Effect of cooling baths on EVOH microporous membrane structures in thermally induced phase separation

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ABSTRACT

The purpose of this work is to investigate the effect of cooling bath on the membrane preparation of crystalline polymer/diluent system via thermally induced phase separation (TIPS), when the cooling bath is compatible with the diluent. In this work, poly(ethylene-co-vinyl alcohol) (EVOH)/PEG300 system with water and methanol as the cooling baths was proposed. Results showed that when water was used as the cooling bath, the membrane presented an asymmetric structure consisting of a porous skin, macrovoids near the top and lacy structures near the bottom. In contrast, when cooled in the bath of methanol, it showed particulate morphology on the top surface and cellular pores near the bottom. The lacy and cellular structures were the typical structures resulted from liquid–liquid thermally induced phase separation, the novel macrovoids and particulate morphology were then supposed to be induced by the mutual diffusion between the diluent and the cooling bath. In the case of water, the diluent’s outflow was much faster than the water’s inflow into the membrane, so the penetrated water acted as a strong nonsolvent and induced macrovoids near the top. In the bath of methanol, the diluent’s outflow was much faster than the methanol’s inflow, which changed the solution composition from a liquid–liquid phase separation region to a solid–liquid phase separation region and resulted in particulate morphology near the top.

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1. Introduction

Microporous membranes can be prepared by approaches such as thermally induced phase separation (TIPS) and nonsolvent induced phase separation (NIPS) with different mechanisms and membrane structures. For the TIPS approach, it has been applied to a number of polymers, such as polypropylene (PP) [2,3], polyethylene (PE) [4], polyvinylidene fluoride (PVDF) [5], poly(ethylene-co-acrylic acid) (EAA) [6] and polystyrene (PS) [7], etc. Generally in the TIPS process, a homogeneous solution is prepared at an elevated temperature by blending the polymer with the diluent, then the solution is cooled to induce solid–liquid (S–L) or liquid–liquid (L–L) phase separation, and finally a microporous structure is formed after the extraction of diluent [1]. Unlike the TIPS process, the mechanism of NIPS process is the induction of phase separation through a change in the composition of the homogeneous solution. Among the several kinds of NIPS process, immersion precipitation is the most widely used approach. In this approach, a homogeneous casting solution is immersed into a nonsolvent coagulation bath, then the phase separation is induced by the exchange of solvent and nonsolvent, by which the membrane is formed [8]. There are many literatures that describe thermodynamic and kinetic aspects of nonsolvent–solvent–polymer systems by this approach [8–12].

As a semi-crystalline random copolymer with good wet strength and hydrophilicity, poly(ethylene-co-vinyl alcohol) (EVOH) can be made into porous membranes by TIPS process [13–15] or immersion–precipitation method [8–12]. Shang et al. [13] prepared EVOH hollow fiber membranes from EVOH/glycerol system via TIPS. The obtained hollow fiber membranes presented larger pores near the outer surface and smaller pores near the inner surface. The authors ascribed it to the enhanced pore growth by the water penetration due to the good compatibility between glycerol and water. According to this article, it can be proposed that when the diluent is not compatible with the cooling bath in the TIPS process, i.e. soybean oil/water, the cooling bath cannot penetrate into the membrane and will result in a usual structure from TIPS. On the other hand, when the diluent is compatible with the cooling bath, i.e. glycerol/water, the cooling bath can diffuse into the membrane and even initiate a nonsolvent induced phase separation and will affect the membrane structure.

Matsuyama et al. [16] reported a combined process of TIPS and immersion precipitation to make PMMA porous membranes. In this article, cyclohexanol was used as the diluent, water and methanol as the cooling baths, respectively. When using water as the cooling bath, due to the low mutual affinity between water
and cyclohexanol, TIPS and the immersion precipitation occurred serially. On the contrary, when using methanol as the cooling bath, TIPS and the immersion precipitation occurred simultaneously because of the fast inflow of methanol. The two cooling baths resulted in different membrane structures. In this literature, the polymer used was amorphous and the cooling temperature was higher than the glass transition temperature of the polymer. Hence, only liquid–liquid demixing occurred. The time of immersion period could be long enough for the penetration of the cooling bath, without the solidification of polymer. However, in general TIPS process crystalline polymers are often used. For the crystalline polymer/diluent systems, i.e. EVOH/PEG, the crystallization temperatures are so high that the process of solid–liquid demixing is inevitable. Thus, the interaction between the cooling bath and crystalline polymer/diluent system could be more applicable but more complex than the amorphous polymer/diluent system.

The purpose of this work is to investigate the effect of cooling bath on the membrane preparation of crystalline polymer/diluent system via TIPS, when the cooling bath is compatible with the diluent. In this work, EVOH/PEG300 system was chosen and two kinds of cooling baths (water and methanol) were used. The effect of cooling bath on the crystalline properties and the membrane structure were studied and discussed, which may be a good guidance for the preparation of crystalline polymeric membranes via TIPS.

