

Effect of Polyethylene Glycol on the Performance of Ultrahigh-Molecular-Weight Polyethylene Membranes

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ABSTRACT: Porous, flat membranes of ultrahigh-molecular-weight polyethylene (UHMWPE) were prepared by thermally induced phase separation, with mineral oil as a diluent and poly(ethylene glycol) with a weight-average molecular weight of 20,000 (PEG20000) as an additive. Through the control of the rheological behavior, crystallite size, and pore structure, the influential factors, including the diluent, poly(ethylene glycol) (PEG) content, and cooling rate, were investigated. The results suggested that PEG could decrease the viscosity of UHMWPE/diluent apparently. The crystal density decreased when mineral oil was added, which made the melting point and crystallinity of UHMWPE lower. The crystallization rate and crystallinity also increased with the addition of PEG. However, the addition of excess PEG restrained crystal growth.

PEG20000 in membranes could be extracted absolutely through the soaking of the membranes with fresh water for 7 days. With increasing PEG content, both porosity and pure water flux first increased and then decreased, reaching a maximum at a PEG mass fraction of 10%. The cooling rate had a direct effect the crystal structure. A slow cooling rate was good for crystal growth and diluent integration. Therefore, the pure water flux increased along with the temperature of the cooling medium, whereas porosity first increased and then decreased, reaching a maximum at 40°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 720–728, 2010

Key words: high performance polymers; membranes; phase separation; polyethylene (PE)

INTRODUCTION

Membrane material is an important part of membrane separation technology. With the development of membrane technology, the requirements should be higher for the performance of membrane material, including its chemical stability, mechanical intensity, and so on, in industry. As a new type of engineering thermoplastic, ultrahigh-molecular-weight polyethylene (UHMWPE) has incomparable properties among plastics because of its physical chemistry stability.^{1–3} However, UHMWPE presents in a rubbery state in melting because of its ultrahigh molecular weight ($>1.0 \times 10^6$). Thus, UHMWPE has almost no liquidity. Furthermore, UHMWPE has a small frictional coefficient and low critical shearing rate. All of these properties make UHMWPE hard to process. Thereby, it is seldom made into membranes with routine methods such as melt stretching.

Thermally induced phase separation (TIPS) was first used by Castro⁴ in the 1980s and has gained much interest. It is a valuable method for producing

microporous structures in some applications.^{5,6} In the TIPS process, a polymer and diluent are blended to a homogeneous phase at a sufficiently high temperature. The diluent is a low-molecular-weight, high-boiling chemical that is not a solvent for the polymer at room temperature but acts as one at higher temperatures. The homogeneous solution undergoes phase separation with the diluent extracted when it is cooled. The voids left by the droplets are referred to as *cells*.^{7,8}

The viscosity of the UHMWPE/diluent system is smaller than that of the UHMWPE melt. Therefore, microporous membranes of UHMWPE can be prepared by TIPS. Lopatin and Yen⁹ first prepared microporous membranes of UHMWPE by the TIPS method, using mineral oil as the diluent. Both the air permeability and water permeability of the UHMWPE membranes were better than these of high-density polyethylene (HDPE) membranes. The porosity was 64% when the extractant was hexane, whereas it was 48% when the extractant was ethanol. Takia et al.¹⁰ investigated different blending ratios of UHMWPE/HDPE. They discovered that the elongation of the membrane increased and the thermal shrinkage of the membrane decreased when UHMWPE was increased. Porous, flat membranes of UHMWPE were prepared as thermally resistant and solvent-resistant membranes by the TIPS method by

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Ding et al. in 2007.¹¹ Diphenyl ether and decalin were chosen as the diluents. The phase diagrams were drawn with the cloud-point temperatures and the crystallization temperatures. According to the phase diagrams, scanning electron microscopy (SEM) images, and porosities of the samples, the influential factors, including the polymer concentration, cooling rate, and viscosity, were investigated.

Poly(ethylene glycol) (PEG) is frequently used as an additive in the preparation of membranes.¹² However, porous UHMWPE membranes, prepared by means of the addition of PEG, have not been reported yet. In this study, poly(ethylene glycol) with a weight-average molecular weight of 20,000 (PEG20000) as an additive not only decreased the viscosity of the UHMWPE/diluent solution but also improved the porous structure. Moreover, to obtain UHMWPE membranes with excellent permeability through the control of the rheological behavior, crystallite size, and pore structure, the influential factors, including the diluent, PEG content, and cooling rate, were investigated.

EXPERIMENTAL

Materials

UHMWPE (MIII) was purchased from Beijing No. 2 Reagent Plant (Beijing, China) and had a weight-average molecular weight of 3,650,000. Mineral oil (7#) and gasoline were produced by the Oil Refinery Plant of Daqing Petrochemical Co. The antioxidant (1076#) was a commercial product of Tianjin Lisheng Chemical Plant (Tianjin, China). PEG20000, alcohol, and glycerol were analytically pure.

