

The Effect of Binary Diluents on the Performance of Ultrahigh Molecular Weight Polyethylene/SiO₂ Hybrid Hollow Fiber Membrane

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ABSTRACT: Ultrahigh molecular weight polyethylene (UHMWPE)/SiO₂ hybrid hollow fiber membranes were prepared by thermally induced phase separation (TIPS) using mineral oil as the first diluent, polyethylene oxide (PEO) as the second diluent, and SiO₂ as additive. The effect of PEO on the rheological behavior, FTIR-ATR spectra, phase diagram, morphology, and permeability was investigated. The results suggested that a proper amount of PEO can decrease the viscosity of UHMWPE/diluent appropriately. Because PEO and UHMWPE were incompatible, the miscibility of membrane dope could be changed by PEO, which directly affect the phase separation. It was also discovered that a

spherulite structure, coming from solid–liquid (S–L) TIPS, was built at any UHMWPE concentration without PEO. Whereas, an open-cell porous structure with better connectivity, owing to liquid–liquid (L–L) phase separation, was produced after adding PEO. The permeability increased firstly, and then decreased because excessive PEO was sensitive for agglomeration. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: E169–E176, 2012

Key words: ultrahigh molecular weight polyethylene (UHMWPE); polyethylene oxide (PEO); hybrid membrane; second diluent

INTRODUCTION

Membrane material is an important part of membrane separation technology. With the development of membrane technology, the requirement should be higher for the performance of membrane material including chemical stability, mechanical intensity, and so on in industry. As a new type of engineering thermoplastic, ultrahigh molecular weight polyethylene (UHMWPE) has incomparable properties, such as good impact resistance, abrasion performance, self-lubricating, solvent resistance, and excellent low-temperature resistance.^{1,2} Thermally induced phase separation (TIPS) method is the one of main techniques for preparation of polymeric porous membranes by controlling phase separation.^{3,4}

Porous UHMWPE membranes could be prepared by TIPS.^{5–7} In our previous study, the UHMWPE membrane⁸ and UHMWPE/SiO₂ hybrid membranes^{9,10} with better permeability were prepared by TIPS. The main aim of our previous work was to improve membrane permeability through building the multipore-structure. And this type of membrane with excellent tensile strength has longer life in water purification. In TIPS process, a polymer is dissolved in a diluent at a high temperature, and then the membrane dope is cooled. When the temperature of the dope reaches the cloud point line, liquid–liquid (L–L) separation is induced.^{11,12} And when the temperature decreases to the crystallines line of the polymer, solid–liquid (S–L) separation occurs. Then the polymer crystallizes is formed, and the membrane structure is fixed. Finally, the diluent is removed by extraction, and the porous membrane is obtained. The microporous membrane was prepared via TIPS using a ternary solution (HDPE, ditrydecylphthalate and hexadecane) by Vadalìa.¹³ And hydrophilic microporous membrane was prepared from two ethylene-acrylic acid copolymers (zinc salt) with different cunit contents via TIPS by Matsuyama.¹⁴ A larger region of L–L phase separation was formed when the acrylic acid in the copolymer was much enough, which affected the membrane morphology

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TABLE I
The Description of Material in Membrane Preparation

Material	Production places and factory	Material type	Average molecular weight (g/mol)	Density (g/cm ³)
UHMWPE	Beijing No. 2 Reagent Plant, China	MIII (fiber grade)	3.65×10^6	0.94
PEO	Shanghai Seebio Company, China	X55K (fiber grade)	5.61×10^4	1.20
Mineral oil	Oil Refinery Plant of Daqing Petrochemical Company, China	7# (industrial grade)	– (Blends)	
SiO ₂	Tianjin Chemical Research Institute, China	TMS-973 (average of 5μm)	60	2.65
<i>n</i> -Octadecyl-β-4-hydroxy-3,5-di-tert-butyl-phenyl propionate (Antioxidant)	Tianjin Lisheng Chemical Plant, China	1076# (industrial grade)	531	1.15
Gasoline	Oil Refinery Plant of Daqing Petrochemical Company, China	120# (industrial grade)	– (Blends)	
Alcohol	Keruishi Fine Chemical Industry Company, China	Analytically pure	45.07	0.79
Glycerol	Keruishi Fine Chemical Industry Company, China	Analytically pure	92.09	1.26

directly. Therefore, the phase separation can be controlled by adjusting the composition of membrane dope.

