

Preparation of Ultrahigh-Molecular-Weight Polyethylene Membranes via a Thermally Induced Phase-Separation Method

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ABSTRACT: Porous, flat membranes of ultrahigh-molecular-weight polyethylene were prepared as thermally resistant and solvent-resistant membranes by the thermally induced phase-separation method. Diphenyl ether and decalin were chosen as the diluents. The phase diagrams were drawn with the cloud-point temperatures and the crystallization temperatures. According to the phase diagrams, scanning electron microscopy images, and porosities of the samples, the influential factors,

including the polymer concentration, cooling rate, and viscosity, were investigated. Porous ultrahigh-molecular-weight polyethylene membranes with thermal and solvent resistance could be prepared with suitable diluents and cooling rates by the thermally induced phase-separation method. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3355–3362, 2007

Key words: phase separation; polyethylene (PE); membranes

INTRODUCTION

Ultrahigh-molecular-weight polyethylene (UHMWPE) is a type of engineering thermoplastic. As an excellent engineering plastic, it is very cheap because its industrialized production was finished early by America Allied Chemical Co. in 1957, and it is often used in many fields, including mechanical and fabric industries, agriculture, mining, transportation, and chemical industries, especially in the form of drawn films and fibers.^{1,2} UHMWPE has been used in several important industrial applications, including the fabrication of surgical prostheses,³ machine parts,⁴ heavy-duty liners,^{4,5} and boat sails.⁵ UHMWPE normally has an ultrahigh-molecular-weight that on average is more than 1,000,000. Therefore, UHMWPE has incomparable properties among plastics. UHMWPE has not only good impact resistance, abrasion performance, and solvent resistance but also excellent low-temperature resistance. It can be used under -269°C .⁶ In recent years, UHMWPE has been investigated because of its excellent properties. UHMWPE is extensively used in orthopedic parts, artificial joints, soft-tissue replacement, and trileaflet valves because of its physical inertia. However, UHMWPE is seldom used in membranes because it

has high viscosity and no suitable solvent at room temperature.

Since the thermally induced phase separation (TIPS) method first was used by Castro⁷ in the 1980s, this method has gained much interest. In the 1990s, Lloyd and coworkers^{7–13} systematically studied the phase-separation mechanism, determining the factors of the TIPS method. The membrane materials used in their studies mainly included polypropylene, polyethylene, and poly(vinylidene fluoride), which could not be used to prepare membranes by the nonsolvent induced phase separation (NIPS) method. Matsuyama's research group^{14–22} further investigated membrane formation by the TIPS method with respect to the influential factors and the control of the porous structure in different systems. To solve the problem of membrane pollution caused by protein absorption in actual applications, hydrophilic membrane materials were used, such as poly(ethylene glycol) and poly(ethylene glycol methacrylate). Recently, work teams in Korea performed much research on poly(lactic acid), poly(D,L-lactic acid-co-glycolic acid), and poly(L-lactic acid), which can be used as biodegradable drug delivery carriers and tissue engineering scaffolds. More and more, research has focused on the special properties of membranes made with the TIPS method. For solvent-resistant and thermally resistant membranes, membrane materials, including fluorinated polymers,^{23,24} poly(ether ether ketone),^{25,26} polyoxymethylene,²⁷ and polyphenylene sulfide (PPS),^{28,29} were investi-

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gated, but the porous structures were not good enough for actual applications.

To obtain solvent-resistant and thermally resistant membranes, UHMWPE membranes were prepared via TIPS in this study. First, UHMWPE is regarded as a suitable membrane material for preparing membranes with excellent solvent and thermal resistance, and the TIPS method also has many advantages, including better mechanical properties, better pore structures, and higher porosity. Therefore, porous, flat membranes of UHMWPE can be prepared as thermally resistant and solvent-resistant membranes by the TIPS method. In our research, diphenyl ether (DPE) and decalin were chosen as the diluents. On the basis of the phase diagrams, scanning electron microscopy (SEM) images, and porosity of the samples, influential factors, including the polymer concentration, cooling rate, and viscosity, were investigated.

EXPERIMENTAL

Materials

The UHMWPE used was a commercial product of Wen Chang Electric Chemical Co., Ltd. (Beijing, China). The weight-average molecular weight was 3,000,000, the melting temperature was 190.6°C, and the crystallization temperature was 135.5°C. The decalin and DPE used were commercial products of Beijing Chemical Factory (Beijing, China).

