

Membrane Formation of Poly(vinylidene fluoride)/Poly(methyl methacrylate)/Diluents via Thermally Induced Phase Separation

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ABSTRACT: The role of the single diluents and mixed diluents on the poly (vinylidene fluoride) (PVDF)/poly (methyl methacrylate) (PMMA) blend membranes via thermally induced phase separation (TIPS) process was investigated. The crystallization behaviors of PVDF in the diluted samples were examined by differential scanning calorimetry. The melting and crystallization temperatures of those diluted PVDF blend were decreased with the enhanced interactions between polymer chains and diluent molecules. The crystallinity of PVDF in the diluent was always higher than that obtained in PVDF blend sample. This can be explained by the dilution effects, which increased the average spatial separation distances between crystallizable chains. Thus, the PVDF

crystallization was favored. Additionally, solid-liquid (S-L) phase separation occurred in the quenched samples. Illustrated by scanning electron microscopy, inter- and intraspherulitic voids were formed in the ultimate membranes, which related to the polymer/diluent interactions, the kinetics of crystallization and diluent rejection from the growing crystal. The porosity of the PVDF blend membranes obtained from the mixed diluents was higher than those obtained from the single diluent samples. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1235–1245, 2009

Key words: membrane; thermally induced phase separation (TIPS); crystallization; morphology

INTRODUCTION

Nowadays, thermally induced phase separation (TIPS) is one of the main techniques for the preparation of polymeric porous membranes by controlling phase separation and it is gaining much interest for the advantages over the conventional membrane preparation technique.^{1–7} This method can be applicable to a wide range of polymers, including the polymers that cannot be formed into membranes because of the solubility problems, such as polypropylene (PP),¹ poly (4-methyl-pentene) (TPX),⁸ poly (vinylidene fluoride) (PVDF),⁹ and poly (lactic acid).¹⁰ In the TIPS process, the thermodynamics of polymer/diluent system, especially for the thermodynamic interaction between polymer and diluent in their mixture during the phase separation process, has been studied systematically.^{11–13} The phase separation dominating solid-liquid (S-L) or liquid-liquid (L-L) phase separation with subsequent polymer crystallization can be controlled through the appropriate choice of diluent,^{1,2,14} and significantly influence the crystallization morphologies of polymer (crystalline or semicrystalline).^{3,15}

PVDF as a semicrystalline polymer has wide applications because of its excellent physical and chemical properties, as well as good thermal stability.¹⁶ Especially, it is quite suitable for membrane manufacture because of the chemical resistance. Currently, the literature on the PVDF microporous membrane via the TIPS method and the crystallization behaviors of PVDF during the process has attracted most attentions.^{9,17–20} However, because of the hydrophobic nature of the PVDF, its membranes often suffer from low flux, changing the solute selectivity with time, and surface fouling, during filtration of oil/protein containing solutions. Thus, a number of efforts have been devoted to the chemical and physical modification of PVDF to improve its surface hydrophilicity. Surface treatment (including physical and chemical methods) is one of the traditional and effective processes to improve the hydrophilicity of PVDF membrane.^{21–23} An alternative method, blending method, as a versatile, straightforward, and relatively inexpensive method, is an efficient method to improve the hydrophilicity of PVDF membranes.^{24,25} Until now, the literature on the PVDF blend membrane via TIPS method is rare. In our previous work, the crystallization behaviors and hydrophilicity of PVDF/poly (methyl methacrylate) (PMMA) polyblend has been studied. It has been demonstrated that PVDF/PMMA with mass ratio of

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70/30 provides the good hydrophilicity²⁶ and the best balance of optical properties, solvent resistance, hardness, mechanical strength, and weatherability.²⁷

In this work, PVDF/PMMA blend with a mass ratio of 70/30 along with a single or mixed diluent was used to prepare hydrophilic PVDF blend membrane via TIPS method. The effect of diluent types and interactions of polymer/diluent on the crystallization behaviors of PVDF in the samples and membrane cross-section morphology were investigated.

EXPERIMENTAL

Materials

PVDF powder (Kynar K-761, $\bar{M}_w = 441,000$) was obtained from Elf Atochem of North America (USA). PMMA resin (HR1000L) was obtained from Kuraray (Japan). Dioctyl phthalate (DOP), dimethyl phthalate (DMP), methyl salicylate (MS), and benzophenone (BP) were purchased from Lingfeng Chemical Reagent of China. Methyl benzoate (MB), diethyl malonate (DEM), triethyl phosphate (TP), and dibutyl sebacate (DBS) were purchased from Sinopharm Chemical Reagent (China). Dibutyl phthalate (DBP) was purchased from Yinxiang Biology (China). Dioctyl adipate (DOA) and dioctyl-sebacate (DOS) were supplied by Shandong Haihua Tianhe Organic Chemical (China). The Soybean oil without antioxidant was bought in the local supermarket. All of these chemicals were used as the diluents without further purification. Methanol, which was supplied by Sinopharm Chemical Reagent (China), was used for extracting the diluents.

Membrane preparation

First, the polymer blend of PVDF and PMMA with mass ratio of 70/30 was prepared by melt blending in a two-roll mixing mill operating at 180°C. Then, 4 g mixture of polymer blend/diluent (the concentration of the polymer blend was always 25 wt %, i.e., the PVDF composition was 17.5 wt %) were weighed into a glass test tube. Homogeneous polymer blend/diluent mixtures were obtained after the tube was heated in an oil bath at 180°C for 4 h. Subsequently, by removing from the oil bath, cooling at the room temperature, and breaking the tube, a solidified mixture was yielded.

To prevent the evaporating the diluent during the membrane preparation, a tailor-made test tube (a ram-type copper tube with inner and outer diameters of 10 and 12 mm, respectively, sealed by a copper plunger) was used. Thus, the sample retained its initial composition throughout the TIPS process, and each flat sheet sample was prepared with approximately the same thickness.

The solid sample was chopped into small pieces, and placed in a tailor-made test tube. After that, it was heated in an oven at 180°C for 10 min. Then, the sample was quenched to 30°C in the water bath for 10 min from the melt and further solidified in the ice water. After recovered from the tube, the sample was immersed in methanol for 48 h to extract the diluent and dried in a vacuum oven at room temperature for 24 h. In the end, the microporous PVDF/PMMA blend membrane was obtained.

Differential scanning calorimetry analysis

The calorimetric measurements were made in a TA Instruments Q-200 differential scanning calorimeter in a dry nitrogen atmosphere. To erase the thermal history of the samples, the solid polymer blend/diluent mixtures (before extraction by methanol) (~ 10 mg) were heated from room temperature to 180°C at a rate of 40°C/min. Maintained at 180°C for 5 min, the mixtures were cooled down to 40°C at a rate of 5°C/min (the cooling run). After 1 min at 40°C, a second heating was done upon to 180°C and the sample was cooled down to 40°C at a rate of 40°C/min. The crystallinity of PVDF (X_c) was recorded below, as in our previous work^{8,20}:

$$X_c = \frac{\Delta H_f / \phi}{\Delta H_f^*} \times 100\% \quad (1)$$

where $\Delta H_f^* = 104.5 \text{ J/g}$ ²⁸ is the melting enthalpy for a 100% crystalline PVDF, ΔH_f is the melting enthalpy of the mixtures measured in differential scanning calorimetry (DSC), and ϕ is the weight fraction of PVDF in the mixture (17.5 wt %).

