

# Miscibility and crystallization of thermosetting polymer blends of unsaturated polyester resin and poly( $\epsilon$ -caprolactone)

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## Abstract

Poly( $\epsilon$ -caprolactone) (PCL) was found to be miscible with uncured polyester resin, i.e. oligoester (OER), as shown by the existence of a single glass transition temperature ( $T_g$ ) in each blend. However, PCL was judged to be partially miscible with crosslinked polyester resin (PER) which was concluded from the results of thermal analysis. Fourier-transform infrared (FT-i.r.) studies revealed that intermolecular hydrogen bonding interaction between the components is an important driving force to the miscibility of PCL/OER blends and the partial miscibility of crosslinked PCL/PER blends. The importance of entropy contribution to the miscibility of thermosetting polymer blends is also shown from the FT-i.r. results. The spherulitic morphology of the blends was remarkably affected by crosslinking. The birefringent spherulites were observed in the uncured PCL/OER blends, whereas a distinct pattern of extinction rings, which was absent either in the pure PCL or in the uncured PCL/OER blends, was apparent in the crosslinked PCL/PER blends. © 1998 Elsevier Science Ltd. All rights reserved.

*Keywords:* Unsaturated polyester resin; Poly( $\epsilon$ -caprolactone); Polymer miscibility

## 1. Introduction

In recent years, glass fibre-reinforced unsaturated polyester (UP) moulding compounds have received an increasing interest in industry. The advantages for the UP composite materials are high strength, dimension stability, low weight, good corrosion properties and cheap price [1]. UP moulding compounds such as sheet moulding compounds, bulk moulding compounds and thick moulding compounds, etc., have been formulated to meet the requirements of specific applications in industry. The compositions of these compounds include UP, low-profile additives (LPAs), catalyst, moulding-release agent, pigments, inorganic fillers, glass fibre reinforcement, etc.

LPAs are used in UP moulding compounds to improve surface quality of moulded parts, and to compensate for resin shrinkage. Poly(vinyl acetate) and poly(methyl methacrylate) were widely used as LPAs. There are many papers concerned with them in the literature [2–5]. The curing kinetics and the mechanism of low profile behaviour in the blends of UP with less than 20 wt% LPA have been the main topics in this field [6–8]. It is generally believed that the two-phase structure in UP/LPA blends plays an

important role in the mechanism of low profile behaviour in polyester systems [9,10]. Poly( $\epsilon$ -caprolactone) (PCL) is a semi-crystalline polymer and was taken as one of the effective LPAs, but only a few patents involved the blends of UP with PCL [11,12]. To our knowledge, no systematic investigation has been conducted on the UP/PCL blends.

On the other hand, there are many works concerned with amorphous/crystallizable thermoplastic polymer blends in the literature [13,14], but little attention is paid to polymer blends containing one crystallizable component and a thermosetting component. We reported blends of poly(ethylene oxide) (PEO) with epoxy resin [15,16], as well as several other miscible/crystallizable thermosetting polymer blends [17–21], and many interesting results were found. As part of a series of our investigations concerning the influence of crosslinking of thermosetting polymers on the miscibility and morphology of their blends, we presented our results on thermosetting polymer blends of a UP resin and PEO in two previous papers [20,21]. Herein, we further describe the miscibility and crystallization in blends of a crosslinked polyester resin (PER) and PCL. Particular attention is given to the effect of crosslinking on those properties in the blends. This research is expected to be also of critical importance for us to understand the low-profile behaviour in these blends.

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## 2. Experimental

### 2.1. Materials and preparation of samples

The poly( $\epsilon$ -caprolactone) (PCL, Placel H-7) was purchased from Daicel Chemical Ind., Ltd. (Japan); it had a number-average molecular weight  $M_n$  of 70 000–100 000. The unsaturated polyester resin (OERS) which contained 67 wt% oligoester resin (OER) ( $M_n = 1000$ ) and 33 wt% styrene as a crosslinking monomer, was supplied by Shanghai Institute of Synthetic Resins (Shanghai, China). The OER was a precopolymer of isophthalic acid (PA), fumaric acid (FA) and propylene glycol (PG) with a molar ratio PA/FA/PG = 1/1/2.2. It was terminated with  $\alpha$ -propylene-glycol. PCL/OER blends were prepared by solution casting from chloroform at room temperature. To remove the residual solvent, the blends were dried in a vacuum oven at room temperature for approximately 2 weeks. In order to prepare PCL/PER blends, OERS and PCL were mixed at 70°C to form a homogenous clear liquid blend, then 1.5 wt% benzoyl peroxide of OERS was added to the blend with continuous stirring until a clear mixture was obtained (in approximately 3 min). The mixture was poured into a stainless steel mould and cured in an oven at 65°C for 14 h, followed by successive postcuring at 90°C for 3 h and 120°C for 3 h.