Fig. 1. SEM photographs of EVOH membrane prepared by immersion in a water bath. (a) Top surface, (b) cross-section, (c) the magnified photograph of cross-section near the top, and (d) the magnified photograph of cross-section near the bottom.
2. Experimental

2.1. Materials

EVOH containing 38 mol% ethylene (EVOH38) with degree of polymerization of 960 was purchased from Kuraray Co. PEG300 (Mn = 300, Shanghai Chemical Reagent Co., AR) was used as diluent. Distilled water (with the conductance of 0.1 μs/cm) and methanol (Shanghai Chemical Reagent Co., AR) were used as the cooling baths. These reagents were all used without further purification.

2.2. Membrane preparation

Homogeneous EVOH/PEG300 sample of 20 wt% polymer concentration was prepared by the method reported in our previous article [15]. The sample was chopped into small pieces, sealed with two cover slips and heated on the hot stage at 200 °C for 5 min. To adjust the membrane thickness, a Teflon ring of 150 μm thickness was inserted between the cover slips. Then the upper cover slip was quickly removed and the sample was immersed in the cooling bath of 25 °C. Finally, the membrane was extracted with acetone (Shanghai Chemical Reagent Co., AR) to further remove residual diluent and dried in vacuum at room temperature overnight.

2.3. SEM observation

The membranes were fractured in liquid nitrogen, coated with gold–palladium and observed by a scanning electron microscope (TESCAN 5136MM).

2.4. DSC

The thermal property of EVOH membranes was studied using differential scanning calorimetry (PerkinElmer DSC, Pyris 1). About 8 mg sample was sealed in an aluminum DSC pan, heated from 50 °C to 200 °C at the rate of 10 °C/min.

3. Results and discussion

3.1. Membrane morphology

Figs. 1 and 2 show the top surfaces and cross-sections of membranes prepared by immersion in water and methanol baths, respectively. Here, the top layer is the layer that contacts with the cooling baths and the bottom layer is the layer that contacts with the cover slip. As shown in Fig. 1, the membrane prepared in the water bath presents an asymmetric structure consisting of a porous skin (a), macrovoids (c), and lacy structures (d). The macrovoids near the top are the typical structures in membranes prepared by immersion precipitation approach [17] and the lacy structures near the bottom are typical in membranes prepared by TIPS [3]. The departure of these two layers might be induced by the shrinkage during post-treatment. In contrast, the membrane prepared in the methanol bath is composed of particles with a diameter of approximately 500 nm on the top surface (a), particles near the top (b) and cellular pores near the bottom. The particle structure is a representative of polymer crystallization [8] and the cellular pores near the bottom are the typical structures resulted from liquid–liquid phase separation in TIPS [3].

As discussed in the literatures [16,18], heat transfer is generally about two orders faster than mass transfer in liquids. Thus, the temperature of the polymer solution decreased to 25 °C almost instantly after the immersion into the cooling baths and thermally induced phase separation occurred at the beginning. According to the phase diagram of EVOH/PEG300 system reported previously [14] (see Fig. 3), the polymer concentration (20 wt%) was lower than the monotectic point (approximately 35 wt%). Thus, liquid–liquid phase separation took place first, followed by crystallization in the polymer-rich phase. However, EVOH crystallization is a slow process [19], which means that before EVOH solidification, mass transfer between the diluent (PEG) and the cooling bath (water or methanol) could occur, thereby affecting the membrane morphology near the top surface.

To quantitatively describe the mass transfer rates between diluent and cooling baths, the diffusion coefficients of solvent 1 in solvent 2 ($D_{1-2}$) were calculated by Eq. (1) [20], with the results shown in Table 1.

$$D_{1-2} = 8.93 \times 10^{-8} \left( \frac{V}{T^{0.267}} \right)^{0.15}$$

where $V$ is the molar volume of solvent, $\eta$ is the viscosity, $\sigma$ is the surface tension of solvent, and $T$ is the temperature.

When a polymer solution is cooled into the liquid–liquid phase separation region, the solution separates into a polymer-rich continuous phase and a polymer-lean droplet phase, or bicontinuous polymer-rich and polymer-lean phases, depending on nucleation and growth (NG) mechanism or spinodal decomposition (SD) mechanism [21]. Before polymer solidification, the exchange of diluent and cooling baths would occur as deduced above.

According to Table 1, when immersed in water, the rate of diluent outflow was a little higher but still comparative with the rate of water inflow. In this case, water’s inflow could compensate some loss of diluent and decrease the polymer concentration on the interface, finally resulted in porous layer on the top surface, as shown in Fig. 1a. The macrovoids near the top can be explained as follows: according to EVOH membrane formation by immersion precipitation, water often acted as a strong nonsolvent for the EVOH solution and resulted in macrovoids via instantaneous liquid–liquid demixing [22]. Water that flowed into the membrane could act as a strong nonsolvent both in the polymer-rich and polymer-lean phases and induced macrovoids until being stopped by polymer crystallization, which resulted in a macrovoids layer with a depth of 20 μm (Fig. 1c). Meanwhile, without the penetration of water, the structure near the bottom was also fixed by crystallization. The inter-connected lacy structure near the bottom (see Fig. 1d) is the representative structure being fixed in the early stage of spinodal decomposition [3]. It suggests that at the first stage, the polymer solution separated into bicontinuous polymer-rich and polymer-lean phases due to SD mechanism, which was beneficial for the fast exchange of the diluent and the cooling bath.