The crystallization half-time ($t_{1/2}$), which is defined as the half-time of crystallization,²⁹ was used as a characteristic parameter of the crystallization process.

Scanning electron microscopy observation

For scanning electron microscopy (SEM) observation, the resulting PVDF/PMMA microporous membranes were fractured in liquid nitrogen and coated with platinum. The cross-section morphologies of the membrane were taken on a Jeol JSM-5900 with an accelerating voltage of 15–20 kV.

Porosity calculation of the membrane

The ultimate PVDF/PMMA blend membranes were immersed in *i*-butanol for 24 h and weighed immediately after the removal of *i*-butanol from the surface. The porosity (A_k) was calculated as reported in our previous work^{8,30}:

TABLE I
Solubility Parameters of PVDF, PMMA, and Diluents³¹

Materials	Solubility of parameters, δ (J/cm ³) ^{1/2}
Poly(vinylidene fluoride) PVDF	19.2
Poly(methyl methacrylate) PMMA	22.7
Diethyl phthalate (DOP)	24.8
Dimethyl phthalate (DMP)	21.9
Methyl salicylate (MS)	21.7
Methyl benzoate (MB)	21.5
Benzophenone (BP)	21.3 ^a
Diethyl malonate (DEM)	19.5 ^a
Dibutyl phthalate (DBP)	19.0
Triethyl phosphate (TP)	18.6 ^a
Dibutyl sebacate (DBS)	18.0
Diethyl adipate (DOA)	17.8
Diethyl-sebacate (DOS)	17.8
Soybean oil	—

^a Calculated by group contribution methods.³¹
—, Indefinite.

$$A_k = \frac{(W_2 - W_1)\rho_1}{\rho_1 W_2 + (\rho_2 - \rho_1)W_1} \times 100\% \quad (2)$$

where W_1 is the initial membrane weight; W_2 is the immersed membrane weight; ρ_1 is the estimated density of the PVDF blend, which was taken as 1.552 g/cm³; and ρ_2 is the density of *i*-butanol, taken as 0.801 g/cm³.

RESULTS AND DISCUSSION

Effect of the single diluents on PVDF blend crystallization and membrane structure

In contrast to the diluted sample in which only one type of polymer exists, the change of the compatibility between the polymer and the diluent should be considered first. According to a simple rule, the compatibility of two components can be estimated by the solubility parameter (δ) of each component; i.e., the closer the value of δ , the more compatible for them when mixing.³¹ The solubility parameters for PVDF, PMMA, and various diluents are summarized in Table I. Although the difference of the value δ between PVDF and PMMA is 3.5 (J/cm³)^{1/2}, making PVDF/PMMA blends are not entirely miscible actually, the interaction between the fluorine atoms and carbonyl groups of the partner polymer makes them highly compatible.³² According to the literature, PVDF/PMMA is a miscible system over the whole range of composition,^{26,33–35} which is linked to the existence of a single phase, and to isotropy. Therefore, PVDF/PMMA (70/30) blend used in this work can be considered as a single phase. The solubility parameter of this PVDF blend is at

about 19.2–22.7 (J/cm³)^{1/2}. Thus, DMP, MS, MB, BP, DEM, and DBP can be used as diluent for PVDF blend membrane preparation, because of the close value δ to PVDF blend. On the contrary, the large difference between the PVDF blend and DOP, TP, DBS, DOA, DOS, or soybean oil suggests that these organic solvents are not suitable to be used as diluents of PVDF blend. The experimental results confirmed that PVDF blend and DOP, TP, DBS, DOA, DOS, or soybean oil systems can not form homogeneous solution at the evaluated temperature.

Figure 1 shows the DSC crystallization curves of PVDF blend and its mixtures with various diluents when cooling from the melt at 5°C/min after removing the thermal history. It is obviously observed that all the diluents induce a significant decrease in the exothermic peak temperature (<120°C), compared with the PVDF blend in which no diluent is added (>120°C). The retardant effects to PVDF crystallization temperature appears in the order of DEM > DMP > MB > MS > DBP > BP when these diluents mixed with PVDF blend. As reported, the addition of diluent lowers the chemical potential of the mixture. So the various diluents used here also can lower the chemical potential of the mixture in different changes, leading to the depression of the crystallization temperature of PVDF diversely.^{12,36}

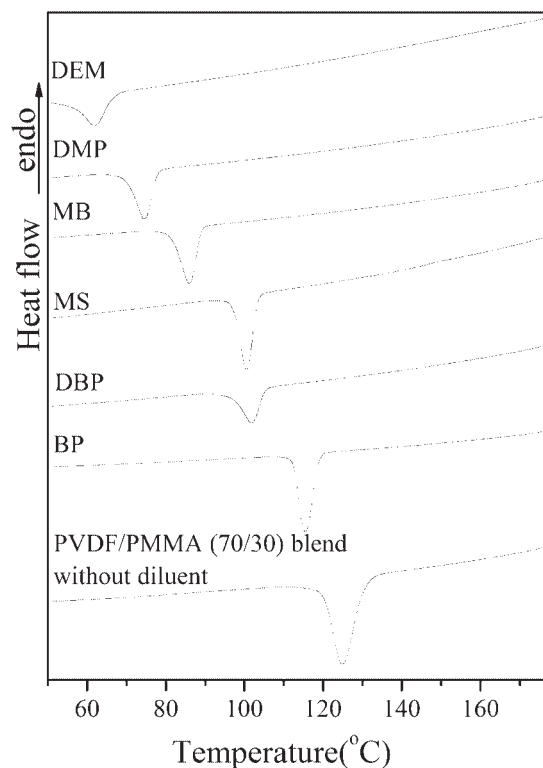


Figure 1 DSC crystallization curves of PVDF blend and its mixtures with diluents when cooling from the melt after removing the thermal history.

TABLE II
DSC Crystallization Results of PVDF Blend and its Mixtures with Diluents when Cooling from the Melt After Removing the Thermal History

Various diluents mixed with PVDF blend	T_c^{on} (°C)	T_c^p (°C)	T_c^f (°C)	ΔT_c (°C)	ΔH_c (J/g)	$t_{1/2}$ (min)
DEM	66.4	62.2	57.3	4.2	9.13	0.76
DMP	77.8	74.6	69.9	3.2	11.57	0.55
MB	88.9	86.0	81.4	2.9	12.54	0.50
MS	103.3	100.5	97.1	2.8	13.66	0.44
DBP	105.2	101.8	96.6	3.4	9.96	0.63
BP	118.7	115.4	112.4	3.3	15.28	0.46
PVDF blend with no diluent	130.5	124.9	119.9	5.6	27.90	0.64

T_c^{on} , onset crystallization temperature of PVDF; T_c^p , peak crystallization temperature of PVDF; T_c^f , final crystallization temperature of PVDF; $\Delta T_c = T_c^f - T_c^{on}$; ΔH_c , crystallization enthalpy of PVDF.

