

EFFECT OF DILUENTS ON CRYSTALLIZATION OF POLY(VINYLIDENE FLUORIDE) AND PHASE SEPARATED STRUCTURE IN A TERNARY SYSTEM *via* THERMALLY INDUCED PHASE SEPARATION*

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Abstract The phase diagram of a ternary system of PVDF, dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) was determined in terms of a pseudo binary system with the same polymer concentration and different DBP content in diluent mixture. The experimental results showed that as the DBP content increased in diluent mixture, the phase separation changed from liquid-liquid phase separation to solid-liquid phase separation, and both the cloudy point for L-L phase separation and crystallization temperature shifted to lower temperature. Molar excess free energy of mixing ΔG^E implying the estimated interaction between PVDF and diluent mixture was characterized to explain the features in the phase diagram. The effects of DBP content in diluent mixture on crystallization behavior and phase separated structure were investigated. The crystallization of PVDF in system with L-L phase separation was perfect, but the crystallinity was lower relative to the system with only S-L phase separation. The phase separated structures can be controlled successfully by varying the DBP content in diluent mixture as the cooling conditions kept constant.

Keywords: Phase separation; Crystallization; Membrane; PVDF; Interaction.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) membranes have been widely used in organic/water separation^[1, 2], membrane distillation^[3, 4], ultrafiltration^[5], fabrication of ion exchange membranes and gel polymer electrolytes^[6, 7], due to its excellent chemical resistance, thermal stability and intrinsic hydrophobicity. In fact, PVDF membranes have been extensively investigated using dry/wet phase inversion processes by many investigators^[8–13]. But few studies have been reported on preparation of PVDF microporous membrane *via* thermally induced phase separation (TIPS) method^[14–16].

Thermally induced phase separation (TIPS) process is also a well known method for obtaining membranes with controlled morphology^[17, 18], and has several well-documented advantages including (1) greater flexibility and ease of control than the conventional casting process, (2) a very low tendency for defect formation, (3) morphology characterized by very high overall porosity and effective control of the final pore size^[17, 18]. In the TIPS process, homogeneous solution needs to be formed by the dissolution of a polymer in a diluent at high temperature, and phase separation is induced by the cooling of the polymer solution. When thermal energy is removed from a homogeneous polymer-diluent mixture, the TIPS can occur *via* solid-liquid (S-L) or liquid-liquid (L-L) phase separation depending on the polymer-diluent interaction, the composition and the thermal driving force.

In preparation of membranes *via* TIPS process, the selection of diluent plays an important role because it affects not only the kinetics of pore growth but also the crystallization behavior of the polymer. The effect of the

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diluent on the diluent mobility and crystallization temperature was examined for S-L phase separation by Kim^[19]. Matsuyama *et al.* also investigated the effect of diluents on the morphology of membranes for S-L phase separation in preparation of poly(ethylene-co-vinyl alcohol) membranes^[20]. In the case of L-L phase separation, the effects of interaction parameter of diluents on the phase diagram and the final phase separated structure were studied by Vadalia *et al.*^[21]. In their work, diluent mixtures were used in preparing microporous membranes by TIPS of a ternary solution of HDPE, ditrydecylphthalate and hexadecane. In addition, Shang *et al.* used 1,3-propanediol, glycerol and their mixture as diluents in the preparation of poly(ethylene-co-vinyl alcohol) hollow-fiber membranes *via* TIPS method and examined the evolution of membrane morphology with the diluents^[22]. However, little work has focused on the effect of diluents on the crystallization behavior of polymers for different phase separation behaviors (S-L and L-L phase separation).

In this study, PVDF is used along with mixtures of two diluents (dibutyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP)). The composition of the diluent mixture was varied to change the interaction between the polymer and the diluent, and to control the position of the cloudy point with respect to the crystallization temperature in phase diagram. Effects of diluents on the phase diagram, the crystallization of PVDF in the blend and the phase separated structures of blends were investigated. The information gained from this study will be useful for choosing the type of diluents in preparation of PVDF membranes *via* TIPS.

EXPERIMENTAL

Materials

The PVDF ($M_n = 59000$, $M_w/M_n = 2.88$) used in the study was provided by Solvay Solexis (1012) with an MFI of 1.5 g/10 min (230°C, 5 kg). DBP and DEHP, supplied by Guangdong Guanghua Chemical Regent Co., Ltd and Shanghai Chemical Reagent Co., Ltd, respectively, were used for preparing diluent mixtures without further purification. Since both DBP (b.p. 340°C) and DEHP (b.p. 386°C) have boiling points much higher than the melting point of PVDF (174°C), they were chosen to form diluent mixtures in preparing PVDF membranes *via* TIPS method. Density and Hansen solubility parameters for PVDF and diluents are listed in Table 1^[23].