Membrane preparation

The steps for preparing the porous, flat UHMWPE samples were as follows. First, UHMWPE and a diluent in a special weight ratio were put in a sample bottle and mixed. After the sample bottle was full of nitrogen, it was sealed with a cap. Then, the sample bottle was put in an electric heating apparatus and heated to 30–50°C above the cloud-point temperature of the solution for 30 min until UHMWPE was dissolved in the diluent completely. Then, the sample was put in a cooling medium (air or water) to solidify. The diluent in the UHMWPE/diluent system was extracted with acetone. After solvent extraction, the samples of the porous membranes were dried in a vacuum-drying oven at 50°C for 12 h.

Phase diagram

The cloud point [liquid–liquid (L–L) phase separation] was observed by optical microscopy as follows. The UHMWPE/diluent sample, sealed in two slides, was first heated on a hot stage into a homogeneous solution. When the solution slowly cooled to the cloud point at which phase separation occurred, the

transparent solution turned out to be turbid. The dynamic crystallization temperature was determined with a differential scanning calorimetry experiment (DSC-7, PerkinElmer, Waltham, MA; cooling rate = 20 K/min). The binodal curve was drawn with the cloud-point temperatures, and the crystallization curve was drawn with the dynamic crystallization temperatures.

SEM observations

The porous samples were fractured in liquid nitrogen and mounted vertically on sample holders. The surfaces of the samples were sputtered with Au/Pd *in vacuo*. An S-4300 scanning electron microscope (Hitachi Co., Tokyo, Japan) was used to observe the porous structures.

Membrane porosity (A_k)

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

$$A_k = \frac{(W_0 - W)\bar{\rho}}{\bar{\rho}W_0 + (\rho - \bar{\rho})W} \times 100\% \quad (1)$$

where W is the total weight of the dry membrane, W_0 is the weight of the wet membrane; ρ is the polymer density, and $\bar{\rho}$ is the absolute alcohol density.

RESULTS AND DISCUSSION

Discussion of the phase diagram

The phase diagrams of the UHMWPE/DPE system and UHMWPE/decalin system were drawn with the cloud points and crystallization temperatures. There are many differences between the two phase diagrams (Fig. 1).

The upper critical solution temperature (UCST) is the highest point in the cloud-point curve. The UCST of the UHMWPE/DPE system is 135°C, and the UCST of the UHMWPE/decalin system is 98°C. For the UHMWPE/DPE system, the UCST is higher than that of the UHMWPE/decalin system. The cloud point of the polymer/diluent system is determined by the properties and contents of the polymer and diluent. When the polymer and its content are limited, the UCST of the polymer/diluent system is determined by the melting point and boiling temperature of the diluent (Table I).

Of the two systems, the phase diagram of the UHMWPE/DPE system has the larger L–L phase-

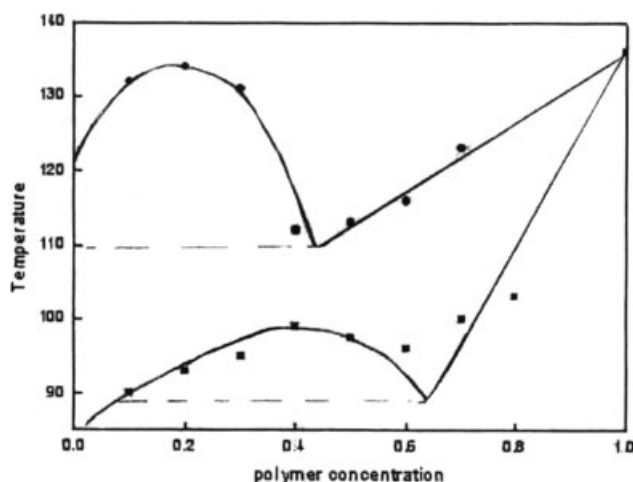


Figure 1 Phase diagram of the UHMWPE/diluent systems (the round points express the phase diagram of the UHMWPE/DPE system, and the square points express the phase diagram of the UHMWPE/decalin system).

separation areas (Fig. 1). For the UHMWPE/decalin system, the temperature gap between the UCST and crystallization temperature is far smaller than that of the UHMWPE/DPE system, so the L–L phase-separation area of the UHMWPE/decalin system is smaller than that of the UHMWPE/DPE system, and the solid–liquid (S–L) phase-separation mechanism should have the predominant effect on membrane formation in the UHMWPE/decalin system.

