# Preparation of Porous Structure in the System of PEEK/PPS/Diphenyl Ketone Via Thermally Induced Phase Separation

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**ABSTRACT:** The porous structure was prepared with polyether ether ketone (PEEK) and polyphenylene sulfide (PPS), which had excellent solvent resistance and thermal resistance as the mixed polymers, and diphenyl ketone as the diluent. The possibility of forming porous structure and the control of porous structure were investigated in the blended system. The effecting factors including the different weight ratios of PEEK/PPS and the total concentration of polymers on the porous structure are discussed, and the two-step phase separation process brings forward the formation of membrane in this system. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1523–1530, 2007

**Key words:** thermally induced phase separation; porous structure; endure high temperature and endure solvents; blended polymer

## INTRODUCTION

The thermally induced phase separation (TIPS) method was developed to solve the problem whereby the porous membranes of some crystallizable polymers were not prepared through non-solvent-induced phase separation (NIPS) method, as these polymers were not a proper diluent at room temperature. Compared with NIPS method, TIPS has some advantages: higher intensity of membranes, higher porosity, and controlling conditions that form a porous structure more easily. Therefore, the TIPS method was comprehensively investigated during the last 20 years.

In 1981, Castro[1] first used the TIPS method to prepare the microporous membranes. Castro mainly solved the problem in which some crystallizable polymers, lacking appropriate solvents at room temperature, were difficult to form membrane. During the 1990s, Lloyd and colleagues[2–8] systematically studied the phase-separation mechanism, effecting the factors of the TIPS method. The membrane material used in their papers mainly included polypropylene (PP), polyethylene (PE), polyvinylidene fluoride (PVDF), which could not prepare the membrane by the NIPS method. Matsuyama's research group[9–17] further investigated the membrane formation of the TIPS method in effecting factors and the control of porous structure in different systems. To solve the problem of membrane pollution caused by protein absorption in the actual application, the hydrophilic membrane materials were used. These investigators chose new materials to form porous structures by the TIPS method, which included poly(ethylene-ethylene acid), poly(ethylene-acrylic acid), etc. The work teams in Korea[18–22] carried out considerable research on poly(lactic acid) (PLA), poly(D,L-lactic acid-co-glycolic acid) (PLGA), and poly(L-lactic acid) (PLLA), which can be used in many fields, such as biodegradable drug delivery carrier and tissue engineering scaffolds. Using PLA, they prepared many kinds of membranes and acquired many good structures.

Nowadays, the membrane materials lean to actual application. To form a membrane with excellent solvent resistance and thermal resistance, the membrane materials included the fluorinated polymers,[23,24] PEEK,[25,26] polyoxymethylene,[27] PPS, HDPE, etc. Caplan et al.[23] prepared Teflon PFA porous membranes in trifluorochloroethylene with the TIPS method. Ramaswamy et al.[24] chose an ethylene-trifluorochloroethylene co-polymer to prepare porous membranes with dibutyl phthalate as the solvent. Matsuyama et al.[27] prepared porous membranes by polyoxymethylene and HDPE. Although many researchers studied this aspect intensively, the porous structures obtained were not good.

Among the above materials, PEEK and PPS have the excellent properties of enduring high temperature and enduring solvents. The end-use temperatures of PEEK and PPS are 250°C and 190°C, respectively. Moreover, the two polymers have no solvents at normal temperature. Therefore, it is difficult to find the

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proper solvent to prepare membranes through NIPS. Through the TIPS method, the microporous membranes could be prepared with PEEK/PPS/diphenyl ketone in our experiment.

Normally, the membrane properties was determined by the physicochemical properties of membrane material and the method of preparing the membrane.[28] Both the TIPS method and the membrane material (PEEK and PPS) had the properties of enduring high temperature and enduring solvents; we chose them to prepare an excellent membrane.

We have already prepared and studied microporous membranes with PEEK and PPS[29]; the effecting factors and the porous structure controlling on pattern formation were also investigated. However, PEEK has the defect of too high a melting temperature ($T_m$ 310°C), and PPS has the shortcoming in toughness. To solve these problems and get the microporous membranes to combine the advantages of PEEK and PPS, the blending of PEEK and PPS was used to prepare the porous structures.

## EXPERIMENTAL

### Materials

PEEK is a commercial product of the JiDa Material Co. (Chang Chun, China); ($\overline{M}_n = 1.6 \times 10^5$). Polyphenylene sulfide (PPS) is a commercial product of Chengdu Letian Plastic Co. (ChengDu, China); ($\overline{M}_n = 9.4 \times 10^4$). Diphenyl ketone (analytical reagent grade, $T_m$, is 48.5°C; $T_b$ is 305.5°C) is a commercial product of Beijing Chemical Factory. Acetone (analytical reagent grade) is a commercial product of Beijing Chemical Factory.

