

Effects of Mixed Diluent Compositions on Poly(vinylidene fluoride) Membrane Morphology in a Thermally Induced Phase-Separation Process

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ABSTRACT: The effects of a mixed diluent (MD) composition [dibutyl phthalate/dioctyl phthalate (DOP)] on poly(vinylidene fluoride) (PVDF) membrane morphology were investigated with scanning electron microscopy, and a bicontinuous morphology could be obtained with MD in a thermally induced phase-separation process. The reasons for the morphology formation were explained according to the effect of MD on the phase diagrams. In addition, the effects of the PVDF concentration on the membrane mor-

phology were examined. For the system with less DOP, the large spherulite morphology was obvious under all investigated concentrations, whereas no large spherulite structure existed in the membrane as the DOP content increased to concentrations other than 20%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3630–3637, 2008

Key words: membranes; morphology; poly(vinylidene fluoride); thermally induced phase separation

INTRODUCTION

More and more attention is being paid to poly(vinylidene fluoride) (PVDF) membranes by thermally induced phase separation (TIPS)^{1–9} because of their excellent physical and chemical properties. Lloyd et al.¹ and Hiatt and Vitzthum² prepared PVDF membranes with a diluent of dibutyl phthalate (DBP), cyclohexane, butyroacetone, and propylene, and the membranes presented a spherulitic structure. Gu and coworkers^{3,4} investigated the membrane structure and crystallization behaviors of PVDF; the morphology of the membranes was also spherulitic. Some patents^{5–8} have reported methods of PVDF membrane formation. A three-dimensional network structure membrane was produced by the addition of inorganic fillers to the TIPS process.⁶ Nucleating agents were used to produce a PVDF membrane with a more uniform microstructure.⁸ In addition, we have prepared a PVDF membrane with a uniform structure.⁹ However, a large amount of CaCO₃ filler is necessary, and this influences other properties of the membrane.

In the TIPS process, the diluent is a very important factor for controlling the membrane morphol-

ogy, which directly influences the thermodynamic properties of a polymer/diluent system, such as the binodal line and crystallization temperature (CT), and significantly influences the final membrane structure.^{10,11} However, for PVDF, it is very difficult to select a single diluent for preparing a membrane with a uniform porous structure. A mixed diluent (MD) was used to prepare polyethylene and polypropylene membranes in which the advantage of MD was indicated.^{12,13}

To obtain a PVDF membrane with a uniform porous morphology, an MD of DBP (good diluent) and dioctyl phthalate (DOP; poor diluent) was adopted. The effects of the MD composition on the membrane morphology were investigated with scanning electron microscopy (SEM). The dynamic phase diagrams of the PVDF/MD system were obtained from the measurement of the CT and cloud point with a differential scanning calorimeter and a hot stage.

EXPERIMENTAL

Materials

PVDF (Solef 1010; melt flow index = 2 at 2.16 kg) was supplied by Solvay (Tavaux, France). Both DBP (density = 1.046 g/cm³; boiling point = 340°C) and DOP (density = 0.985 g/cm³; boiling point = 370°C) were analytical reagents bought from Tianjin Yongda Chemical Reagent Co. (Tianjin Chemical Solvent Factory, Tianjin, China). The ethanol was an industrial product.

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Preparation of the blend materials and membranes

PVDF/MD pseudobinary blend materials were prepared via these steps: a definite ratio of MD to PVDF (all PVDF concentrations are weight percentages in this article) was weighed into a test tube with a total sample weight of 10 g, purged with nitrogen, and melted at 220°C for about 12 h. In the melting period, the blends were periodically agitated manually to form a homogeneous solution and then quenched in a 20°C water bath to be solidified, and the blend materials were used for cloud-point measurements, differential scanning calorimetry (DSC), and the preparation of membranes.