The data of the DSC crystallization results from Figure 1 are summarized in Table II. The crystallization temperatures and the value ΔH_c (enthalpy of crystallization) for PVDF in the mixtures depend upon various diluent types. The onset crystallization temperature T_c^{on} , peak crystallization temperature T_c^p , and final crystallization temperature T_c^f decrease in comparison with the PVDF blend. As reported, the lower crystallization temperature of the mixture indicates a higher degree of supercooling or a larger driving force needed for PVDF crystallization.³⁶ This suggests that the crystallization driven force needed for PVDF in the diluted mixture is higher than that with no diluent, and dramatically depends on the diluent type under the cooling conditions (i.e., non-isothermal process).

The difference between the onset and peak crystallization temperature ΔT_c obtained from each PVDF blend/diluent system is listed in Table II. Beck and Ledbetter³⁷ suggested that the smaller the values ΔT_c , the faster the overall crystallization rate, because the free expansion of crystals occurs between the onset and peak of crystallization temperatures.³⁶ With regard to the PVDF blend sample, the higher crystallization temperatures, ΔT_c (5.6°C) are observed, compared with the diluted samples (2.8–4.2°C). This indicates that the crystallization rate of PVDF is the lowest in the PVDF blend sample. It has been demonstrated that the crystallization of PVDF is reduced by PMMA addition because of the trapped PMMA chains in PVDF lamellar crystals.²⁶ However, adding diluents to PVDF blend induces a decrease in half-crystallization times ($t_{1/2}$), except for DEM (Table II). As reported,^{38,39} increased $t_{1/2}$ are correlated to lower crystallization rates. The shorter the value $t_{1/2}$, the faster the crystallization rate, and *vice versa*. The reduced value $t_{1/2}$ and ΔT_c in the diluted samples suggests that the crystallization rate of PVDF is promoted by diluents except for DEM diluted sample. This enhanced crystallization can be attributed to the various dilution effects (changing the average spatial

separation distances between crystallizable chains). In addition, among these diluted samples, the value ΔH_c of those having a larger value of $t_{1/2}$, is lower than those having a small value of $t_{1/2}$. That is to say, the sample having a comparative of high crystallization rate will obtain the high crystallization ability. The value ΔT_c obtained in the diluted samples is far smaller than that of the PVDF blend with no diluent, which is due to the decrease of PVDF quantity in the diluted samples (17.5 wt %) in comparison with the PVDF blend (70 wt %).

Figure 2 shows the melting curves of PVDF blend/diluent samples after cooling from the melt.

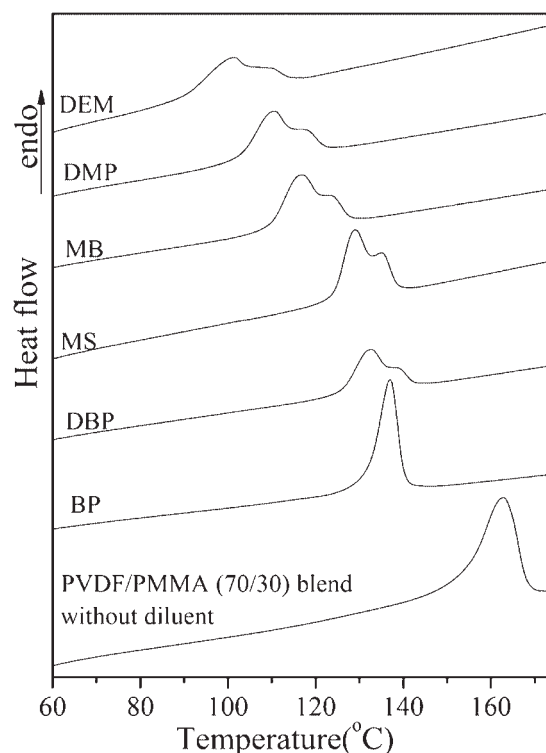


Figure 2 DSC melting curves of PVDF blend and its mixtures with diluents during melting after the cooling process.

TABLE III
DSC Melting Results of PVDF Blend and its Mixtures with Diluents During Melting After the Cooling Process

Various diluents mixed with PVDF blend	T_m^{on} (°C)	T_m^{p} (°C)	T_m^{f} (°C)	ΔT_m (°C)	ΔH_m (J/g)	X_c (%)
DEM	89.0	100.9	114.9	25.9	11.62	63.5
DMP	102.4	110.3	122.2	19.8	11.62	63.5
MB	109.5	116.5	128.0	18.5	12.60	68.9
MS	124.1	129.0	138.8	14.7	13.12	71.2
DBP	125.8	132.3	142.4	16.6	9.54	52.2
BP	131.7	136.9	140.2	8.5	14.98	81.9
PVDF blend with no diluent	152.7	162.7	168.1	15.4	26.39	36.1

T_m^{on} , onset melting temperature of PVDF; T_m^{p} , peak melting temperature of PVDF; T_m^{f} , final melting temperature of PVDF; $\Delta T_m = T_m^{\text{f}} - T_m^{\text{on}}$; ΔH_m , melting enthalpy; X_c , crystallinity of PVDF.

It is observed that the melting temperature is decreased as the diluents added into PVDF blend. The melting peak observed in the melting curves for the different diluted samples ranks DEM < DMP < MB < MS < DBP < BP. As reported,^{33,40} depression of the melting points, because of a decrease in the chemical potential of the crystalline polymer, can provide the information on miscibility and strength of intermolecular interactions in the mixture. The higher depth of a depression of the melting points is the stronger interaction between the components of the mixture will be. So, it is suggested that the interaction between the PVDF blend and diluent in these mixtures decreases in the order DEM > DMP > MB > MS > DBP > BP.

In Figure 2, when the PVDF blend mixed with DEM, DMP, MB, DBP, and MS, a high temperature shoulder is observed. The appearance of the double melting peaks has observed in many polymers. As demonstrated,^{19,20,41} PVDF crystallizing from the melt only forms into the α phase. Thus, the polymorphism or the crystal transformation can be excluded. Other possible explanations can be assigned to the melting–recrystallization process^{28,42} and the melting of a series of crystallite sizes.^{8,43} Herein, the melting–recrystallization process or the difference of lamellar thickness and perfection of PVDF crystals formation may be the most possible explanations for the double melting peaks on the DSC melting curves. Further identification that whether melting–recrystallization leads to the two endotherms in the DSC curves will be studied in our future work. In both melting–recrystallization process and the difference degree of crystallization, the appearance of the lower temperature melting peak is due to the melting of small or imperfect crystals formed, while the higher one is partially because of the melting of the large or perfect crystals during the DSC heating scans. Thus, the small or imperfect crystals melt first and some large or perfect crystals melt at higher temperature during the heating process. However, as for the PVDF blend sample and the PVDF blend/

BP mixture, only one melting peak is observed on the melting curves. This suggests that more homogeneous in PVDF crystal size or perfection is obtained in these two samples than any other PVDF blend/diluent mixtures. This can be attributed to the weakest interactions between PVDF chains and BP molecules, resulting in the similar melting behaviors of PVDF to that of the PVDF blend sample.