Preparation of the UHMWPE membranes

The steps for preparing the porous, flat UHMWPE membranes were as follows. First, the UHMWPE, diluent, antioxidant, and PEG20000 were mixed well at 50°C at a high rotating speed (45 rpm) in a stirred autoclave for 1 h to uniformly disperse the polymer in the diluent. Then, the mixture was heated to 140°C for 1 h. After it swelled enough, the solution was stirred strongly for 3–4 h at 175°C to prepare the homogeneous casting solution. All of these steps were done *in vacuo* to avoid bubbles in solution. The resulting homogeneous solution was cast onto a steel plate to form a flat gel membrane (the diameter of the scraping stick was 0.4 mm) by immersion in a cooling medium (water). The cooling medium was 20°C. The gel membranes were put into gasoline for 48 h to extract the diluent, and the last step was to take some measures to extract the gasoline.

The methods used to extract the gasoline in this study included the following two types. The extraction of the residuary gasoline in a relaxed state with alcohol after the gasoline was volatilized in air for 12

h is intitled *extracting method I*. The extraction of the residuary gasoline in an intension state with alcohol after the gasoline was volatilized in air for 12 h is intitled *extracting method II*. The resulting membranes were soaked with fresh water for 7 days to extract the PEG20000 in the membrane. When studying the effect of the PEG content on the melting behavior and crystallization membranes, we used extracting method I. When studying the effect of the PEG content and cooling rate on the permeability of membranes, we used extracting method II. Before the SEM tests, the resulting membranes were put into glycerol–water solution (3 parts glycerol to 2 parts water) for 24 h. Then, the membranes were dried in air.

Pure water flux experiments

The membranes were kept in fresh water for at least 48 h. The pure water flux of the UHMWPE membranes were calculated as follows:¹³

$$J = \frac{V}{S \times t} \quad (1)$$

where J is the flux, V is the total permeation (L), S is the total permeation area (m²), and t is the total permeation time (h). The operating pressure difference across the membrane was 0.1 MPa, and the operating temperature was 25 ± 1°C.

Porosity measurement

We determined the porosity of the blend membrane by measuring the true density (ρ_t) and bulk density (ρ_b).¹⁴ The sample was put into a density bottle (10 mL) filled with alcohol, and the equation of cubage was expressed as follows:

$$10 = \frac{M_a}{\rho_a} + \frac{M_m}{\rho_t} \quad (2)$$

where M_a and M_m are the weights of the residual alcohol in the density bottle and the dry membrane, respectively, and ρ_a is the density of alcohol. Therefore, ρ_t was calculated as follows:

$$\rho_t = \frac{M_m \times \rho_a}{10\rho_a - M_a} \quad (3)$$

To measure ρ_b , the blend membrane was swollen at 20°C for 12 h, and the wet weight (M_{wm}) was measured. The free liquid on the surface of the swollen membrane was padded dry with filter paper before weighing. The dry weight (M_{dm}) was measured after the sample was dried *in vacuo*. The bulk volume (V_b) was calculated as follows:

$$V_b = \frac{M_{wm} - M_{dm}}{\rho_a} + \frac{M_{dm}}{\rho_t} \quad (4)$$

ρ_b was calculated as follows:

$$\rho_b = \frac{M_{dm}}{V_b} \quad (5)$$

The porosity of the sample (ε) was calculated as follows:

$$\varepsilon(\%) = \left(1 - \frac{\rho_b}{\rho_t}\right) \times 100 \quad (6)$$

Rheological behavior experiments

A rotary rheometer (AR1000, TA Instruments, New Castle, DE) equipped with parallel plates 25 mm in diameter with 1-mm plate spacing was used to measure the viscoelastic properties at a temperature of 160°C. The samples were compression-molded disks. All samples were pretreated at a constant temperature of 160°C for 3 min. The shear rate ranged from 0.10 to 100.00 s⁻¹.

Morphology examination

The structure and morphology of the membranes were observed by SEM (Quanta 200, FEI Company, Eindhoven, Netherlands). Cross sections of membranes were freeze-fractured under liquid nitrogen. The membrane samples were gold-sputtered and analyzed by SEM.

Differential scanning calorimetry (DSC) experiments

The melting point, crystallization temperature, melting limit, and crystallinity were determined with DSC (model 200F3, Netzsch Company, Bavarian, Germany). The samples were heated from 0 to 200°C at a heating rate of 1°C/min under a nitrogen atmosphere. After waiting at least 5 min to ensure complete melting and equilibrium, the samples were cooled at a cooling rate of 1°C/min. The sample weight was approximately 5 mg. The crystallinity of the sample was calculated from the heats of fusion taken from the thermograms, with the assumption that a purely crystalline polyethylene had a heat of fusion of 289 J/g.¹⁵ When the mineral oil was present in sample, the values were those measured for the mixture of UHMWPE and mineral oil. Therefore, the crystallinity was relative. The quantity of mineral oil present in the samples was not measured and could not be assumed to be the original content because there was visual evidence that some of the oil migrated to the membrane surface during processing. Analyses of the mineral oil content of extrudates will be carried out in the future with a technique based on supercritical fluid extraction.

