

Influences of Extractant on the Hydrophilicity and Performances of HDPE/PE-*b*-PEG Blend Membranes Prepared via Thermally Induced Phase Separation (TIPS) Process

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ABSTRACT: Blending the block copolymer into the membrane matrix is a convenient and efficient way for membrane modification. In this study, HDPE/PE-*b*-PEG membranes were prepared via TIPS process, and the extractant effect was investigated. An interesting finding was that a non-polar extractant (*n*-hexane) was more conducive to the surface enrichment of PEG chains than a polar solvent (ethanol). The reason was deemed to be the combined effect of entropy drive, interfacial energy, and the swelling behavior. Besides, membrane performances related to the surface chemical properties were studied. Results suggested that the prepared blend membranes extracted by *n*-hexane showed enhanced hydrophilicity, anti-fouling property and water flux. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2680–2687, 2013

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INTRODUCTION

Polyethylene (PE) has excellent chemical and thermal stability, good mechanical properties, and low prices, which is currently the most widely used polymer membrane materials.¹ However, the hydrophobic property is considered to be the key factor to limit the application of PE membrane, especially for water-treatment.^{2,3} First, the hydrophobicity of membrane would cause high energy consumption in use due to a higher pressure being required for water to penetrate the membrane. Second, the hydrophobicity could easily cause membrane fouling, leading to the rapid decay of the flux. Thus, hydrophilic modification is an important direction for high performance polyethylene membranes. Lots of efforts have been done to improve the hydrophilicity of membranes, such as surface coating,^{4,5} chemical grafting,^{6,7} blending,^{8–10} and plasma treatment,^{11,12} etc. Among them, the blending method is a kind of convenient and effective way for surface modification.¹³ The membranes modified by blending method could not only avoid the disadvantages of the original component, but also own some new features.

An important consideration for the blending method is the choice of the modifier. Extensive works have focus on the amphiphilic copolymers.^{14,15} Because the hydrophobic segments usually has good compatibility with the matrix and it could act

as an anchor in membrane matrix to prevent the losing of the copolymer during membrane preparation and operation process. Meanwhile, the hydrophilic moiety always enriches onto the surface of the membrane, giving the membrane improved hydrophilicity.¹⁶ In this respect, the maximization of the surface enrichment would have extremely vital significance. Generally, the content of the hydrophilic segments in the surface layer is regulated by changing the dosage amount of the amphiphilic copolymer.^{17,18} Even so, there are two drawbacks. First, the addition of too much copolymer would absolutely lead to higher membrane cost. Second, the adopted copolymer usually has a relatively low molecular weight, which might cause unaccepted reduction of the mechanical strength of the blend membranes.¹⁹ Hester et al.²⁰ have reported that the temperature of the coagulating bath would obviously affect the surface enrichment behavior of the hydrophilic moieties in the non-solvent induced phase separation (NIPS) process. This result indicates that the preparation conditions could also influence the surface chemical composition of the blend membranes. And when the addition amount is fixed, the optimization of the surface modification could be achieved by choosing the suitable preparation conditions. However, few studies have been reported to explore the relationship between the preparation conditions of TIPS process and the surface composition of the obtained blend membranes.

PE-*b*-PEG has been used to modify PE membrane via TIPS process and has been proved to enhance membrane hydrophilicity and water flux effectively.^{3,21} The advantage of TIPS method lies in that the preparation and modification could be achieved simultaneously. In this study, we would explore the effect of extractant on surface composition for preparing HDPE/PE-*b*-PEG blend membranes via TIPS process. Furthermore, in previous researches, DPE is used as the diluent, which is not suitable for application in the industry field. In this article, environmentally friendly liquid paraffin (LP) is chosen as diluent, and the preparation and performances of HDPE/PE-*b*-PEG blend membrane are also investigated.

EXPERIMENTAL

Materials

HDPE (5200B, $M_w = 3.68 \times 10^5$) was provided by Lanzhou Petrochemical Co. (China). PE-*b*-PEG (50 wt % PEG, $M_n = 1400$) was bought from Aldrich. Liquid paraffin (LP), *n*-hexane and ethanol were all provided by Shanghai Chemical Reagents Co. (China).

Phase Separation Behavior of the Casting Solution System

A proportion of HDPE, PE-*b*-PEG, and LP (Table I) were added into a flask equipped with a stirrer. The mixture was stirred into homogeneous solution at 180°C and it was then quenched by liquid nitrogen to yield solid HDPE/PE-*b*-PEG/LP mixture samples for phase diagram determination and membrane preparation. The obtained solid sample (about 10 mg) was placed between a pair of microscope cover slips and was heated on a hot stage (Linkam, THMS600, UK) at 180°C for 2 min and then cooled to 20°C at 10°C min⁻¹. The cloud point (T_{cloud}) and the dynamic crystallization temperature (T_c) were determined visually by observing the appearance of turbidity and crystallization of polymer under an optical microscope (Nikon, Eclipse E600POL, Japan). The phase separation behaviors of HDPE/LP were determined same as that of the HDPE/PE-*b*-PEG/LP system.