Table III lists the data obtained from the melting curves in Figure 2, and summarizes the influence of the diluents on PVDF blend crystallization during the heating. The onset of melting temperature (T_m^{on}), the peak melting temperature (T_m^{p}), and the final melting temperature (T_m^{f}) of PVDF blend/diluent samples are lower than those obtained in PVDF blend. The degree of melting point depression in PVDF blend/diluent samples is in the order DEM > DMP > MB > MS > DBP > BP. This suggests the reduced interaction between PVDF blend and diluent in the same order. The difference in value ΔT_m ($\Delta T_m = T_m^{\text{f}} - T_m^{\text{on}}$) indicates that the different PVDF crystal size may be formed in different diluents. Therefore, the crystallinity of PVDF (in the PVDF region of the samples) varies with the different diluent types. It seems that the stronger interaction between PVDF blend and diluent, the lower crystallinity of PVDF will be obtained in these samples. However, when DBP is chosen as the diluent, the lowest crystallinity is obtained in the diluent samples. This may be caused by other factors that affect the PVDF crystallization in this case.

An increased interaction between PVDF and diluents reduced the PVDF melting and crystallization temperatures, which has been analyzed by DSC measurement above. This is consistent with the Su et al.'s work.^{17,18} So the crystallization behavior of PVDF blend in diluents will influence the ultimate membrane structure via TIPS process.

The mixtures of PVDF blend and several diluents with 25 wt % PVDF blend were melted at 180°C and quenched in a 30°C water bath. After extraction by methanol, the resulting membrane structure is

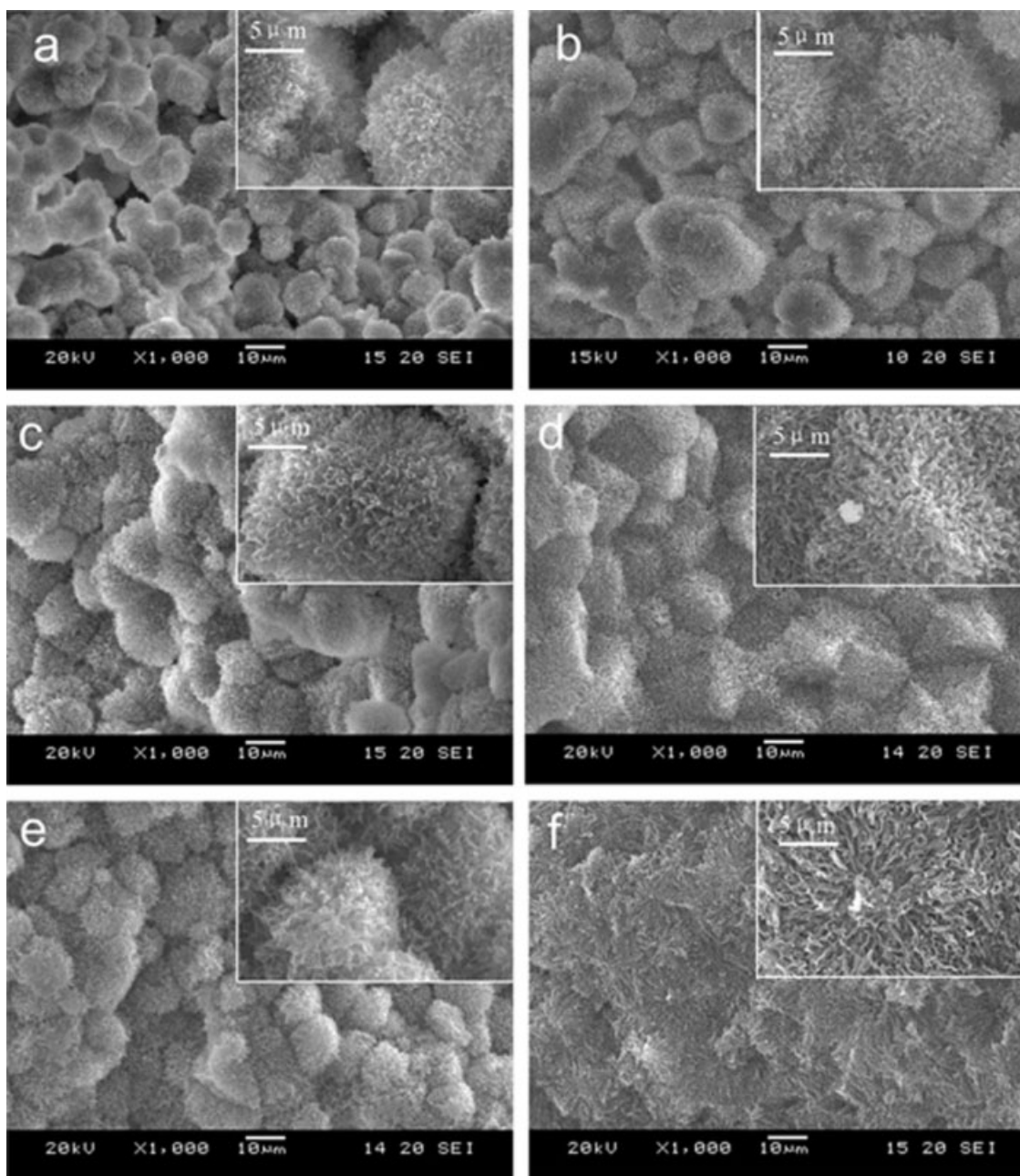


Figure 3 SEM micrographs of cross-sections of 25 wt % PVDF blend membranes from single diluent quenched from 180°C to 30°C: a-DEM; b-DMP; c-MB; d- MS; e-DBP; f-BP.

examined by SEM, as shown in Figure 3. The discernable spherulitic structure can be observed in the quenched samples except the quenched BP sample, because of PVDF crystallization during the quenching. These spherulitic structures are attributed to the S-L phase separation via nucleation and growth of the polymer with accompanying rejection of the liquid diluent.^{3,14} In a quenched sample, the PVDF blend/diluent mixture is essentially frozen in time, and the spherulitic structure is representative of crystallization from a homogeneous mixture. The

difference in spherulitic surface structure is attributed to the kinetics of crystallization and diluent rejection from the growing crystal.¹ Herein, the morphologies of the membrane structures can be divided into two types. One includes the quenched DEM, DMP, MB, DBP samples. The surfaces of the spherulites shown to be textured by branched lamellae. This is due to the increased amount of rejected diluent from the growing spherulite at the surface of each spherulite.¹ Consequently, the interspherulitic voids (the region between spherulites) is formed in

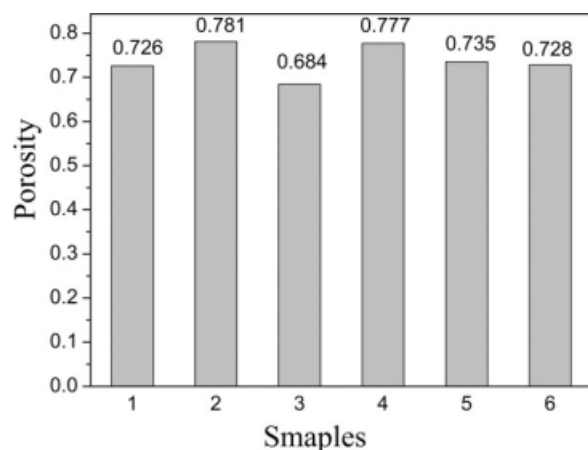


Figure 4 Porosity of PVDF blend/diluent samples with 25 wt % PVDF blend: 1-DEM; 2-DMP; 3-MB; 4-DBP; 5-MS; 6-BP.

these samples. The other type includes MS and BP samples, in which the interspherulitic voids are not observed, but the intraspherulitic structure (location between lamellae within the spherulite) is predominant.

