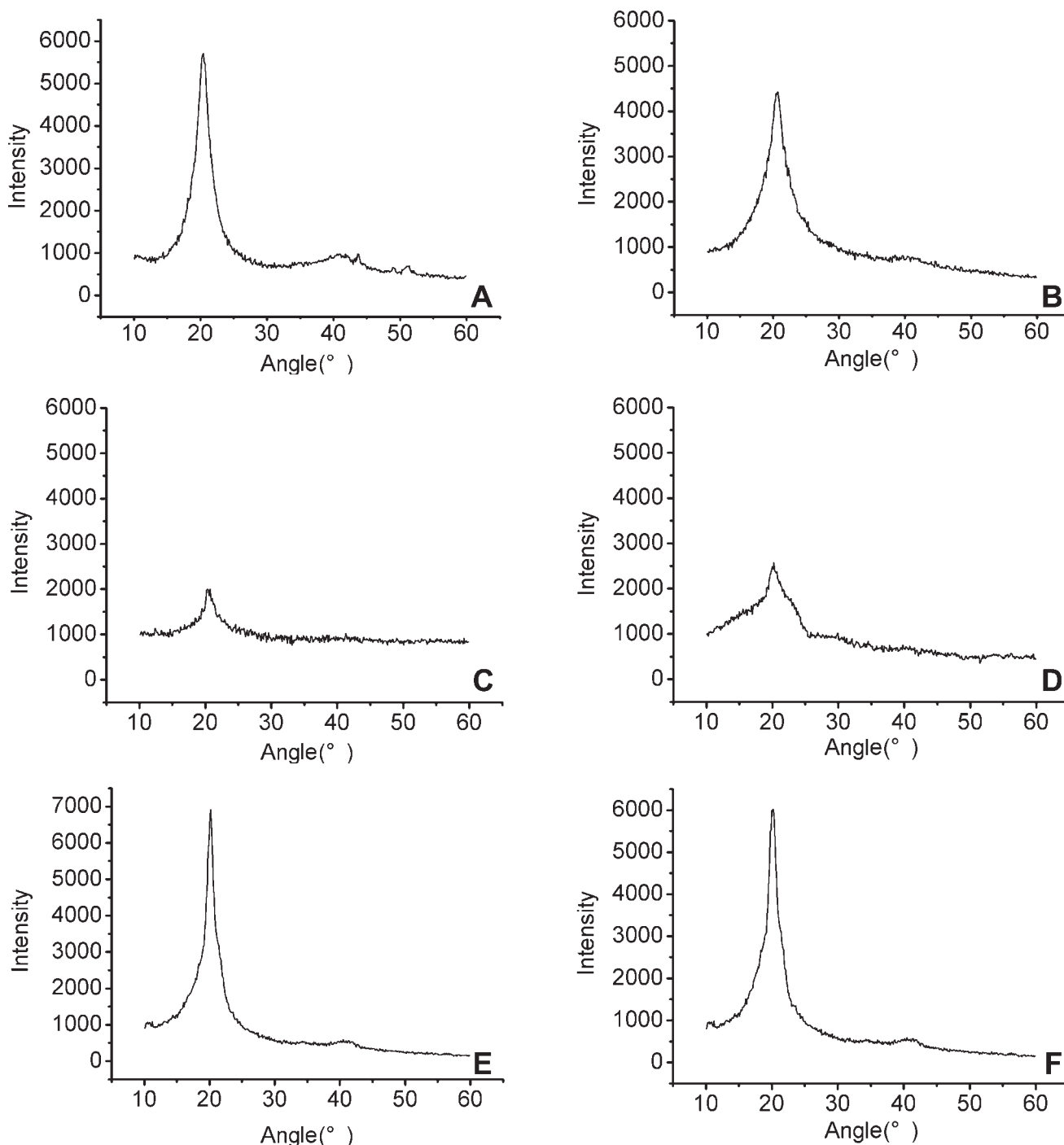


Figure 2 The X-ray diffractograms of EVOH and hollow fiber in extraction state and dried state. (A) EVOH38; (B) hollow fiber being extracted by acetone; (C) hollow fiber being extracted by water; (D) hollow fiber being extracted by methanol; (E) dried hollow fiber after extracted by water; (F) dried hollow fiber after extracted by methanol.