In this study, the binary diluents including mineral oil as the first diluents and polyoxyethylene (PEO) as the second diluents was used to prepared UHMWPE/SiO₂ hybrid hollow fiber membranes. The results showed that the proper amount of PEO could change the phase separation from S-L separation to L-L separation, which benefited to build the open-cell porous with better connectivity. The objective of this work is to confirm the relationship between diluents composition and phase separation mechanism, and get the optimum composition of membrane dope. The resulting membrane could be used in water purification.

EXPERIMENTAL

Materials

The correlated description of material in membrane preparation was shown in Table I.

Preparation of UHMWPE/SiO₂ hybrid hollow fiber membranes

The porous, UHMWPE/SiO₂ hybrid hollow fiber membranes were prepared using following steps.¹⁵ First, mineral oil and SiO₂ were mixed well at 20°C at high rotating speed (45 rad/min) in stirred autoclave for 1 h. Then, UHMWPE, PEO, and antioxidant were dissolved in the mixture of mineral oil/SiO₂ and stirred 3 h (the mass ratio of SiO₂/UHMWPE = 4/5, and the mass ratio of diluent/UHMWPE/antioxidant = 91.7/8/0.3). After blending enough, the solution was filled into twin-screw.

In spinning, the spinneret with the outer diameter of 10.5 mm and the inner tube diameter of 7.8 mm was used. The hollow fibers were spun by the gel-spinning process (air-gap = 15 cm).¹⁶ The environment temperature was 20°C and the relative humidity was 65%. The take-up velocity was 11–12 m/min. The extrusion rate of membrane dope was in the range 35–36 mL/min. The flow rate of internal cooling bath was in the range 3–3.5 mL/min. The gel hollow fibers were obtained by immersing the extruding material in cooling medium (20°C water), while mineral oil was used as internal cooling bath. Then the gel hollow fibers were put into gasoline for 48 h to extract the mineral oil. After that, the gasoline was extracted by alcohol. The resulting membranes were washed with 80°C water to remove PEO. Before SEM test, the resulting membranes were put into glycerol-water solution (3 parts glycerol to 2 parts water) for 24 h and then were dried in air, which can retain the porous structure.

Rheological behavior experiment

Rotary rheometer (AR1000, TA, America), equipped with parallel plates of 25 mm diameter and 1 mm plate spacing, was used to measure the viscoelastic properties at a temperature of 170°C. Samples were compression-molded disks. All samples were pre-treated at a constant temperature of 170°C for 3 min. The shear rate ranged from 0.10 s⁻¹ to 100.00 s⁻¹.

FTIR-ATR experiment

The membranes without putting into glycerol-water solution were dried in air. And then the spectra of group in membranes could be measured by FTIR-ATR (SENSOR37, BRUKER, Germany).

Pure water flux experiment

The membranes were kept in fresh water for 48 h. The pure water flux of hybrid membrane was calculated by eq. (1)¹⁷:

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

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

Porosity measurement

The porosity of the hybrid membrane was determined through measuring the true density and the bulk density.¹⁸ The porosity (ε) of the sample was calculated by eq. (2):

$$\varepsilon(\%) = \left(1 - \frac{\rho_b}{\rho_t}\right) \times 100 \quad (2)$$

where ρ_b and ρ_t are the bulk density of membrane and the true density (ρ_t) of polymer, respectively.

Bubble point pore diameter measurement

The bubble point pore diameter was measured using the gas permeation method. The membranes were put into the wetting fluid for 2 h, and then operated increasing from 0 MPa to higher pressure in capillary flow porosimetry system (CFP-1100-A*, Laurel, India). The bubble point pore diameter can be defined as Laplace eq. (3)¹⁹:

$$r = \frac{2\sigma \cos \theta}{\Delta P} \quad (3)$$

where σ is the coefficient of surface tension of the wetting fluid, θ the contact angle between wetting fluid and membrane, ΔP the operating pressure when the first bubble appears.