The blend materials were sliced into small pieces, placed between two microscope glass slips with interspaces produced by brass wires (diameter = 0.2 mm), and sealed with vacuum grease, and then they were clipped by two alloyed plates (thickness = 0.5 mm) and melted at 220°C for 30 min to remove the thermal history. They were solidified by quenching in a 20°C water bath. As a result, the membranes were obtained.

MD1–MD4 were prepared through the mixing of DBP and DOP in ratios of 9/1, 7/3, 5/5, and 4/6, respectively.

Cloud point and CT

The blend material was placed between a pair of microscope cover slips. To prevent MD volatilization, Teflon films (thickness = 120 μm) with a small opening and vacuum grease were inserted between the cover slips. The sample was heated on a Linkam LK-600PH hot stage at 220°C for 5 min and cooled to room temperature at a 10°C/min cooling rate. Cloud points were determined visually by the appearance of turbidity via an Olympus BX50 optical microscope (Tokyo, Japan); each sample was observed three times, and the average was shown.

DSC (DSC-7, PerkinElmer, Wellesley, MA) was used to determine the dynamic CT for the phase diagram. About 10 mg of the blend material was sealed in an aluminum DSC pan, melted, and kept at 220°C for 5 min to ensure complete melting; it was then cooled at 10°C/min to room temperature. The onset of the exothermic peak was taken as the CT.

To investigate the crystallization behavior of a membrane sample, the ascending DSC was also obtained at a 10°C/min heating rate. The melt heat (ΔH_m) was determined from the melting peak area. The crystallinity was evaluated as follows:

$$\Phi_{\text{DSC}} = \Delta H_m / \Delta H_{100}$$

where Φ_{DSC} is crystallinity and $\Delta H_{100} = 104.7$ J/g is the melting heat for a 100% crystalline sample of PVDF.¹⁴

Morphology characterization of the PVDF membrane

MD was extracted by ethanol, and the membranes were dried naturally and fractured in liquid nitrogen. The surface and cross-sectional morphologies of the membranes were coated with gold and observed with SEM (Quanta 200, GG Eindhoven, Netherlands FEI).

Wide-angle X-ray diffraction (WAXD)

The WAXD patterns of representative samples were recorded with a Bruker (Madison, WI) AXS D8 Discover apparatus with a general area detector diffraction system for investigating the polymorphism of PVDF crystals. Cu K α radiation ($\lambda = 1.5418$ Å) was employed.

RESULTS AND DISCUSSION

Effect of the MD composition on the phase diagram

The effects of the MD composition on the phase diagram are shown in Figure 1. The area between the CT and cloud-point temperature increases gradually in the order of MD1, MD2, MD3, and MD4 (the cloud point of the MD1 system is not shown because it cannot be distinguished from the CT). In other

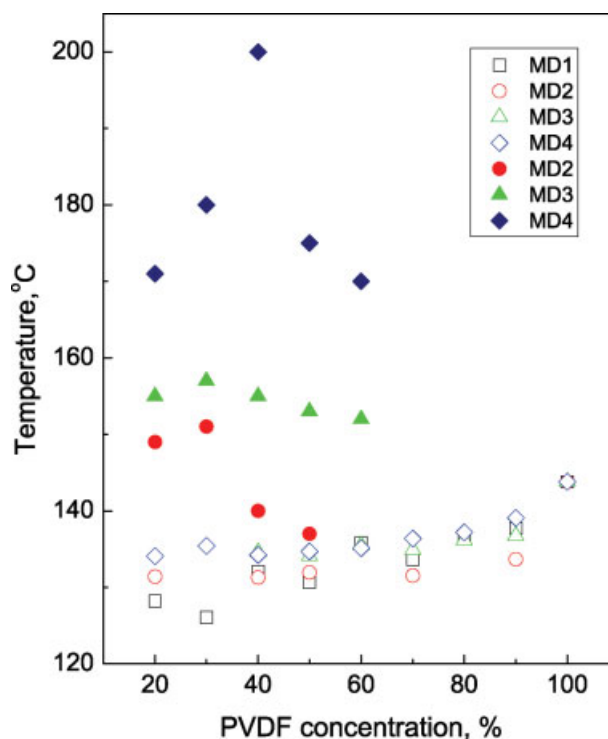


Figure 1 Phase diagram of the PVDF/MD system. Hollow symbols show CT; solid symbols show the cloud point. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

