

PREPARATION OF HIGH DENSITY POLYETHYLENE/POLYETHYLENE-BLOCK-POLY(ETHYLENE GLYCOL) COPOLYMER BLEND POROUS MEMBRANES VIA THERMALLY INDUCED PHASE SEPARATION PROCESS AND THEIR PROPERTIES*

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Abstract High density polyethylene (HDPE)/polyethylene-*block*-poly(ethylene glycol) (PE-*b*-PEG) blend porous membranes were prepared *via* thermally induced phase separation (TIPS) process using diphenyl ether (DPE) as diluent. The phase diagrams of HDPE/PE-*b*-PEG/DPE systems were determined by optical microscopy and differential scanning calorimetry (DSC). By varying the content of PE-*b*-PEG, the effects of PE-*b*-PEG copolymer on morphology and crystalline structure of membranes were studied by scanning electron microscopy (SEM) and wide angle X-ray diffraction (WAXD). The chemical compositions of whole membranes and surface layers were characterized by elementary analysis, Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS). Water contact angle, static protein adsorption and water flux experiments were used to evaluate the hydrophilicity, antifouling and water permeation properties of the membranes. It was found that the addition of PE-*b*-PEG increased the pore size of the obtained blend membranes. In the investigated range of PE-*b*-PEG content, the PEG blocks could not aggregate into obviously separated domains in membrane matrix. More importantly, PE-*b*-PEG could not only be retained stably in the membrane matrix during membrane formation, but also enrich at the membrane surface layer. Such stability and surface enrichment of PE-*b*-PEG endowed the blend membranes with improved hydrophilicity, protein absorption resistance and water permeation properties, which would be substantially beneficial to HDPE membranes for water treatment application.

Keywords: High density polyethylene; Polyethylene-*block*-poly(ethylene glycol) copolymer; Blend porous membrane; Thermally induced phase separation.

INTRODUCTION

Porous polymeric membranes have been used in a wide variety of commercial applications including separating membranes, battery separators, support materials, thermal and sound insulators, air-permeable clothing, sanitary articles, *etc.* The performances of membranes in these applications vary obviously depending on the morphological features of the membranes such as symmetry, pore shape, pore size and the chemical nature of the polymeric materials used to form the membranes.

Polyethylene is an attractive candidate for porous membranes due to its good mechanical properties, chemical stability, low cost, *etc.* Numerous fundamentally different techniques have been developed for fabricating porous membranes based on polyethylene. The most important techniques include sintering,

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irradiation, stretching^[1, 2], template-leaching^[3, 4] and thermally induced phase separation (TIPS)^[5–9]. TIPS process is currently receiving much attention in industrial applications for the production of porous membranes from polyolefin. In general, a homogeneous polymer/diluent solution made at elevated temperature is cooled to induce phase separation and solidification. Subsequently the diluent is removed by extraction, evaporation or freeze drying to obtain the porous membrane. The porous morphology of the resulting membrane can be controlled by a delicate balance of various parameters^[10–23]: the cooling depth, cooling rate, polymer concentration, diluent composition and the presence of additives. However, polyethylene membranes are susceptible to adsorptive fouling of proteins or oils because of their strong hydrophobicity. The consequence is a sharp decline in permeate flux and changing solute selectivity with operation time, which have detrimental effects on the efficiency and economics of the membrane process. Thus, hydrophilic modification of polyethylene membranes should be performed to reduce membrane fouling.

The polymer blending approach has been widely utilized to improve hydrophilicity, permeability and antifouling properties of the porous polymeric membranes formed *via* nonsolvent induced phase separation (NIPS) process^[24–26]. Also in TIPS process, several studies have reported on the formation of porous membranes from two-polymer blend/diluent systems. Castro produced microporous membranes from polypropylene/chlorinated polyethylene/diluent and polyethylene/chlorinated polyethylene/diluent systems^[19]. The membrane formation from polypropylene/polybutene/diluent^[20], poly(vinyl butyral)/poly(ethylene-co-vinyl alcohol)/diluent^[21], and poly(vinyl butyral)/Pluronic F127/diluent^[22] systems was reported by Matsuyama *et al.* The preparation of poly(ethylene-co-vinyl alcohol)/polyvinylpyrrolidone blend membranes was described by Lv *et al.*^[23]. The advantage of the use of polymer blends in TIPS process is that the pore size and morphology can be controlled by the addition of a second polymer due to the changes in thermodynamics and kinetic properties of the blend system. Furthermore, the membrane performances such as hydrophilicity, water permeability and antifouling property can be enhanced.