Morphology examination

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

Differential scanning calorimetric experiment

Crystallization temperature was determined using the differential scanning calorimeter (DSC 200F3, NETZSCH,

Germany). The samples were heated from 0 to 200°C at a heating rate of 20°C/min under nitrogen atmosphere. After at least 5 min, the samples were melting completely and equilibrium. And then they were cooled at the rate of 20°C/min. The sample weight was ~ 5 mg. The onset of the exothermic peak during the cooling was taken as the dynamic crystallization temperature.

Cloud point measurement

The mixtures placed between two glass slides were put on the polarizing microscope at 200°C for 5 min. After the sample becoming transparency, it was cooled at the rate of 7°C/min. The cloud point was determined by the appearance of turbidity.

RESULTS AND DISCUSSION

Effect of PEO content on rheological behavior of UHMEPE/SiO₂/diluent membrane dope

Figure 1 displays the rheological curve of UHMWPE/SiO₂/diluent membrane dope with difference PEO content. As can be seen, the apparent viscosity of UHMWPE/SiO₂/mineral oil dope is higher than that of UHMWPE/SiO₂/PEO/mineral oil dope. Moreover, the apparent viscosity decreases with the increase of PEO content. This may be attributed to the good fluidity of PEO. However, the apparent viscosity increases rapidly when the PEO mass fraction reaches 15%, due to UHMWPE macromolecular chains can't disentangle in less mineral oil.

The FTIR-ATR spectra of UHMWPE/SiO₂ blends and UHMWPE/SiO₂/PEO blends

As can be seen in Figure 2, the strong absorbencies at 2845 and 2913 cm⁻¹ result from the stretching vibration of -CH₂-.²⁰ The weak absorbency at 1472 cm⁻¹ results from the plane deformation vibration of -CH₂-. The absorbencies at 720 and 800 cm⁻¹ result from the rocking vibration of -CH₂-in -CH₂CH₃. Compared with the spectrum of UHMWPE, the new absorbencies appear at 2887, 1342, 1279, 1102, 956, and 846 cm⁻¹ appear in UHMWPE/PEO blend. Considering the less -CH₃ groups in UHMWPE, the absorbencies at 2887, 1342, and 1279 cm⁻¹ can be attributing to the -CH₃ end group in PEO. The absorbencies at 1472 cm⁻¹, resulting from the plane deformation vibration of -CH₂-, shifts to low frequency direction for about 5 cm⁻¹ after adding PEO. At the same time, the absorption intensity of this peak increases owing to the oxygen atom in PEO. The peak at 1102 cm⁻¹ and the shoulder-peak at 1144 cm⁻¹ result from the stretching vibration and the out-of-plane bending vibration of -CO-, respectively. The absorption intensity of the shoulder-peak increases owing to the direct connection between oxygen atom

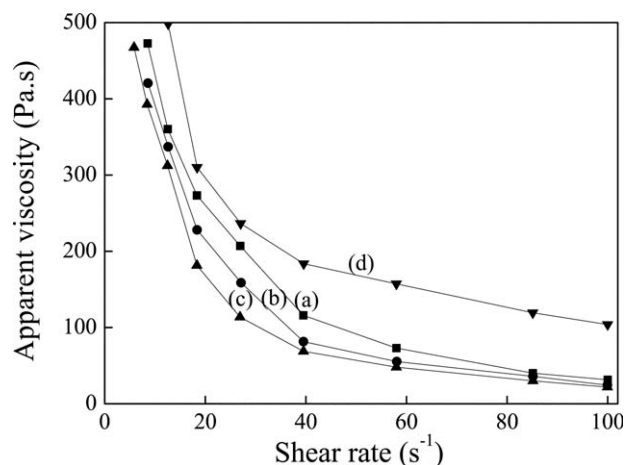


Figure 1 The rheological curves of UHMWPE/Mineral oil with different mass fraction of PEO. (a) 0% PEO, (b) 5% PEO, (c) 10% PEO, and (d) 15% PEO.

and carbon atom. The higher PEO concentration, the more apparent these spectra change. The peaks at 956 and 846 cm^{-1} are the characteristic abstraction of PEO. Compared with the characteristic peaks ($-\text{CH}_2-$) in UHMWPE, those in UHMWPE/PEO blends have no significant change, which displays that PEO and UHMWPE aren't miscible.

As can be seen in Figure 3, the FTIR-ATR spectrum of UHMWPE/ SiO_2 /PEO blends washed by hot water accords with that of UHMWPE basically. This result shows that PEO can be fully extracted by 80°C water.