The monotectic point is at the intersection of the binodal curve (or cloud-point curve) and the dynamic crystallization curve, and it is also the intersection of L–L and S–L (Fig. 1). If the polymer concentration is less than the monotectic point, the porous structure can be formed through L–L phase separation followed by polymer crystallization. If the polymer concentration is larger than the monotectic point, the porous structure can be formed only by S–L phase separation (or polymer crystallization). The polymer concentration of the monotectic point of the UHMWPE/DPE system is 42 wt %, and that of the UHMWPE/decalin system is 63 wt %. Therefore, the UHMWPE/decalin system has a wider concentration range of L–L phase separation than the UHMWPE/DPE system. These aforementioned differences have a great effect on UHMWPE membrane formation.

UHMWPE/DPE system

The phase diagram of the UHMWPE/DPE system has the largest region of L–L phase separation, and its UCST is also the higher of the two systems (Fig. 1). Figure 2 shows SEM images of the UHMWPE/DPE system cooled in air. The open-cell pores are shown in Figure 2. The open-cell pores should be

TABLE I
Properties of the Diluents

Diluent	Melting temperature	Boiling temperature	Density
Decalin	−43.3	194.6	0.896
DPE	27	159	1.084

formed through L–L phase separation. On the basis of the thermodynamic phase diagram (Fig. 1), this kind of pore structure should be formed by two mechanisms: nucleation and growth of the polymer-rich phase in the L–L phase-separation process and crystallization of the polymer in the polymer-rich phase. Under this condition, the L–L phase separation plays a major role in the two competitive mechanisms and forms the open-cell pore structure.

A comparison of Figure 2(f,h,j) can lead to the conclusion that the pore size decreases with increasing polymer concentration. When the polymer content increases, the polymer-lean phase decreases, and the increasing viscosity restrains the coarsening process. Therefore, the pore size decreases.

Figure 3 shows SEM images of the UHMWPE/DPE system cooled in water. The SEM images show a branchlike structure that may be formed by spinodal decomposition (from 10 to 40 wt %; Fig. 3). Because water has a high thermal capacity, the cooling rate in 20°C water is higher than that in 20°C air. The higher cooling rate makes the driving force of phase separation increase and makes the mechanism of phase separation change from nucleation and growth to spinodal decomposition. In Figure 3(a–d,f–i), the branchlike, porous structure can be seen clearly, and it is typical of spinodal decomposition. The decomposition leads to the formation of the polymer-rich phase and the polymer-lean phase. After coarsening of the polymer-rich phase, growth, and solidification, a bicontinuous structure is formed.

The viscosity of the solution plays an important role. The high viscosity of a UHMWPE solution comes from its ultrahigh molecular weight. In Figure 2(a,f), there are pores of different sizes in a sample because of the nonuniform solution. The polymer and diluent system cannot be mixed into a homogeneous solution because of the high viscosity of the UHMWPE solution. In Figures 2(c,d) and 3(c,d), similar pore structures and pore sizes can be seen. This is because the coarsening process is limited by the higher viscosity of the UHMWPE solution. The same conclusion can be drawn from Table II; there are the similar porosities from 20 to 40 wt % at different cooling rates. Therefore, the viscosity affects the UHMWPE membrane formation. The porosity of the UHMWPE/DPE system is almost higher than 45% when the polymer concentration is 10–40 wt % (Fig.