In previous work,⁹ it reveals that the system possessing stronger interaction between polymer and diluent can yield more discernable spherulitic structure because of the better compatibility of PVDF and diluent. As analyzed in DSC results, the interactions between PVDF blend and diluents rank in the order DEM > DMP > MB > MS > DBP. Therefore, in the quenched PVDF blend/DEM and PVDF blend/DMP samples, the membrane cross-section clearly illustrates the numerous spherulites. On the contrary, in the quenched MB, MS, and DBP samples, more connections among spherulites are formed. As for the quenched PVDF blend/BP sample, there are no discernable spherulites but small-size pores observed in it [Fig. 3(f)]. The reason can be related to the L-L phase separation before the crystallization of PVDF, which restricts subsequent PVDF crystallization to small isolated domains of limited PVDF supply and limited growing space.³ The further studies about the thermal dynamic phase diagram will continue in our group.

As shown in Figure 4, the value of porosity of the above six PVDF blend/diluent samples ranges from 68% to 78%, which are higher than that obtained in PVDF/diluent system.⁹ This result suggests that the PVDF blend/diluent system is better for preparing higher porosity microporous membrane.

Effect of the mixed diluents on PVDF blend crystallization and membrane structure

It has been demonstrated that the mixed diluents can change the interactions between the polymer

and diluent by varying the composition of each diluent.^{17,44-46} Thus, the membrane structure can be controlled by changing each diluent composition. Analogously, using the proper composition of good and poor diluents under the same thermal conditions can control the membrane structure of the resulting products. Herein, several suitable mixed diluents were applied for preparing the PVDF blend membranes, and simultaneously the crystallization behavior of PVDF in these systems was studied.

Table IV lists the composed solubility parameter (δ_c) of each mixed dilute which is estimated as our previous work,⁴⁵ according to the equation is as follows³¹:

$$\delta_1 = \delta_1\phi_1 + \delta_2\phi_2 \quad (3)$$

where, δ_1 , δ_2 are the solubility parameters of each diluent, and ϕ_1 , ϕ_2 are the volume fraction of each component. By solving this equation with the values of solubility parameter are listed in Table I, the calculated solubility parameters for the mixed diluents are given in Table IV. It can be seen that these values range from 19 to 23 (J/cm^3)^{1/2}, which is very close to that of PVDF blend. Therefore, these mixed diluents are suitable for preparation of PVDF blend membranes.

Figure 5 shows the DSC crystallization curves of PVDF blend/mixed diluent systems during cooling from the melt at 5°C/min after removing the thermal history. A significant shift of the exothermic peak to the low temperature is obvious in these samples in comparison with that of PVDF blend without diluent (Fig. 1), because of the decreased chemical potential of the mixture.^{12,36} When DMP/TP/soybean oil (7/2/1) used as the mixed diluent, the greatest degree of crystallization depression is observed. DMP/DOP (5/5), DMP/DOS (7/3), DMP/DBS (5/5), and DMP/DOA (5/5) diluted samples have higher crystallization peak temperatures and they are very close. The DBP/DBS (4/6) sample possesses the highest PVDF crystallization peak temperature in these samples.

TABLE IV
Calculated Solubility Parameters of the Mixed Diluents
Calculated by Group Contribution Methods³¹

Mixed dilutes	Calculated solubility of parameters (J/cm^3) ^{1/2}
DMP/DOP (5/5)	23.4
DMP/DOS (7/3)	20.7
DMP/DBS (5/5)	20.0
DMP/DOA (5/5)	19.9
DMP/TP/soybean oil (7/2/1)	>19.1
DBP/DBS (4/6)	18.4

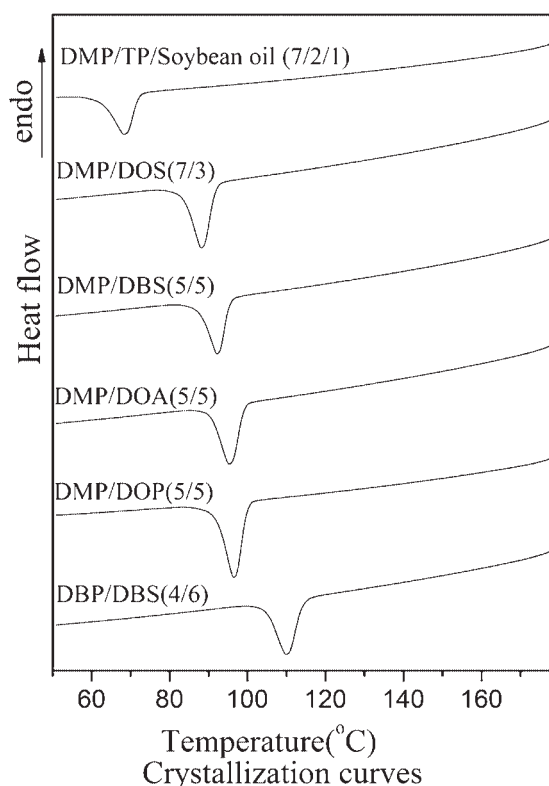


Figure 5 DSC crystallization curves of PVDF blend/mixed diluent systems when cooling from the melt after removing the thermal history.

The data for the DSC crystallization results obtained from Figure 5 are detailed in Table V. The onset crystallization temperature T_c^{on} , peak crystallization temperature T_c^{p} , and final crystallization temperature T_c^{f} are ranked in the order DMP/TP/soybean oil (7/2/1) < DMP/DOS(7/3) < DMP/DBS(5/5) < DMP/DOA(5/5) < DMP/DOP(5/5) < DBP/DBS(4/6). This indicates that the need of supercooling degree or driving force is ranked in the inverse order. On the other hand, the difference between the onset and peak crystallization temperature, and half-crystallization times ($t_{1/2}$), which both related to the overall crystallization rate,³⁶ are listed

in Table V. The close values of ΔT_c and $t_{1/2}$ obtained from all of the mixed diluents indicate the approaching crystallization rate of PVDF in these systems. However, the value ΔH_c of each sample has a small change. Therefore, the crystallization temperature of PVDF can be affected by changing the composition of each component in the mixed diluents, as demonstrated by the previous work.^{17,45} Thus, the S-L phase separation boundary can be controlled by using the mixed diluents.