Wide-angle X-ray diffraction (WAXD) experiments

WAXD patterns were taken with a diffractometer (X'Pert MPD, Philips Company, Eindhoven, Netherlands). The X-ray beam was graphite-monochromator-filtered (wavelength = 1.54 Å) with Cu K α radiation at 40 kV and 45 mA. The scanning speed was 8°/min. The scanning area of the Bragg angle was from 2 to 40°.

The crystallite size was calculated with the Sherrer equation:¹⁶

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta_{hkl}} \quad (7)$$

where θ_{hkl} is the Bragg angle of a certain diffraction plane (hkl), λ is the wavelength of the incident wave, D_{hkl} is the average size of the normal direction of the crystal plane, β is the peak width, and k is the Sherrer constant. The value of k is about 0.89 when β is the peak width at half-height.

RESULTS AND DISCUSSION

Effect of the PEG content on the rheological behavior of the UHMWPE/diluent solution

Figure 1 displays the rheological curve of the UHMWPE/diluent solution with difference PEG contents. As shown, the viscosity of the UHMWPE/diluent solution was higher than that of the UHMWPE/PEG/diluent solution. Moreover, the viscosity decreased as with increasing PEG content. The apparent viscosity decreased markedly at slow shear rates when the PEG mass fraction reached 15%.

Melting behavior and crystallization of the UHMWPE/diluent solution

Figure 2 and Table I show the effect of the diluent on the melting behavior and crystallization of

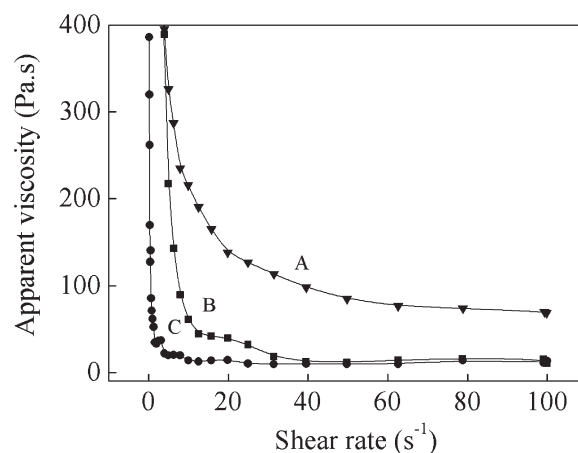


Figure 1 Rheological curves of (A) UHMWPE/diluent, (B) UHMWPE/PEG20000 (10%)/diluent, and (C) UHMWPE/PEG20000 (15%)/diluent.

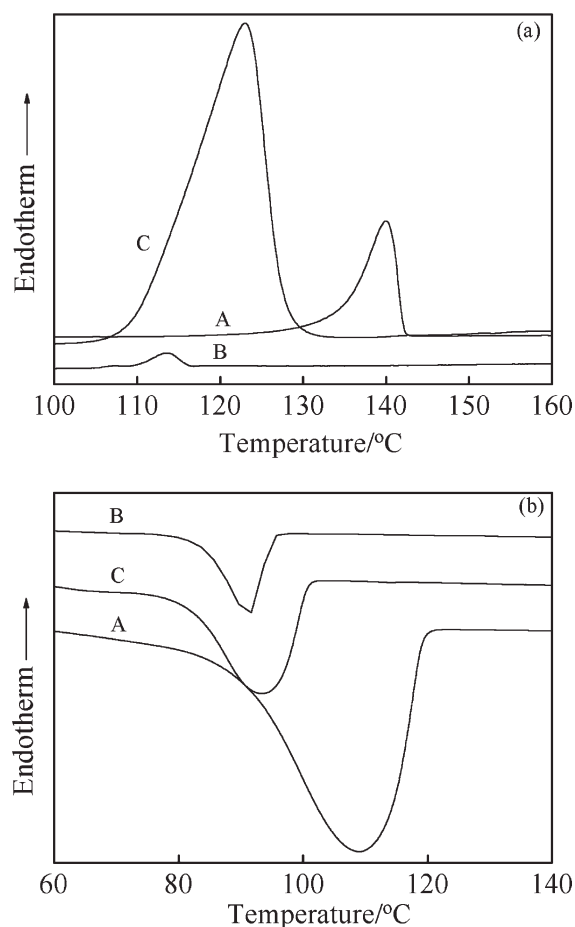


Figure 2 Effect of the diluent on DSC curves in (a) the ascending range and (b) the descending range: (A) UHMWPE powder, (B) UHMWPE/diluent, and (C) UHMWPE membrane (with extraction method III).