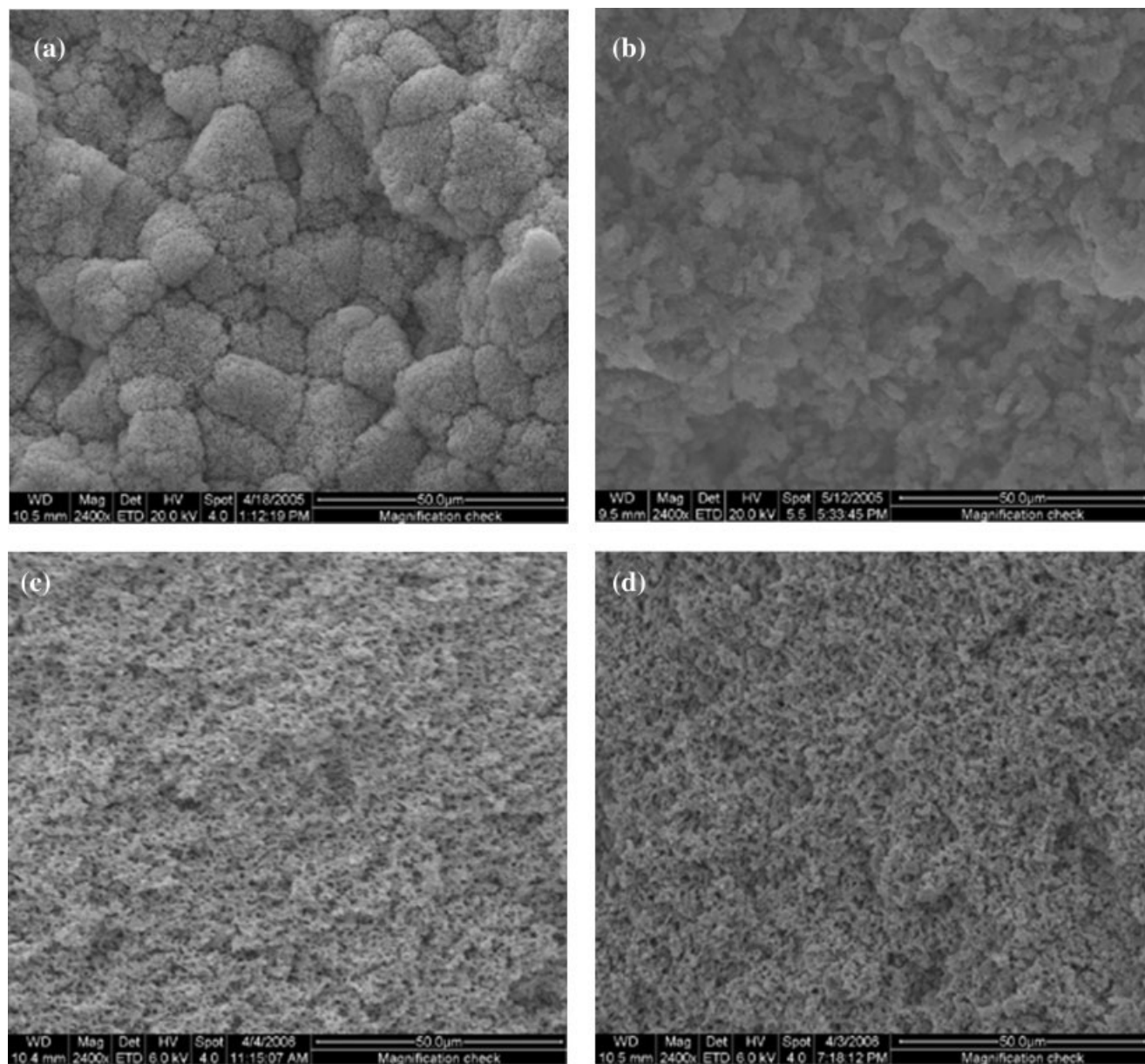


Figure 2 Effect of the MD composition on the membrane morphology: (a) MD1, (b) MD2, (c) MD3, and (d) MD4 (PVDF concentration = 30%).

