Porous Polyphenylene Sulfide Membrane with High Durability Against Solvents by the Thermally Induced Phase-Separation Method

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ABSTRACT: Porous polyphenylene sulfide membranes were prepared as new solvent-resistant membranes by the thermally induced phase-separation (TIPS) method. Porous structures were either formed by solid–liquid phase separation (polymer crystallization) or liquid–liquid phase separation. The effects of solvents, cooling rates, and polymer concentrations on the porous structures were investigated. Various characteristics of pore structure can be obtained with suitable diluents and cooling rates using the TIPS method. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2959–2966, 2006

Key words: polyphenylene sulfide; porous membranes; thermally induced phase separation; chemical resistance

INTRODUCTION

Porous membranes have been widely applied in various areas such as the food industry, oil–water separation, and water and wastewater treatment. Nowadays, porous membranes are mainly used for aqueous separation.[1] In this field, organic separation is an important aspect which attracts much work to research the porous membranes that have high durability against solvents. Iwama and Kazuse[2] have investigated the solvent-resistant polyimide membrane, which showed excellent stability to common organic solvents, even at elevated temperature. The membrane in their work was made by the immersion-precipitation method. In this method a homogeneous polymer solution was first prepared before it was solidified to be a porous membrane in a nonsolvent bath. This meant that the membrane had no durability against the solvents in membrane preparation solutions.

Polyphenylene sulfide (PPS) is a common semicrystalline polymer that has high glass transition and high melting temperatures (T_g is 103.9°C and T_m is 265.6°C). The properties of commercial available PPS have excellent solvent resistance and thermal stability. However, PPS is generally regarded as being insoluble in most common solvents; thus, the immersion-precipitation method cannot be used for PPS because of solubility problems.

Vaorbach et al.[3] investigated an approach to prepared PPS porous membrane. The material was first melted at a high temperature, and then the melted PPS was extruded out to be a hollow fibre filament. When the filament was cooled to a special temperature, it was stretched to be a porous membrane. The pores in their samples were too small. The stretch forming method had its shortcoming to enlarge the pore structure.

Some groups have investigated the phase-separation mechanism and effecting factors of microporous membrane formation, and many different materials have been used. According to their research, the phase-separation mechanism can be elucidated through view of thermodynamics. That is, membrane is formed by solid–liquid phase separation or liquid–liquid phase separation via TIPS, and nucleation and growth mechanism and spinodal decomposition mechanism are two mechanisms of liquid–liquid phase separation. Douglas R. Lloyd et al.[4–11] first researched the microporous membrane with use of PP, PE, PVDF, ethylene-acrylic acid compolymers. Furthermore, Hideto Matsuyama et al.[16–22] investigated some other materials (cellulose acetate, EVAL, etc.). Recently, Doo Sung Lee et al.[23–26] prepared PLGA membranes as biodegradable material. However, these polymeric material in previous research studies do not have sufficient durability against solvents;

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therefore, PPS may be used as material of membrane with high durability against solvents.

In order to prepare porous PPS membranes with various pore structures, another approach to prepare porous PPS membranes was investigated in this article by the thermally induced phase separation (TIPS) method. In this process, PPS was first dissolved in a diluent at an elevated temperature, and then phase separation occured through cooling or quenching of the polymer solution. After the diluent was extracted, the porous structures were formed. The TIPS method is applicable to these polymers that have few solvents at room temperature and cannot be made via the precipitation method. Another advantage of TIPS is that the porous structure is varied due to the different phase-separation mechanisms. This strongly contrasts with the stretch-forming method that shows monotonous porous structures.

EXPERIMENTAL

Materials

Polyphenylene sulfide (PPS) is commercial product of Chengdu Letian Plastic Co. ($Mn = 94000$ Dalton, density ρ is 1.36 g/m^3, melting temperature T_m is 265.6°C, and glass transition temperature T_g is 103.9°C). Both diphenyl sulfone (chemical pure, T_m is 128~129°C and boiling point T_b is 378 ~ 379°C) and diphenyl ketone (analytical reagent grade, T_m is 48.5°C, T_b is 305.5°C) are commercial products of Beijing Chemical Factory.