Table 1. Density and Hansen solubility parameters for PVDF and diluents

Substance	Density (g/cm ³)	δ_d ((MPa) ^{1/2})	δ_p ((MPa) ^{1/2})	δ_h ((MPa) ^{1/2})
BP	1.045	17.8	8.6	4.1
DEHP	0.985	16.6	7	3.1
PVDF	1.78	17.2	12.5	9.2

Preparation of PVDF/DBP/DEHP Blend Samples

The diluent mixtures (DBP/DEHP) of known concentration were prepared beforehand. Since PVDF hardly dissolves in pure DEHP at higher temperature (240°C), the diluent mixtures with the ratio of DBP/DEHP over 27.5:72.5 (*W/W*), in which PVDF dissolves more quickly to form homogenous solution at 240°C, were chosen as the latent diluents for this study. PVDF and the diluents were mixed at an elevated temperature (240°C) under nitrogen atmosphere for at least 3 h in a glass vessel with a stirrer. Then the glass vessel was quenched in liquid nitrogen to solidify the sample and broken to obtain the solid polymer-diluent sample. Because it was difficult to cast films when the polymer concentration in the polymer-diluent solution is below 30 wt%, homogeneous samples of 30 wt% PVDF blend with diluent mixtures of various DBP ratios were prepared.

Determination of the Phase Diagram

The cloudy point (T_{cloud}), crystallization temperature (T_c) and melting temperature (T_m) were measured according to the method reported by Shang *et al.*^[22]. The sample was heated on a hot stage (Linkam THMS600) to a required temperature at 10 K/min and held for 1 min until forming homogenous solution. The solution then was cooled to 40°C at a certain rate of 10 K/min. T_{cloud} was determined visually by the appearance of turbidity under an optical microscope (Nikon eclipse E600 POL). The crystallization curve and melting curve were determined by a perkin-Elmer DSC-7. All DSC measurements were performed under the nitrogen atmosphere, and sample

weights varied from 4 mg to 7 mg. The solid sample was melted at 240°C for 5 min to erase thermal history and cooled to 40°C at 10 K/min and then heated to 240°C at 10 K/min again. The onset temperatures of the exothermic peak during cooling and the endothermic peak during heating were taken as the T_c and T_m , respectively.

Observation of the Phase Separation Structure

The structure evolution due to different phase separation was investigated by optical microscopy. The prepared sample was heated slowly to 240°C and held at that temperature for 1 min to ensure complete dissolution. Subsequently, the sample was cooled to a required temperature at 10 K/min to give rise to phase separation. The observation of the droplet growth for L-L phase separation and final crystal conformation in various samples was done under an optical microscope.

RESULTS AND DISCUSSION

Phase Diagram

Figure 1 shows the phase diagram of 30 wt% PVDF samples prepared with several diluent mixtures with different DBP ratios. As seen in Fig. 1, the T_{cloud} decreased significantly with the increased DBP content in the diluent mixture, while the T_c decreased slowly. When the DBP content in diluent mixtures increased and reached to 40/60 (W/W), L-L phase separation was no longer observed experimentally, and only the polymer crystallization process was present.

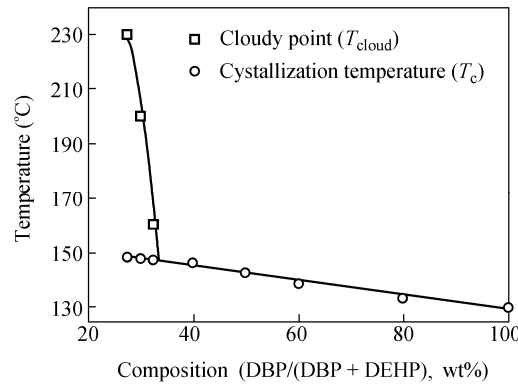


Fig. 1 Phase diagram of 30 wt% PVDF samples prepared with several diluent mixtures with different DBP content

The overall feature in Fig. 1 is analyzed in terms of the interaction between PVDF and the diluent mixture. The estimated interaction parameter χ^* , typically used to interpret the interaction between the polymer and the diluent, was estimated from the difference of the solubility parameters between the polymer and the diluent using the following expression^[24]:

$$\chi^* = \frac{V_m}{RT} ((\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2) \quad (1)$$