words, the cloud-point curve appears and shifts to a higher temperature with the DOP content increasing, whereas the CT changes slightly. The PVDF/MD4 system, which contains the largest amount of DOP, shows the highest cloud-point temperature. This result also suggests that liquid–liquid (L–L) phase separation can take place as a specific amount of DOP is added; however, for the pure DBP system, only solid–liquid (S–L) phase separation occurs.^{1,9}

The changes in the cloud points and phase-separation mechanism can be explained by the system's miscibility. The major factor determining whether S–L or L–L phase separation occurs is the miscibility of

the polymer/diluent system.¹⁰ If there is strong polymer/diluent interaction, the mixture undergoes S–L phase separation when cooled. If there is a weak interaction, the blend undergoes L–L phase separation when cooled.¹⁵

The miscibility becomes lower as the DOP content increases, the lower miscibility brings about the increase in the cloud-point temperature, and then the binodal line shifts to a higher temperature, whereas the CT is less influenced in contrast to the cloud-point temperature. This means that the region between the binodal line and CT becomes wider as the DOP content increases. This result agrees

approximately with the shape of the hypothetical phase diagram in which only interaction parameter χ changes.¹⁵

Effect of the MD composition on the membrane morphology

The cross-sectional morphologies of the membranes are shown in Figure 2. For the MD1 system, the large spherulite morphology represents the membrane body. For the MD2 system [Fig. 2(b)], the spherulitic morphology becomes indiscernible at the same magnification, although the small particle can be discerned at a high magnification. It is a pleasure to find that the membrane changes into a uniform porous morphology when the DOP content increases further [Fig. 2(c,d)]; this structure can be named a bicontinuous morphology. High-magnification SEM shows that the bicontinuous structure is composed of crystallites. The reason for the formation of the membrane morphology depends on the thermodynamics and dynamics of the phase separation. Here, the morphology change should be attributed mainly to the phase-separation mechanism.

Phase-separation mechanisms have been widely discussed for semicrystalline polymer/diluent systems.^{15–17} In all cases, the solution system proceeds via S–L or L–L phase separation when cooled. S–L phase separation usually leads to a spherulitic structure, and L–L phase separation is more complex; usually, there are two phase-separation mechanisms: nucleation and growth (between the binodal and the spinodal) or spinodal decomposition (below the spinodal).

Figure 1 shows that the cloud point is adjacent to CT, which increases linearly with the PVDF concentration when the DOP content is low. This suggests that TIPS will occur by S–L phase separation via PVDF crystallization. Hence, the obvious spherulitic morphology is present.

As the DOP content increases, the PVDF/MD miscibility becomes low. L–L phase separation can occur. The system will experience a driving force for both L–L separation and PVDF crystallization while quenching to 20°C. That is, when L–L phase separation occurs, PVDF will nearly simultaneously crystallize rapidly in the polymer-rich phase, and the combination of L–L phase separation and crystallization will lead to the bicontinuous morphology. To confirm L–L phase separation in the MD3 system, a different cooling condition was adopted. At first, the solution films were put into a 145°C glycerin bath, kept there for 1 min, and then quenched at 20°C. The membrane morphology is shown in Figure 3. The circular pore and leafy structure present in the membrane can be seen.