Membrane preparation

The steps for preparing the porous PPS samples are given below. First, the PPS and the diluent (diphenyl sulfone or diphenyl ketone) with the special weight ratio were put in a test tube, and mixed. After the test tube was full of nitrogen, it was sealed with aluminum leaf. Then the test tube was put in an electric heating apparatus, and heated to 20 ~ 30°C above the temperature of cloud point of solution for 30 minutes until the PPS was completely dissolved in the diluent. At last the test tube was suddenly put in a cooling media (air or water) to solidify.

The diluents in the PPS/diluents system were extracted by acetone (for diphenyl sulfone) or alcohol (for diphenyl ketone). After solvent extraction, the samples of porous membrane were dried in vacuum drying oven at 80°C for 12 h.

Phase diagram

All the phase diagrams show the UCST-type L-L phase behavior. Since PPS is a semi-crystalline polymer, the L-L phase boundary intersects with the dynamic crystallization curve at the monotectic point. The cloud point (L-L phase separation) is observed by optical microscopy, as in the steps given below. The PPS/diluents sample sealed in two slides were first heating on a hot stage to be a homogeneous solutions. When the solution was slowly cooling down to the cloud point at which phase separation occurred, the transparent solution turned out to be turbid.

The dynamic crystallization temperature is determined by DSC experiment as the steps below. A 2–4 mg sample was sealed in an aluminum differential scanning calorimetry (DSC) pan, melted, usually at the endothermic peak for 3–5 min, and then cooled at 20°K/min in a PerkinElmer DSC-7. The onset of the exothermic peak during cooling was taken as the dynamic crystallization temperature.

Scanning electron microscopy (SEM) observation

The microporous samples were fractured in liquid nitrogen and mounted vertically on sample holders. The surfaces of the samples were sputtered with Au/Pd in vacua. A scanning electron microscope (Hitachi Co., Tokyo, Japan; S-4300) with an accelerating voltage of 25 kV was used to observe the porous structures.
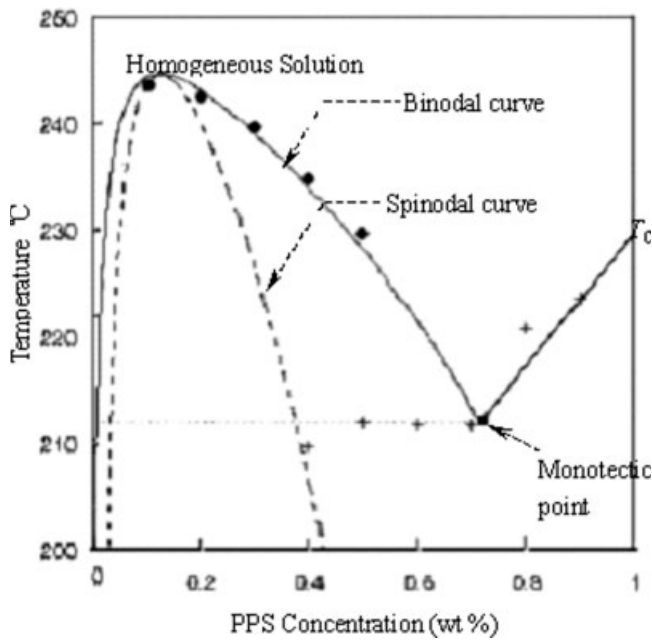
RESULTS AND DISCUSSION