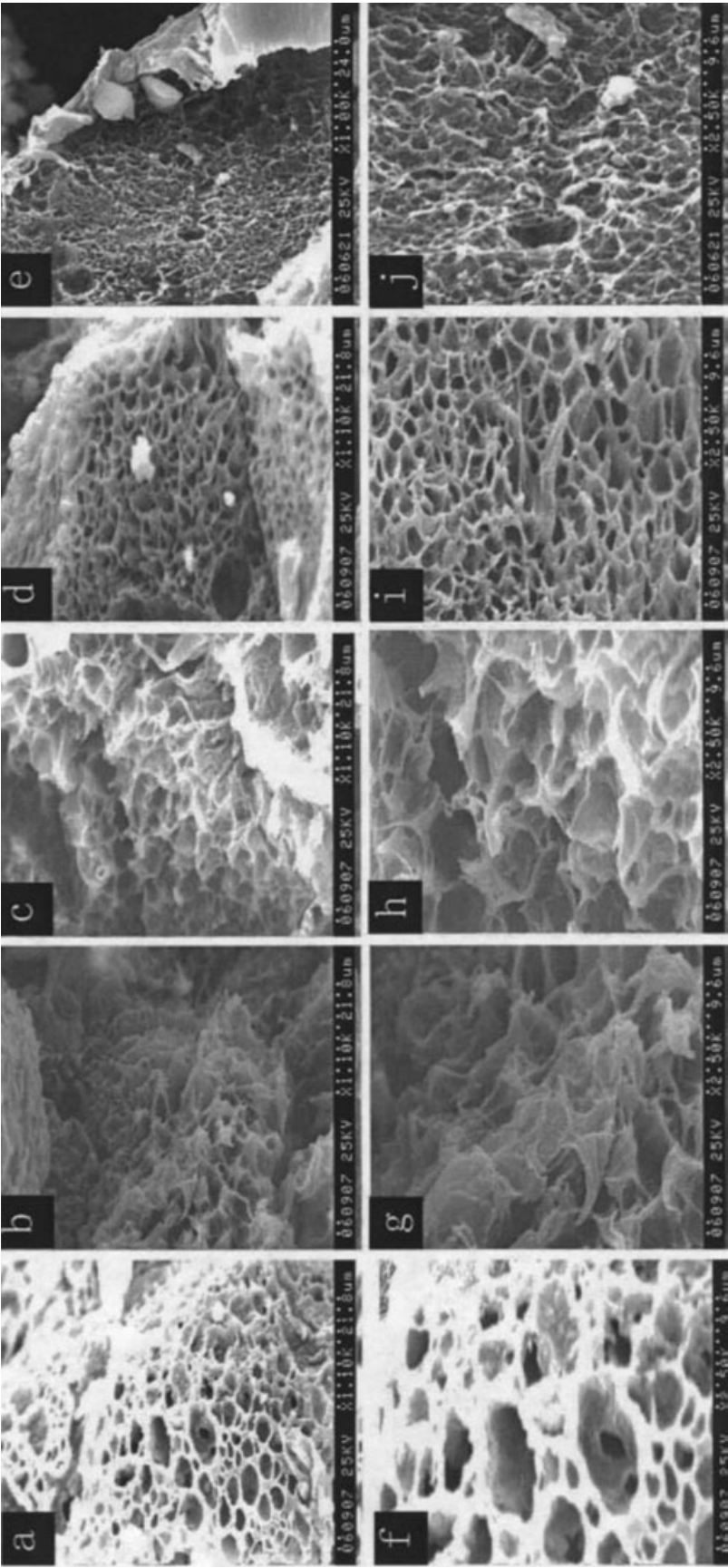


Figure 2 Porous structures of the UHMWPE/DPE system with various UHMWPE concentrations (cooled in 20°C air): (a) 10, (b) 20, (c) 30, (d) 40, and (e) 50 wt % (low power) and (f) 10, (g) 20, (h) 30, (i) 40, and (j) 50 wt % (high power).