UHMWPE. As shown, the melting point of the UHMWPE powder was higher than that of the UHMWPE membrane, which was attributed to the decrease in the molecular weight of UHMWPE as a result of the thermal degradation of UHMWPE in the membrane preparation.¹⁷ The decrease in the molecular weight of UHMWPE made both the molecular symmetry and the intermolecular force decrease; thus, the melting of UHMWPE decreased.¹⁸ The melting point of the UHMWPE/diluent was the lowest. The crystallization temperature showed the opposite trend.

Generally, the decrease of melting point is the result of the strong interaction between two kinds of compatible polymeric melting state.¹⁹ In this study, the mineral oil as a diluent was beneficial to the increase in the crystallization rate. However, the diluent could not be excluded from the crystal region completely in the high crystallization rate. Thus, the crystal defect made the crystalline density decrease, which presented as loose molecular chain packing, weak intermolecular interactions, melting enthalpy, and a decrease in the melting point and crystallization.²⁰ The effect of various small molecular diluents, including the plasticizer, unreacted monomer, and soluble additive, on the decrease of the polymeric melting point can be defined as follows:²¹

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{RV_A}{\Delta H_m^0 V_1} \left[\frac{\phi_1}{P_1} - \chi_1 \phi_1^2 \right] \quad (8)$$

where R is a constant, and V_A and V_1 are the molar volumes of the polymeric repeating units and diluent repeating units, respectively; ϕ_1 is the volume fraction of the diluent; P_1 is the polymerization degree; χ_1 is the interaction coefficient between the polymeric molecule and diluent; T_m^0 is the melting point of the polymer; ΔH_m^0 is the molar enthalpy of the polymeric repeating units; and T_m is the melting point of the polymer after the addition of the diluent. The decreasing degree of the melting point may have been related to the diluent content and the interaction between the polymeric molecule and the diluent. The mineral oil in this study was a good solvent for UHMWPE.²² We concluded that T_m was lower than T_m^0 ; this resulted from χ_1 being less than zero.

As shown in Figure 3, the diffraction peak at $2\theta \approx 17.70^\circ$ was attributed to the interference of mineral oil. In the UHMWPE powder and UHMWPE/diluent, the diffraction peaks at 20.98° and 23.36° were the orthorhombic (110) and (200) reflections.²³ The results indicate that mineral oil had no effect on the crystal form of UHMWPE. The crystallite size increased through the addition of diluent, as shown in Table I. This was because the diluent decreased the concentration of the UHMWPE crystalline molecule, which made the UHMWPE molecular chains disperse in the diluent and separate from each other.

TABLE I
Effect of the Diluent on the Melting and Crystallization Behaviors

Sample	Melting point of UHMWPE (°C)	Crystallization temperature of UHMWPE (°C)	Crystallinity (%)	D_{110} (nm)	D_{200} (nm)
UHMWPE powder	139.99	109.00	68.50	7.27	6.64
UHMWPE/diluent	113.54	91.07	—	13.10	16.71
UHMWPE membrane	123.03	93.36	20.05	—	—

D_{110} and D_{200} are the sizes of crystal plane (110) and (200) respectively.

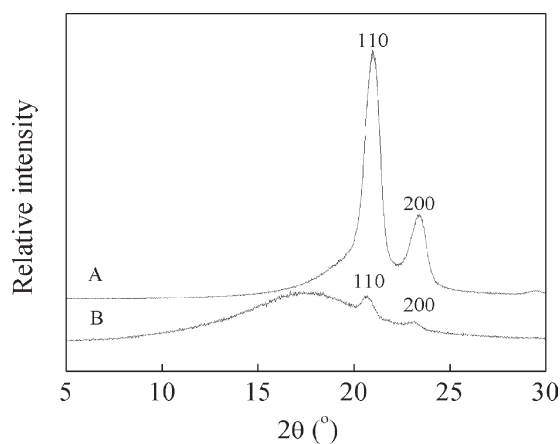


Figure 3 Effect of the diluent on the X-ray diffraction pattern: (A) UHMWPE powder and (B) UHMWPE/diluent.

By preventing the entanglement of molecular chains, the crystallites grew better.²⁴

As are shown in Figure 4 and Table II, PEG had an apparent effect on the melting behavior and crystallization of UHMWPE in UHMWPE/diluent, including the increase of the melting point, crystallization temperature, relative crystallinity, and crystallite size. In addition, a small shoulder peak was more obvious at the mass fraction of PEG reached 10%. Figure 5 shows that the diffraction peaks at 20.6° at a PEG mass fraction of 10% were hexagonal (100); this resulted from a part of the orthorhombic transforming to the hexagonal.