Phase diagram

Figure 1 shows a phase diagram for the PPS/diphenyl ketone system. The monotectic point is at the intersection of binodal curve (or cloud point curve)
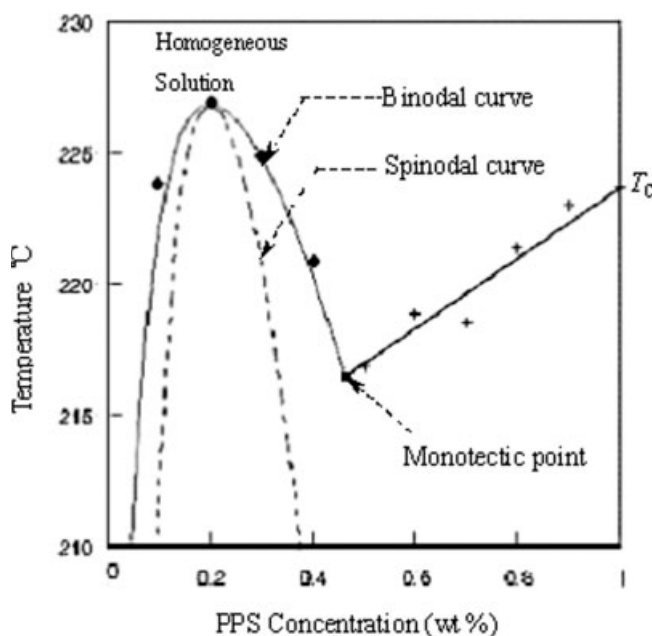

Figure 1 Phase diagram of polyphenylene sulfide/diphenyl ketone system: (●) cloud-point temperature; (+) crystallized temperature; (■) monotectic point.

Figure 2 Phase diagram of polyphenylene sulfide/diphenyl sulfone systems: (●) cloud-point temperature; (+) crystallized temperature; (■) monotectic point.

and the dynamic crystallization curve (45 wt%, 217°C). If the PPS concentration is larger than 45%, the porous structure may be formed by polymer crystallization. If the PPS concentration is less than 45%, the porous structure may be formed by liquid–liquid phase separation. Since the larger pore structure could be formed by liquid–liquid phase separation, in order to obtain a PPS porous membrane with a larger pore structure, the polymer solution should be less than that of the monotectic point. The up-critical solvent temperature (UCST) in Figure 1 is 227°C. The polymer/diluents system should be heated above the UCST so as to be a homogenous solution.