Where V_m is a reference volume which equals to the molar volume of the specific repeating unit size of the polymer, δ_d and δ_p are the dispersive and the polar term of the solubility parameter, respectively. δ_h is the hydrogen-bonding contribution to the solubility parameter, and 1 and 2 refer to the diluent and the polymer. By assuming that V_m is the same for every system, the interaction between PVDF and diluent for blends at a certain temperature and the same polymer concentration may be compared by molar excess free energy of mixing ΔG^E ^[23]:

$$\Delta G^E = ((\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2) \quad (2)$$

Smaller values of χ^* and ΔG^E present better interaction between PVDF and the diluent.

In order to validate the effect of interaction between polymer and mixed diluent on the phase diagram, four systems had been utilized (30/70, 32.5/67.5, 50/50 and 100/0 DBP/DEHP, *W/W*). Subsequently, the value of solubility parameter for mixed diluent can be calculated by using the following equation:

$$\delta_i = \delta_{i1}\Phi_1 + \delta_{i2}\Phi_2 \quad (3)$$

where Φ_1 is the volume fraction of one diluent, Φ_2 is the volume fraction of another diluent and *i* represents d, *p* and h. The values of solubility parameter for the four diluent mixtures, calculated by Eq. (3) using the data in Table 1, are listed in Table 2.

Table 2. The values of solubility parameter for four diluent mixtures

Diluent mixture (DBP/DEHP, <i>W/W</i>)	δ_d ((MPa) ^{1/2})	δ_p ((MPa) ^{1/2})	δ_h ((MPa) ^{1/2})
30/70	16.95	7.46	3.39
32.5/67.5	16.97	7.50	3.41
50/50	17.18	7.78	3.59
100/0	17.80	8.60	4.10

By solving Eq. (2) with the values of solubility parameter for PVDF and diluent mixtures in Table 1 and Table 2, ΔG^E can be determined as a function of the DBP content in diluent mixture as shown in Fig. 2. In Fig. 2, it showed that a plot of ΔG^E against the DBP content in diluent mixture gave a straight line. Simultaneously, it was clearly that the value of ΔG^E was decreasing proportionally with the increasing DBP content in the diluent mixture, which expressed that the increase of DBP content in diluent mixtures enhanced the interaction between polymer and diluent mixture. The change from the liquid-liquid phase separation to solid-liquid phase separation as shown in Fig. 1, owed to the increased interaction between polymer and diluent. On the other hand, T_{cloud} decreased sensitively than T_c with the interaction between polymer and diluent mixture increasing.

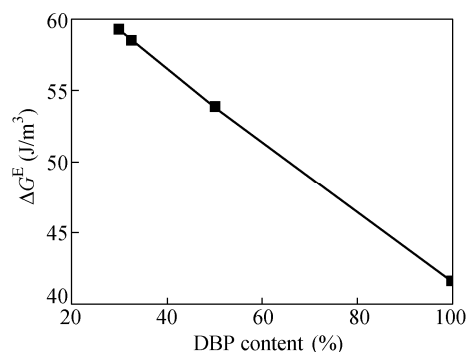


Fig. 2 Relation between DBP content in diluent mixture and molar excess free energy of mixing (ΔG^E)

Effect of Diluents on the Crystallization Behavior of PVDF in Blends

Figure 3 shows the typical DSC curves of heat flow as a function of temperature at 10 K/min cooling rate for different PVDF/DBP/DEHP blends.

The onset temperature of crystallization (T_c^o), the exothermic peak temperature (T_c^p) and the end temperature of crystallization (T_c^e) are determined from these curves, and the results have been shown in Table 3. It was clear that all the parameters namely T_c^o , T_c^p and T_c^e shifted to lower temperature with increasing the DBP content in diluent mixtures as seen in Table 3. These results were related to the enhanced interaction between PVDF and diluent mixture when the DBP content increased in diluent mixture. Stronger interaction between PVDF and diluent mixture prevented the formation of crystal nuclei of PVDF in the blend at primary crystallization.