The polymerization degree of PEG20000 was higher. Therefore, eq. (8) could be simplified as follows:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_A}{\Delta H_m^0 V_1} \chi_1 \phi_1^2 \quad (9)$$

At first, χ_1 was greater than zero because PEG was a nonsolvent for UHMWPE. The weak attraction between PEG and UHMWPE made the dissolving process an endothermic reaction. Thus, the melting point increased with the addition of PEG. Second, the dissolving ability of mineral oil decreased with the addition of nonsolvent. This may have increased the crystallization temperature and provided enough time for UHMWPE to crystallize. Furthermore, the viscosity of the UHMWPE/diluent solution decreased with the addition of PEG20000,

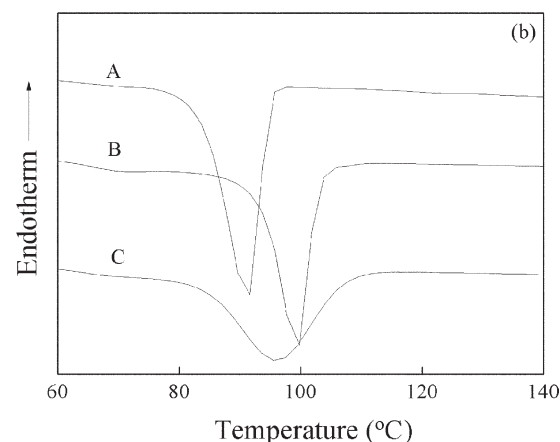
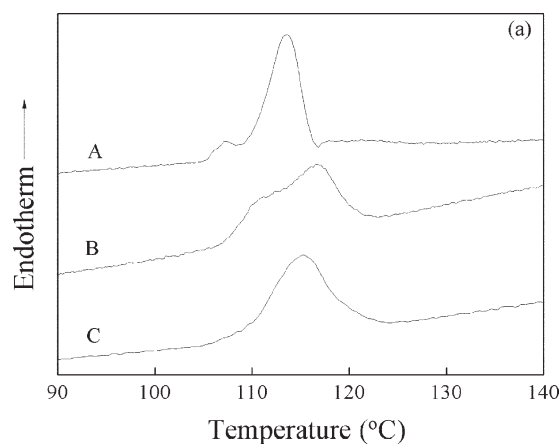


Figure 4 DSC curves of UHMWPE/diluent solutions with different PEG20000 contents in (a) the ascending range and (b) the descending range: (A) UHMWPE/diluent, (B) UHMWPE/PEG (10%)/diluent, and (C) UHMWPE/PEG (15%)/diluent.

as shown in Figure 1. The UHMWPE molecular motion was strong in a low-viscosity solution, which was beneficial to the growth of crystallites.

However, the melting point, crystallization temperature, and crystallite size decreased at a PEG mass fraction of 15%. At the same time, the small shoulder peak disappeared in the DSC curve. The results indicated that some small crystallites disappeared because of the low-viscosity solution with the addition of excess PEG. Nevertheless, the excess

TABLE II
Effect of the PEG20000 Content on the Melting and Crystallization Behaviors

Sample	Melting point of UHMWPE (°C)	Crystallization temperature of UHMWPE (°C)	Relative crystallinity (%)	D_{100} (nm)	D_{110} (nm)	D_{200} (nm)
UHMWPE/diluent	113.54	91.07	5.52	—	7.89	8.37
UHMWPE/PEG (10%)/diluent	116.72	99.32	6.37	15.51	9.00	8.83
UHMWPE/PEG (15%)/diluent	115.26	96.07	6.62	—	6.64	7.18

D_{100} , D_{110} and D_{200} are the sizes of crystal plane (100), (110), and (200) respectively.

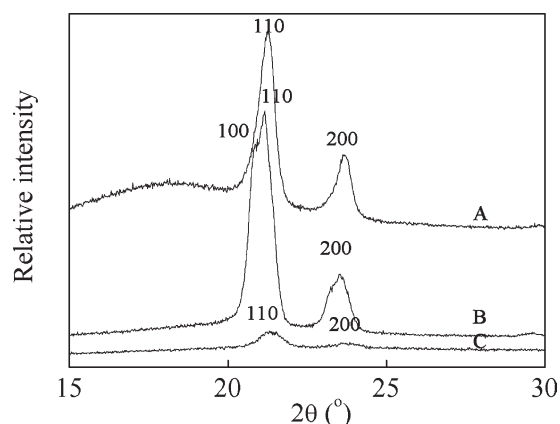


Figure 5 Effect of PEG20000 on the X-ray diffraction patterns of the membranes: (A) no PEG, (B) 10% PEG, and (C) 15% PEG.

PEG restrained the UHMWPE molecules from contacting each other and forming steady crystallites. Thus, the crystallite size decreased.