Phase diagram

The miscibility of polymer and diluent directly reflects the thermodynamic properties such as the

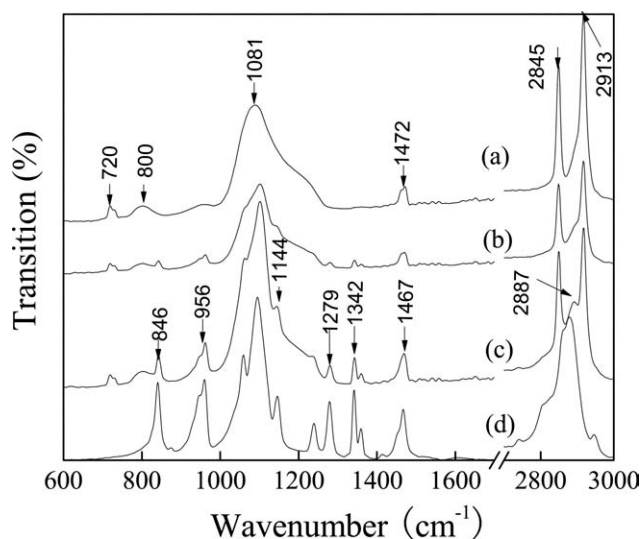


Figure 2 The FTIR-ATR spectra of UHMWPE/ SiO_2 /PEO blends with different PEO concentration (extracting by hot water). (a) 0% PEO; (b) 5% PEO; (c) 15% PEO.

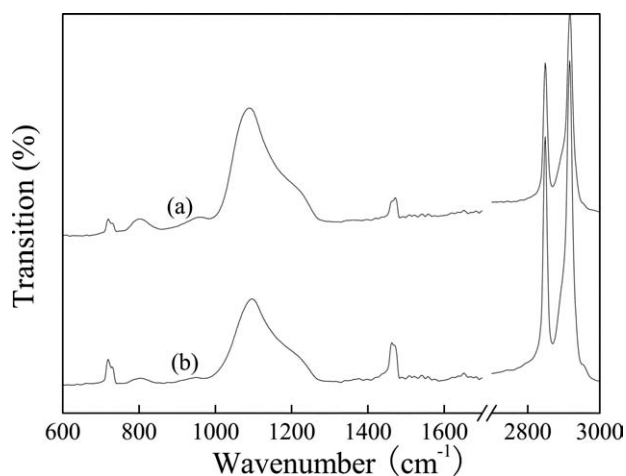


Figure 3 The FTIR-ATR spectrum of UHMWPE/ SiO_2 /PEO (10%) blends extracted by hot water (a), and without extracting (b).

binodal line and crystallization temperature. In membrane preparation by TIPS, phase separation mainly occurs after membrane dope extruding from the spinneret. Although the phase separation effect decreases with the shear rate increasing,²¹ the direct reason of phase separation is temperature decrease. Therefore, interpretation of the interactions of polymer, diluent and the structure of TIPS membranes requires thermodynamics phase diagram.²² In previous researches by other peoples, TIPS was mainly described by binary diagram.^{23–25} In their researches, the phase separation process could better describe by phase diagram including cloud point curve and crystallization temperatures curve. The diluent has different effects on membrane properties through changing phase diagram. As for UHMWPE/mineral oil system (Fig. 4), there is only

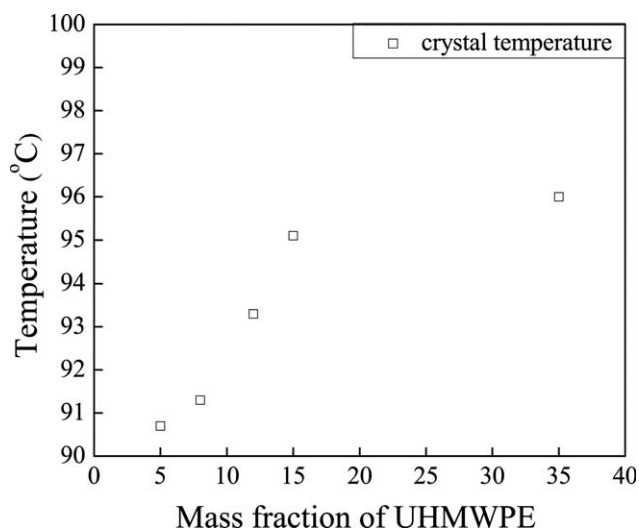


Figure 4 Dynamic phase diagram of UHMWPE/Mineral oil systems.