Preparation of HDPE/PE-*b*-PEG Blend Membranes

The casting solution and corresponding solid sample were prepared same as those in previous section. The small pieces of HDPE/PE-*b*-PEG/LP solid sample were put into a cube mould (thickness: 200 μm)³ and thoroughly melted at 180°C. Then the casting solution was compressed into thin liquid film. The liquid film sandwiched in the template was quenched in a water bath (15°C) for 10 min and the solid film (called precursor film) was formed. The diluent LP in precursor film was extracted by a specific extractant (ethanol or *n*-hexane) for 24 h at 25°C. The resultant porous membranes (coded as M0, M1,

Table I. Composition of Casting Solutions for Preparing Membranes

Membrane code	HDPE/PE- <i>b</i> -PEG/LP(wt/wt/wt)
M0	30/0/70
M1	27/3/70
M2	24/6/70
M3	21/9/70

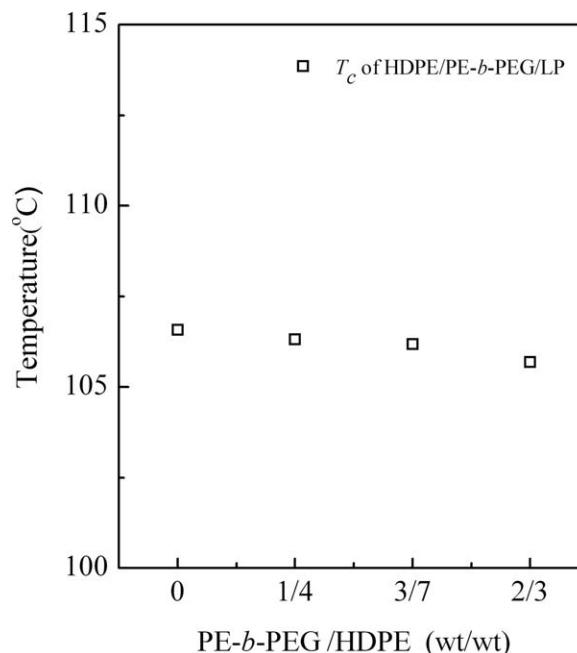


Figure 1. Phase diagrams of the casting solution system.

M2, and M3) were dried for 12 h in a vacuum oven at 30°C before characterization.

Characterization of Membranes

Membrane structure was observed by a field emission scanning electron microscope (FESEM, Hitachi S4800, Japan). Surface pore size was evaluated basing on the SEM images by the software of Image Pro. Plus. Porosity (P) was calculated by the equation: $P(\%) = (1 - \rho_m/\rho_p) \times 100$, where, ρ_m and ρ_p are the density of porous membrane and membrane matrix, respectively.²² Thermal behaviors of membranes were characterized by a differential scanning calorimeter (Perkin-Elmer Pyris-1 DSC). The sample (5–8 mg) was sealed in an aluminum pan and the DSC curves were recorded from 40°C to 160°C at 10°C min⁻¹ under the atmosphere of N₂. The crystallinity (X_c) was calculated according to $X_c (\%) = H_f/\Phi H_f^0 \times 100$, where, H_f and H_f^0 is the fusion enthalpy of the blend membrane and HDPE with 100% crystallinity [(273 J g⁻¹)²³]. Φ is the weight fraction of HDPE in blend membrane. The chemical composition was investigated by X-ray photoelectron spectroscopy (XPS, PHI Co., PHI 5000C ESCA system). The contact angle was measured by a contact angle measurement system (Dataphysics, OCA20, Germany) at 25°C.

Static BSA Adsorption

The protein antifouling characteristics of the membranes were evaluated with BSA as a model sample. The membrane was cut into a square, which had an external surface area of 8 cm². BSA solutions with various concentrations were prepared by dissolving BSA in the phosphate buffer solution (pH = 7.4). Then the prepared samples were immersed in 10 mL BSA solution at 30°C for 12 h and shaken at a speed of 150 rpm. The protein adsorption amount was determined as the different value of the concentrations of BSA solution before and after the adsorption

test divided by the surface area. The concentration was indicated by the UV-absorption intensity at 280 nm, which was determined on the UV-Vis spectrophotometer (Shimadzu, UV-1601, Japan).

Water Flux

Water flux was determined on a homemade device with a pressurized stirred test cell. The effective area is 12 cm². Samples were stabilized at 0.15 MPa with deionized water for about 0.5 h. Then the test was performed under 0.1 MPa and the flux was recorded when it was stable. The flux (J_w) is calculated by the equation $J_w = V/A\Delta t$, where V represents the volume of the percolating water, A is the effective membrane area, and Δt is the test time.