Figure 6 shows the melting traces of PVDF blend/mixed diluent systems after cooling from the melt. The results, similar to in PVDF blend/single diluent systems, are obtained. The melting point depression is occurred in these systems, in comparison with PVDF blend in which no diluent is added. The melting peak temperature in different diluents ranks DMP/TP/Soybean oil (7/2/1) < DMP/DOS(7/3) < DMP/DBS(5/5) < DMP/DOA(5/5) < DMP/DOP(5/5) < DBP/DBS(4/6). The quantitative values of T_m^{on} , T_m^{p} , and T_m^{f} are listed in Table VI. The melting point depression phenomenon is attributed to the changes in the strength of intermolecular interactions of the mixtures.^{33,40} The higher this interaction exists, the more the melting point will be depressed. Therefore, the interaction between polymer and diluent in PVDF blend/DMP/TP/soybean oil (7/2/1) system is the highest, while that in PVDF blend/DBP/DBS(4/6) system is the lowest.

Additionally, the double melting peaks are observed in each sample, which due to the different degrees of perfection of PVDF crystals, as discussed in PVDF blend/single diluent systems. The small or imperfect crystals melt first and some large or perfect crystals melt at higher temperature during the heating process. It is observed that when DBP/DBS(4/6) mixed diluent is applied, the double melting peak is less obvious than others. It indicates that the more perfect PVDF crystals are formed in this sample than those formed in other mixed diluents. As mentioned in "Conclusion", in PVDF blend/BP system, only one melting peak is observed, which means perfect crystals are formed (Fig. 2).

TABLE V
DSC Crystallization Results of PVDF Blend/Mixed Diluent Systems when Cooling from the Melt After Removing the Thermal History

Samples with various mixed diluents	T_c^{on} (°C)	T_c^{p} (°C)	T_c^{f} (°C)	ΔT_c (°C)	ΔH_c (J/g)	$t_{1/2}$ (min)
DMP/TP/soybean oil (7/2/1)	72.2	68.4	62.6	3.8	9.85	0.70
DMP/DOS (7/3)	91.9	88.3	83.5	3.6	11.59	0.60
DMP/DBS (5/5)	95.5	92.4	87.5	3.1	10.68	0.58
DMP/DOA (5/5)	99.2	95.5	90.5	3.7	11.65	0.60
DMP/DOP (5/5)	100.0	96.5	91.8	3.5	13.27	0.58
DBP/DBS (4/6)	114.2	110.2	104.6	4.0	11.61	0.65

T_c^{on} , onset crystallization temperature of PVDF; T_c^{p} , peak crystallization temperature of PVDF; T_c^{f} , final crystallization temperature of PVDF; $\Delta T_c = T_c^{\text{on}} - T_c^{\text{p}}$; ΔH_c , crystallization enthalpy of PVDF.

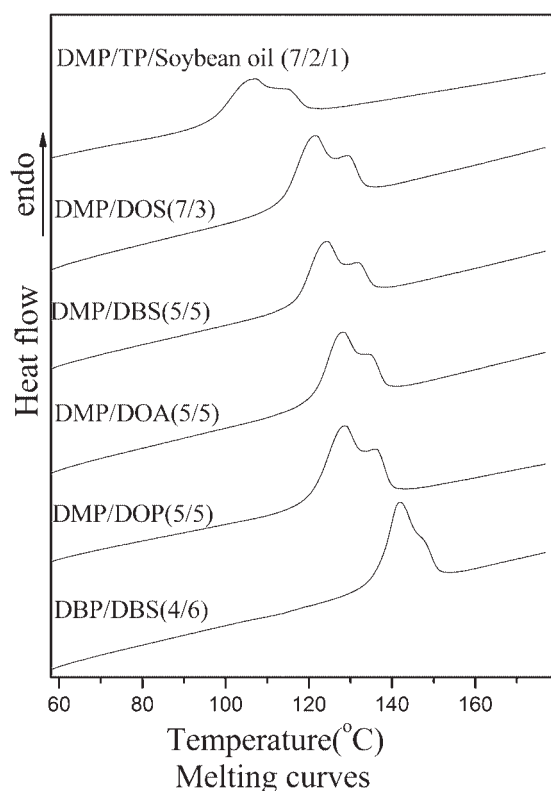


Figure 6 DSC melting curves of PVDF blend/mixed diluent systems during melting, after the cooling process.

In Table VI, the values of ΔT_m ($\Delta T_m = T_m^f - T_m^{on}$), the melting enthalpy ΔH_m , and the calculated crystallinity of PVDF are illustrated. As discussed above, the difference in value ΔT_m indicates that the different PVDF crystal size may be formed in different diluents. The PVDF blend/DMP/TP/Soybean oil (7/2/1) system has the greatest value ΔT_m , which indicates the most inhomogeneity in PVDF crystals size. In this system, the melting temperatures of PVDF depresses most deeply in these mixed diluent system, suggesting the strongest interactions between molecules in DMP/TP/Soybean oil (7/2/1) diluted system.^{33,47} So the retardance to PVDF crystallization is most predominant, resulting in the

widest range of PVDF crystal size. The four systems, in which DMP/DOS(7/3), DMP/DBS(5/5), DMP/DOA(5/5), and DMP/DOP(5/5) are used as the diluents, have the smaller values of ΔT_m (18°C–20°C) than the DMP/TP/soybean oil (7/2/1) sample (24°C). This implies that more homogeneous PVDF crystals are formed in these four samples. With regard to DBP/DBS(4/6) sample, the smallest value of ΔT_m (15°C) is obtained, suggesting that most homogeneous PVDF crystals are formed. The crystallinity of these six samples fluctuates with the different types of the mixed diluents in the smaller range (58%–64%) than those obtained in the PVDF blend/single diluent systems (52%–82%). To some extent, this may be due to the difference in the molecule interactions between PVDF and diluent.

Compared with the DSC results of PVDF blend/DMP system, the melting and crystallization temperatures are decreased in PVDF blend/mixed diluent (containing DMP), and other data also changed more or less. This confirms that the melting behaviors of PVDF blend can be controlled by changing the mixed diluent (including diluent type and composition of each component).