As far as the blending method is concerned, extensive work focusing on the blending of conventional hydrophobic membrane materials with amphiphilic polymers has been reported. Usually, the hydrophilic component in amphiphilic polymers is poly(ethylene glycol) (PEG) since PEG is well-known for its extraordinary ability to resist protein adsorption, which is thought to arise from its hydrophilicity, large excluded volume, and unique coordination with surrounding water molecules in aqueous solutions^[26, 27]. Selection of an amphiphilic diblock polymer with a PEG block as the membrane additive might be expected to improve the permeability, hydrophilicity and antifouling abilities of high density polyethylene (HDPE) membranes effectively. In this work, an amphiphilic polyethylene-*block*-poly(ethylene glycol) (PE-*b*-PEG) diblock copolymer was used as additive for the preparation of blend porous HDPE membranes *via* TIPS process. The effects of PE-*b*-PEG content on phase diagram and membrane morphology were studied. The properties of the blend membranes such as hydrophilicity, water permeability and protein-resistance were also investigated.

EXPERIMENTAL

Materials

HDPE (5200B, $M_w = 150000$) was supplied by Lanzhou Petrochemical Co. Ltd. (China). Diblock copolymer PE-*b*-PEG ($M_n = 1400$, ethylene oxide content = 50 wt%) and bovine serum albumin (BSA, $M_n = 67000$) were purchased from Aldrich. Diphenyl ether (DPE) and ethanol were obtained from Shanghai Chemical Reagents Co. (China). All the chemicals were used as received.

Determination of Phase Diagrams

HDPE, PE-*b*-PEG copolymer and DPE with desired weight ratios were added into a flask equipped with a nitrogen inlet, a condenser and a stirrer. The mixture was heated to 200°C, mixed until homogeneous, and then quenched in liquid nitrogen, yielding a solid HDPE/PE-*b*-PEG/DPE mixture (namely, a solid solution) sample for determination of phase diagrams and membrane preparation. The obtained homogeneous sample was cut into small pieces and placed between a pair of microscope cover slips, while a Teflon film of 100 μm thickness with

a square opening in the center was inserted between the cover slips to prevent diluent loss by evaporation. The sample was heated on a hot stage (Linkam, THMS600, UK) at 200°C for 5 min and then cooled to 20°C at a controlled rate of 10 K/min. The temperature of the stage was manipulated by a programmable temperature controller (Linkam, CI94, UK) and an automated liquid nitrogen cooling pump (Linkam, LNP94/2, UK). The cloud point (T_{cloud}) was determined visually by observing the appearance of turbidity under an optical microscope (Nikon, Eclipse E600POL, Japan). Each T_{cloud} value reported represents the average temperature of three measurements.

The dynamic crystallization temperature (T_c) and melting temperature (T_m) were estimated using a differential scanning calorimeter (Perkin-Elmer Pyris-1 DSC, USA). Approximately 5–7 mg of sample sealed in an aluminum pan was melted at 160°C for 5 min, cooled at a rate of 10 K/min to 20°C, and then heated at a rate of 10 K/min to 160°C again. The onset temperatures of the exothermic peak on cooling and the endothermic peak on heating in the thermograms were taken as T_c and T_m , respectively.

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

The homogeneous solid HDPE/PE-*b*-PEG/DPE mixtures for membrane preparation were prepared as described above. Table 1 shows the corresponding solution composition for each membrane sample. The solid HDPE/PE-*b*-PEG/DPE mixture was placed between a stainless steel mould and a stainless steel slip^[17]. This assembly was heated on a hot-press apparatus (Huzhou Shunli Rubber Machinery Co., Ltd., XLB-D, China) at 200°C for 5 min and the mixture sample was pressed into film after melting. The thickness of the film was adjusted by the mould to be (100 ± 2) μm . Then the assembly was taken out and immediately immersed into a water bath of 20°C. The formed solid HDPE/PE-*b*-PEG/DPE film was peeled off and subsequently immersed in ethanol of 20°C for 24 h to extract DPE. The resulting porous HDPE/PE-*b*-PEG blend membrane was dried for 12 h in a vacuum oven at about 40°C before characterization.