### Preparation of membrane

The steps prepared for the porous PEEK or PPS samples are stated below. First some PEEK, PPS, and diluent (diphenyl ketone) with special weight ratios were put in a test tube and mixed. After the test tube was full of nitrogen, it was sealed by a stopper with aluminum leaf. The test tube was then put into an electric heating apparatus and heated to 20–30°C above the cloud point of solution for 30 min, until PEEK and PPS were dissolved completely in the diluents. Finally, the test tube was suddenly placed into cooling media (air or water) to solidify.

The diluents in the PEEK/PPS/diluents system were extracted for 2–3 times (4 h each time) by acetone. After solvent extraction, the samples of porous membrane were dried in vacuum drying oven at 60°C for 12 h; the samples were then obtained before characterization tests.

### Scanning electron microscopy 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 vacuo. A scanning electron microscope (SEM; Hitachi, Tokyo, Japan; S-4300) with an accelerating voltage of 25 kV was used to observe the porous structure.

### Membrane porosity

The membrane porosity, $A_k$, is defined as the volume of the pores divided by the total volume of the porous membrane. The dry membrane was dip in the pure alcohol for 10 h. Then the membrane was taken out; the alcohol on the surface of the membrane was softly wiped up by filter paper. Finally, the membrane was weighed quickly. The formula for membrane porosity is as follows:

$$\overline{\rho} = \frac{W}{W_1/\rho_1 + W_2/\rho_2} \tag{1}$$

$$A_k = \frac{(W_0 - W)\overline{\rho}}{\overline{\rho}W_0 + (\rho - \overline{\rho})W} \times 100\%, \tag{2}$$

where $W$ is the total weight of the dry membrane; $W_1$ is the weight of PEEK; $W_2$ is the weight of PPS, $W_0$ is the weight of the wet membrane; $\overline{\rho}$ is the average polymer density; $\rho_1$ is the PEEK density; $\rho_2$ is the PPS density; and $\rho$ is the absolute alcohol density.

## RESULTS AND DISCUSSION

The melting temperature of the PEEK/diphenyl ketone system is nearly 310°C, when blended the PEEK and PPS as mixed polymers, the melting temperature of the PEEK/PPS/diphenyl ketone system nearly decreased to 270°C. The melting temperature of blended system was lower than that of PEEK and diphenyl ketone system, and the toughness of blended system membrane is larger than the toughness of PPS membrane in our experiment. So the problems improving the toughness and decreasing the melting temperature were solving of membrane through blending PPS and PEEK.

By analyzing the results (SEMs and porosity), the two-step phase separation process is brought forward. When the membrane of the PEEK/PPS/diphenyl ketone system was prepared, the two-step phase separation process occurred. The crystallization temperature of PEEK is higher than that of PPS; thus, in the PEEK/PPS/diphenyl ketone system, the phase separation of PEEK/diphenyl ketone system occurred first,
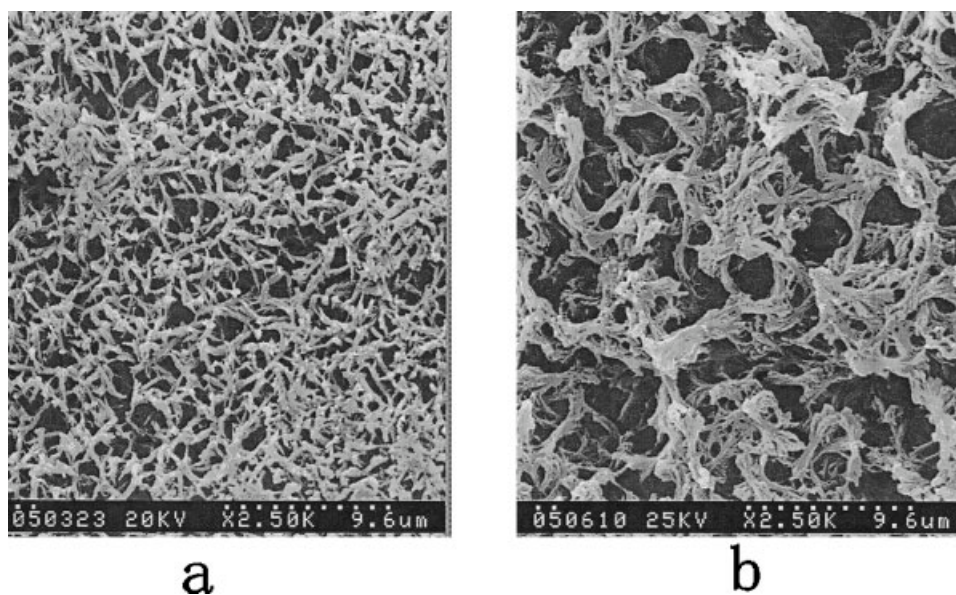
**Figure 1** SEMs of microporous membrane at 10 wt % (cooled in air). (a) PPS; (b) PEEK.

followed by the phase separation of the PPS/diphenyl ketone system. This is two-step phase separation process. In fact, the process was affected by many factors, including the ratio of PEEK and PPS, and the cooling rate.