Figure 7 shows the cross sections of 25 wt % PVDF blend membranes in PVDF blend/mixed diluent systems quenched from 180°C to 30°C. The spherulitic structure is more discernable in DMP/TP/soybean oil (7/2/1), DMP/DOS (7/3), and DMP/DBS (5/5) quenched samples than that in the other three samples. This is due to the better compatibility of PVDF blend with these three mixed diluents, in which these systems have stronger interactions between polymer chains and diluent molecules.⁹ In these three systems, more dramatically S-L phase separation occurs and the interspherulitic voids are obvious, because of the kinetics of crystallization and diluent rejection from the growing crystal.^{1,14} As PVDF crystallized, the diluents are rejected from the spherulitic regions and form the interspherulitic voids (the region between spherulites). The lack of discernible spherulites in the DMP/DOA (5/5), DMP/DOP (5/5), and DBP/DBS

TABLE VI
DSC Melting Results of PVDF Blend/Mixed Diluent Systems During Melting After the Cooling Process

Samples with various mixed diluents	T_m^{on} (°C)	T_m^p (°C)	T_m^f (°C)	ΔT_m (°C)	ΔH_m (J/g)	X_c (%)
DMP/TP/soybean oil (7/2/1)	95.8	106.1	119.8	24.0	10.24	56.0
DMP/DOS (7/3)	113.2	121.2	133.4	20.2	11.53	63.0
DMP/DBS (5/5)	116.7	123.9	135.8	19.1	10.59	57.9
DMP/DOA (5/5)	120.9	127.8	138.7	17.8	11.56	63.2
DMP/DOP (5/5)	120.7	128.3	139.9	19.2	13.07	71.5
DBP/DBS (4/6)	136.2	141.7	151.3	15.1	11.66	63.8

T_m^{on} , onset melting temperature of PVDF; T_m^p , peak melting temperature of PVDF; T_m^f , final melting temperature of PVDF; $\Delta T_m = T_m^f - T_m^{on}$; ΔH_m , melting enthalpy; X_c , crystallinity of PVDF.

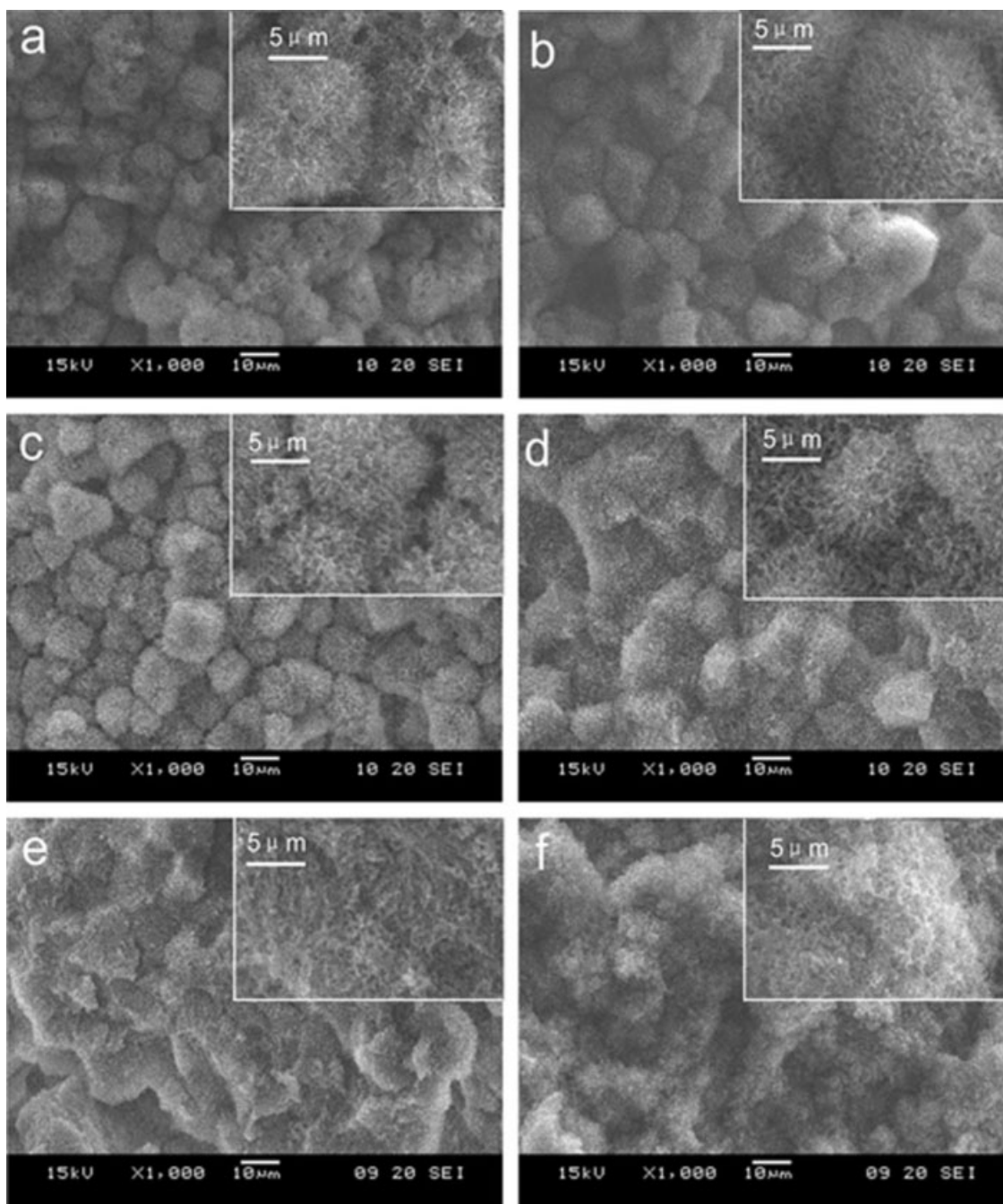


Figure 7 SEM micrographs of cross-sections of 25 wt % PVDF blend membranes from the mixed diluent systems quenched from 180 to 30°C: a-DMP/TP/Soybean oil (7/2/1); b-DMP/DOS (7/3); c-DMP/DBS (5/5); d-DMP/DOA (5/5); e-DMP/DOP (5/5); f-DBP/DBS (4/6).

(4/6) quenched samples is related to the L-L phase separation before the crystallization of PVDF, during which the phase separation restricts subsequent PVDF crystallization to small isolated domains of limited PVDF supply and limited growing space.³ This result is in agreement with that obtained in PVDF blend/single diluent system.

The porosity of PVDF blend/mixed diluent systems is shown in Figure 8. They are very close, which range from 76% to 79%. Compared with the

values obtained in PVDF blend/single diluent systems, the mixed diluent with proper ratio of each component can be used to prepare PVDF blend membrane with higher porosity.

CONCLUSIONS

This study reported that the different diluent types had a remarkable effect on PVDF crystallization behaviors and the resulting membrane structures.

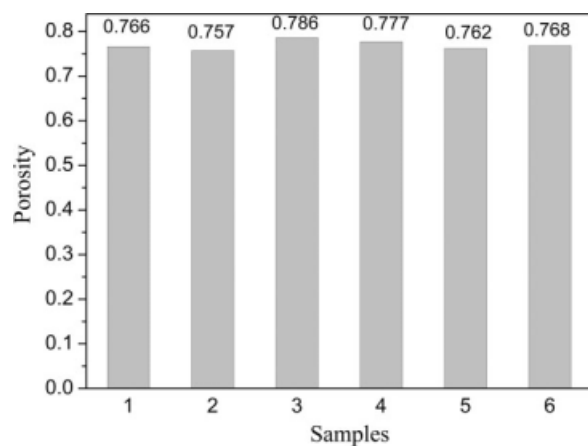


Figure 8 Porosity of PVDF blend/mixed diluent systems with 25 wt % PVDF blend: 1-DMP/TP/soybean oil (7/2/1); 2-DMP/DOS (7/3); 3-DMP/DBS (5/5); 4-DMP/DOA (5/5); 5-DMP/DOP (5/5); 6-DBP/DBS (4/6).