RESULTS AND DISCUSSION

Phase Separation Behavior of the Casting Solution System

Figure 1 shows the phase diagrams of the HDPE/PE-*b*-PEG/LP system in which total polymer concentration (HDPE and PE-*b*-PEG) is fixed at 30 wt %. In all the investigated cases, only solid-liquid phase separation occurs. This is because the solubility parameter of LP is 16.4 (J/cm³)^{1/2}, close to that of HDPE [16.2 (J/cm³)^{1/2}], which means better interaction between HDPE and LP. When the thermal energy is removed, phase separation is induced by polymer crystallization. Furthermore, the crystallization temperature decreases slightly (from 106°C to 105°C) with increasing PE-*b*-PEG concentration in casting solution. The reason is that with total polymer concentration being fixed, the addition of PE-*b*-PEG leads to lower average molecular weight of polymer and lower viscosity of system. This is benefit for the movement of polymer segments. So polymer crystallization occurs at lower temperature.

Comparing to the pure HDPE/LP system, it could be found that T_c of HDPE/PE-*b*-PEG/LP system is slightly higher than that of HDPE/LP system with same HDPE concentration. The reason is deemed as lower solution viscosity for HDPE/LP system, which goes against with polymer crystallization. But for all

this, it is worth noting that the discrepancies caused by the existence of PE-*b*-PEG are very small.

Surface Chemical Composition

A typical TIPS process includes preparation of casting solution, high temperature melting process in the template, cooling process to form the precursor film, extracting process, and drying process to obtain the final porous membrane. The extracting process could be regulated by changing the extractant. Two kinds of completely different extractants (ethanol and *n*-hexane) are chosen. Discrepancies of the surface chemical compositions of prepared membranes are investigated.

The surface composition was quantitatively characterized by XPS (Figure 2). PE-*b*-PEG contents in surface layer calculated based on the XPS results are listed in Table II. For all prepared blend membranes, PE-*b*-PEG content in membrane surface is much higher than the corresponding theoretical value, no matter what kind of extractant is used, indicating enrichment of the PEG segments in the surface layer. This result is consistent with previous studies.^{3,17} However, an interesting result is that the enrichment degree is obviously discrepant when different kinds of extractants are used. When non-polar *n*-hexane is chosen as extractant, much more PEG chains enrich in the surface layer. As can be seen, if the dosage amount of PE-*b*-PEG is increased by 3 times (From 10% to 30%), the copolymer content on the surface would only change from 21.2 wt % to 34.2 wt % when ethanol is used as extractant. While, PE-*b*-PEG content in surface layer could be elevated by 2–3 times when the extractant is changed from ethanol to *n*-hexane. The results suggest that the surface enrichment behavior could be effectively regulated by choosing the extractant, which is more effective than adjusting the content of the additive.

Enrichment ratio is defined as the ratio of PE-*b*-PEG content in the surface layer and the theoretical value. High enrichment ratio indicates that the difference between surface PE-*b*-PEG content and the amount of PE-*b*-PEG in membrane matrix is much larger, e.g., much more PEG chains migrate onto the

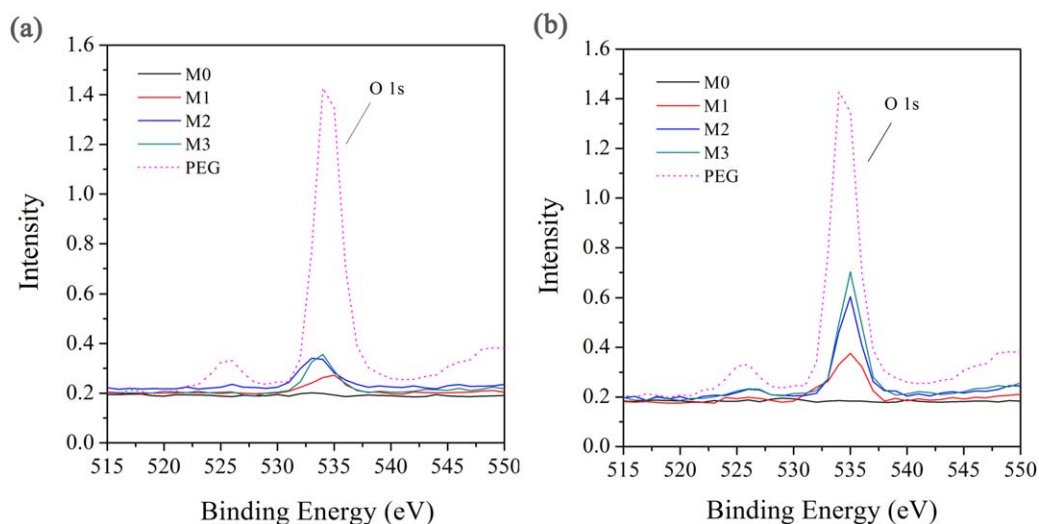


Figure 2. XPS results of prepared membranes with (a) ethanol and (b) *n*-hexane as extractant, respectively. (The value of Y axis was adjusted by defining the height of C 1s peak as 1.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Chemical Composition of Prepared Separators