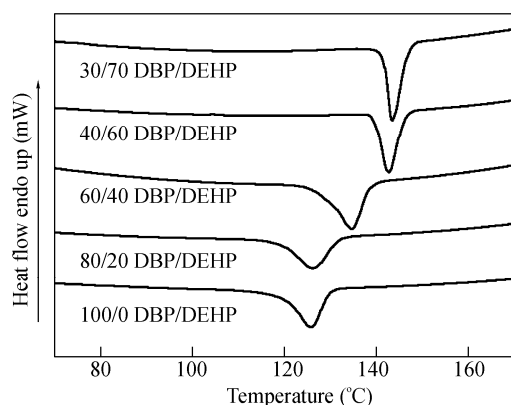


Fig. 3 DSC cooling curves of 30 wt% PVDF samples prepared with several diluent mixtures with different DBP content (DBP/DEHP, *W/W*) at 10 K/min cooling rate

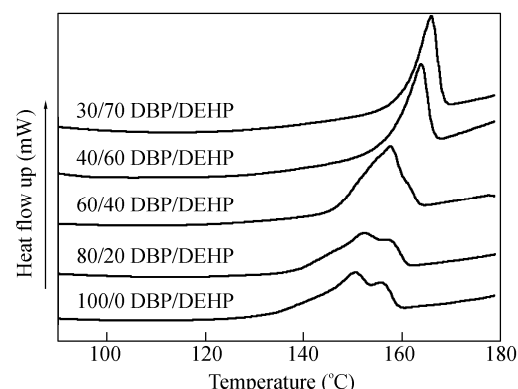


Fig. 4 DSC melting curves of 30 wt% PVDF samples prepared with several diluent mixtures with different DBP content (DBP/DEHP, *W/W*) at 10 K/min heating rate

Table 3. Effects of DBP/DEHP ratio on crystallization temperatures of PVDF in blends with different diluent mixture

Crystallization parameters (°C)	DBP/DEHP (30/70)	DBP/DEHP (40/60)	DBP/DEHP (60/40)	DBP/DEHP (80/20)	DBP/DEHP (100/0)
T_c^o	147.0	146.2	138.5	131.9	129.9
T_c^p	143.6	142.7	134.7	126.4	125.7
T_c^e	139.0	137.7	122.9	116.1	110.5

The melting curves of different PVDF/DBP/DEHP systems are shown in Fig. 4. It was found that the sharp melting-peak for 30/70 (*W/W*) DBP/DEHP system began to collapse as the DBP content increased in diluent mixture. When the DBP content increased to 80/20 (*W/W*) and 100/0 (*W/W*), a weakened shoulder-peak appeared instead of the sharp melting peak. This phenomenon implied that the secondary crystallization existed in the process of the crystallization of PVDF and enhanced by the increase of DBP in the diluent mixture. DBP exhibits stronger interaction with PVDF than DEHP. On the other hand, DBP possesses higher viscosity than DEHP (DBP 163 mPa·s (20°C) and DEHP 80 mPa·s (20°C)), so the viscosity of system increased with the DBP ratio increasing. These two factors lowered the mobility of polymer segments and prevented crystal nucleation as DBP content increased. As a result, the spherulite growth at the late stage of crystallization transformed into the two-dimensional or lamellar-like crystal growth, namely the secondary crystallization.

The melting temperatures for different systems determined from the melting curves were shown in Table 4. The peak temperatures of melting for 80/20 and 100/0 DBP/DEHP (*W/W*) samples, given in Table 4, were the melting temperatures corresponding to primary crystallization. All of the onset temperature of melting (T_m^o), the endothermic peak of melting (T_m^p) and the end temperature of melting (T_m^e) decreased as the DBP content increased in diluent mixture as shown in Table 4. The crystallinity of PVDF in various blends was calculated using the following equation:

$$X_c = \Delta H_f / \Delta H_f^0 \times 100\% \quad (4)$$

where X_c means the crystallinity of PVDF in PVDF/diluent mixture blends, ΔH_f represents the fusion enthalpy of PVDF in PVDF/diluent mixture blends which was determined from the endothermic peak area of DSC melting curve of blends. ΔH_f^0 was the fusion enthalpy of PVDF with 100% crystallinity which was previously reported as 105 J/g^[25]. The fusion enthalpy and the crystallinity of PVDF in blends with different diluent mixtures were listed in Table 4. PVDF in blends with different diluent mixtures showed the crystallinity varying from 15.0% to 18.5%. Although there was no obvious correlation between the crystallinity and the DBP content,

it is noticed that the crystallinity of PVDF in the system with 30/70 DBP/DEHP (*W/W*) is the lowest, but the crystallization is most perfect as shown in Fig. 4. This phenomenon was explained that the polymer-rich phase for L-L phase separation in this system contributed to the formation of perfect crystals, and polymer-lean phase contributed to the lower crystallinity.