Table 1. Compositions of HDPE/PE-*b*-PEG/DPE mixtures for membrane preparation

Membrane	Composition (wt%)			PE- <i>b</i> -PEG/HDPE ratio (W/W)
	HDPE	PE- <i>b</i> -PEG	DPE	
M0	20.0	0	80.0	0
M1	20.0	2.0	78.0	1/10
M2	20.0	4.0	76.0	2/10
M3	20.0	6.0	74.0	3/10

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

The surface and cross-section (fractured in liquid nitrogen) morphologies of prepared membranes were inspected on a field emission scanning electron microscope (FESEM, FEI, SIRION-100, USA) after being coated with a gold layer. The average pore size was analyzed based on such FESEM images with the Image-Pro Plus software. The porosity of membranes was measured by a mercury porosimeter (Micromeritics, AutoPore IV 9500, USA). The chemical compositions of whole membranes and the retention ratio of PE-*b*-PEG in membranes were calculated basing on elemental contents of carbon and hydrogen determined with an elemental analyzer (Elementar, Vario EL III, Germany). The chemical compositions of membrane surface layers were characterized by Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR, Bruker Optics, Vector 22, Switzerland) and X-ray photoelectron spectroscopy (XPS, PHI Co., PHI 5000C ESCA system, USA). The thermal behaviors of membranes were studied by a differential scanning calorimeter (Perkin-Elmer Pyris-1 DSC, USA). Approximately 5–7 mg of samples were sealed in aluminum pans and thermograms were recorded from –10°C to 150°C at a heating rate of 5 K/min under a constant flow of nitrogen gas. The crystalline structures of membranes were investigated by wide-angle X-ray diffraction (WAXD) on an X-ray diffractometer (PANalytical, X'Pert PRO, The Netherlands) with $\text{CuK}\alpha$ radiation. The static contact angles of water on membrane surfaces were measured at 25°C on a contact angle goniometer (Dataphysics, OCA20, Germany), and 5 measurements were done for each sample to get the average value. Water flux experiments were performed at 25°C on a dead-end membrane evaluation cell with an effective filtration area of 12 cm^2 . Each membrane sample

was stabilized at 0.15 MPa for at least 30 min with deionized water before testing. Then the operation pressure was reduced to 0.1 MPa and the water flux was recorded after the flux was stable. The flux of pure water (J_w) is determined as: $J_w = V/A\Delta t$, where V is the volume of the permeated water during the experiment, A represents the membrane area, and Δt denotes the operation time.

Static Protein Adsorption on Membrane Surfaces

BSA was used as a model protein to evaluate the protein-resistant characteristics of the prepared membranes. The studied membranes with external surface area (including top and bottom surfaces) of about 8 cm² were immersed in 10 mL of phosphate buffer solution (PBS, 0.01 mol/L, pH 7.4) containing BSA with various concentrations at 30°C for 24 h with a shaking speed of 150 rpm to reach adsorption equilibrium. The amount of the adsorbed protein was determined by measuring the difference between the concentrations of albumin in the solution before and after adsorption indicated from the absorbance intensity at 280 nm recorded on a UV-Vis spectrophotometer (Shimadzu, UV-1601, Japan). The reported data were the average values of triplicate samples for each membrane.

RESULTS AND DISCUSSION

Phase Diagram

Figure 1 shows the phase diagrams of the HDPE/PE-*b*-PEG/DPE systems in which the concentration of HDPE was fixed at 20 wt%. The cloud point curve of the systems containing PE-*b*-PEG shifts to higher temperatures as the amount of additive increases from 2 wt% to 6 wt%. The result indicates that phase separation could be assisted by the addition of a diblock copolymer. This assistance is induced by the amphiphilic effect of the added additive serving as a nucleus for phase separation. The tendency of the cloud point can be explained by the change in the compatibility of systems. An increase in ethylene oxide content in the system can decrease the compatibility relative to that in the pure HDPE/DPE system, thus raising the cloud point to a higher temperature. On the other hand, the dynamic crystallization temperatures and melting temperatures are not influenced so much by the addition of PE-*b*-PEG.