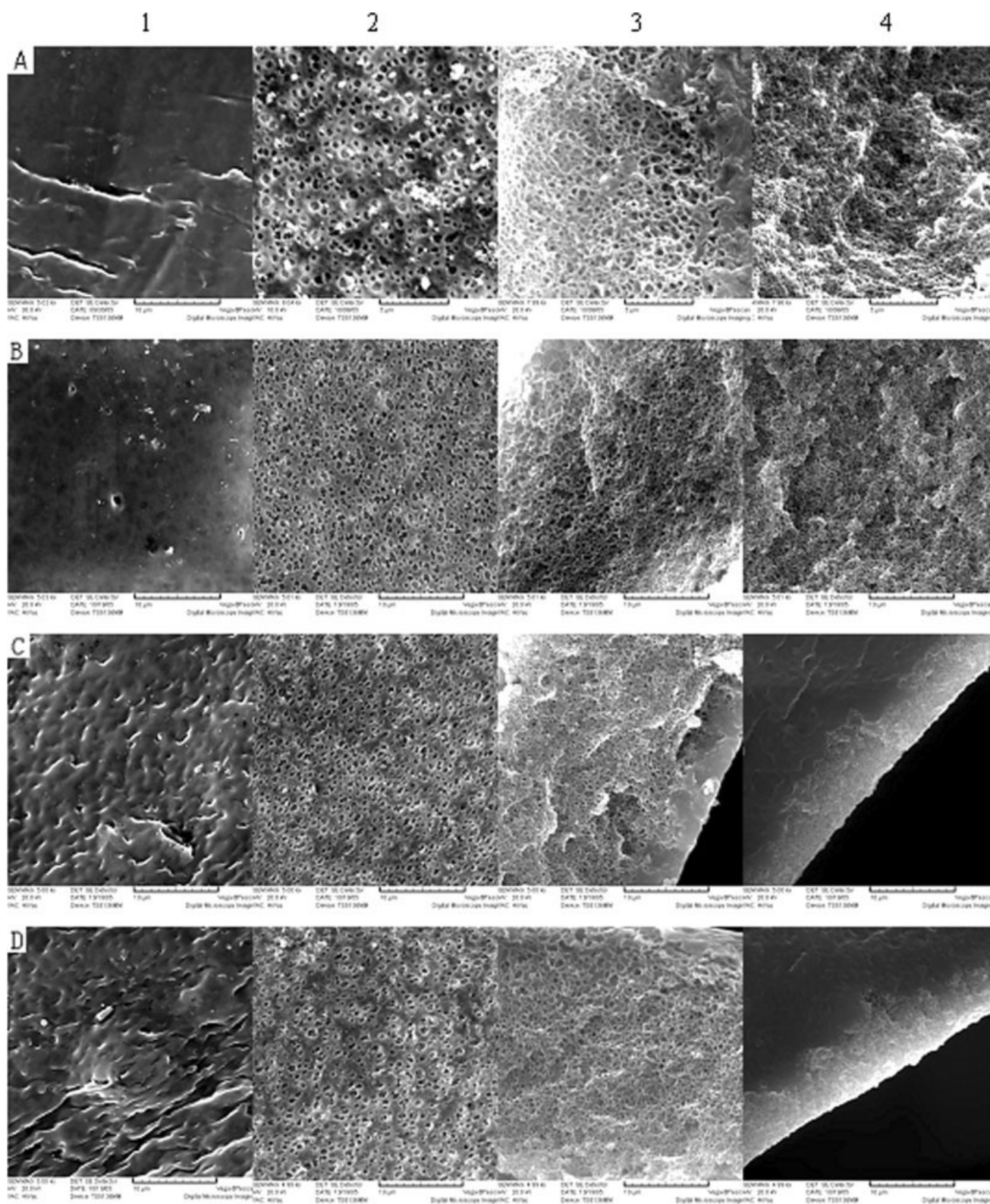


Figure 3 Micrographs of hollow fiber. (A) freeze-dried; (B) acetone-extracted; (C) water-extracted; (D) methanol-extracted; (1) outer surface; (2) inner surface; (3) cross section of outer layer; (4) cross section of inner layer.

area of Figure 2(c,d) was greatly weakened, whereas the peak area of Figure 2(b) did not change much. This can be explained from the interaction of the solvent and polymer. It has been known that the pres-

ence of solvent or diluent can cause depression of the melting point of crystalline polymer. Flory¹⁵ has given the relation of interaction parameter χ and melting point of the polymer.