Table 4. Effects of DBP/DEHP ratio on melting temperatures, fusion enthalpy and crystallinity of PVDF in blends with different diluent mixture

DBP/DEHP ratio (<i>W/W</i>)	T_m^o (°C)	T_m^p (°C)	T_m^e (°C)	ΔH_f (J/g)	X_c (%)
30/70	160.8	166.08	170.2	15.8	15.0
40/60	158.08	164.0	168.2	17.1	16.3
60/40	146.8	157.6	164.1	19.4	18.5
80/20	143.38	152.4	161.9	16.1	15.3
100/0	141.5	150.6	160.8	17.5	16.7

Effect of Diluent on Phase Separated Structure

As described in the experimental part, the phase separated structure for four systems was investigated under optical microscope. For the systems with diluent mixtures of 30/70 and 32.5/67.5 DBP/DEHP (*W/W*), the L-L phase separation was observed before crystallization. The whole process of phase separation for the system with 30/70 DBP/DEHP (*W/W*) was shown in Fig. 5. The observation revealed that liquid droplets started to nucleate and grow and finally were fixed in the spherulites of PVDF during cooling. In the case of the diluent mixture with 32.5/67.5 DBP/DEHP (*W/W*), visible droplets appeared in the cooling process, but could hardly be observed in the spherulites when PVDF completely crystallized at 100°C. It was interpreted that the binodal point was so closer to its T_c for the system with 32.5/67.5 DBP/DEHP (*W/W*) that the droplets did not have enough time to grow as shown in Fig. 1. The observation of small droplets was greatly disturbed by the appearance of PVDF crystallization. The size of spherulites was comparable for the systems with 30/70 and 32.5/67.5 DBP/DEHP (*W/W*) as shown in Fig. 6. The size of the spherulites was bigger for the system with less favorable interaction (30/70 DBP/DEHP, *W/W*). Since the binodal point was higher in case of a worse diluent, enough time for L-L phase separation was available in the 30/70 DBP/DEHP (*W/W*) system, resulting in a bigger size of liquid droplets under the identical thermal condition. Bigger liquid droplets contributed to higher polymer concentration in rich polymer region, which resulted in more perfect spherulites.

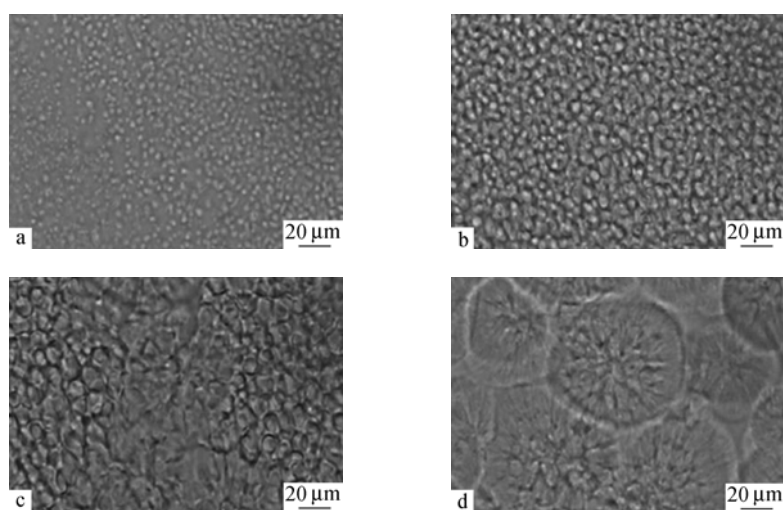


Fig. 5 The process of phase separation for PVDF/DBP/DEHP solution with 30 wt% PVDF and 30/70 DBP/DEHP (*W/W*)

a) 198°C; b) 170°C; c) 145°C; d) 135°C; Cooling rate: 10 K/min

On the other hand, the systems with 60/40 and 100/0 DBP/DEHP (*W/W*) showed no evidence for L-L phase separation and only spherulite growth during cooling. The size of spherulites grows bigger when the interaction of system enhanced as shown in Fig. 7. The stronger interaction prevents the nucleation activity of PVDF, which leads to the formation of fewer primary nuclei at the beginning of crystallization. In the systems with the same polymer concentration, less primary nuclei formation allows more nuclei growth. Thus bigger spherulites were observed.