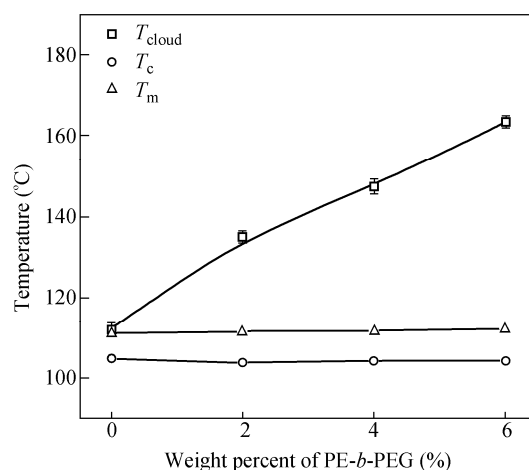


Fig. 1 Phase diagrams of the HDPE/PE-*b*-PEG/DPE systems

Membrane Morphology

Figure 2 shows the surface and cross-section FESEM photomicrographs for the membranes formed by quenching in water at 20°C with varying composition of PE-*b*-PEG. The cellular pores formed from typical liquid-liquid phase separation were observed in the cross-sections of all the membranes. This result can be explained by Fig. 1. In all the investigated cases, the cloud point exists above the dynamic crystallization temperature, and this means that liquid-liquid TIPS will occur prior to crystallization during cooling. Therefore, all the formed membranes exhibited similar cellular structure.