**Porous structures prepared from mixed polymers/ diphenyl ketone system with a ratio of 10 wt %**

Figure 1 shows SEMs of porous structures at 10 wt % of PEEK/diphenyl ketone [Fig. 1(a)] and PPS/diphenyl ketone [Fig. 1(b)]. From the images, we can see the branch-like porous structure clearly, which is the typical characteristic of spinodal decomposition. This decomposition leads to the formation of the polymer-rich phase and the polymer-lean phase. After the polymer-rich phase coarsening, growth, and solidification, the bicontinuous structure is formed. The porous structures of the two systems are continuous, and the porosities are 83.8% and 80.0%, respectively, which are very high.

Figure 2 presents the porous structures of different weight percent of PEEK and PPS in the blended system. When the weight ratio of PPS/PEEK is 2 : 8 [Fig. 2(a–d)], the spherical structure is observed. The mechanism of formation this kind of porous structure is nucleate-growth (NG) mechanism. The spherical structure originates from nucleating and growth of the polymer-rich phase; the porous structure is formed when polymers crystallize and the solvent separates from the polymer-rich phase, and the porosity is nearly 71.1%. Because of the lower content of PPS, the NG mechanism of PEEK/diphenyl ketone has the leading role. Because the ratio of PPS/PEEK is changed in the blended system, the phase separa-

tion mechanism is also changed. When the weight ratio of PPS/PEEK is 5 : 5 [Fig. 2(b–e)] or 8 : 2 [Fig. 2(c–f)], the branch-like structure, originating from spinodal decomposition, is observed. For the 10 wt % sample, the two-step phase separation process is not expressed remarkably from the SEMs.

Comparing the porosity of different weight ratio of PEEK/PPS with porous structure, when the concentration of the blended polymer system is 10%, the porosity is higher; however, the porous structures are not so good. Compared with the porous structures of PPS/diphenyl ketone and PEEK/diphenyl ketone, the porous structures in the blended system are not uniform and are worse under the same condition (Table I).