Figure 2 shows a phase diagram for the PPS/diphenyl sulfone system. The PPS concentration of the monotectic point in Figure 2 is 70 wt %, which is larger than its counterpart in Figure 1. The UCST in Figure 2 is also higher than that in Figure 1. This means that although the PPS concentration of the PPS/diphenyl sulfone system for L-L phase separation has a larger scope than that of PPS/diphenyl ketone system, the PPS/diphenyl sulfone system should be heated at a higher temperature to be homogeneous solutions.
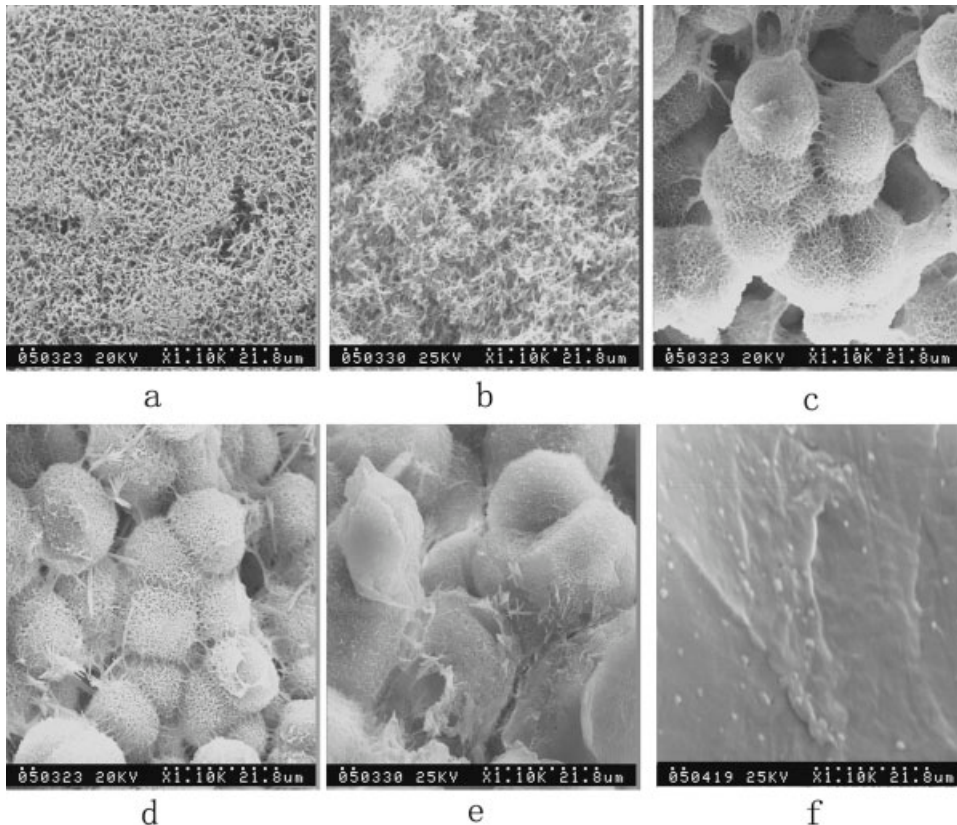
Figure 3   Porous structures of PPS/diphenyl ketone system with variant PPS concentration: (a) 10 wt %, cooled in air; (b) 20 wt %, cooled in air; (c) 30 wt %, cooled in air; (d) 40 wt %, cooled in air; (e) 50 wt %, cooled in air; (f) 80 wt %, cooled in air.
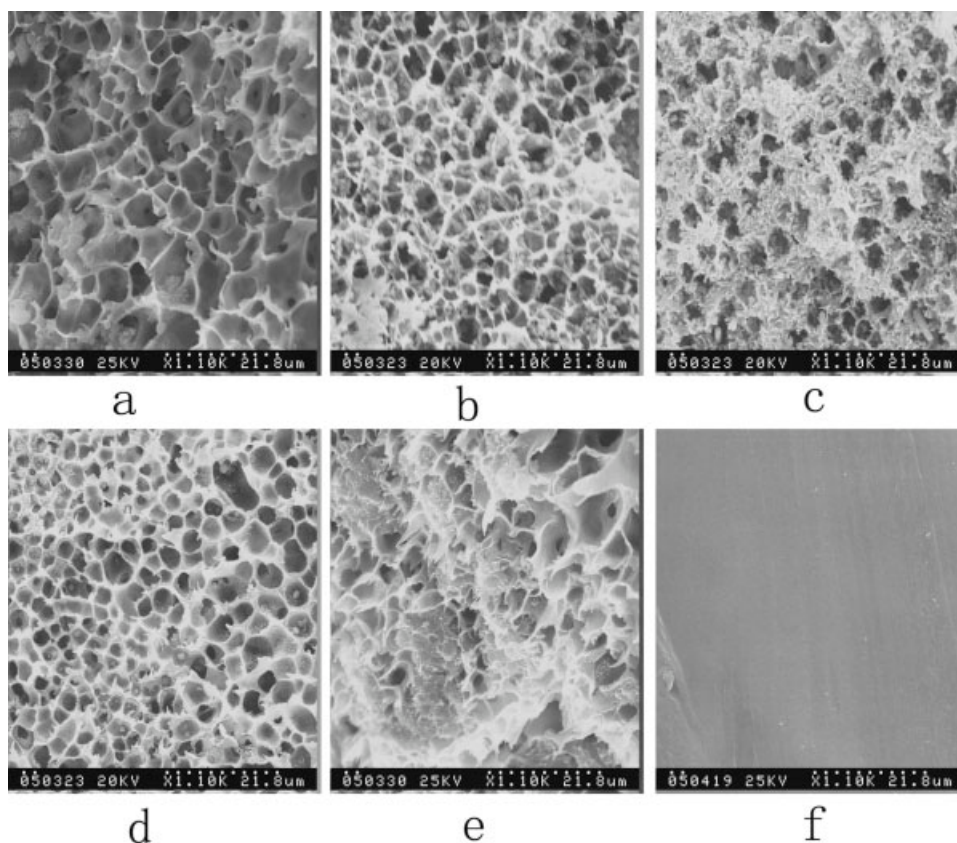
Figure 4 Porous structures of PPS/diphenyl sulfone system with variant PPS concentration: (a) 20 wt %, cooled in air; (b) 30 wt %, cooled in air; (c) 40 wt %, cooled in air; (d) 50 wt %, cooled in air; (e) 60 wt %, cooled in air; (f) 80 wt %, cooled in air.