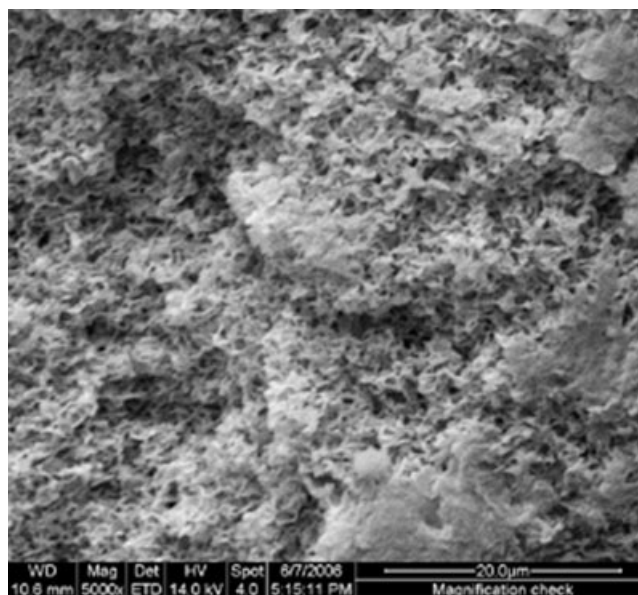


Figure 3 Morphology of a membrane under a different cooling condition (PVDF concentration = 30%).

Effect of the PVDF concentration on the membrane morphology

Figure 4 shows the morphology of the membrane from MD1 with different PVDF concentrations quenched at 20°C. A clear spherulite is formed at all investigated concentrations (from 20 to 70%); the only differences brought by the concentration are in the spherulite size and packing density. The isolated spherulites become closer and even impinge on one another with the increase in the PVDF concentration, but the boundary around the spherulites is still quite distinct. A similar morphology was obtained from isotactic polypropylene by Lloyd et al.¹⁵ A comparison of Figure 5 with Figure 4 for the PVDF/MD2 system shows that the membrane morphology is obviously different. No large spherulite is found, and a nearly bicontinuous morphology is exhibited at all concentrations other than 20%, although many crystallites are discernable at a high magnification.

The change in the phase-separation mechanism accounts for the different membrane morphology. It can be seen from the phase diagram (Fig. 1) that, for the PVDF/MD1 system, crystallization will predominate in the TIPS process because of S–L phase separation, so a spherulitic morphology is formed. For the PVDF/MD2 system, L–L phase separation can occur before crystallization. Hence, as discussed previously, the isolated spherulitic structure is prevented, and a nearly bicontinuous structure is formed. For the 20% PVDF concentration, the membrane presents a particle morphology. This is perhaps related to the position of the phase diagram. When the concentration is lower than the upper