**Porous structures prepared from mixed polymers/diphenyl ketone system with a ratio of 20 wt %**

Figure 3 shows SEMs of the porous structures at 20 wt % of PEEK/diphenyl ketone [Fig. 3(a)] and PPS/diphenyl ketone [Fig. 3(b)]. The porous structure of PPS/diphenyl ketone is a leaf-like structure, and the porous structure of PEEK/diphenyl ketone is a branch-like structure. In the two blended systems, the leaf-like porous structure is formed by complete phase separation. From the two kinds of porous structures, both may originate from spinodal decomposition. The polymer solution is extracted to form symmetrical porous structures after the spinodal decomposition and then crystallization and solidification. From Table II, the porosities of porous structures are very high; then, the porosity of Figure 3(b) is better than that of Figure 3(a).
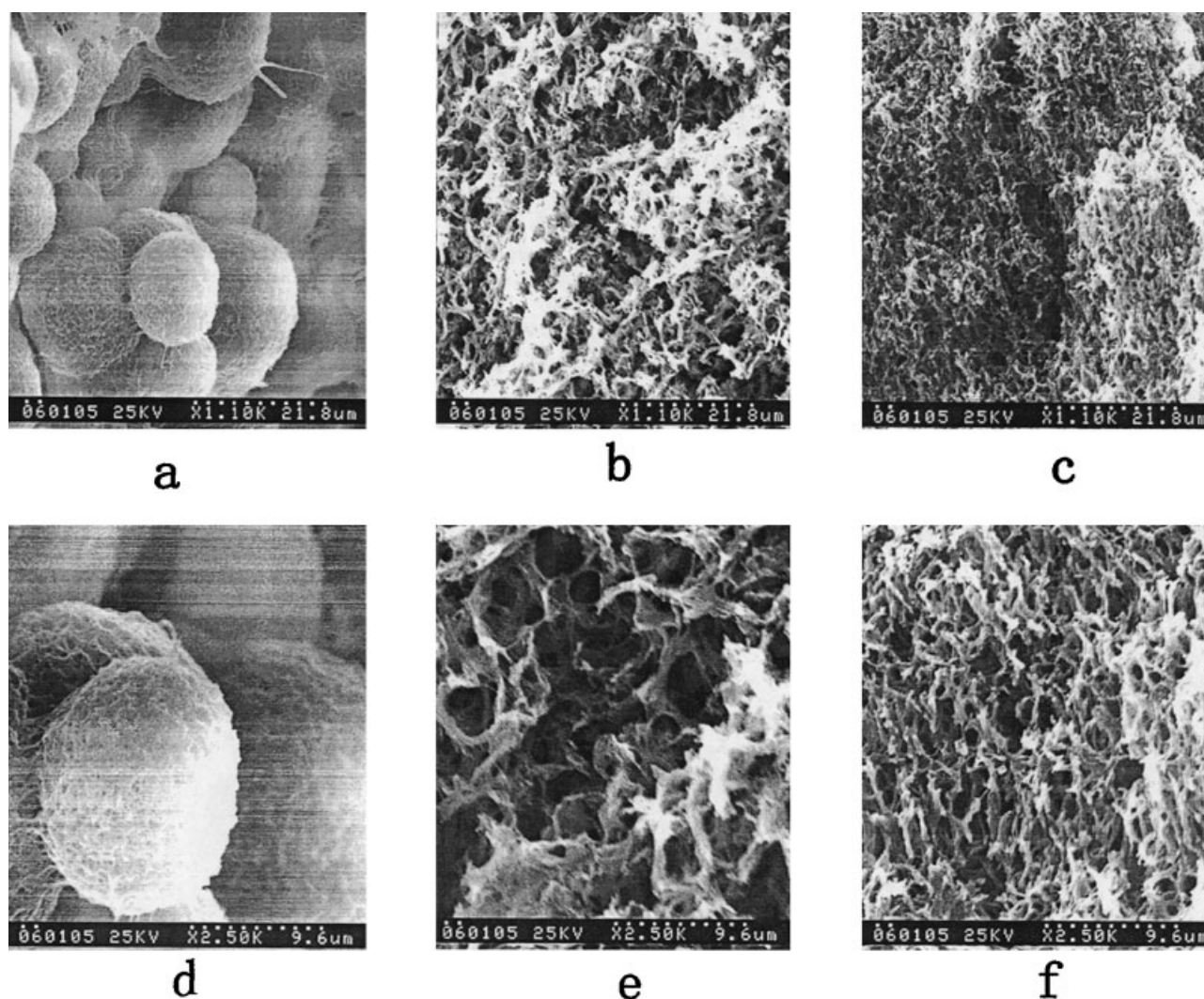
**Figure 2**   SEMs of microporous membrane at 10 wt % (cooled in air). (a) PPS : PEEK = 2 : 8; (b) PPS : PEEK = 5 : 5; (c) PPS : PEEK = 8 : 2, low power; (d) PPS : PEEK = 2 : 8; (e) PPS : PEEK = 5 : 5; (f) PPS : PEEK = 8 : 2, high power.

When the weight ratio of PPS/PEEK is 2 : 8 [Fig. 4(a–d)], the sheet-like structure is obtained. It is produced by solid–liquid (S–L) phase separation. Because of the change of the ratio of PEEK and PPS, the S–L phase separation holds the leading position during the competition of the S–L phase separation and liquid–liquid (L–L) phase separation. From Figure 4(a–d), we can see clearly that there are no visible porous structures in the leaf-like structures. This can also be proved by the porosity. The porosity is only 57.2%, which is far smaller than that of the 8 : 2 or 5 : 5 ratio of PPS/PEEK at 20 wt % of polymers.

When the weight ratio of PEEK/PPS is 5 : 5 [Fig. 4(b–e)], the branch-like porous structure is observed. It is originated from L–L phase separation. From Figure 4(b), we can see the porous structures formed through the spinodal decomposition of L–L phase separation. When the blended system is heated to the homogeneous solution, the temperature of the system decreases lead to the L–L phase separation.

During the spinodal decomposition phase separation of the blended system, because the crystallization temperature of PEEK is higher than that of PPS, PEEK crystallizes before PPS, which inducing crystallization of PPS, and the chains between the interfaces extend and gather. Finally, the uniform porous structures are formed. According to the SEMs, the two-step phase separation of PEEK and PPS produces the larger spherical structures because PEEK induces PPS to crystallize on the basis of PEEK phase separation.