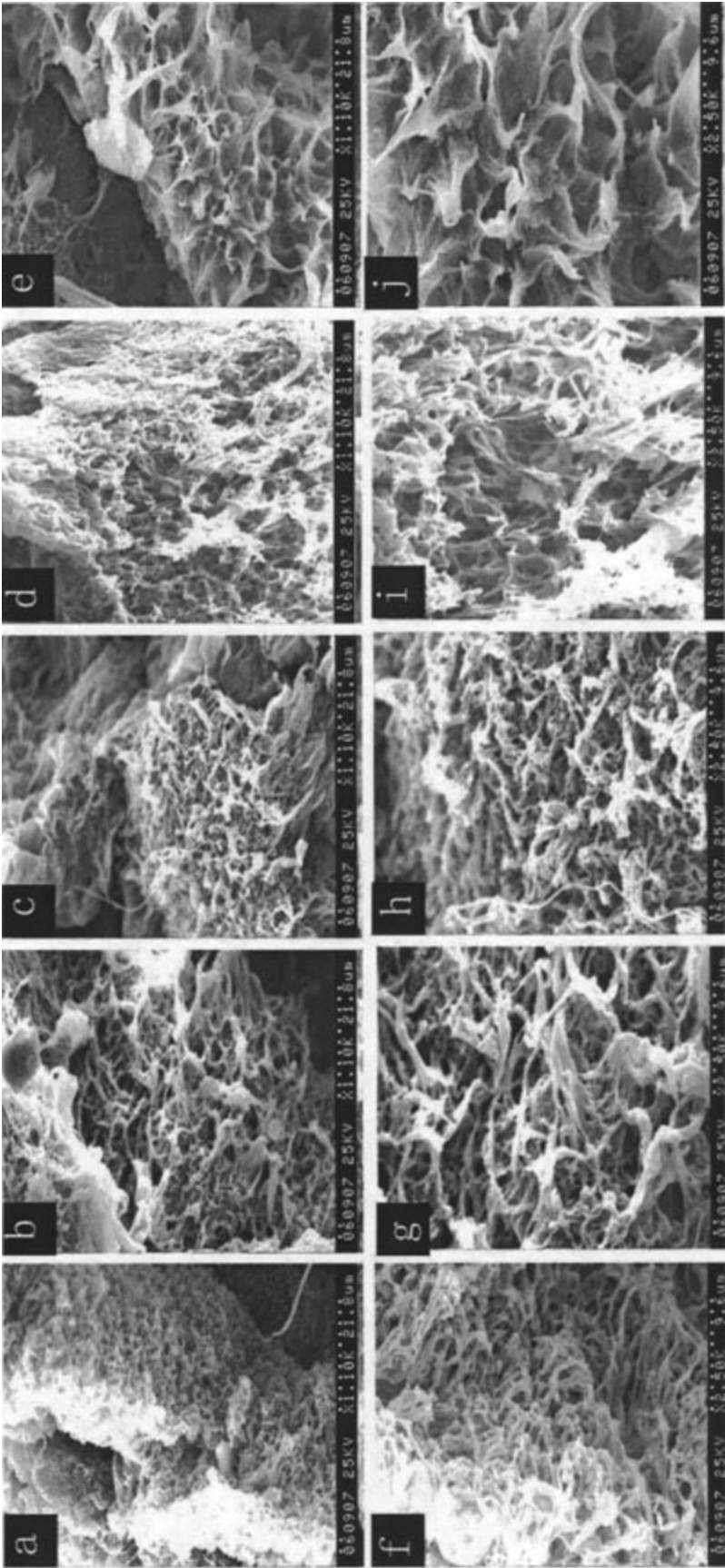


Figure 3 Porous structures of the UHMWPE/DPE system with various UHMWPE concentrations (cooled in 20°C water): (a) 10, (b) 20, (c) 30, (d) 40, and (e) 50 wt % (low power) and (f) 10, (g) 20, (h) 30, (i) 40, and (j) 50 wt % (high power).

TABLE II
Porosity of the UHMWPE/DPE System at Different Cooling Rates

UHMWPE/DPE	10%	20%	30%	40%	50%
Porosity with cooling in air	60.0	56.6	45.2	50.3	23.3
Porosity with cooling in water	66.5	50.0	47.4	50.6	28.0

3). That is, a UHMWPE membrane with a better pore structure and porosity can be obtained with the UHMWPE/DPE system via TIPS.

UHMWPE/decalin system

The phase diagram of the UHMWPE/decalin system has a smaller region of L-L phase separation and a wider concentration range of L-L phase separation from 10 to 50 wt % than that of the UHMWPE/DPE

system (Fig. 1). The temperature gap between the UCST and crystallization is only 10°C at the same concentration; it is too short for L-L phase separation.

Figures 4 and 5 present SEM images of the UHMWPE/decalin system cooled in air and water. A sheetlike structure can be observed in Figure 4(a,b,d,e). This kind of pore may be formed through S-L phase separation. Because the L-L phase-separation region is too small (Fig. 1), the S-L phase separation and L-L phase separation take place at the same time, and the S-L phase separation plays a major role in this system. Therefore, the sheetlike structures are formed by S-L phase separation. No pore can be seen in Figure 4(c,f) because of the S-L phase separation and higher polymer concentration. Figure 5 shows the same sheetlike structures obtained through the S-L phase-separation mechanism. When the S-L phase-separation mechanism