Effect of the concentration of the PPS solution

According to a thermodynamic consideration of the L-L phase separation, the most important factor affecting the pore structure is the polymer concentration. Figure 3 shows the SEM images of the porous samples with different polymer concentration at the same cooling condition. These photographs clearly show that both the pore density and the average pore diameter decrease when the polymer concentration increases. This is easy to elucidate by the view of thermodynamics (Fig. 1).

The branchlike pore structure shown in Figure 3(a,b) is due to spinodal decomposition of the L-L phase separation for PPS/diphenyl ketone system. Following the L-L phase separation, the poly-rich phase solidifies to be a branchlike structure. Some large spherical structures are observed in Figure 3(c,d), and inside the spherical structures there are many small cavities. Based on the thermodynamic phase diagram, this kind of pore structure should be formed by two mechanisms: nucleation growth of the polymer-rich phase in the L-L phase-separation process and the crystallization of the polymer in the polymer-rich phase. No pore structure is presented

in Figure 3(e,f). This is because the polymer concentrations of these two solutions are larger than that of monotectic point; only polymer crystallization occurs (there is no L-L phase separation).

As a rough rule, when the polymer concentration increases, the phase-transition mechanisms in the TIPS process transform from L-L phase separation to polymer crystallization. All the characteristics of the porous structure can be explained by the two mechanisms. Nucleate growth and spinodal decomposition are the two mechanisms of L-L phase separation. Only spinodal decomposition occurs in the PPS/diphenyl ketone system for low PPS concentration.

The characteristic of the porous structure of the PPS/diphenyl sulfone system (Fig. 4) is different from that of the PPS/diphenyl ketone system (Fig. 3). Unlike PPS/diphenyl ketone system [Fig. 3(a,b)], the PPS/diphenyl sulfone system at low PPS concentration [Fig. 4(a)] shows a clearly cellulous structure. The difference between PPS/diphenyl sulfone and PPS/diphenyl ketone system may be explained by observing their phase diagram. In the phase diagram of PPS/diphenyl ketone system (Fig. 1), the bimodal curve is much narrower, therefore, when the solu-
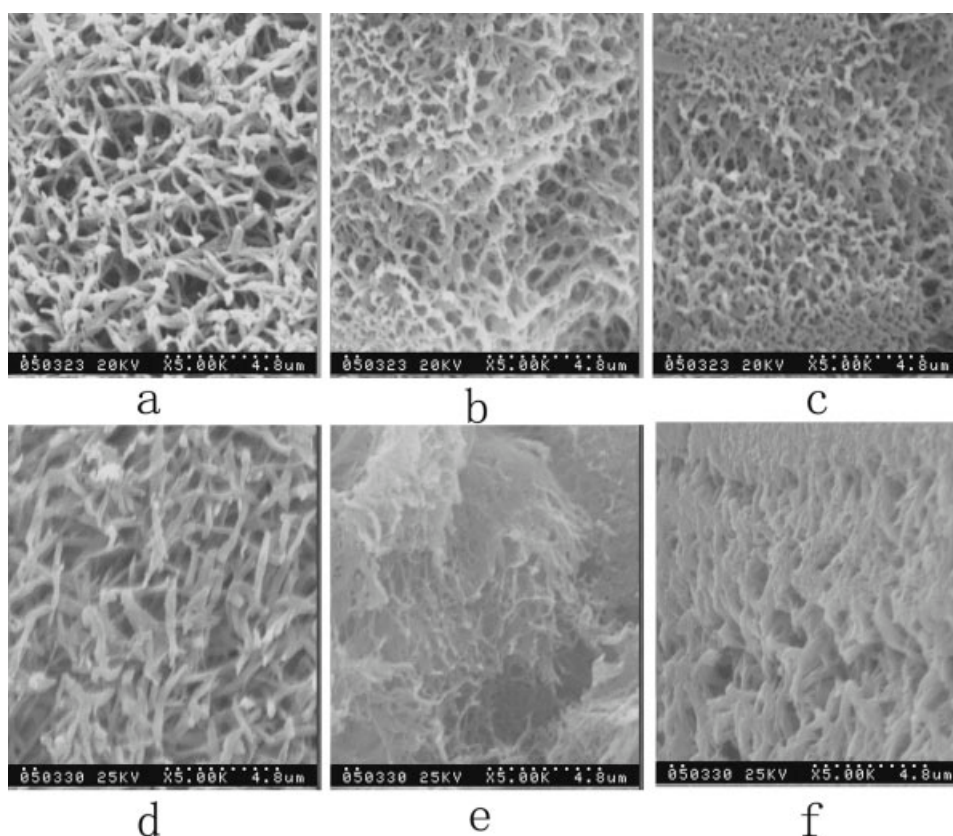
Figure 5 Porous structures of PPS/diphenyl ketone system with variant PPS concentration and cooled rates: (a) 10 wt %, cooled in air; (b) 30 wt %, cooled in air; (c) 40 wt %, cooled in air; (d) 10 wt %, 20°K/min; (e) 30 wt %, 20°K/min; (f) 40 wt %, 20°K/min.