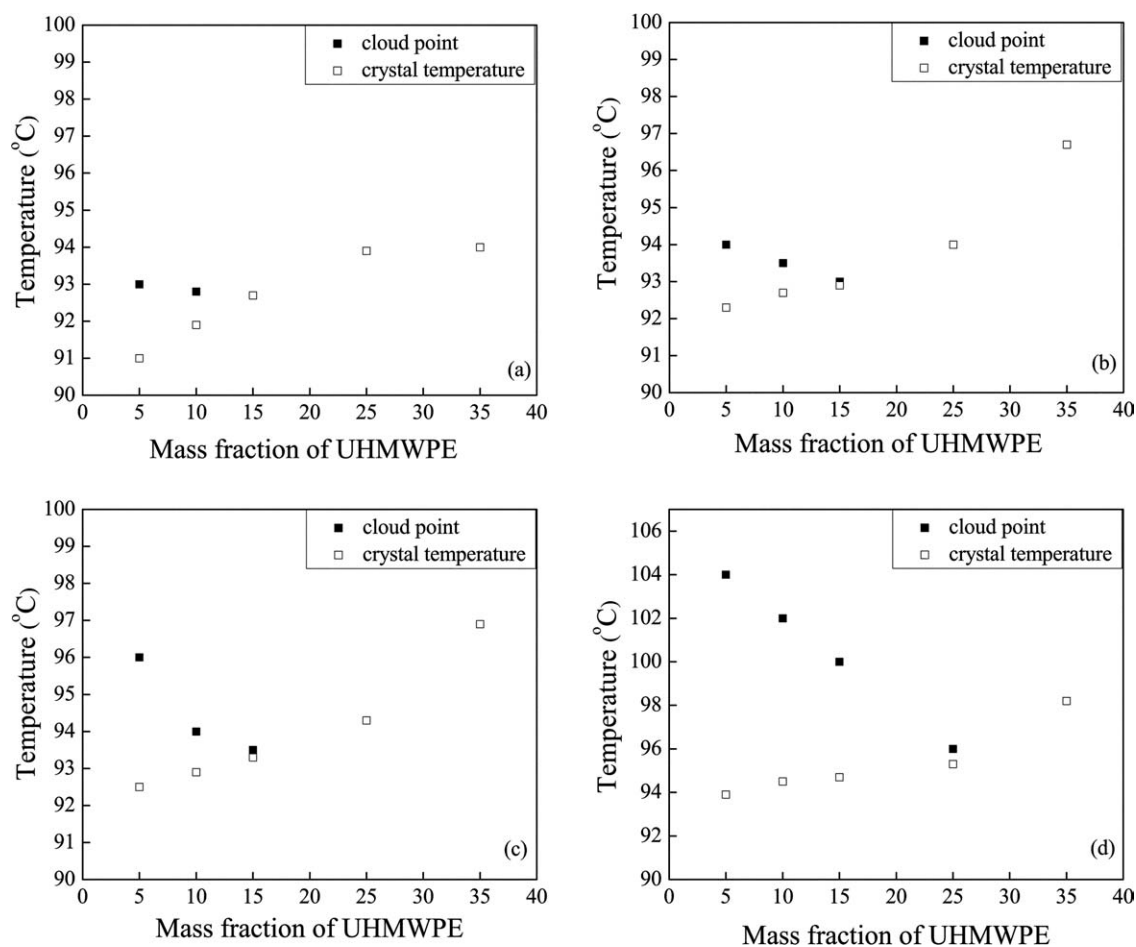


Figure 5 Dynamic phase diagram of UHMWPE-Mineral oil-PEO systems. (a) 5% PEO, (b) 10% PEO, (c) 15% PEO, and (d) 40% PEO.

crystallization temperature line in phase diagram. As a result, the spherulite structure can be formed by S-L TIPS in any UHMWPE concentration.²⁶ Moreover, shear rate also affect the phase separation.