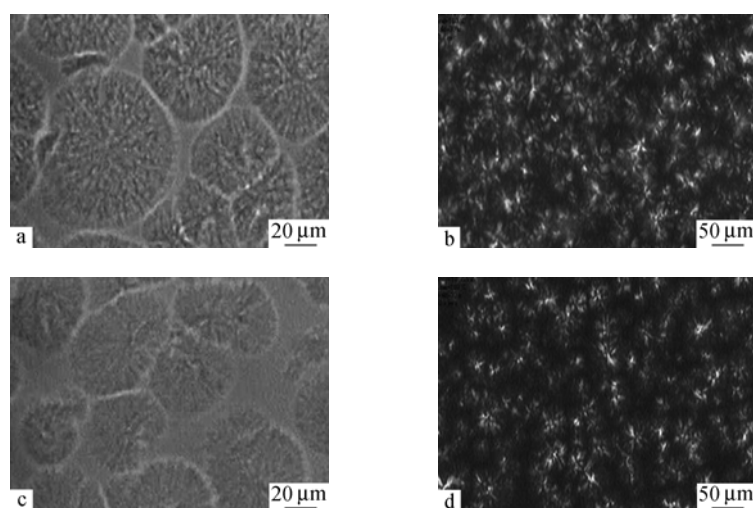


Fig. 6 (a) Micrograph and (b) polarized light micrograph for the system with 30/70 DBP/DEHP (*W/W*), (c) and (d) for the system with 32.5/67.5 DBP/DEHP (*W/W*)
Cooled to 100°C at 10 K/min

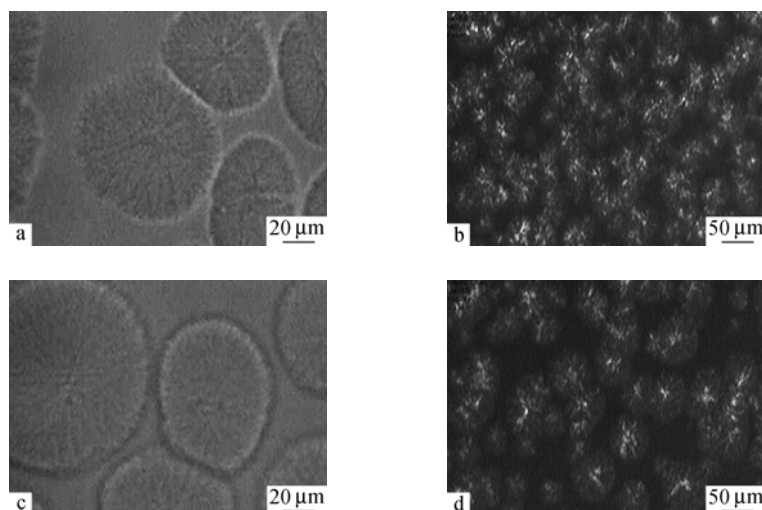


Fig. 7 (a) Micrograph and (b) polarized light micrograph for the system with 60/40 DBP/DEHP (*W/W*), (c) and (d) for the system with 100/0 DBP/DEHP (*W/W*)
Cooled to 100°C at 10 K/min

CONCLUSIONS

The phase behaviors of a ternary system of PVDF/DBP/DEHP and the crystallization of PVDF in blend were investigated by changing the composition of the two diluents. The phase diagram of blends with the same polymer concentration and different DBP contents in diluent mixture was determined by an optical microscope

and DSC. By changing the DBP content in diluent mixtures, we were able to successfully control the type of phase separation (liquid-liquid (L-L) phase separation or solid-liquid (S-L) phase separation).

The crystallization behavior of PVDF with different phase separation behavior was distinguishable. In the system with L-L phase separation, the crystallinity of PVDF in system with 30/70 DBP/DEHP (*W/W*) was the lower, but the crystallization was more perfect relative to the system with only S-L phase separation.

The phase separated structures of four systems were obtained under optical microscope. In the system for L-L phase separation, liquid droplet fixed in the spherulites of PVDF could be observed in the final phase separated structure. On the other hand, the size of the spherulites in system with less favorable interaction was bigger. When the interaction between PVDF and mixed-diluent farther enhanced, it showed only spherulite growth. The size of spherulites grew bigger in system with favorable interaction, because the strong interaction limited the nucleation activity of PVDF, and more polymer molecules were provided for spherulite growth.

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