tion cooled, the solution directly goes into the area of the Spinodal curve and thus the phase-separation mechanism of the L-L phase separation is spinodal decomposition. This kind of structure originates from the nucleation of solvent-rich phase during L-L phase separation. Before having contact with the spherical solvent-rich phase, the polymer-rich phase will have solidified. Polymer crystallization is the most important reason for the solidification of the polymer-rich phase. If the rate of crystallization increases, the rate of solidification of the polymer-rich phase may also increase, and so the average diameter of the porous structure will decrease. Figure 4(a–e) clearly elucidates this rule. All these porous structures are formed at the same cooling condition, and the polymer concentration is the only variable. It is easily seen that with an increase of polymer concentration, the rate of solidification of the polymer-rich phase will also increase. Since the polymer crystallization will prohibit the growth of the solvent-rich phase, average diameter of the pore structure will decrease when the polymer concentration increases. No pore structure is observed in Figure 4(f) because the polymer concentration is higher than that of the monotectic point (Fig. 2).

The porous structure of PPS/diphenyl sulfone system can also be explained by the L-L phase separation and polymer crystallization. Unlike the PPS/diphenyl ketone system, the nucleation-growth mechanism, not the spinodal mechanism, plays an important role here.

Effect of the cooling rate

The driving force of phase separation in the TIPS process comes from the cooling process. When the cooling rate increases, the driving force of phase separation will also increase. At the same time, the solidification rate of the polymer-rich phase will also be faster. Solidification and L-L phase separation are two competitive factors affecting the characteristic of the resultant pore structure.