The UHMWPE/mineral oil/PEO system is showed in Figure 5, where the cloud points decrease and crystallization temperatures slightly increase with UHMWPE increasing. It was found that the cloud points and the crystallization temperatures shift to a higher temperature with PEO increasing. This indicates that there is weaker miscibility between mineral oil/PEO and UHMWPE than that between mineral oil and UHMWPE. The pore growing time prolong when the cloud points shift to higher temperature, which is better to produce large pore. Moreover, the area between cloud point line and crystallization line increases with PEO increasing. Thereby, the monotectic point (ϕ_m , the point of intersection of cloud point line and crystallization line) shifts to high temperature. The L-L phase separation occurs at the left of ϕ_m . The S-L phase separation region occurs at the right of ϕ_m and below ϕ_m . Therefore, the phase separating

time can be prolonged by adding PEO, which is better to pore growing. When the polymer concentration reaches high enough, polymer is prior to crystallize. Then, the spherulite structure can be formed caused by S-L phase separation. In this study, L-L phase separation plays a major action, because the polymer concentration is less than 15%.

The morphology of UHMWPE/SiO₂ hybrid hollow fiber membranes

Figure 6 shows the outer skin layer SEM results of UHMWPE/SiO₂ hybrid hollow fiber membranes. As can be seen in Figure 6(a), the outer skin layer of membrane prepared without PEO is very dense, having no sign of pores. With PEO increasing, the outer skin layer becomes coarsening, due to the effect of PEO on the stability of membrane dope. When there is PEO in the membrane dope, L-L phase separation plays a leading role. As a result, the open-cell porous structures are produced in membranes [Fig. 6(b,c)].²⁷ Nevertheless, excessive PEO is sensitive for agglomerating. The big

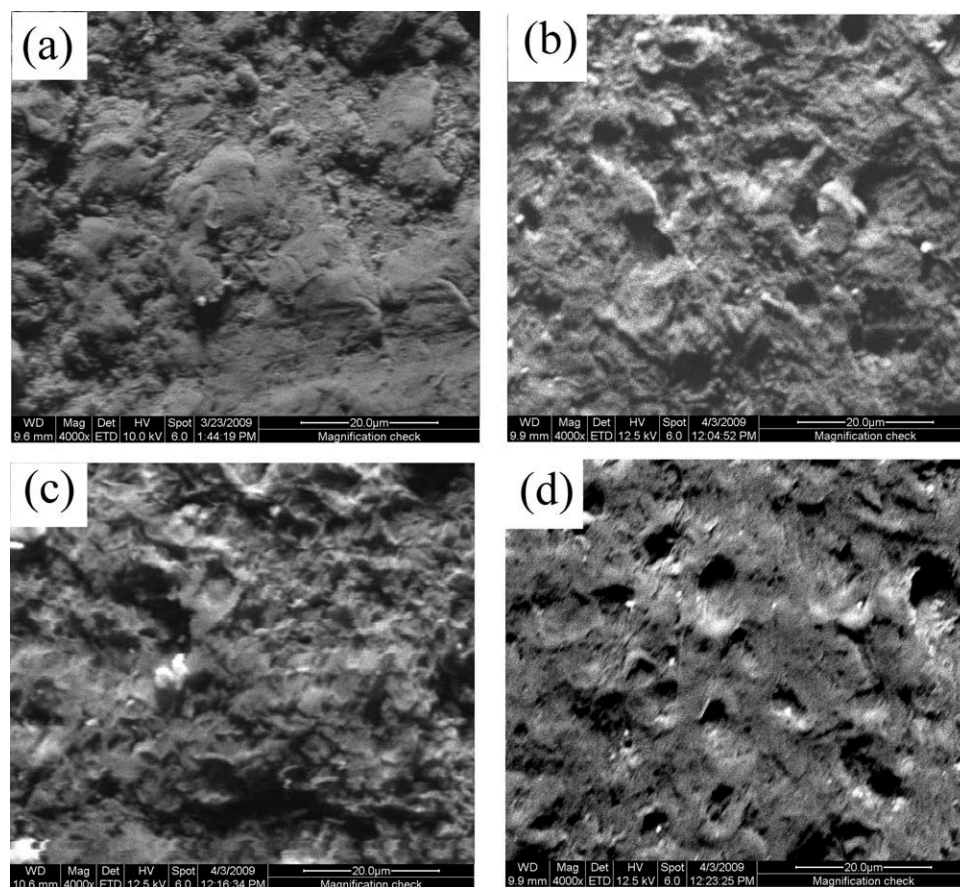


Figure 6 Outer skin layer SEM results of UHMWPE/SiO₂ hybrid hollow fiber membranes. (a) 0% PEO, (b) 5% PEO, (c) 10% PEO, and (d) 15% PEO.

superficial pores are formed by extracting these agglomerated PEO [Fig. 6(d)].