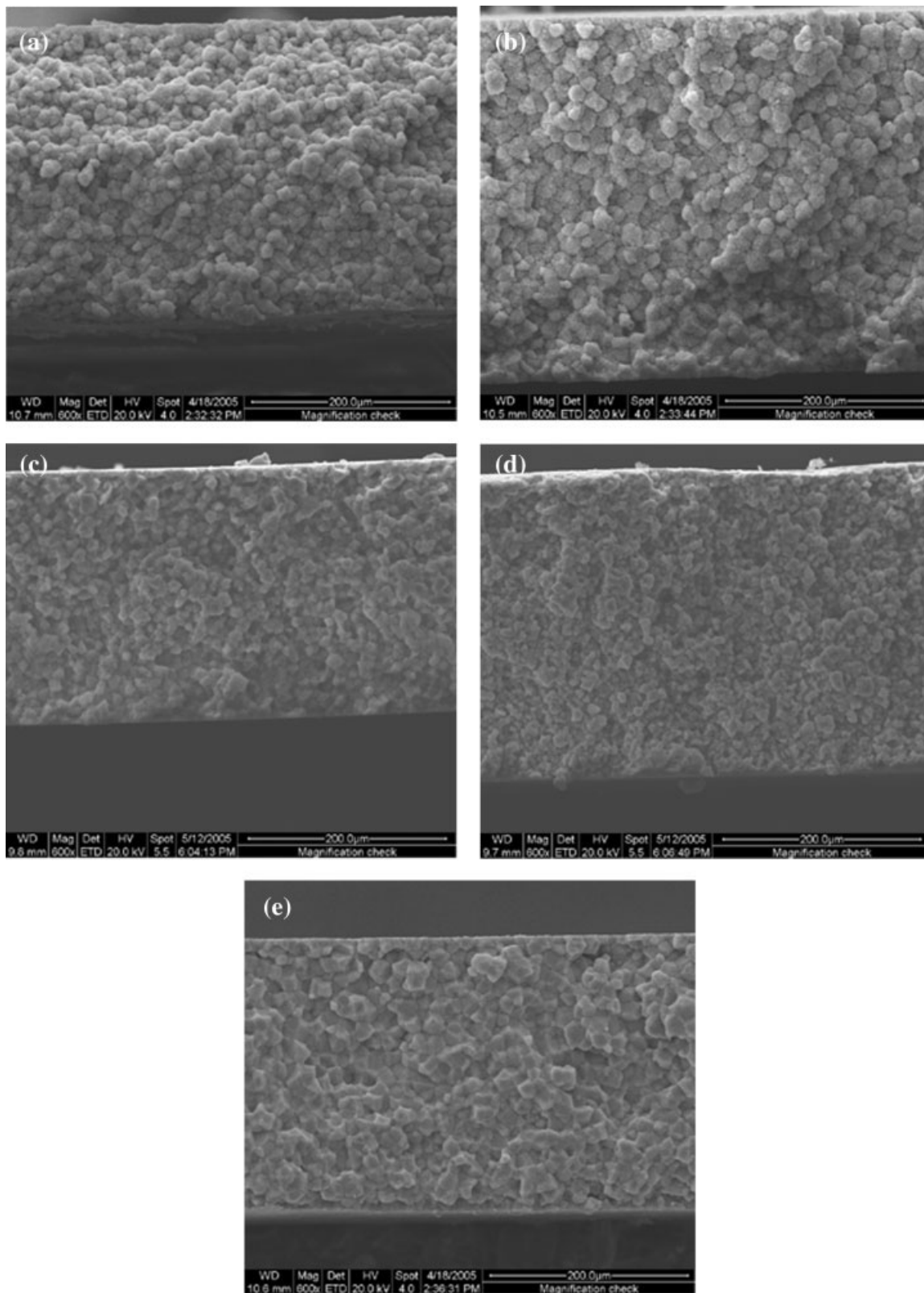


Figure 4 Cross-sectional morphology of membranes by the PVDF/MD1 system: (a) 20, (b) 30, (c) 40, (d) 50, and (e) 70% PVDF.

critical solution concentration, the solution will demix by nucleation and growth of a droplet of a polymer-rich phase,¹⁶ and this often will lead to

polymer particles. However, it has not been excluded that polymer particles might result from the L-L phase separation and further coarsening.¹⁸