Figure 5 presents the effect of cooling rates on the resultant porous structures in PPS/diphenyl ketone system with variant PPS concentrations. Figure 5(a, d) shows a similar branchlike structure, which originates from spinodal decomposition. Little difference between Figure 5(a) and Figure 5(d) could be observed. The pore density shown in Figure 5(d) is less than that in Figure 5(a). This means that the
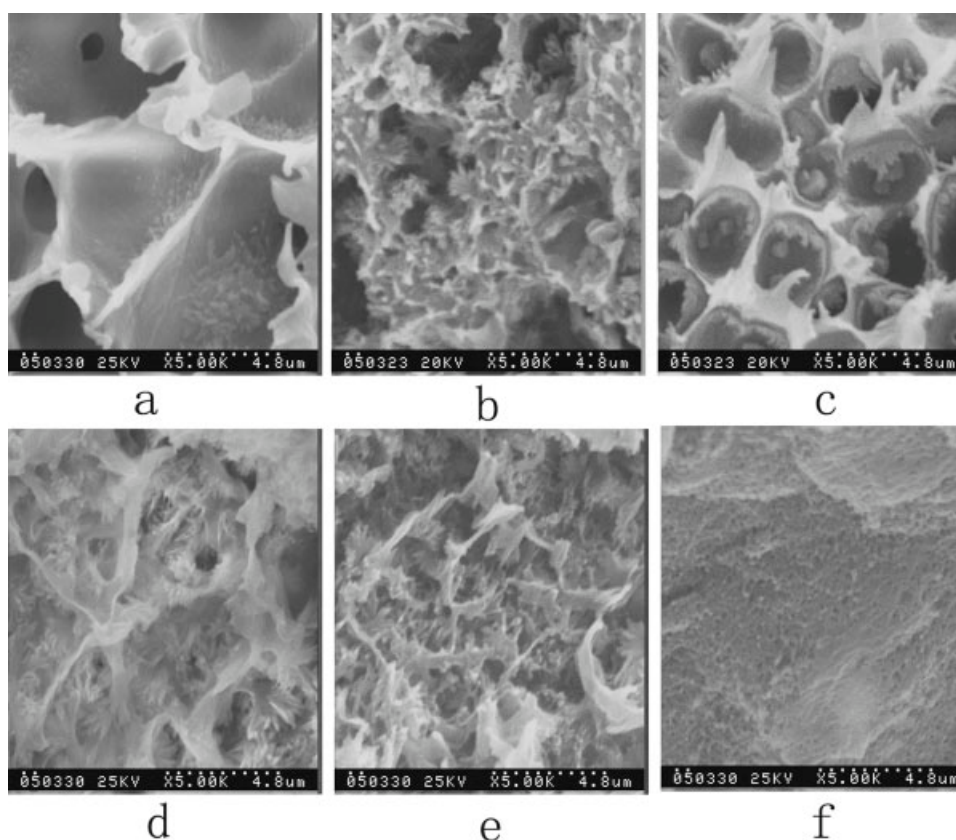
Figure 6 Porous structures of PPS/diphenyl sulfone system with variant PPS concentration and cooled rates: (a) 20 wt %, cooled in air; (b) 40 wt %, cooled in air; (c) 50 wt %, cooled in air; (d) 20 wt %, 20°K/min; (e) 40 wt %, 20°K/min; (f) 50 wt %, 20°K/min.

cooling rate of 20°K/min is smaller than that of cooling in air (20°C, 150°K/min), and leads to the smaller driving force for phase separation. This rule can also be observed by comparing the Figures 5(b), 5(c), 5(e), and 5(f). There are fewer pore structures in Figures 5(e) and 5(f) than Figures 5(b) and 5(c) because the larger driving force for phase separation cooled in air than that in water.
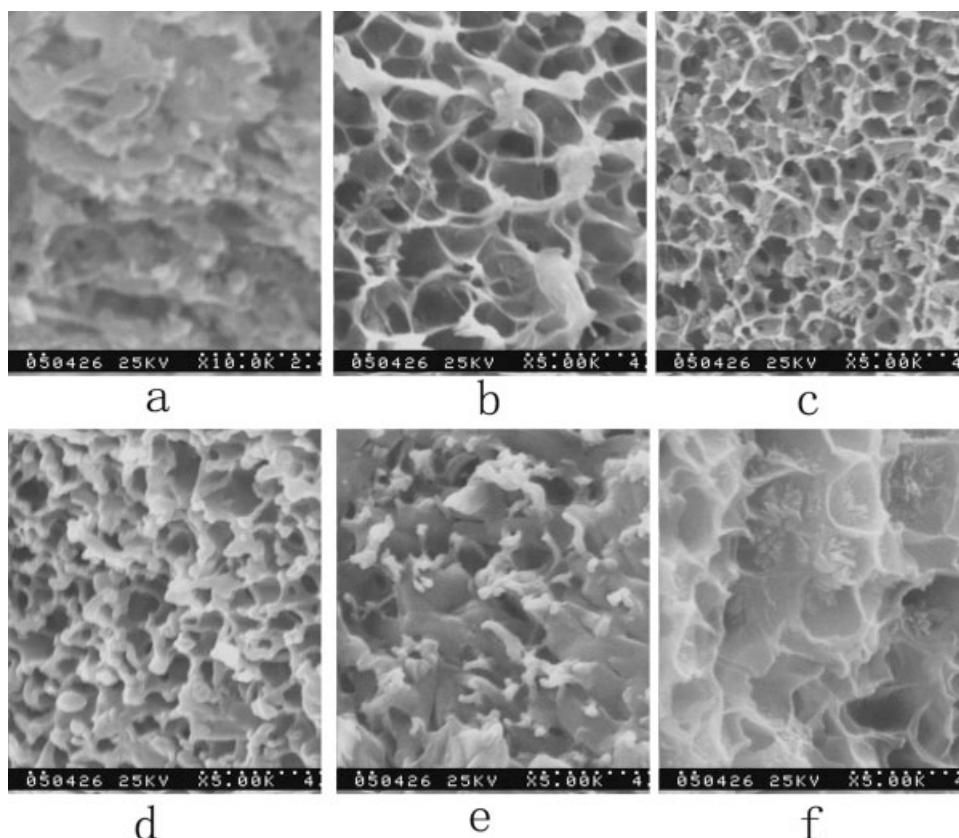
Figure 6 presents the effect of cooling rates on the resultant porous structures of PPS/diphenyl sulfone system with variant PPS concentrations. The effect of cooling rate on the porous structure in PPS/diphenyl sulfone system is similar to that of PPS/diphenyl ketone system. At the cooling rate of 20°K/min, the driving force for phase separation is too small, and this prohibits the L-L phase separation. Thus fewer pore structures can be observed [Fig. 6(d–f)]. If the polymer solutions were cooled in air (20°C, 150°K/min), the large cellulous porous structure would be clearly seen. This confirms the conclusion that the cooling rate of 20°K/min is smaller than that of cooling in air, and this leads to the smaller driving force for phase separation.