Remnant of PEG20000 in the UHMWPE membrane

PEG20000 as an additive not only decreased the viscosity of the UHMWPE/diluent solution but also improved the porous structure by means of PEG dissolving in water. Figure 6 shows the DSC curves of the membrane (with extracting method III) after PEG was extracted (with extracting method III) and the UHMWPE/PEG (10%)/diluent solution. As shown in Figure 6 and Table III, the two endotherm peaks at 56.94 and 107.74°C corresponded to the melting of PEG20000 and UHMWPE, respectively. The melting peak of PEG20000 disappeared, and the melting peak of UHMWPE shifted toward a high

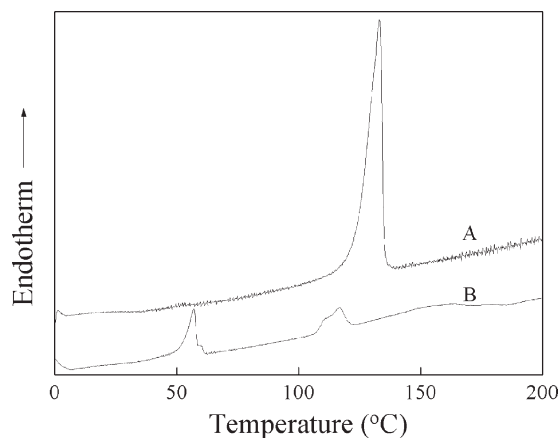


Figure 6 DSC curves in the ascending range of (A) the UHMWPE membrane (with extraction method III) after the extraction of PEG and (B) UHMWPE/PEG (10%)/diluent.

TABLE III
Effect of Extracting PEG20000 on the Melting and Crystallization Behaviors

Sample	Melting point of PEG20000 (°C)	Melting point of UHMWPE (°C)
UHMWPE/PEG (10%)/diluent	56.94	107.74
UHMWPE membrane	—	133.00

temperature after the membrane was soaked with fresh water for 7 days, which indicated that PEG20000 was extracted completely by water. The removal of PEG20000 supplied a lot of free space for UHMWPE molecular motion, which was beneficial for crystallization. Moreover, the space of PEG dissolution could be considered as a porous structure, which greatly contributed to the improvement of the permeability of the UHMWPE membranes.

Effect of the PEG20000 content on the membrane permeability

As shown in Figure 7, the pure water flux of the UHMWPE membrane without additive was very low, which was probably because of the dense pore structure formed by the molecular network [Fig. 8(a)].

With the mass fraction of PEG increased, the viscosity of the UHMWPE/diluent decreased, which had a great influence on the diluent droplet growth. The lower viscosity was beneficial for the flowing and coalescence of the diluent droplets. Thus, through extracting diluent, the occupied space by diluent increased. Moreover, both the quantity and pore diameter of the PEG dissolving pores increased with increasing PEG content, as shown in Figure 8(b,c). Therefore, the pure water flux and porosity of

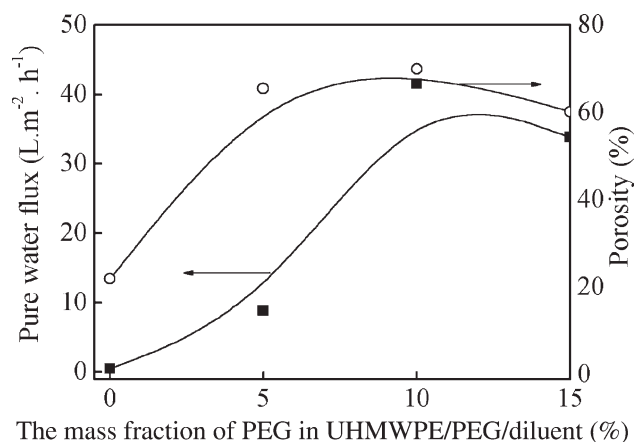


Figure 7 Effect of the PEG20000 content on the pure water flux and porosity of the membranes.