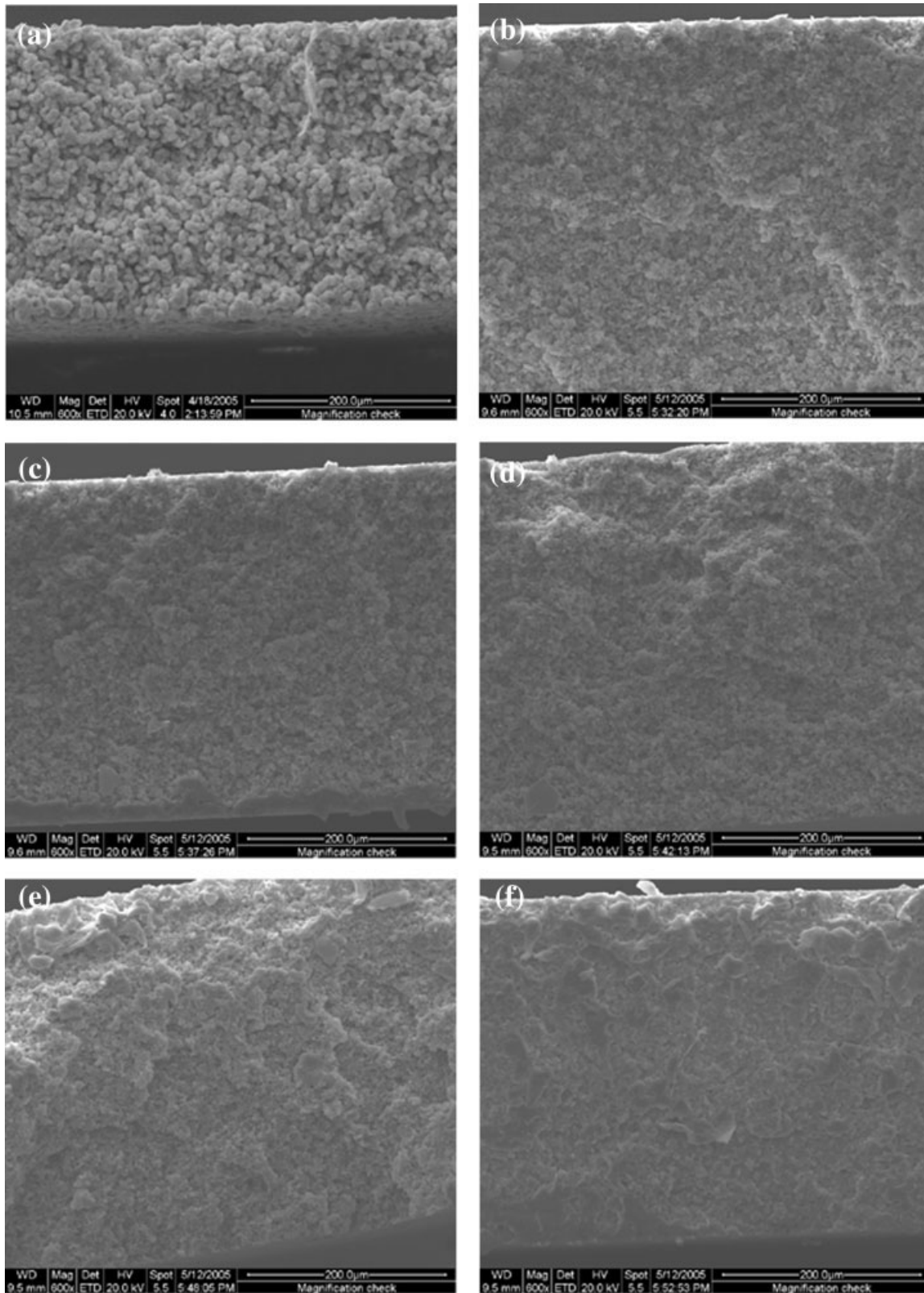


Figure 5 Cross-sectional morphology of membranes by the PVDF/MD2 system: (a) 20, (b) 30, (c) 40, (d) 50, (e) 70, and (f) 90% PVDF.

Effect of the MD composition on the crystallization behavior

DSC (Fig. 6) has been employed for investigating the crystallization behavior of the PVDF membrane, and it shows that multiple melt peaks are present for all three representative samples and that the height and temperature of the first peak (weak peak) increase as the DOP content increases. The multiple melting phenomenon of crystalline polymers has been reported in many publications,^{19,20} and its formation mechanism is complicated. The variation of the morphology, perfection of crystals, polymorphism, and recrystallization all can lead to a multiple melting phenomenon. Neidhöfer et al.²⁰ emphasized that secondary crystallization could result in a low-temperature peak.