**TABLE I**
**Porosity (10 wt % of Polymers)**

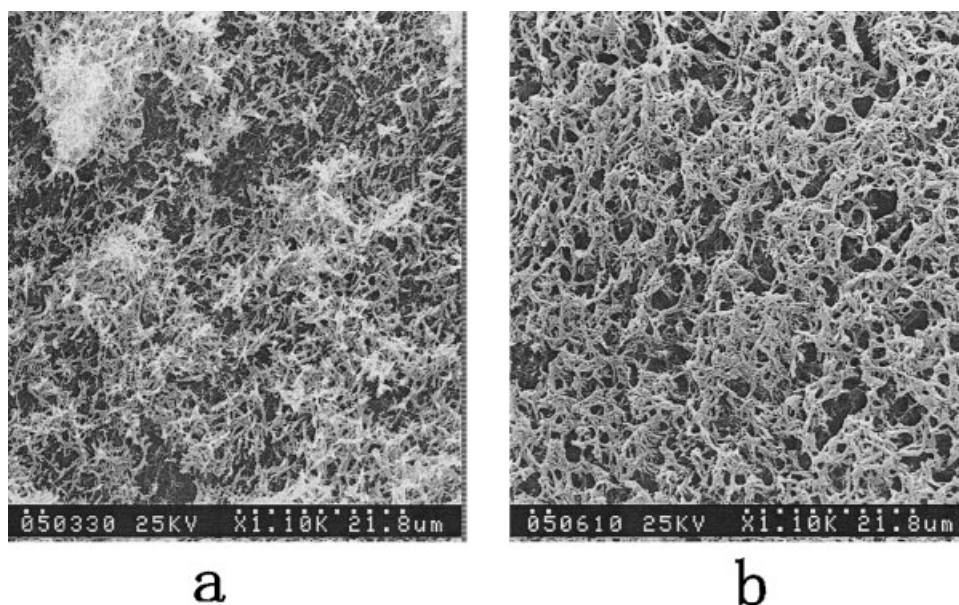| Weight ratio of PPS/PEEK | Porosity (%) |
|---|---|
| 2 : 8 | 71.1 |
| 5 : 5 | 84.6 |
| 8 : 2 | 87.1 |
| 100/0 | 83.8 |
| 0/100 | 80.0 |

**Figure 3** SEMs of microporous membrane at 20 wt % (cooled in air). (a) PPS; (b) PEEK.

When the weight ratio of PPS/PEEK is 8 : 2 [Fig. 4(c–f)], there are no clear porous structures. This also results mainly from the S–L phase separation, just like Figure 4(a–d). The porosity, only 59.3%, is small.

Compared with Figures 3 and 4, at the total 20 wt % of the polymers, when the weight ratio of PEEK/PPS is 5 : 5, better porous structures are formed. The porosity, 89.9%, is far larger than that of any other sample porosity.

**Porous structures prepared from mixed polymers/diphenyl ketone system with a ratio of 30 wt %**

Figure 5(a) shows a spherical porous structure at 30 wt % PPS. The phase separation mechanism should be NG. Figure 5(b) presents the leaf-like porous structures at 30 wt % PEEK. The leaf-like porous structure is formed because polymer-rich phase nucleates and grows during the L–L phase separation process and then coalesces fully.

Figure 6 shows the different porous structures at the different ratio of PPS/PEEK at 30% of polymers. Figure 6 shows the branch-like porous structures, which originate from spinodal decomposition. Because the compatibility of a single polymer/solvent is changed in the blended system, it is expressed with the interaction parameter of system. The L–L phase separation mechanism changes at the same time. However, when the weight ratio of PPS/PEEK is different, the structures differ distinctly from each other.

When the weight ratio of PPS/PEEK is 2 : 8 [Fig. 6(a–d)], porous structures are branch-like, and the porosity is small, only 62.1%. This may be because the crystallization temperatures of PPS and PEEK are different in the blended system, causing the phase

separation to divide into two steps. In the two-step phase separation, first, phase separation of PEEK and diphenyl ketone occurs. Next, phase separation of PPS and diphenyl ketone occurs, induced by PEEK. As shown in Figure 6(d), the branch-like pores spread around and congregate. Because the crystallization temperature of PEEK is higher than that of PPS, PEEK crystallizes before PPS and forms a branch-like porous structure. Crystallization of PEEK will induce PPS to crystallize. However, as the concentration of PPS is lower, the second step cannot be performed. Only the chains among the molecules entangle each other, producing this kind of porous structure [Fig. 6a].

When the weight ratio of PPS/PEEK is 5 : 5 [Fig. 6(b–e)], the large spherical porous structure formed by the penetrating branch-like structures is observed. IN Figure 6(b), the porous structure is easily observed. This porous structure may be explained by the two-step phase separation. The structure is formed through PEEK crystallization and PPS crystallization. Because the content of PEEK is lower and the phase separation of PEEK occurs first, the crystallized PEEK as the cores induce the PPS crystallization. It can be seen in Figure 6(e) that the porosity of the branch-like structures is high and the porous structure is uniform. As a result, when the weight ratio of PPS/PEEK is 5 : 5,