On the contrary, as shown in Table 1, the diffusion coefficient of PEG in methanol is more than twice that of methanol in PEG, indicating that diluent’s outflow was much faster than methanol’s inflow. With the outflow of diluent, the composition on the top surface would shift from a liquid–liquid phase separation region to a higher concentration in a solid–liquid phase separation region. Fig. 4 shows the schematic composition change in this case. As a result, particulate morphology resulted from crystallization formed on the top surface (see Fig. 3a). From the top to the bottom in the cross-section, the change of morphology from particles to cellular pores (Fig. 3d) suggested the change of polymer concentration from high to low.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Diffusion coefficients between PEG and cooling baths.</th>
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<tr>
<td>Solvent 1</td>
<td>Solvent 2</td>
</tr>
<tr>
<td>PEG300 Water</td>
<td>6.19</td>
</tr>
<tr>
<td>PEG300 Methanol</td>
<td>10.42</td>
</tr>
</tbody>
</table>
At this concentration and cooling condition, the cellular pores near the bottom could be ascribed to the later stage of spinodal decomposition rather than nucleation and growth mechanism. Nucleation and growth is the expected mechanism when a system leaves the thermodynamically stable condition and slowly enters the metastable region of the phase diagram, while spinodal decomposition takes place in a fast quench into the two phase region limited by the spinodal curve [21]. From the phase diagram of EVOH/PEG300 shown in Fig. 3, we can deduce that the 20 wt% EVOH/PEG300 solution underwent spinodal decomposition when immersed in methanol of 25°C. Therefore, the cellular pores near the bottom were the structure fixed in the later stage of spinodal decomposition, which is distinct from the case of water.

The heat transfer rate can be used to explain the distinct stages of spinodal decomposition fixed respectively in water and methanol baths. Table 2 shows the heat conductivities of water and methanol, indicating that the rate in water is three times more than that in methanol. The higher heat transfer rate in water meant shorter time for the phase growth before being fixed at the early stage of spinodal decomposition. In contrast, the lower heat transfer rate in methanol allowed more time for the phase growth to the later stage of spinodal decomposition before polymer crystallization.

Fig. 2. SEM photographs of EVOH membrane prepared by immersion in a methanol bath. (a) Top surface, (b) cross-section, (c) the magnified photograph of cross-section near the top, and (d) the magnified photograph of cross-section near the bottom.
3.2. Crystalline properties

The crystalline properties of membranes can be found in the DSC thermograms, as shown in Fig. 5, with the melting peaks and enthalpies of fusion calculated in Table 3. As shown in Table 3, membranes prepared in water and methanol baths had almost the same melting temperatures but different enthalpies of fusion, which suggested that crystallinities of membranes prepared by immersion in different baths were different. The lower enthalpy of fusion of the membrane prepared in water indicated lower crystallinity. From the reports of Young et al. [24], the enthalpies of fusion were similar for membranes with cellular morphologies and membranes with particulate morphologies. Therefore, the different crystallinities might originate from different cooling rates for the membrane formation rather than different structures. As discussed above, the cooling rate in water was much higher than that in methanol, which meant shorter time for the arrangement of polymer chains and imperfect crystallization and resulted in lower crystallinity. On the contrary, the lower cooling rate in the bath of methanol allowed perfect crystallization and resulted in higher crystallinity.

It is noticed that in Fig. 5, there was an unobvious endothermic peak at about 160 °C for the membrane prepared by immersion in water. In the literature of Young et al. [24], an unobvious peak at about 160 °C was also found for EVOH membranes prepared by immersing in water using immersion–precipitation method, but was not found for the membranes prepared by immersing in 2-propanol. Considering the different structures of these membranes, this unobvious peak might be related to the macrovoids resulted from instantaneous liquid–liquid demixing, which could induce lattice distortion during the following crystallization. The reason of the unobvious endothermic peak shown in Fig. 5 could also be the same one.

4. Conclusion

EVOH microporous membranes were prepared by cooling in two kinds of cooling baths via thermally induced phase separation. It was found that when water was used as the cooling bath, the membrane presented structures consisting of a porous skin, macrovoids near the top and lacy structures near the bottom. In contrast, in the case of methanol, it showed particulate morphology on the top surface and cellular pores near the bottom. The mutual diffusion coefficients between diluent and cooling baths, the heat conductivities of cooling baths, and DSC melting endotherms were used to explain the membrane formation. It can be concluded that during the membrane preparation via thermally induced phase separation, the cooling bath had a strong effect on the membrane morphology, especially for the membrane surface. The combination of TIPS
and immersion–precipitation method can be used to develop novel porous membrane structures.

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**References**