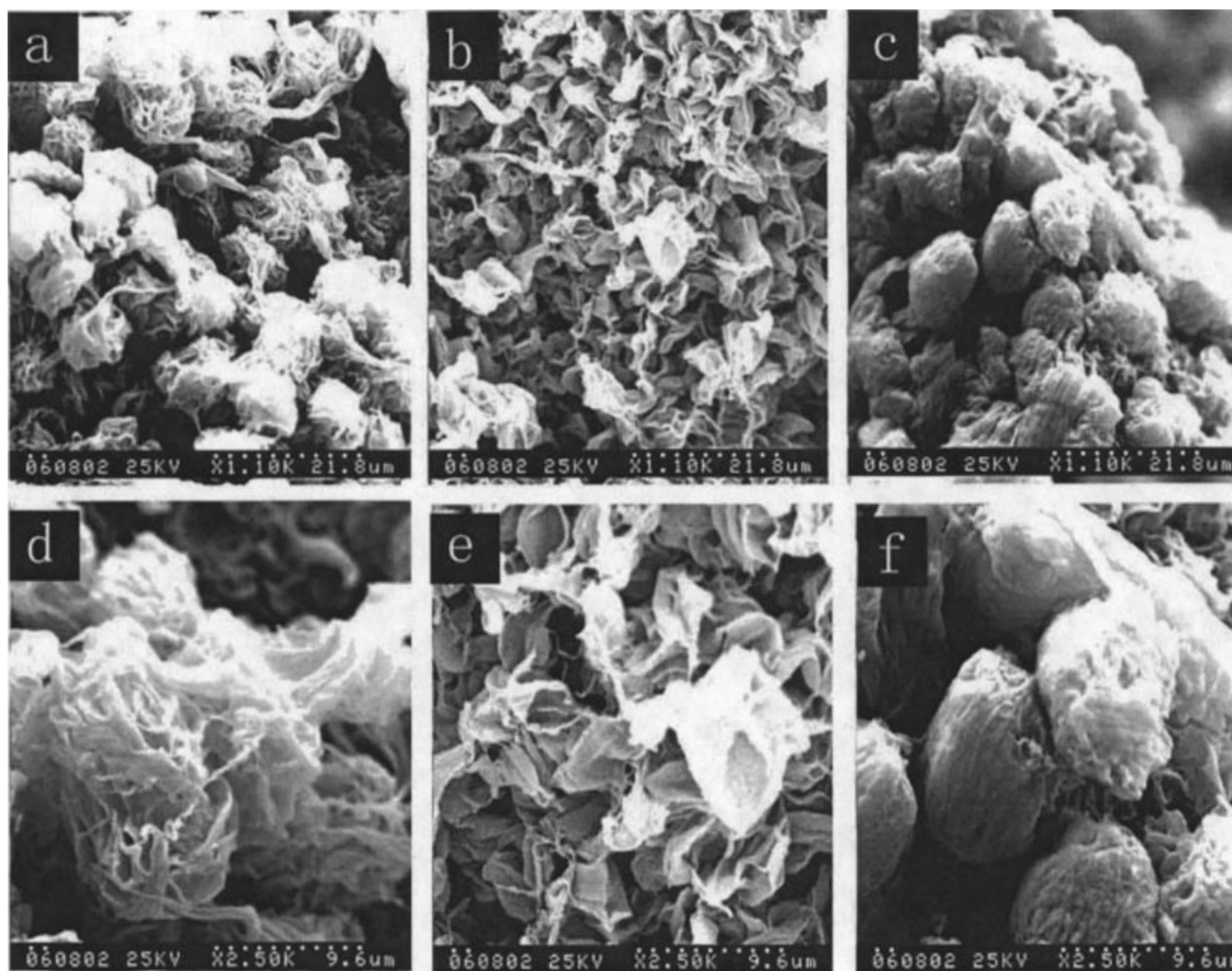


Figure 4 Porous structures of the UHMWPE/decalin system with various UHMWPE concentrations (cooled in 20°C air): (a) 20, (b) 30, and (c) 40 wt % (low power) and (d) 20, (e) 30, and (f) 40 wt % (high power).