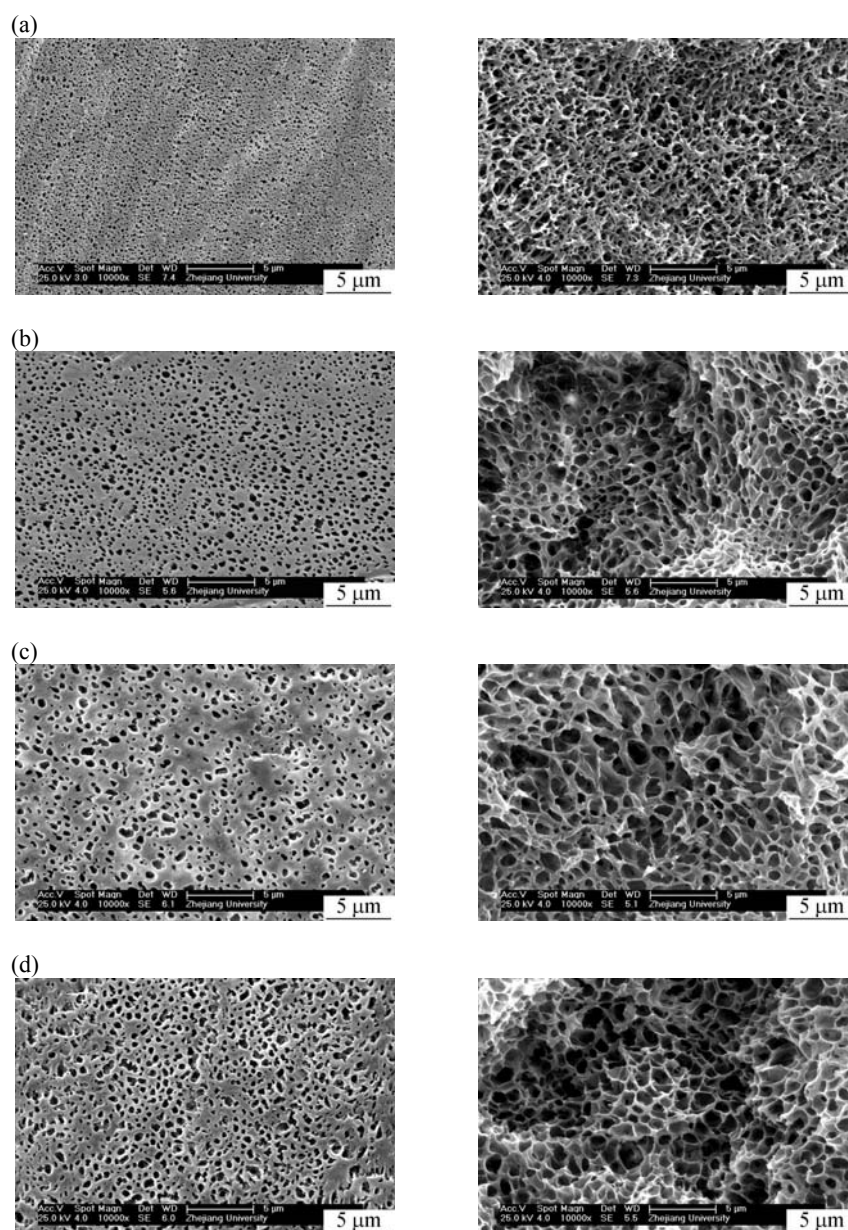


Fig. 2 Surface (left) and cross-section (right) FESEM photomicrographs for the membranes of (a) M0, (b) M1, (c) M2 and (d) M3

When a homogeneous polymer/diluent solution is cooled from the one-phase region of the phase diagram to a temperature below the coexistence curve, liquid-liquid phase separation occurs and droplets of one phase form within a continuous matrix of a second phase. These two phases have compositions given by the coexistence curve. In the formation of cellular membranes *via* TIPS, the droplet phase is polymer-poor and the matrix phase is polymer-rich. In many systems, these droplets grow in size and decrease in number with time through a process known as coarsening once they have reached their equilibrium compositions^[29, 30]. The thermodynamic driving force for this droplet growth is the minimization of interfacial free energy *via* reduction of the interfacial area. Two factors contributing to the droplet size are droplet growth rate and growth duration^[31]. The growth rate depends on the viscosity of the system (the higher the viscosity, the slower the

growth) and the interfacial tension between the phases (the higher the interfacial tension, the faster the growth), while the growth duration depends on the cooling rate and the temperature difference between the cloud point and the crystallization temperature. When the polymer is solidified by a further drop in temperature and the diluent is removed, the droplets become cellular pores in the membrane. The size of the droplets in a phase-separated system is directly related to the size of the pores in the resulting membrane.

The average pore size of the membranes was measured by FESEM image analysis method and given in Table 2. It can be seen that the average pore size increases in the order of $M0 < M1 < M3 < M2$, generally coincident with the increase of PE-*b*-PEG content. The first reason is that the temperature range between T_{cloud} and T_c becomes wider with increasing PE-*b*-PEG content (as illustrated in Fig. 1), which can provide longer time interval for the droplet growth. The second reason is that the interfacial tension (between the droplet phase and continuous matrix phase) increases with increasing PE-*b*-PEG content, which can lead to higher droplet growth rate. As a result, the final pore size in the membrane generally increases with the increase of PE-*b*-PEG content. However, it seems the viscosity and interfacial tension yield contradicting effects on the droplet growth in this investigated system. Although the viscosity will increase due to the increasing PE-*b*-PEG content, concerning the low molecular weight of PE-*b*-PEG, the viscosity of the system containing lower PE-*b*-PEG content only increases slightly. On the other hand, the interfacial tension should increase obviously with the increase of PE-*b*-PEG content. By comparison, it should be the increased interfacial tension rather than the increased viscosity which yields the dominant effect on droplet growth rate. While the PE-*b*-PEG content reaches much higher values, on the contrary, the greatly increased viscosity might yield the dominant effect on droplet growth rate, which will slow the droplet growth and generate smaller pore size in the resulting membrane. Basing on this mechanism, the observation that the blend membrane with a PE-*b*-PEG/HDPE ratio of 3/10 (M3) exhibits smaller pores than that with a PE-*b*-PEG/HDPE ratio of 2/10 (M2) could be explained reasonably.

Table 2. Structure parameters of the pure and blend HDPE membranes

Membrane	Average pore size (μm)		Porosity (%)	Retention ratio of PE- <i>b</i> -PEG (wt%)
	Interior	Surface		
M0	0.54	0.15	65.4	—
M1	0.76	0.35	65.3	97.7
M2	1.24	0.52	63.8	99.1
M3	1.08	0.48	61.2	98.6

For all the cases, the pore sizes at the surfaces of membranes are smaller than the interior pore sizes (Table 2). The smaller pores at the surfaces may be attributed to the higher cooling rate in surface layers brought about by contacting with water. There would be less time for the formed droplets to coarsen in surface layers in cooling process. As summarized in Table 2, the porosity of the membranes varies in a small range and shows a slight decreasing tendency with increase in the total polymer concentration. This may be associated with the reduced volume fraction of the polymer-poor phase in the high polymer concentration case.