$$\frac{1}{T_m} = \frac{1}{T_m^0} = \frac{RV_u}{\Delta H_u V_d} (\phi_d - \chi \phi_d^2) \quad (7)$$

where T_m and T_m^0 are the melting temperatures of the crystalline polymer in solution and in melt, respectively, V_d and V_u are the molar volume of the solvent and the repeat unit, respectively, ΔH_u is the heat of fusion for the repeat unit, ψ_d is the volume fraction of the solvent, and χ is the Flory–Huggins interaction parameter between polymer and solvent. This equation indicates that the lower the value of the interaction parameter is, the more depression of the melting point is caused. From Table III, it has been found that the values of the interaction parameter of EVOH with methanol or water are much lower than the value with acetone. Therefore, during extraction with methanol or water, the melting point of EVOH would be severely depressed due to the strong interaction between solvent and polymer, and consequently, the crystalline EVOH tends to melt. That is the reason why the peak area of Figure 2(c,d) was greatly weakened. After the solvent evaporated, the polymer molecules would crystallize again.

Hollow fiber morphology

Figure 3 shows the SEM photos of surface and cross sections of the hollow fiber extracted by different extractants. As shown in Figure 3, the hollow fiber presented asymmetric porous structure with denser

TABLE V
The Shrinkage of Hollow Fiber Extracted by Different Extractants After Vacuum Drying

	TS (%)	ODS (%)	VS (%)
Acetone	0.12	0.07	0.16
Water	0.21	0.20	0.34
Methanol	0.23	0.21	0.34

outer surface and porous inner surface. When immersed in the cooling bath of water, the polymer solution would separate into polymer-lean phase and polymer-rich phase by TIPS. Removing of the diluent resulted in the porous structure. The skin of outer surface was formed due to a high ratio of the outflow of the diluent compared with the inflow of the water in cooling bath, which resulted in high polymer concentration near the outer surface. But this phenomenon would not appear at inner surface, because solvent used as bore liquid could compensate the loss of diluent. The formation of asymmetric structure has been explained in the Ref. 3.

To compare conveniently, the hollow fiber was also prepared using freeze-drying method because this method could almost keep the original morphology.⁷ From SEM of cross section, the sample extracted by acetone had similar morphology with the sample freeze-dried, but when water and methanol was used as extractant, it was found that the pore size and porosity at their inner layer of fibers