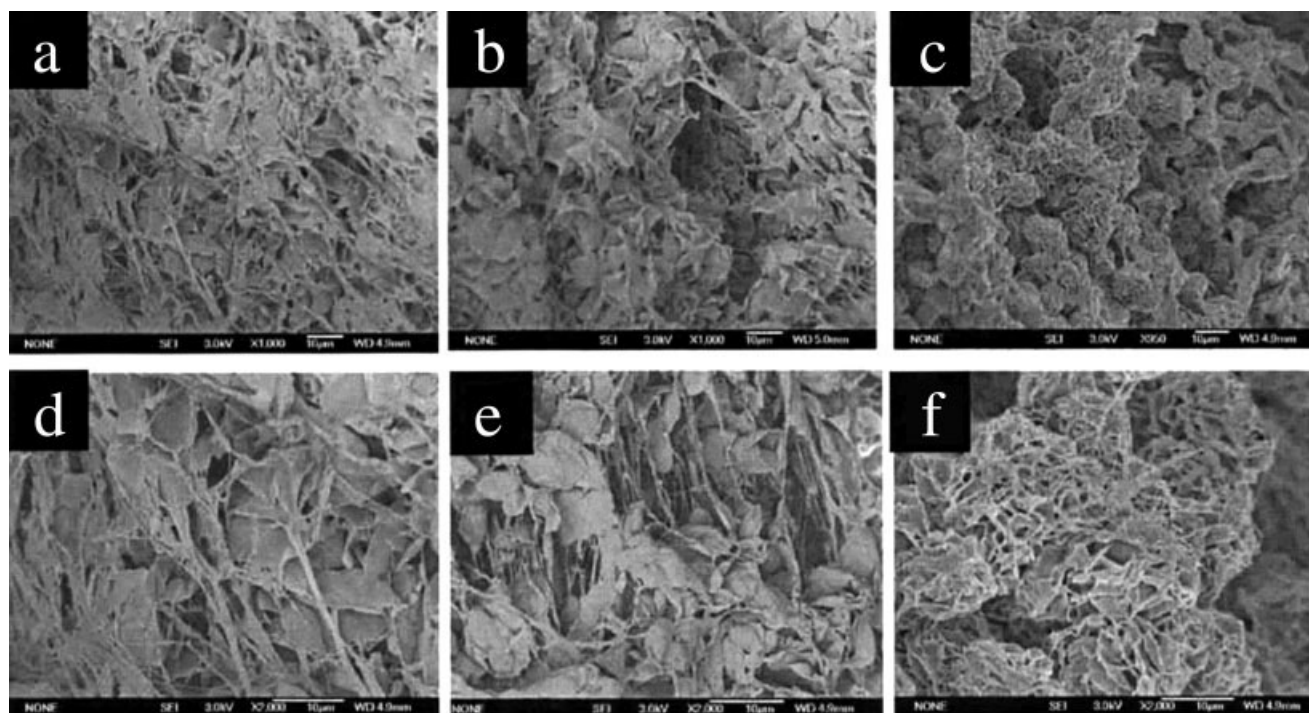


Figure 5 Porous structures of the UHMWPE/decalin system with various UHMWPE concentrations (cooled in 20°C water): (a) 20, (b) 30 and (c) 40 wt % (low power) and (d) 20, (e) 30, and (f) 40 wt % (high power).

has the major role in the UHMWPE/decalin system, the cooling rate and longer range of L–L phase separation can hardly change the pore structure (Figs. 4 and 5).

Table III shows that the sheetlike structure has a lower porosity in the UHMWPE/decalin system. A comparison of the pore structures and porosities in the two systems can lead to the conclusion that the UHMWPE membranes have better pore structures and higher porosities than those from the UHMWPE/decalin system.

CONCLUSIONS

Phase diagrams of the UHMWPE/DPE system and UHMWPE/decalin system have been drawn with the cloud-point and crystallization temperatures. The differences between the two phase diagrams with respect to the UCST, monotectic point, and L–L phase-separation region have been discussed.

The membrane obtained with the UHMWPE/DPE system has open-cell and branchlike pore structures under different conditions, and the porosity is higher

than 45% when the polymer concentration is 10–40 wt %. The membrane obtained with the UHMWPE/decalin system has only a sheetlike pore structure, and the porosity is lower than 45%. Therefore, a better membrane can be prepared with the UHMWPE/DPE system through the TIPS method.

The viscosity of the solution plays an important role in UHMWPE membranes. Nonuniform pores and similar pore structures and sizes with different polymer concentrations are obtained because of the higher viscosity of the polymer solution.

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TABLE III
Porosity of the UHMWPE/Decalin System at Different Cooling Rates

UHMWPE/decalin	10%	20%	30%	40%	50%
Porosity with cooling in air	38.3	37.6	22.5	29.4	21.2
Porosity with cooling in water	40.0	30.4	44.9	19.5	13.7

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