Figure 7 displays the cross-sectional SEM results of UHMWPE/SiO₂ hybrid hollow fiber membranes. As for membrane papered without PEO [Fig. 7(a)], the spherulite structure can be made from S-L phase separation, which accords with the phase diagram (Fig. 4). The resulting porous connectivity is bad. After adding PEO [Fig. 7(b,c)], the open-cell porous structure can be built in membrane, which comes from L-L phase separation. With PEO increasing, the cell pore size increases, and the fluidity of membrane dope is improved. The better fluidity is beneficial to the coalescence of diluent. Thereby, the size of pore coming from diluent extracting increases. Moreover, the agglomeration of excessive PEO goes against the connectivity of pore structure [Fig. 7(d)].

The permeability of UHMWPE/SiO₂ hybrid hollow fiber membranes

Figures 8 and 9 show the effect of the mass fraction of PEO on the porosity, pure water flux and bubble point pore diameter of membrane. As can be seen,

the porosity, pure water flux and bubble point pore diameter increase at first then decrease, with PEO increasing. These results are mainly due to the effect of PEO on the phase separation mechanism. The open-cell porous structure, which has better connectivity, is sensitive to be built after adding a proper amount of PEO. Thereby, the porosity, pure water flux and bubble point pore diameter increase with PEO increasing in a certain range. Furthermore, the porosity, pure water flux, and bubble point pore diameter decrease when PEO concentration excess 10%, resulting from the excessive PEO going against the connectivity of pore structure. These phenomena are in agreement with the results of phase diagram and SEM.

CONCLUSIONS

UHMWPE/SiO₂ hybrid hollow fiber membranes were prepared by TIPS, using mineral oil as the first diluent, PEO as the second diluent and SiO₂ as additive. The results indicated a proper amount of PEO can not only improve the fluidity of membrane dope, but also control the phase separation. By adding PEO into membrane dope,