Retention of PE-*b*-PEG in Blend Membranes

To understand the retention of PE-*b*-PEG in the blend membranes, the chemical compositions of the whole membranes were characterized by elementary analysis. The retention ratio of PE-*b*-PEG in each blend membrane was calculated according to the different elemental contents of carbon and hydrogen in HDPE, PE-*b*-PEG, and the membrane. As listed in Table 2, PE-*b*-PEG exists in the blend membranes and the retention ratio of PE-*b*-PEG exceeds 97 wt% for all the blend membranes. This means that the amphiphilic PE-*b*-PEG copolymer is well compatible with HDPE and most of the copolymer can be retained stably in the formation of membranes.

Besides, the FTIR-ATR spectra of PE-*b*-PEG and the membranes of M0 and M1 are shown in Fig. 3. For the membrane M1, the appearance of the characteristic absorption peak at around 1110 cm^{-1} assigned to the stretching vibrations of C—O bonds in PEG blocks reveals the existence of PEG chains in the surface layer of

blend membrane. To further examine the chemical compositions in membrane surface layers, XPS analysis was also employed, and the typical survey spectra for the membranes of M0 and M1 are shown in Fig. 4. Two major emission peaks in the spectrum of M1 can be observed at 288.4 eV for C(1s) and 536.1 eV for O(1s), respectively. Concerning no oxygen existing in HDPE, the presence of O(1s) peak confirms the existence of PEG chains at the surface of blend membrane. Further calculation from the XPS spectrum of M1 indicates the O/(O+C) atomic ratio at the membrane surface layer (0.084) is three times higher than that in the whole membrane (0.02), suggesting substantial enrichment of the PEG segments of PE-*b*-PEG at the surface layer of blend membranes.

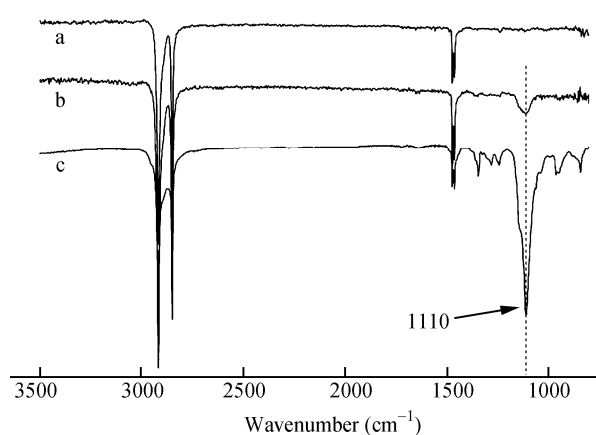


Fig. 3 FTIR-ATR spectra of (a) M0, (b) M1 and (c) PE-*b*-PEG copolymer

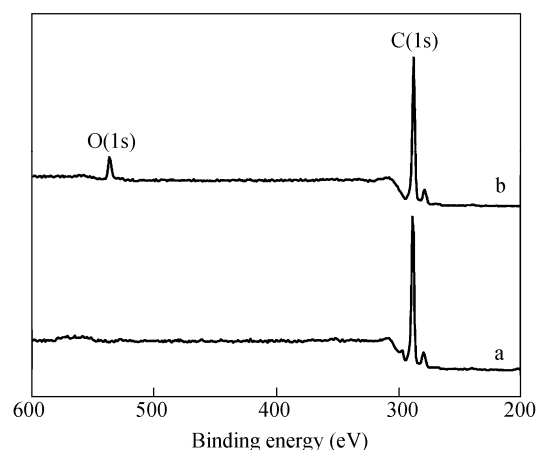


Fig. 4 Survey XPS spectra for the membranes of (a) M0 and (b) M1

Thermal Behavior and Crystalline Structure of Membranes

The thermal behaviors of PE-*b*-PEG and the membranes were determined *via* DSC measurements. The obtained thermograms are presented in Fig. 5. The pure PE-*b*-PEG exhibits two obvious endothermic peaks due to the sequential melting of the crystalline PEG block and the crystalline PE block at 27.3°C and 104.9°C, respectively. The four membranes exhibit similar melting peaks of HDPE at 128–130°C. The melting peak of PEG block disappears in the thermograms, indicating the separated domains of PEG can not be formed in the blend membranes.