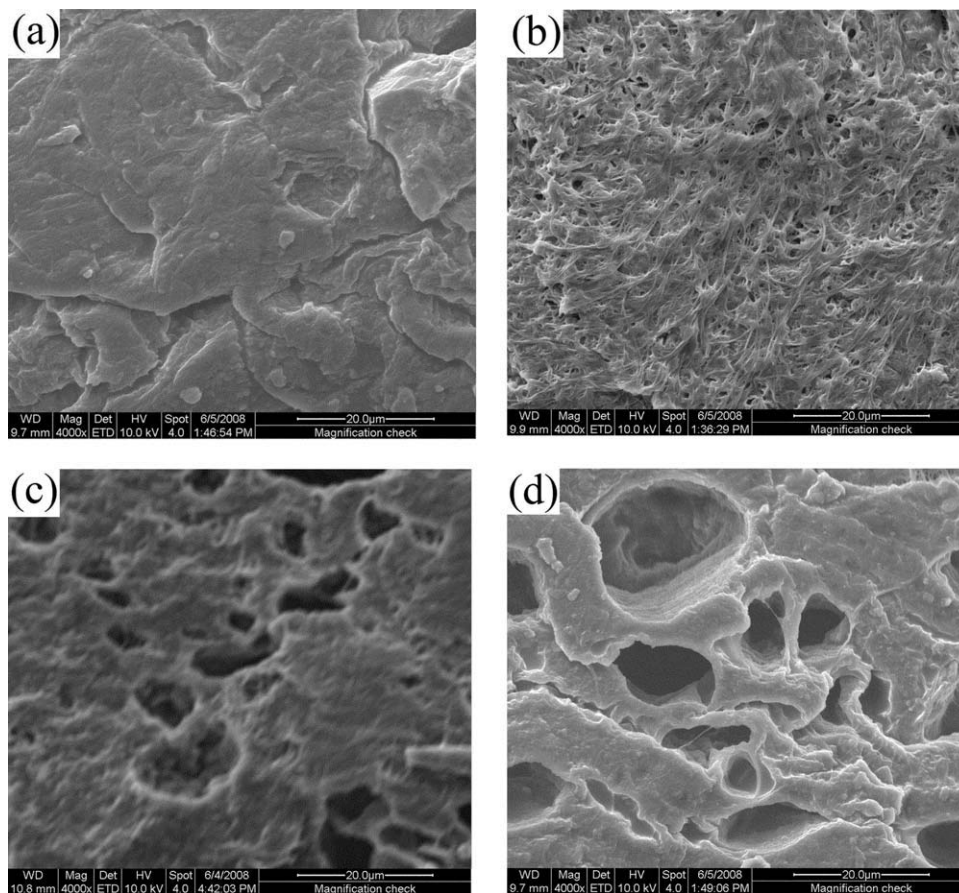


Figure 8 Cross-sectional SEM graphs of the UHMWPE membranes: (a) no PEG, (b) 5% PEG, (c) 10% PEG, and (d) 15% PEG.

the UHMWPE membrane increased with increasing PEG content.

When the PEG content was too large, the quantity of PEG dissolving pores decreased because of PEG aggregation and the bad connectivity of the pores [Fig. 8(d)]. Therefore, the pure water flux and porosity of the UHMWPE membrane decreased with the addition of excess PEG.

Because of the low glass-transition temperature of UHMWPE,²⁵ the UHMWPE membrane is easily deformed under high pressure. Thus, the bubble-point pore diameter of the membranes is not discussed in this article.

Effect of the cooling rate on the permeability of the UHMWPE membrane

As are shown in Figure 9, pure water flux increased with the temperature of the cooling medium, whereas the porosity first increased and then decreased, reaching maximum at 40°C. These trends were attributed to the effect of the cooling rate on the diluent droplet growth and crystal state.^{26–28}

When the cooling rate was high, the diluent became stringy before the crystallization of the poly-

mer. The density of the crystal nucleus was large, and the crystallite size was small, which evidently resulted from the polymer crystallization being hindered by the stringy diluent. The gap between the two crystallites was very small.²⁹ Therefore, the pore diameter and pure water flux of membrane were greatly small at the high cooling rate. Furthermore,

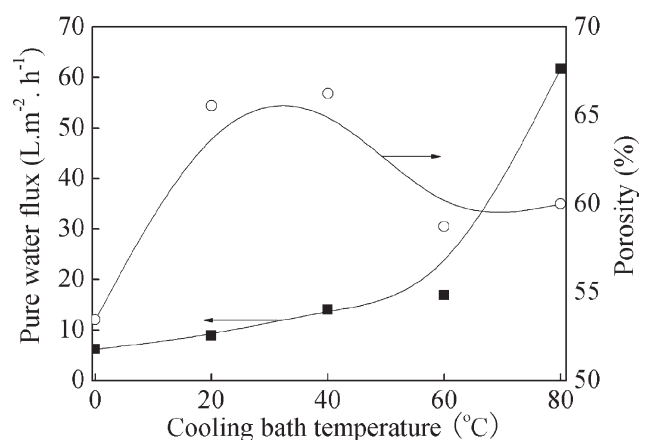


Figure 9 Effect of the cooling medium temperature on the pure water flux and porosity of the membranes (5% PEG).