WAXD (Fig. 7) shows that the peaks at 2θ values of 17.66, 18.30, 19.90, and 26.56°, corresponding to diffraction in the (100), (020), (110), and (021) planes, respectively, present all the characteristics of the α phase. This indicates that PVDF tends to form the α phase for MD2 and MD4 systems. The merge of the peaks at 2θ values of 17.66 and 18.30° and the deviation of the peak at 19.90° indicate the possibility of coexistence of the α and γ phases for the pure DBP diluent. However, the three WAXD patterns do not present a well-defined peak at $2\theta = 20.26^\circ$, which is the characteristic peak of the β phase. The latest studies²¹ showed that the crystallization of a PVDF solution always resulted exclusively in the β phase as long as the solvent was good. However, DBP and its mixture cannot be defined as good solvents, so no β phase appears in the membranes. Hence, the multiple melting peak of DSC cannot be attributed to polymorphism.

The combination of DSC curves and membrane morphology allows us to suppose that the double peak perhaps results from the different sizes of crys-

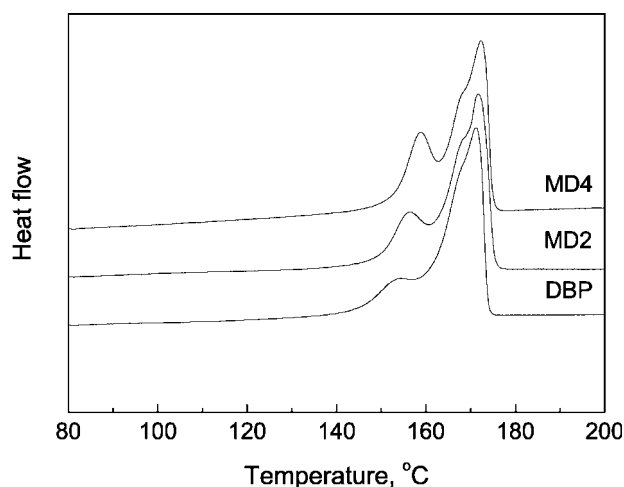


Figure 6 DSC curves of membranes from different MDs.

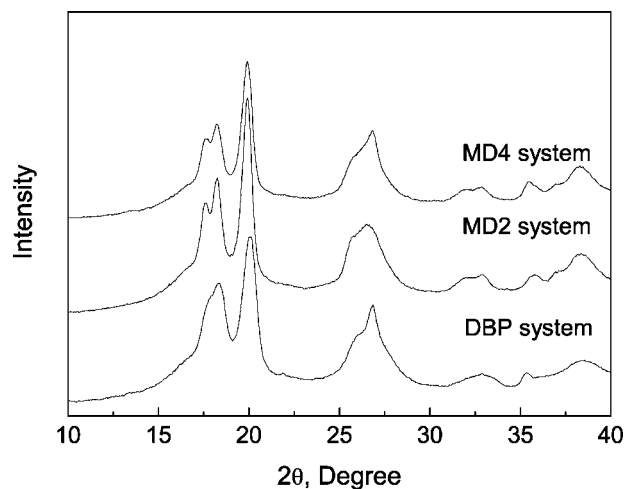


Figure 7 WAXD of membranes from different MDs.

tallites or perfection of crystals. It may be related to the membrane morphology, which needs further investigation.

The crystallinity of pure DBP, MD2, and MD4, calculated from the melting heat, is 64.89, 65.38, and 63.00%, respectively. The effect of the MD composition on PVDF crystallinity is not systematic.

CONCLUSIONS

Cloud-point curves appeared and shifted to higher temperatures with an increase in the DOP content in MD, and this means that L–L phase separation could occur via the adjustment of the MD composition. As a result, a bicontinuous morphology could be obtained from MD3 and MD4 systems when the PVDF concentration was 30%. For PVDF/MD1, the spherulite characterized the membrane morphology at all investigated concentrations, whereas a nearly bicontinuous structure presented in the membrane from the MD2 system at all concentrations other than 20%. DSC showed that the height and temperature of the weak peak increased as the DOP content increased. This may be related to the membrane morphology, which needs further investigation.

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