The melting and crystallization temperatures of those PVDF blend/diluent systems were depressed with the enhanced interactions between polymer chains and diluent molecules. The crystallinity of PVDF in the diluent systems was always higher than that obtained in PVDF blend sample. This can be explained by the various dilution effects, which increased the average spatial separation distances between crystallizable chains. Thus, the PVDF crystallization was favored. Additionally, S-L phase separation occurred in the quenched samples. The cross-section of the membranes illustrated the inter- and intraspherulitic voids, depending on the polymer/diluent interactions, the kinetics of crystallization, and diluent rejection from the growing crystal. The porosity of the PVDF blend membranes for the mixed diluent system was higher than those obtained in the single diluent systems.

It also revealed that the crystallization behavior and membrane structure could be efficiently controlled by changing the composition of the mixed diluent.

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References

- Lloyd, D. R.; Kinzer, K. E.; Tseng, H. S. *J Memb Sci* 1990, 52, 239.
- Lloyd, D. R.; Kim, S. S.; Kinzer, K. E. *J Memb Sci* 1991, 64, 1.
- Kim, S. S.; Lloyd, D. R. *J Membr Sci* 1991, 64, 13.
- Kim, S. S.; Lim, G. B. A.; Alwattari, A. A.; Wang, Y. F.; Lloyd, D. R. *J Membr Sci* 1991, 64, 41.
- Lim, G. B. A.; Kim, S. S.; Ye, Q. H.; Wang, Y. F.; Lloyd, D. R. *J Membr Sci* 1991, 64, 31.
- Alwattari, A. A.; Lloyd, D. R. *J Membr Sci* 1991, 64, 55.
- McGuire, K. S.; Lloyd, D. R.; Lim, G. B. A. *J Membr Sci* 1993, 79, 27.
- Tao, H.; Zhang, J.; Wang, X.; Gao, J. *J Polym Sci Part B: Polym Phys* 2007, 45, 153.
- Gu, M.; Zhang, J.; Wang, X.; Tao, H. *Desalination* 2006, 192, 160.
- Lee, J. S.; Lee, H. K.; Kim, J. Y.; Hyon, S. H.; Kim, S. C. *J Appl Polym Sci* 2003, 88, 2224.
- Kim, S. S.; Lloyd, D. R. *Polymer* 1992, 33, 1026.
- Kim, S. S.; Lloyd, D. R. *Polymer* 1992, 33, 1036.
- Kim, S. S.; Lloyd, D. R. *Polymer* 1992, 33, 1047.
- Lee, H. K.; Myerson, A. S.; Levon, K. *Macromolecules* 1992, 25, 4002.
- Zha, L.; Hu, W. *J Phys Chem B* 2007, 111, 11373.
- Seiler, D. A., Ed. *Modern Fluoropolymers*; Wiley: Chichester, 1997; p 487.
- Su, Y.; Chen, C. X.; Li, Y. G.; Li, J. D. *J Macromol Sci Part A: Pure Appl Chem* 2007, 44, 305.
- Su, Y.; Chen, C. X.; Li, Y. G.; Li, J. D. *J Macromol Sci Part A: Pure Appl Chem* 2007, 44, 99.
- Gu, M.; Zhang, J.; Xia, Y.; Wang, X. *J Macromol Sci Part B: Phys* 2008, 47, 180.
- Gu, M.; Zhang, J.; Wang, X.; Ma, W. *J Appl Polym Sci* 2006, 102, 3714.
- Chen, Y. W.; Liu, D. M.; Zhang, N. *Surf Rev Lett* 2005, 12, 709.
- Hietala, S.; Skou, E.; Sundholm, F. *Polymer* 1999, 40, 5567.
- Zhai, G. Q.; Toh, S. C.; Tan, W. L.; Kang, E. T.; Neoh, K. G. *Langmuir* 2003, 19, 7030.
- Nunes, S. P.; Peinemann, K. V. *J Membr Sci* 1992, 73, 25.
- Ochoa, N. A.; Masuelli, M.; Marchese, J. *J Membr Sci* 2003, 226, 203.
- Ma, W.; Zhang, J.; Wang, X.; Wang, S. *Appl Surf Sci* 2007, 253, 8377.
- Lin, S. C.; Argasinski, K. In: *Fluoropolymers 2 Properties*; Hougham, G.; Cassidy, P. E.; Johns, K.; Davidson, T., Eds.; Plenum Press: New York, 1999; pp 121-136.
- Nakawa, K.; Ishida, Y. *J Polym Sci: Polym Phys Ed* 1973, 11, 2153.
- Long, Y.; Shanks, R. A.; Stachurski, Z. H. *Polymer* 1995, 20, 651.
- Luo, F.; Zhang, J.; Wang, X. L.; Chen, J. F.; Xu, Z. Z. *Acta Polym Sin* 2002, 566.
- Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; Wiley: New York, 1999.
- Alfonso, G. C.; Turturro, A.; Pizzoli, M.; Scandola, M.; Ceccorulli, G. *J Polym Sci Part B: Polym Phys* 1989, 27, 1195.
- Nishi, T.; Wang, T. T. *Macromolecules* 1975, 8, 909.
- Sasaki, H.; Bala, P. K.; Yoshida, H.; Ito, E., *Polymer* 1995, 36, 4805.
- Roerdink, E.; Challa, G. *Polymer* 1978, 19, 173.
- Lim, G. B. A.; Lloyd, D. R., *Polym Eng Sci* 1993, 33, 529.
- Beck, H. N.; Ledbetter, H. D. *J Appl Polym Sci* 1965, 9, 2131.
- Pillin, I.; Pimbert, S.; Levesque, G. *Polym Eng Sci* 2002, 42, 2193.
- Wang, J.; Dou, Q.; Wu, S.; Chen, X., *Polym Eng Sci* 2007, 47, 889.
- Wang, T. T.; Nishi, T. *Macromolecules* 1977, 10, 421.
- Gregorio, J. R.; Nociti, N. C. P. S. *J Phys D: Appl Phys* 1995, 28, 432.
- Marega, C.; Marigo, A. *Eur Polym J* 2003, 39, 1713.
- Alamo, R.; Mandelkern, L. *J Polym Sci Part B: Polym Phys* 1986, 2087, 24.
- Vadalia, H. C.; Lee, H. K.; Myerson, A. S.; Levon, K. *J Membr Sci* 1994, 89, 37.
- Tao, H.; Zhang, J.; Wang, X. *J Appl Polym Sci* 2008, 108, 1348.
- Ji, G. L.; Du, C. H.; Zhu, B. K.; Xu, Y. Y. *J Appl Polym Sci* 2007, 105, 1496.
- Wang, Y. D.; Cakmak, M. *J Appl Polym Sci* 1998, 68, 909.