Membrane ID	PE- <i>b</i> -PEG content in whole membrane (wt %) ^a	PE- <i>b</i> -PEG content in surface layer ^b (wt %)		Enrichment ratio	
		Extracted by ethanol	Extracted by <i>n</i> -hexane	Extracted by ethanol	Extracted by <i>n</i> -hexane
M0	0.0	-	-	-	-
M1	10.0	21.2	55.4	2.1	5.5
M2	20.0	28.0	80.4	1.4	4.0
M3	30.0	34.2	100.0	1.1	3.3

^a Added in casting solution.^b Calculated from XPS measurements.

surface in the TIPS process. Enrichment ratio reaches 5.5 for M1 with *n*-hexane as extractant, while when polar ethanol is used, the Enrichment ratio is only 2.1. All the results suggest that the non-polar extractant *n*-hexane is more favorable for the enrichment of PEG chains. In previous reports, the enrichment of PEG chains is deemed to be originally formed in the high temperature melting processing in the template and the cooling process.^{3,24} Since other preparation conditions are equal, the discrepancy of the enrichment degree in this study should be caused in the extracting process. To explore the reason for the extractant effect, the solubility parameter and surface energy of HDPE, LP and PEG and extractant are compared and listed in Table III. Solubility parameter for non-polar *n*-hexane ($\delta_{n\text{-hexane}} = 14.6 \text{ (J/cm}^3)^{1/2}$) is near to that of non-polar HDPE ($\delta_{\text{HDPE}} = 16.96 \text{ (J/cm}^3)^{1/2}$). So HDPE matrix of the prepared membranes could be swelled by the non-polar *n*-hexane²⁵ and this could enhance mobility of polymer segments. Meanwhile, low molecular weight PE-*b*-PEG chains embedded in the amorphous area of HDPE could be dissolved into the extractant and show enough migration ability, which would be further proved by DSC determination in the following section. Thermodynamically, dissolved PE-*b*-PEG chains would also tend to diffuse from the center of the membrane to the surface and the extractant bath, which is all driven by entropy. Furthermore, comparing the surface energies of HDPE, LP, and the extractants, it could be concluded that the surface energy of the precursor film is obviously higher than that of the extractants. That means in the interface layer between the precursor film and the extractant bath, the PEG blocks would tend to migrate into the precursor film rather than diffuse into the extractant bath due to the characteristics of the amphiphilic block copolymer, e.g., lowering the interfacial energy. Obviously, these two kinds of forces from the entropy drive and interfacial energy are in the opposite directions. But the enhanced surface enrichment suggests that entropy and swelling effects dominate the interfacial

energy effects. The reason might be that in the extracting process, the real interfacial layer is not the layer between pure HDPE and pure *n*-hexane. LP exists in the precursor film and in the *n*-hexane, which could effectively decrease the interfacial energy effect. So under the together actions of entropy drive and interfacial energy, the surface enrichment of the copolymer is further enhanced. While, membrane matrix could not be swelled by polar ethanol ($\delta_{\text{Ethanol}} = 25.8 \text{ (J/cm}^3)^{1/2}$) and so the motion of PE-*b*-PEG chains is prohibited, finally causing totally different surface enrichment amount for blend membranes with same copolymer dosage.

As we know, the more PEG chains aggregate in membrane surface, the better modification effect would be obtained.^{3,17} Table II shows that PEG content in surface layer calculated based on XPS is up to 50 wt % for M3 when *n*-hexane is chosen as extractant. This is beneficial for preparing high performance PE membranes.

Thermal and Crystalline Properties

The thermal properties of prepared membranes were studied via DSC measurements (Figure 3). In the DSC curves, endothermic peaks at about 124 and 130°C correspond to the melting of crystalline HDPE in the blend membranes extracted by ethanol and *n*-hexane, respectively. The differences in T_m might be caused by rearrangement of polymer chains in the extracting process. M2 and M3 extracted by ethanol show melting peaks of crystalline PE segments in PE-*b*-PEG chains at 90.9°C, while M3 extracted by *n*-hexane show the peak at 95.7°C. These results suggest that independent crystalline regions for PE-*b*-PEG chains form when the addition amount of the copolymer increases to a certain degree.²⁴

The crystallinity of membrane, HDPE and PE block in PE-*b*-PEG are calculated and listed in Table IV. Crystallinity of membranes extracted by ethanol decreases first and then increases. Since only HDPE chains could crystallize when addition

Table III. Solubility Parameters and Surface Energies for HDPE, PEG, LP, *n*-Hexane, and Ethanol

Material	HDPE	PEG	LP	<i>n</i> -Hexane	Ethanol
Solubility parameter δ [(J/cm ³) ^{1/2}]	16.9	22.5	16.2	14.6	25.8
Surface energy (mN/m)	31.9	42.9	33	18.4	22