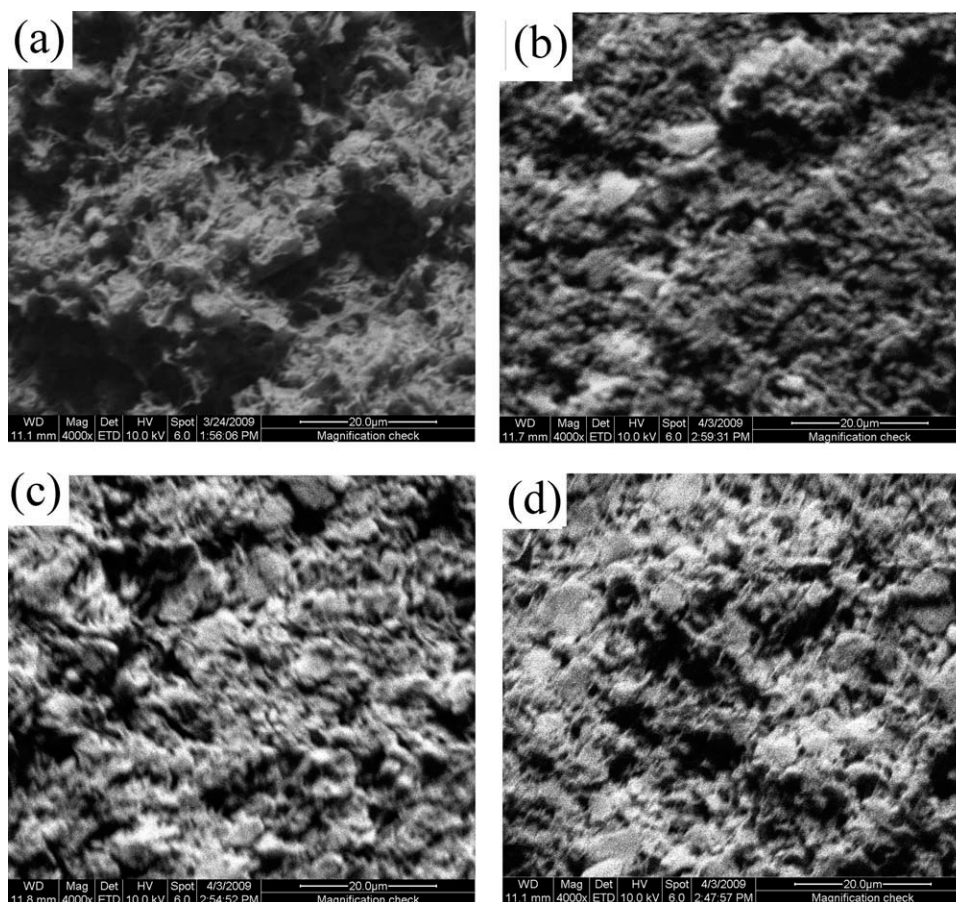


Figure 7 Cross-sectional SEM results of UHMWPE hollow fiber membranes. (a) 0% PEO, (b) 5% PEO, (c) 10% PEO, and (d) 15% PEO.

the phase separation was changed from L-L to S-L, while the porous structure was translated from spherulite into open-cell porous having better connectivity. And the cell pore size increased with PEO increasing. That is to say, some PEO was better to the growth of membrane pore. As a

result, the porosity, pure water flux and bubble point pore diameter of membrane increased at first and then decreased, with PEO increasing. Nevertheless, the excessive PEO was sensitive for agglomeration, being bad to membrane connectivity.

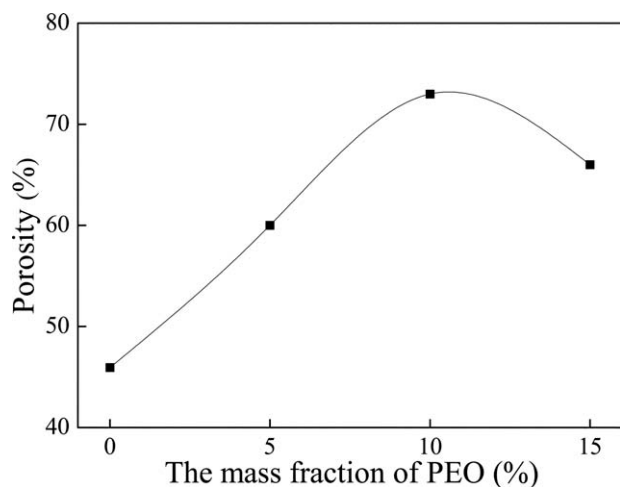


Figure 8 The effect of the mass fraction of PEO on porosity of membrane.

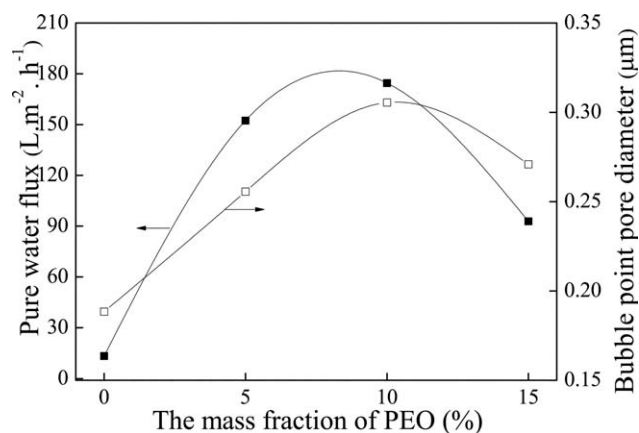


Figure 9 The effect of the mass fraction of PEO on pure water flux and bubble point pore diameter of membrane.

NOMENCLATURE

ε	Porosity, %
ρ_b	Bulk density of membrane, g/cm ³
ρ_t	True density of membrane, g/cm ³
J	Pure water flux, L/m ² /h
V	Total permeation, L
S	Total permeation area, m ²
t	Total permeation time, h
γ	Bubble point pore diameter, μm
σ	Coefficient of surface tension of the wetting fluid, –
θ	Contact angle between wetting fluid and membrane, rad
ΔP	Operating pressure when the first bubble appears, MPa

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