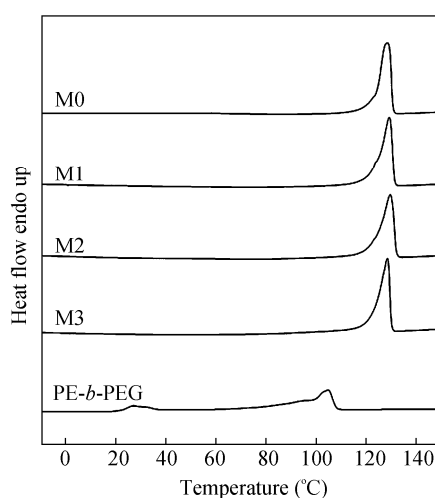


Fig. 5 DSC thermograms for the pure and blend HDPE membranes

To investigate the effect of the addition of PE-*b*-PEG on the crystalline structures of the membranes, WAXD measurements were performed to examine the crystalline structures of PE-*b*-PEG and the membranes. As shown in Fig. 6, all the membranes have three most distinctive diffraction peaks at around 21.5°, 23.9° and 36.3°, corresponding to the reflections of (110), (200) and (020) lattice planes of the orthorhombic crystalline form of polyethylene, respectively. It is suggested that the addition of PE-*b*-PEG could not disturb the crystallization of HDPE molecules. The two peaks at 19.2° and 23.3°, corresponding to monoclinic crystalline PEG (120) reflection and a combination of PEG (032) and (112) reflections, can not be clearly observed in the WAXD patterns for the blend membranes containing PEG segments less than 11.5 wt% (calculated from the highest PE-*b*-PEG/HDPE weight ratio of 3/10 for M3). Though more proof seems needed to conclude that PE-*b*-PEG can be mixed with HDPE on a molecular level, at least in the range of PE-*b*-PEG content in this work, the PEG blocks can not aggregate into obvious separated domains in membrane matrix, and the PE blocks in PE-*b*-PEG might be involved into the crystalline domains of HDPE. These results are in good agreement with those from DSC analysis. From application consideration, the homogenous dispersion and stability of PE-*b*-PEG in HDPE matrix should contribute to the expected reliability in structure and properties of the blend membranes.

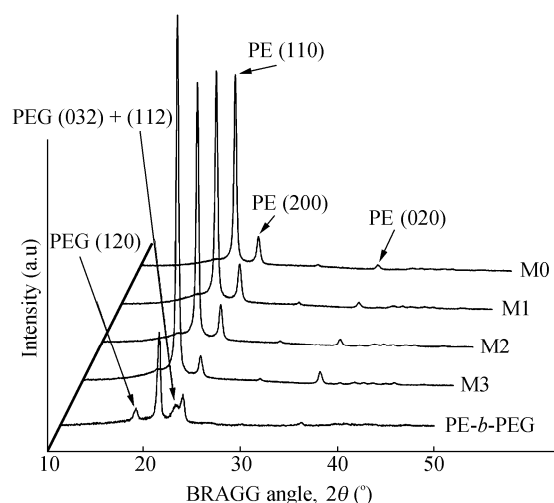


Fig. 6 WAXD patterns for the pure and blend HDPE membranes

Hydrophilicity, Protein Absorption and Permeation Properties of Membranes

Water contact angle measurements were used to characterize the hydrophilicity of membrane surface. The static contact angles of the membranes are shown in Table 3. The water contact angles of the membranes decrease with the content of PE-*b*-PEG increasing. The contact angle of pure HDPE membrane (M0) is about 126°, showing an inherently hydrophobic behavior for pure HDPE membrane. While the blend membrane with a PE-*b*-PEG/HDPE ratio of 3/10 (M3) exhibits a lower contact angle of about 81°. The changes in water contact angles suggest that the addition of amphiphilic PE-*b*-PEG copolymer can enhance the hydrophilicity of HDPE membranes effectively. Principally, such improved hydrophilicity could be ascribed to the enriched existence of PEG segments at the membrane surfaces, which has been confirmed by XPS. This hydrophilicity improvement will certainly benefit the protein resistance and permeability of the blend membranes.