In order to prove the rule that the faster the cooling rate, the larger the driving force for phase separation, the experimental results that polymer solutions were cooled at the same cooling agent (water) of different temperature are presented below.

The specific heat capacity of water is so large that the cooling rate of water with different temperatures may differ greatly. The lower the water temperature, the faster the cooling rate. The porous structures shown in Figure 7(a–c) were solidified at 80°C water, and the porous structure could be clearly seen. When the porous structures in Figure 7(e,f) were solidified at 18°C water, fewer porous structures were observed. The above phenomenon elucidates that L-L phase separation will be prohibited when the cooling temperature is too lower. Because the system does not have enough time to carry out L-L phase separation, the porous structures in Figures 7(e,f) are formed by polymer solidification.

A nodular structure can be observed in Figure 7(a,d). It is believed[27] that this nodular structure is formed at the initiate stage of L-L phase separation through spinodal decomposition. Based on the thermodynamic phase diagrams (Figs. 1 and 2), the driving force for spinodal decomposition should be larger than that of the nucleate-growth mechanism. When the PPS/diphenyl sulfone solutions were cooled at 20°K/min or in 20°C air, only the cellulous structure formed by nucleate-growth mecha-

Figure 7 Porous structures of PPS/diphenyl sulfone system with variant PPS concentration and cooled rates: (a) 20 wt %, 80°C water; (b) 40 wt %, 80°C water; (c) 50 wt %, 80°C water; (d) 20 wt %, 18°C water; (e) 40 wt %, 18°C water; (f) 50 wt %, 18°C water.

nism was observed (Fig. 6). As the specific heat capacity of water is far larger than that of air, the cooling rate of water is much faster than that of air. Therefore, the driving force of L-L phase separation for the system in water may be larger than that in air.

CONCLUSIONS

A porous PPS membrane with variant pore structure can be formed using the TIPS method. The diluents, polymer concentration, and cooling rates are major factors affecting the mechanism of L-L phase separation and polymer crystallization.

The pore structure can be explained by two competitive mechanisms, L-L phase separation and polymer crystallization. For the PPS/diphenyl ketone system, spinodal decomposition occurs. For the PPS/diphenyl sulfone system, nucleate-growth mechanism plays an important role; at the cooling agent of 18°C water and 20 wt % PPS concentration, spinodal decomposition was also observed.

An open or semi-open cellulous pore structure and a branchlike porous structure are achieveable for PPS via the TIPS method.

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