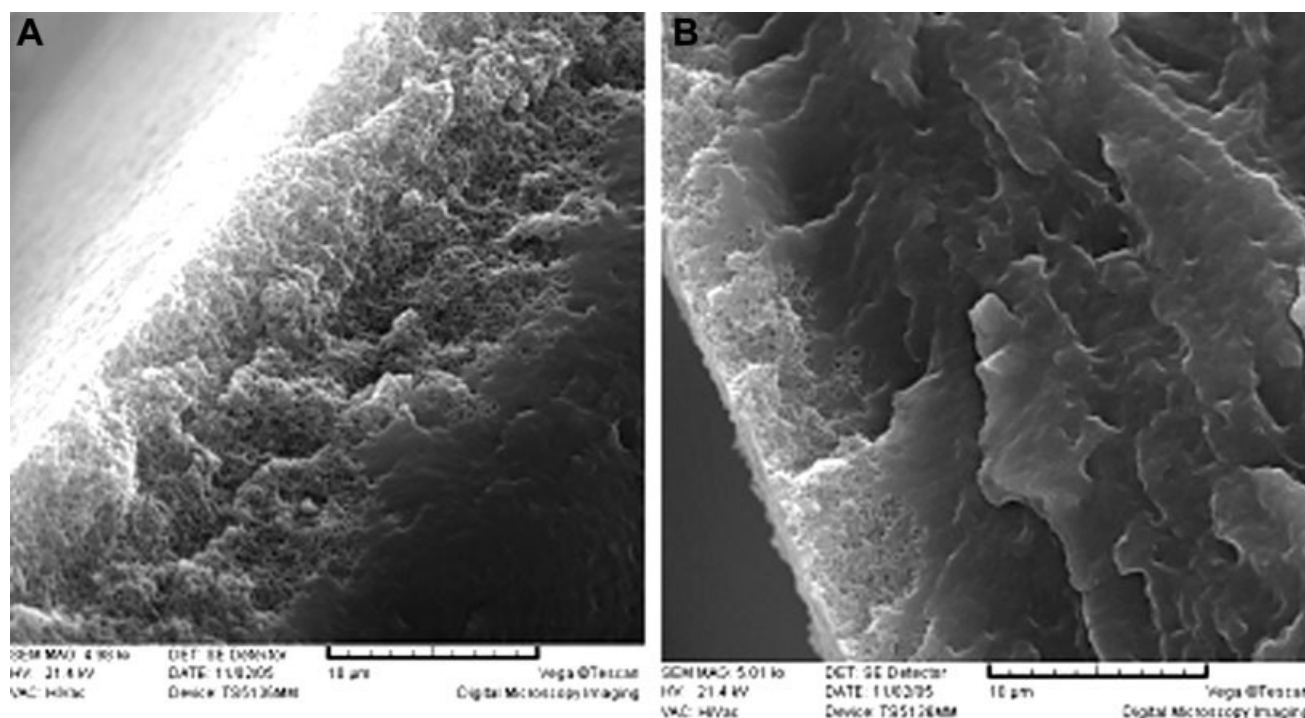


Figure 4 Cross section micrographs of hollow fiber extracted with water: (A) by vacuum drying; (B) by natural drying.

TABLE VI
The Gas and Water Permeability of Hollow Fiber Treated with Different Extractants and Different Drying Methods

	Flux _{N₂} (mL s ⁻¹ cm ⁻² MPa ⁻¹)		Flux _{H₂O} (L m ⁻² h ⁻¹ MPa ⁻¹)	
	Naturally dried	Vacuum-dried	Naturally dried	Vacuum-dried
Acetone	11.2	11.8	496	541
Pure water	0.32	2.39	32	130
Methanol	Undetectable	0.21	Undetectable	Undetectable

became smaller, which must result from the larger volume shrinkage and the pore collapse caused by the extractants due to the better affinity of the two extractants with the polymer. As shown in Figure 3, there was no obvious difference in inner surface morphology of all the samples. However, the outer surface of sample extracted by acetone was smoother than those by water and methanol. This is because water and methanol would give a stretch force resulting in crackle on outer surface, when the two ends of fiber were fixed on a frame during drying.

The mechanism of pore collapse was the result of movement of molecules. To find out whether the extent of shrinkage could be controlled by the evaporation speed, vacuum-drying method was carried out to speed evaporation of extractant. Table V listed the shrinkage of hollow fiber via vacuum drying. If compared with the data of Table IV, it can be found that the shrinkage of vacuum-dried hollow fiber extracted by water was smaller than the fiber naturally dried. As shown in Figure 4, the pore structure was clearer for the fiber vacuum-dried. Hence, the pore structure collapse was a kinetic process; the membrane morphology could be controlled by the speed of the extractant evaporation.

When acetone and methanol were used as extractant, the shrinkage seems not changed (see Tables V and IV). This is because the boiling point of these two solvents was lower, and the difference of evaporation speed between natural drying and vacuum drying was small.

Properties of hollow fiber

Table VI shows the gas and water permeability of hollow fibers treated with different extractants and by different drying method. It was indicated that the permeability of vacuum-dried hollow fibers was better than naturally dried, and the fibers extracted by acetone showed much better performance than the fiber by other two extractants. The results are coincident with the SEM images and shrinkage data.

CONCLUSIONS

EVOH38 hollow fibers were prepared via TIPS process. Water, methanol, and acetone were used to

extract the diluent in the fibers, respectively. Bigger shrinkage of fibers during extractant evaporation was observed when water or methanol was used. The results of calculation for interactive parameters indicated that the molecules of water and methanol had stronger interaction with EVOH38. Therefore, the affinity of extractant with polymer would be the crucial factor for the shrinkage during extractant evaporation. Besides, the analysis of X-ray diffraction in extraction process indicated that water and methanol could cause the crystalline polymer to melt partly, and after the solvent evaporated, the polymer can recrystallize. The smaller pore size and porosity at inner layer of fibers were observed on the SEM images of cross section of hollow fibers treated with water and methanol. The denser morphology must result from the larger volume shrinkage and the collapse of porous structure caused by the extractants due to the better affinity of the two extractants with the polymer. The measurement results of water and gas permeability are coincident with the SEM images and shrinkage data.

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