Figure 7 shows the results of BSA adsorption on the pure and blend HDPE membranes. The amounts of BSA adsorption on the blend membranes are much smaller than those on the pure HDPE membrane. Meanwhile, the adsorbed amounts of BSA decrease with the increase of PE-*b*-PEG content. The effective reduction in protein adsorption is attributed to the increased hydrophilicity of the HDPE/PE-*b*-PEG blend membranes. In detail, the PEG segments of PE-*b*-PEG anchored at the membrane surface stretch out into the

surrounding aqueous environment to form a hydrated layer, which can prevent protein molecules from contacting the membrane surface. With the increase of PE-*b*-PEG content in the membranes, more PEG segments immobilized at the blend membrane surfaces would enhance the capability of reducing protein adsorption.

Table 3. Water contact angles and water fluxes of the membranes

Membrane	Contact angle (°)	Flux (J_w , $L \cdot m^{-2} \cdot h^{-1}$)
M0	126 ± 2	< 50
M1	112 ± 2	500 ± 15
M2	95 ± 2	648 ± 15
M3	81 ± 2	551 ± 15

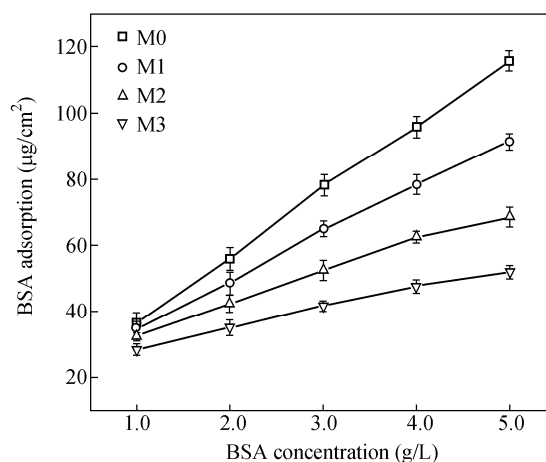


Fig. 7 BSA adsorption on the pure and blend HDPE membranes

The tested water fluxes of the prepared membranes are listed in Table 3. It can be observed that the water flux of pure HDPE membrane (M0) is lower than $50 L \cdot m^{-2} \cdot h^{-1}$. The stronger hydrophobicity of pure HDPE made higher water permeation resistance for M0 with surface pore size of $0.15 \mu m$. Considering the pore size of membrane surfaces no more than $0.52 \mu m$, the blend membranes of M1, M2 and M3 should also perform strong water permeation resistance and the fluxes should be small. However, the water fluxes increase dramatically as PE-*b*-PEG is blended into the membranes due to the efficiently rendered hydrophilicity. The water flux variation of blend membranes is consistent with the pore size difference of membrane surfaces. Although the water flux results suggest PE-*b*-PEG can be blended into HDPE membrane as a hydrophilic modifier, what must be noted is that the absolute water flux of blend membranes in this work is still relatively small. This is probably caused by the cellular and poorly interconnected structure in membrane matrix. In order to prepare hydrophilic HDPE/PE-*b*-PEG blend membranes with larger water flux and better antifouling performance, ongoing work is directed toward changing membrane formation conditions and adopting a post-stretching step.

CONCLUSIONS

The phase diagrams of the HDPE/PE-*b*-PEG/DPE systems were determined *via* thermally induced phase separation. The cloud point temperature shifted to higher temperatures as the ethylene oxide content increased. The porous HDPE/PE-*b*-PEG blend membranes were prepared following a typical TIPS process. The membrane morphology can be influenced by the PE-*b*-PEG content due to the changes in thermodynamic and kinetic behaviors during phase separation. Because of the good compatibility between HDPE and PE-*b*-PEG, the copolymer can be retained stably in the blend membranes and the separated domains of PEG can not be formed in membrane matrices. The PEG segments in PE-*b*-PEG copolymer can enrich at the membrane surface layers

and endow the blend membranes with enhanced hydrophilicity, protein absorption resistance and water permeation properties, which will contribute a new suggestion for the preparation of modified HDPE membranes *via* TIPS process. With further exploration, the high performance of HDPE/PE-*b*-PEG blend membranes for water filtration should be achieved.

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