**TABLE II**
**Porosity (20 wt % of Polymers)**

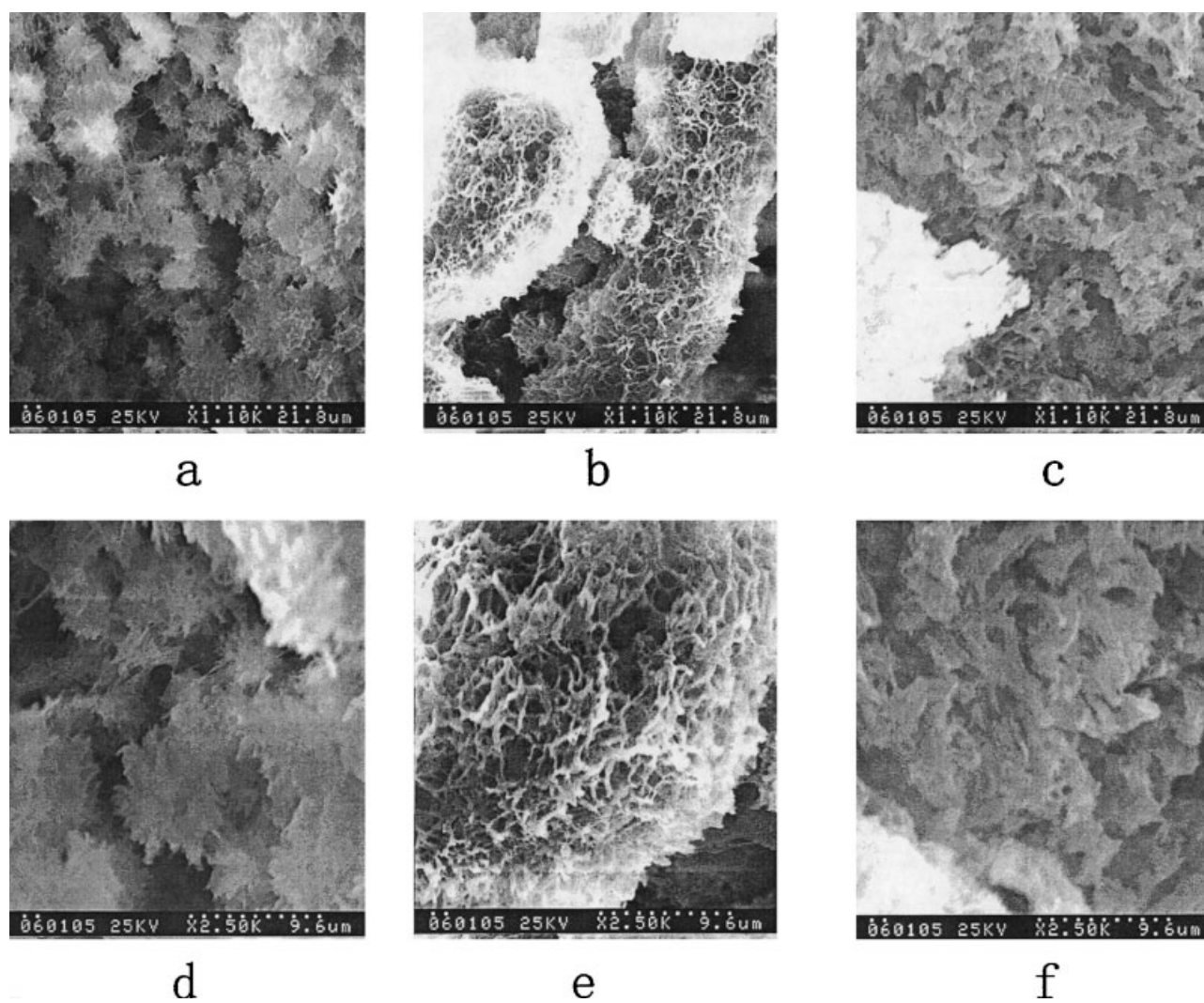| Weight ratio of PPS/PEEK | Porosity (%) |
|---|---|
| 2 : 8 | 57.2 |
| 5 : 5 | 89.9 |
| 8 : 2 | 59.3 |
| 100/0 | 78.4 |
| 0/100 | 83.2 |

**Figure 4**   SEMs of microporous membrane at 20 wt % (cooled in air). (a) PPS : PEEK = 2 : 8; (b) PPS : PEEK = 5 : 5; (c) PPS : PEEK = 8 : 2, low power; (d) PPS : PEEK = 2 : 8; (e) PPS : PEEK = 5 : 5; (f) PPS : PEEK = 8 : 2, high power.