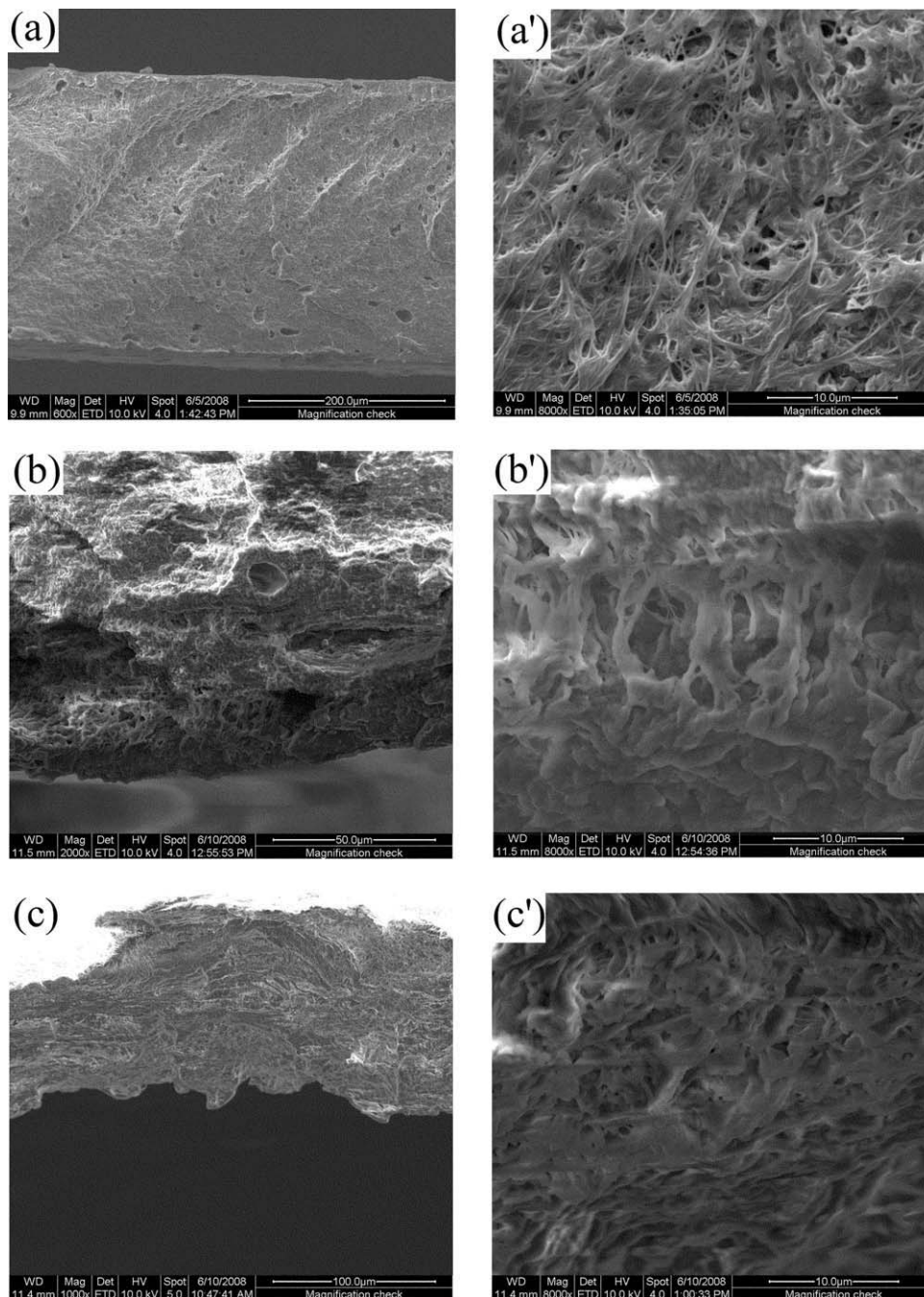


Figure 10 Cross-sectional SEM graphs of membranes (5% PEG) with cooling medium temperatures of (a,a') 20, (b,b') 60, and (c,c') 80°C.

at the high cooling rate, the time of phase separation before solidification was shortened, and then, the polymer-rich phase and polymer-lean phase did not have enough time to coarsen. Thus, the diluent could not conglomerate into bigger droplets. This also made the pore diameter decrease, as shown in Figure 10(a,a'). The results were contrary when the temperature of the cooling medium increased. Moreover, a slow cooling rate was good for the macromolecular chain entanglement once again. The micelle pores could form, as shown in Figure 10(b,b'). The

micelle pores had a larger size than the molecular network pores. Accordingly, a proper high temperature of the cooling medium could be used to prepare UHMWPE membranes with a high pure water flux.

As the temperature increased further, a part of PEG20000 dissolved in the cooling medium (hot water) before the extraction process. The PEG dissolving porous structure collapses were attributed to the shrinking of the membrane, as shown in Figure 10(c,c'). Therefore, the porosity decreased at too high cooling temperature. However, the high temperature

was beneficial for the crystallization of UHMWPE. The large gap between the two crystallites made the membrane have a high pure water flux.

CONCLUSIONS

Porous, flat UHMWPE membranes were prepared by TIPS, with mineral oil as the diluent and PEG20000 as an additive. Through the control of the rheological behavior, crystallite size, and pore structure, the influential factors, including the diluent, PEG content, and cooling rate, were investigated. The results indicate that the addition of mineral oil decreased the crystal density, which made the melting point and crystallinity of UHMWPE decrease. PEG decreased the viscosity of the UHMWPE/diluent apparently. The lower viscosity was beneficial to the improvement of the crystallization rate and crystallization. However, the overaddition of PEG went against crystal growth because excess PEG restrained the UHMWPE molecules from contacting each other and forming steady crystallites. PEG20000 as an additive not only decreased the viscosity of the UHMWPE/diluent solution but also improved the porous structure by means of obtaining PEG dissolving pores. With increasing PEG content, both the porosity and pure water flux first increased and then decreased, reaching a maximum at a PEG mass fraction of 10%. The cooling rate had a direct effect on the crystallization of UHMWPE. A slow cooling rate was beneficial for crystal growth and diluent integration. Therefore, the pure water flux increased along with the temperature of the cooling medium, whereas the porosity first increased and then decreased, reaching a maximum at 40°C.

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