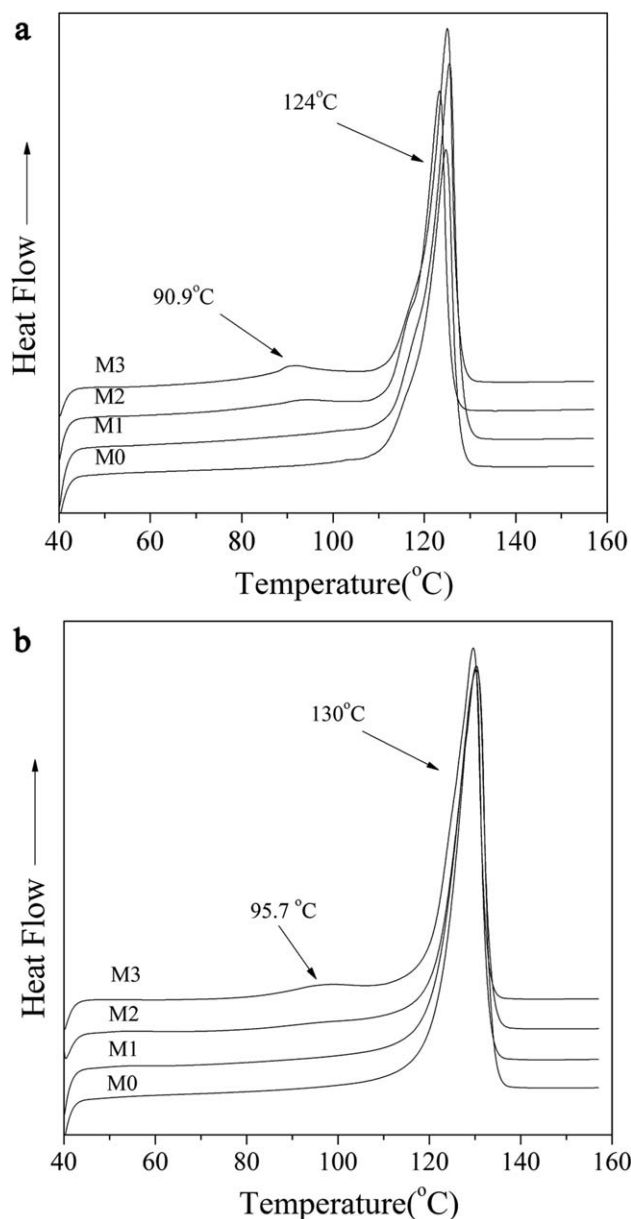


Figure 3. DSC curves of the membranes prepared with (a) ethanol and (b) *n*-hexane as extractant, respectively.

amount of PE-*b*-PEG is relatively low, the crystallinity of membrane first decreases because the HDPE content decreases. When the copolymer dosage is raised, PE block in copolymer

could also crystallize, as shown in Table IV, so the total crystallinity is also elevated. The crystallinities for membranes extracted by *n*-hexane show same trend. However, they are higher than that for membranes extracted by ethanol. This could be attributed to the increase of HDPE crystallinity, which suggests that rearrangement of chain segments and secondary crystallization occur during extraction process. Furthermore, the crystallinity of PE block in membranes extracted by *n*-hexane is lower than that in membrane extracted by ethanol. The explanation might be that, since the copolymer has low molecular weight, the crystalline region could be easily swelled and even might be totally dissolved by the *n*-hexane,²¹ and the copolymers tend to diffuse to the membrane surface due to entropy drive rather than recrystallized. So the crystallinity for the PE blocks decreases. While, the crystal structure of membrane extracted by ethanol might hardly change because ethanol could not effectively swell membrane matrix. From this perspective, the effect of extractant on the chemical composition and the crystallinity is in accordance.

Membrane Morphologies

Figure 4 gives the surface and cross-section morphologies of the prepared membranes. As can be seen, all the membranes show a similar pore structure on the surface and a similar spherulite structure in the cross-section, which is caused by the solid-liquid phase separation in the TIPS process. Comparing M0 and M3, the result suggests that the introduction of PE-*b*-PEG hardly influence membrane structure, which is different with previous reports with DPE as the diluent.^{3,17} Pore size tends to increase when blend membranes are prepared by HDPE/PE-*b*-PEG/DPE system. The reason lies in different mechanism of pore formation. In the HDPE/PE-*b*-PEG/DPE system, since the dynamic crystallization temperature hardly varies, the pore size strongly depends on the liquid-liquid phase separation temperature, which changes obviously when PE-*b*-PEG is introduced.²⁶ In the HDPE/PE-*b*-PEG/LP system, pore structure is induced by the solid-liquid phase separation. However, the phase separation behavior is less affected by the addition of PE-*b*-PEG, so the membrane structure and surface pore size (Table V) hardly changes. In theory, this kind of membrane structure should contribute to the penetration of water due to the existence of a more interconnected tunnel between the spherulites.²⁴ Besides, the extractants have made no obvious difference on membrane structures. This might be because although the swelling phenomenon exists, it only occurs in the surface layer of the surface and the pores rather than in the whole membrane matrix.