**Figure 5**   SEMs of microporous membrane at 30 wt % (cooled in air). (a) PPS; (b) PEEK.

**Figure 6** SEMs of microporous membrane at 30 wt % (cooled in air). (a) PPS : PEEK = 2 : 8; (b) PPS : PEEK = 5 : 5; (c) PPS : PEEK = 8 : 2, low power; (d) PPS : PEEK = 2 : 8; (e) PPS : PEEK = 5 : 5; (f) PPS : PEEK = 8 : 2, high power.
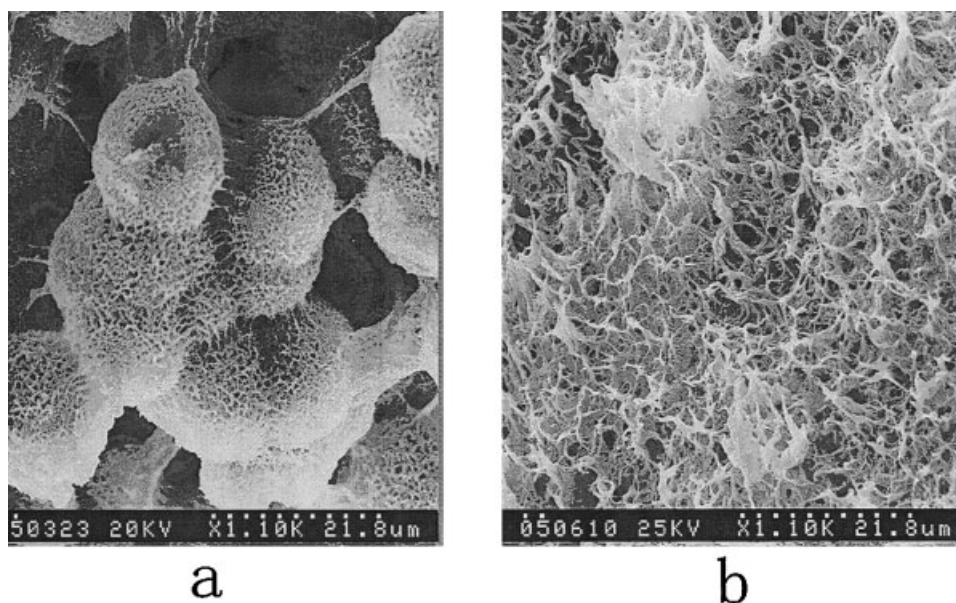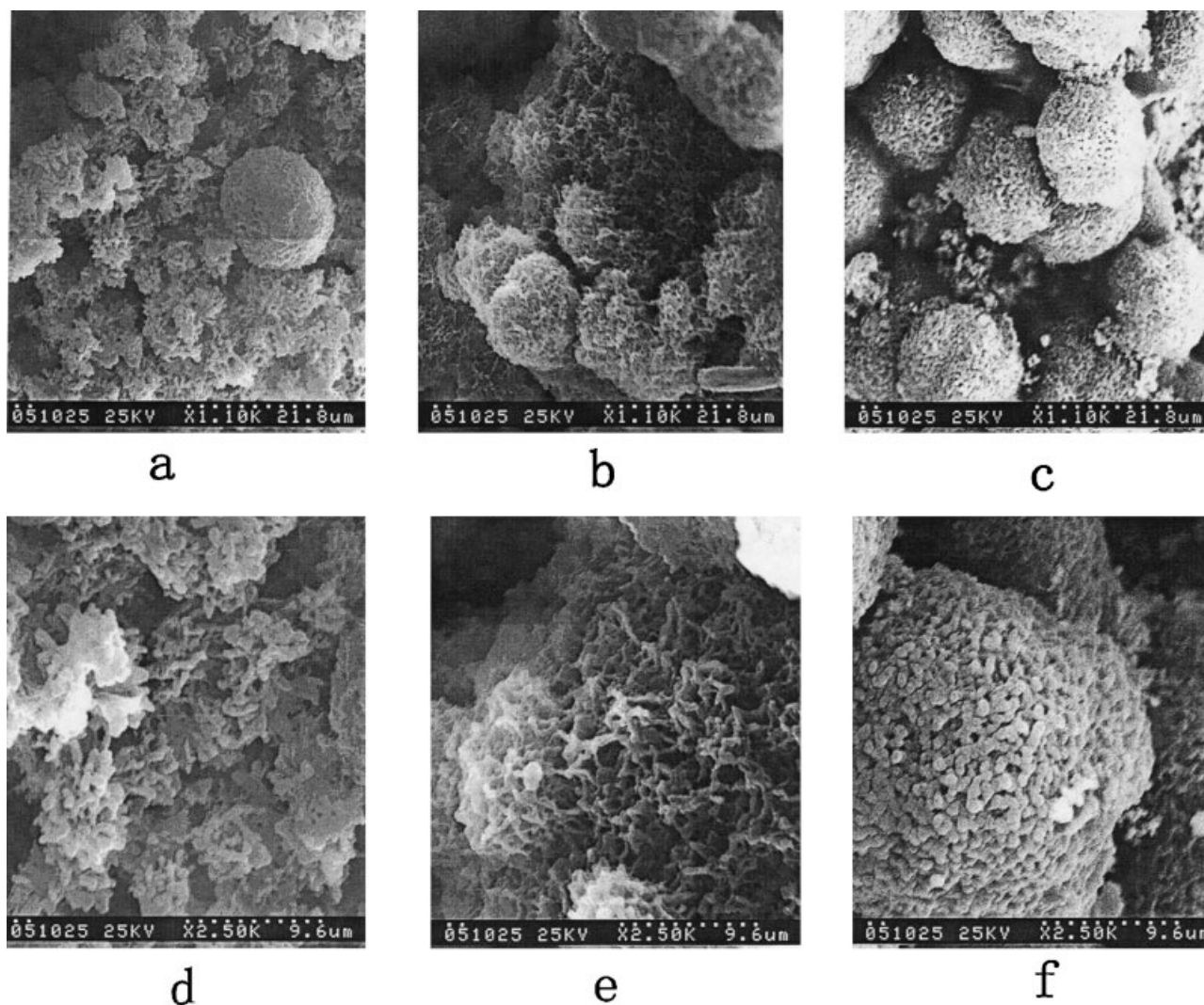
better porous structures are formed than that of 2 : 8 PPS/PEEK.