Table IV. The Melting Point and Crystallinity of the Prepared Membranes

Membrane ID	T_m (°C)	Extracted by ethanol			Extracted by <i>n</i> -hexane			
		X_c (%)			X_c (%)			
		Membrane	HDPE	PE block	T_m (°C)	membrane	HDPE	PE block
M0	124.7	52.7	52.7	-	130.0	63.8	63.8	-
M1	125.5	36.5	40.6	-	130.1	62.8	69.8	-
M2	123.3	38.4	47.5	7.5	130.3	56.3	70.4	0.0
M3	125.0	45.0	42.2	15.2	129.6	60.5	80.4	8.3

Table V. Porosity and Pore Size of Prepared Membranes

Membrane code		M0	M1	M2	M3
Porosity(%)	<i>n</i> -Hexane	64.2	64.5	66.2	65.8
	Ethanol	65.3	63.1	65.9	67.3
Surface pore size (μm)	<i>n</i> -Hexane	0.43	-	-	0.40
	Ethanol	0.41	-	-	0.39

The porosities of prepared membranes are shown in Table V, which changes little. This result is in accordance with the observation of SEM results. In explanation, pores are essentially the location for the diluent. So the porosity is mainly determined by the diluent content in the casting solution. Since the concentration of

LP stays same in this study, the porosity for all the prepared membranes keeps consistent. The similar membrane structure provides an experimental foundation for investigating the influences of surface chemical composition on membrane performances.

Membrane Hydrophilicity

The hydrophilicity of membranes is evaluated by the contact angle, which is given in Figure 5. As can be seen, the contact angle is decreased effectively by adding the amphiphilic copolymer PE-*b*-PEG. M3 extracted by *n*-hexane shows the lowest contact angle of 64° , while the lowest contact angle of M3 extracted by ethanol reaches about 96° . Improved hydrophilicity is attributed to the enhanced surface enrichment of PEG chains. The results suggest that hydrophilicity of membranes could be effectively regulated by controlling the extracting process, especially by choosing different kinds of extractants.

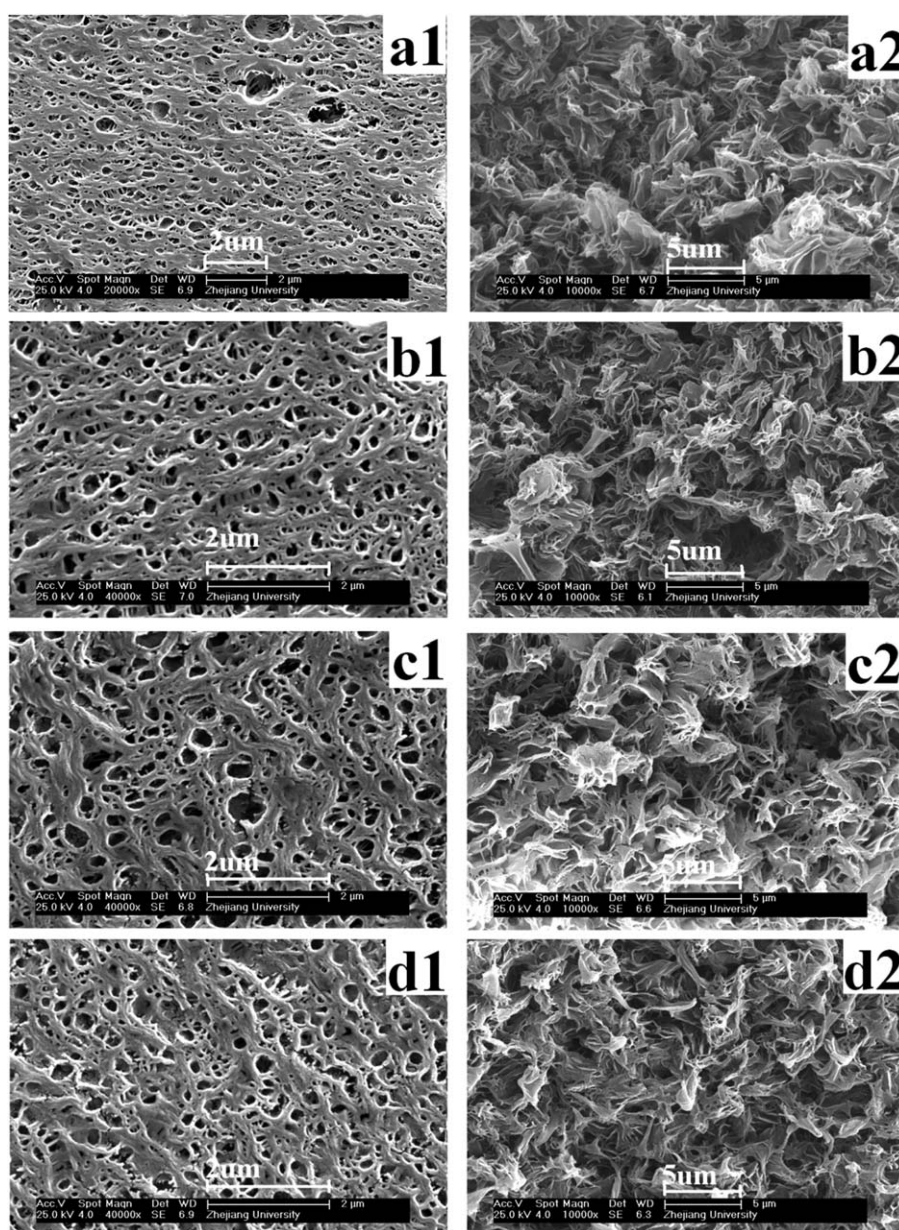


Figure 4. The surface (left) and cross-section (right) morphologies of membranes. (a) M0-*n*-hexane; (b) M3-*n*-hexane; (c) M0-ethanol; (d) M3-ethanol.

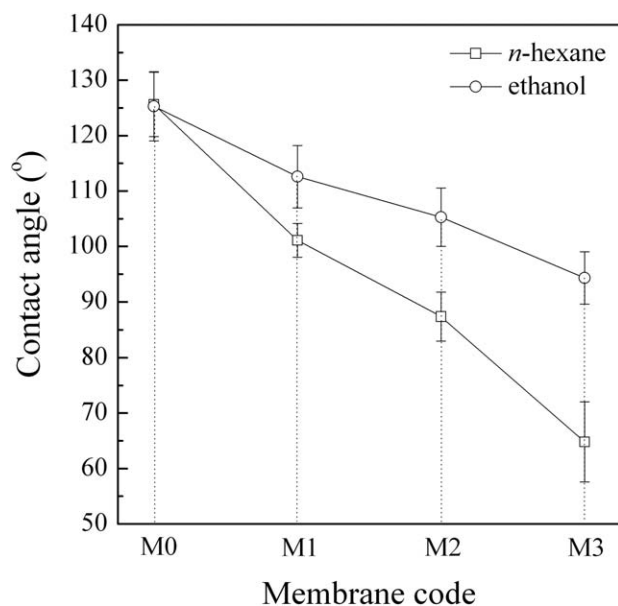


Figure 5. Contact angles of the prepared membranes.

Membrane Performances

Figure 6 shows the BSA adsorption of membranes as a function of the BSA concentration. The adsorption is greatly depressed when more PE-*b*-PEG is introduced. M3 extracted by *n*-hexane has the BSA adsorption amount of $6.3 \mu\text{m cm}^{-2}$ in 1.0 g L^{-1} BSA solution, which is far below that for M0 ($36 \mu\text{m cm}^{-2}$) under same experimental condition. Meanwhile, all the adsorption values are lower than the results extracted by ethanol. It is well known that PEG chains possess exceptional resistance for the protein to contact with membrane surface,²⁷ so more PEG chains aggregating in membrane surface, membranes would show enhanced capability of reducing protein adsorption. That is to say, the enhanced surface enrichment of membranes extracted by *n*-hexane yields the membranes better anti-fouling properties

The pure water permeation is determined at 0.1 MPa and shown in Figure 7. The pure HDPE membrane extracted by *n*-hexane has the flux of $103 \text{ L m}^{-2} \text{ h}^{-1}$, which is basically same with that of M0 extracted by ethanol. This could be attributed to similar membrane structure and porosity. Besides, the flux (membranes extracted by *n*-hexane) increases dramatically when the addition amount of PE-*b*-PEG is elevated. For M3, the water flux reaches $481 \text{ L m}^{-2} \text{ h}^{-1}$. Meanwhile, membranes extracted by ethanol show same trend. However, the flux is much lower than that of the corresponding membranes extracted by *n*-hexane. Since all the prepared membranes own basically same structure, the changes of flux should be ascribed to the enhanced hydrophilicity.

Here, the flux is deemed to be dominated by two processes. First, the water infiltrates from membrane surface into the pores. Second, the water flows in membrane pores. The first stage could be analyzed by the cylindrical capillary model.²⁸ The pores on membrane surface are regarded as the capillaries. According to the Laplace equation: $r_p = 2\gamma\cos\theta/\Delta P$, where, r_p is the pore size. γ and θ represent the surface tension and the

water contact angle, respectively. ΔP is the difference between the external pressure and the internal pressure of the pore, which represents the critical pressure needed from the outside world to make the water to penetrate into the pores. When $\theta > 90^\circ$, $\cos\theta < 0$. Since r_p and γ are positive, ΔP would be less than zero, which means the water penetration could not occur spontaneously. When θ is becoming closer to 90° , $\cos\theta$ and ΔP tend to decrease to zero, suggesting the critical pressure needed from the outside world would become smaller. Furthermore, when $\theta < 90^\circ$, $\cos\theta > 0$, and $\Delta P > 0$, indicating that the penetration behavior could take place spontaneously. The second stage, the water flowing in the pores, could be described by the Hagen-Poiseuille law.²⁸ In theory, the flow rate would be determined by the hydrophilicity of the wall of the pores, since the pore size is small enough. However, once the pore wall is fully wetted, and the flux test is performed on same pressure, the difference on the flow rate should be very small.²⁸