When the weight ratio of PPS/PEEK is 8 : 2 [Fig. 6(c–e)], the large spherical porous structures with compact branch-like porous structures inside are obtained. From Figure 6(c), the reason of large spherical porous structure is same as Figure 6(b). However, the internal structure is different because the weight ratios are changed. This kind of internal porous structure can be illustrated by the two-phase separation processes. The first is the phase separation of PEEK and diphenyl ketone. Because the concentration of PEEK is small, it forms inner structure. Second, during the phase separation of PPS and diphenyl ketone, the influence of PEEK induce crystallization of PPS near the PEEK molecular chains. Therefore, when spinodal decomposition of PPS/diphenyl ketone happened, the pore structure with compact branch-like structure was formed. The porosity is very high, 86.5%.

By changing the weight ratio of PEEK/PPS, we could get various shapes of porous structure. The blending system could not only change the phase separation mechanism, but also improve the connectivity and porosity. When the ratio of PEEK/PPS is 5 : 5 or 2 : 8 for a 30 wt % sample, better porous structures were obtained. Moreover, the porosity of the two kind structures is far higher than that of PEEK/PPS (8 : 2) (see Table III).

**TABLE III**
**Porosity (30 wt % of Polymers)**

| Weight ratio of PPS/PEEK | Porosity (%) |
|---|---|
| 2 : 8 | 62.1 |
| 5 : 5 | 83.0 |
| 8 : 2 | 86.5 |
| 100/0 | 83.8 |
| 0/100 | 65.4 |

When the concentration of the polymer is 10%, 20%, and 30%, we get different kinds of porous structures, as shown in Figures 2, 4, and 6. Some have better connectivity, resulting from the two steps of phase separation and PEEK. This induces the crystallization of PPS during the phase separation of PPS/diphenyl ketone, which accelerates the crystallization of PPS. In addition, the chains between the interfaces entangle with each other, extend, and gather. When the concentration of polymer is 20%, the mixture of PEEK and PPS, whose weight ratio is 5 : 5, can form the better branch-like porous structure. When the concentration of polymer is 30%, better porous structure can be formed; the porosity is also high.

When the weight ratio of PEEK and PPS is 8 : 2 [Figs. 2(d), 4(d), 6(d)] and 2 : 8 [Figs. 2(f), 4(f), 6(f)], the porous structure is not good and the porosity is lower. Except for the large symmetrical spherical porous structure in Figure 6(f), there are compact branch-like porous structure inside. When the weight ratio of PEEK and PPS is 5 : 5, the porous structures gained are the best, and all have a branch-like structure. Under this condition, the phase separation mechanism is spinodal decomposition. Furthermore, the particular large spherical porous structures are formed, as shown in Figures 4(e) and 6(e). This kind of structure is made up of the penetrating loosen branch-like pores.

## CONCLUSION

1. Various kinds of porous structure were prepared, using the blended system of polymers, PEEK and PPS, and taking diphenyl ketone as the solvent.
2. In the blended system, a multifarious porous structure was obtained, such as sphericity, branch-like, leaf-like, and sheet-like by changing the weight ratio of PEEK, PPS, and diphenyl ketone.
3. By changing the weight ratio of PEEK and PPS, when the weight ratio is 5 : 5, the branch-like pores under the condition of cooling in the air were prepared. The porous structure have better connectivity, higher porosity, and a symmetrical structure. When the weight ratio of PEEK and PPS is 8 : 2, under the condition that the concentration of polymer is 30%, large spherical porous structures that are compact branch-like particular pores are obtained.

4. In this article, the two-step phase separation process is used to explain the structure of Figure 4(b) (20 wt %, PPS : PEEK = 5 : 5), Figure 6(b) (30 wt %, PPS : PEEK = 5 : 5), and Figure 6(c) (30 wt %, PPS : PEEK = 8 : 2), which had special porous structures.

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