As reported by Vladislavljevic et al.,²⁸ for the hydrophilic membrane, trans-membrane pressure needed is zero, since the water

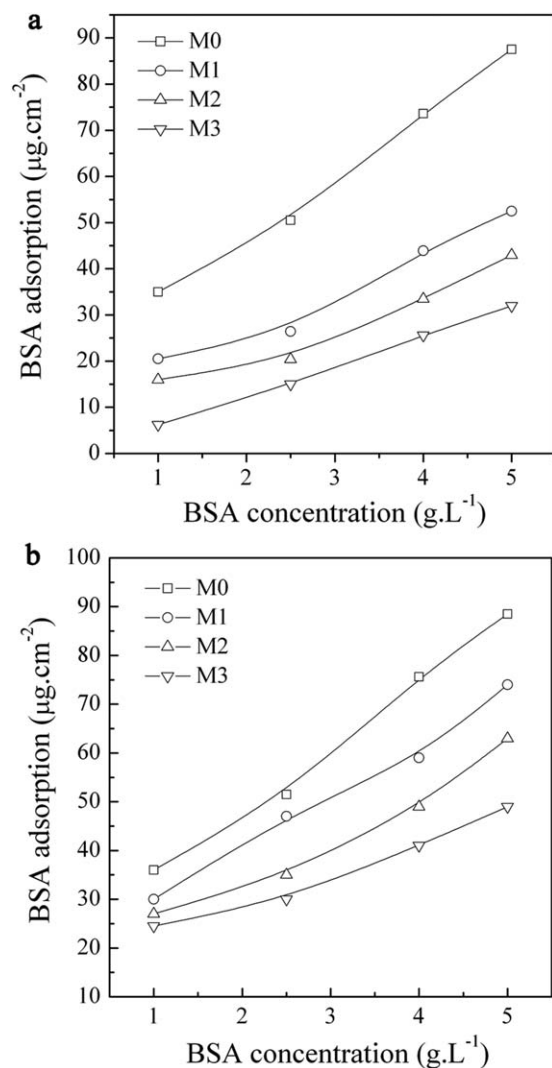


Figure 6. The BSA adsorption of the prepared membranes. (a) Extracted by *n*-hexane; (b) extracted by ethanol.

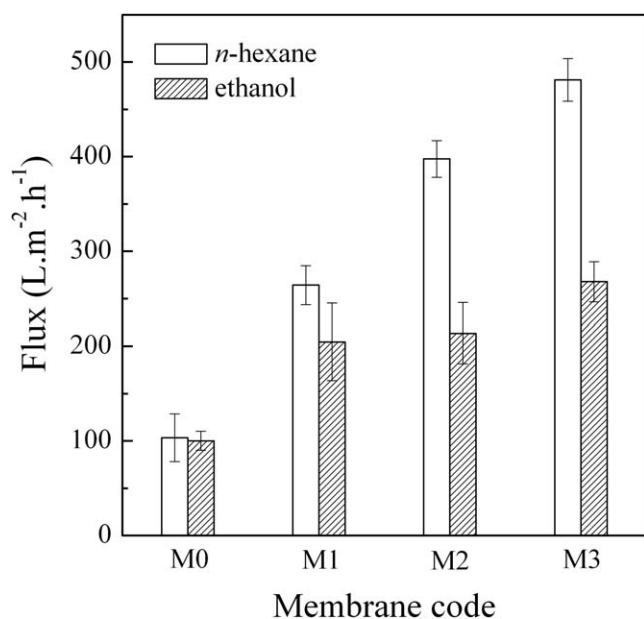


Figure 7. The water flux of the pure PE membrane and the blend membranes (Pressure: 0.1 MPa).

penetration could start up autonomously. However, for the hydrophobic membranes, the critical pressure for water filtration is relatively high. For example, the critical trans-membrane pressure needed for membrane with pore size $3.8 \mu\text{m}$ is reported as 30 kPa.²⁸ For the prepared membranes, in this study, the hydrophilicity is enhanced with increasing PE-*b*-PEG dosage, yielding a lower critical pressure ΔP or even a spontaneous force ($\Delta P > 0$) for water permeation at the first stage. When the membranes are subjected under same pressure (0.1 MPa), the critical pressure needed to overcome decreases, and the remaining pressure for water flowing in the pores would be elevated. So the water flux would tend to increase with increasing PEG chains on the surface.

CONCLUSIONS

HDPE/PE-*b*-PEG blend membranes were successfully prepared via TIPS process. Environmentally friendly LP was used as diluent. Only solid-liquid phase separation occurred in the membrane formation process, yielding membranes a spherulite structure. The effect of extractant was investigated. Results suggested that the non-polar *n*-hexane was more conducive to the surface enrichment of PEG chains than the polar ethanol, which was the result of the swelling effect combined with the entropy drive and interfacial energy effect. The modified membranes extracted by *n*-hexane showed enhanced hydrophilicity, antifouling property, and flux. These above results would contribute helpful understanding and technology in enhancing the properties of membranes related to chemical composition.

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