### 2.2. Differential scanning calorimetry (d.s.c.)

The calorimetric measurements were carried out on a Perkin-Elmer DSC-7 differential scanning calorimeter. The instrument was calibrated with an indium standard, and the measurements were conducted under a nitrogen atmosphere. The sample weight used in the d.s.c. cell was kept in the range 8–12 mg. All samples were first heated to 140°C at a heating rate of 20°C/min (the first heating scan) and were maintained at that temperature for 5 min. The second scan was conducted by the same heating rate after the sample was quenched to –70°C. The midpoint of the slope change of the heat capacity plot of the second scan was taken as the glass transition temperature ( $T_g$ ). The crystallization temperature ( $T_c$ ) was taken as the minimum of exothermic peak, whereas the melting point temperature ( $T_m$ ) was taken as the maximum of the endothermic transition. The heat of fusion ( $\Delta H_f$ ) and the heat of crystallization ( $\Delta H_c$ ) were evaluated from the areas of melting and crystallization peaks, respectively.

### 2.3. Fourier-transform infrared (FT-i.r.) spectroscopy

FT-i.r. measurements were made with a Nicolet 750 Fourier-transform infrared spectrometer. For the PCL/OER blends, thin films were cast on to a KBr window from 1% (w/v) chloroform solutions. After evaporation of most of the solvent, the films were transferred to a vacuum oven to remove residual solvent. For the PCL/PER blends,

little lumps scraped from the cured samples were mixed with KBr in a mortar and then ground into fine powder, which was further, pressed into thin sheets for FT-i.r. measurements. All spectra were recorded at room temperature and stored on a magnetic system. A minimum of 50 scans at a resolution of 2 cm<sup>-1</sup> were signal-averaged. The films used in this study were sufficiently thin to obey the Beer–Lambert law.

### 2.4. Morphological observations

The overall morphology of the pure PCL, the PCL/OER blends, as well as the crosslinked PCL/PER blends, was investigated by optical microscopy using a Jiangnan XPR-2 optical microscope equipped with cross-polarizers. The samples between two glass covers were crystallized from the melt before observation.

## 3. Results and discussion

### 3.1. PCL/OER blends

The PCL/OER blends casting from chloroform with PCL content of 10 wt% or more were opaque at room

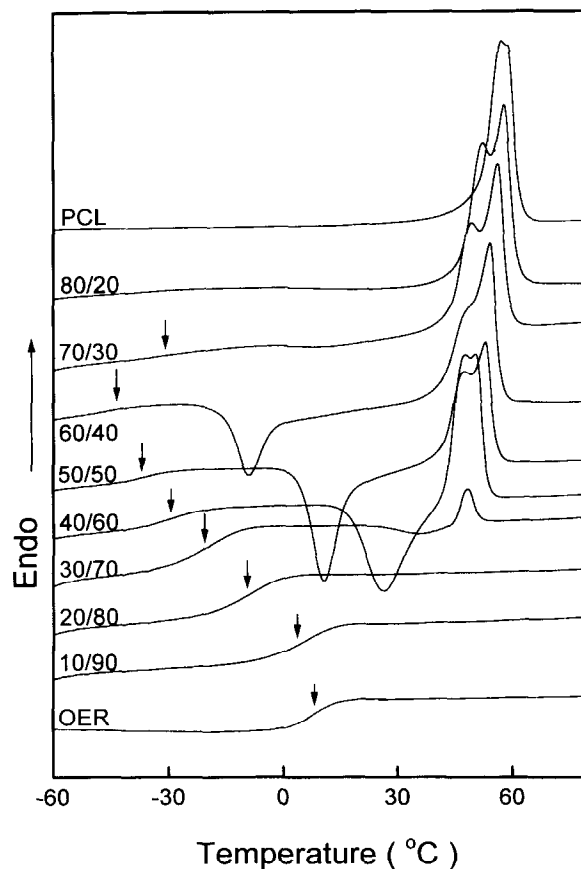


Fig. 1. D.s.c. thermograms of PCL/OER quenched samples. PCL/OER: (A) 0/100, (B) 10/90, (C) 20/80, (D) 30/70, (E) 40/60, (F) 50/50, (G) 60/40, (H) 70/30, (I) 80/20, and (J) 100/0.

Table 1  
Thermal properties of PCL/OER blends

| PCL/OER | $T_g$ (°C)       | $T_{m1}/T_{m2}$ (°C) | $\Delta H_f$ (J/g blend) | $T_c$ (°C) | $\Delta H_c$ (J/g blend) | $X_{c(\text{blend})}$ (%) | $X_{c(\text{PCL})}$ (%) |
|---------|------------------|----------------------|--------------------------|------------|--------------------------|---------------------------|-------------------------|
| 100/0   | -65 <sup>a</sup> | 57/58                | 82.7                     |            |                          | 60.8                      | 60.8                    |
| 80/20   |                  | 52/57                | 68.4                     |            |                          | 50.3                      | 62.8                    |
| 70/30   | -30              | 49/56                | 63.5                     |            |                          | 46.7                      | 66.7                    |
| 60/40   | -44              | 48/54                | 56.1                     | -9         | 27.6                     | 21.0                      | 35.0                    |
| 50/50   | -37              | 47/52                | 42.4                     | 10         | 40.0                     | 1.8                       | 3.6                     |
| 40/60   | -29              | 47/49                | 30.0                     | 26         | 28.0                     | 1.5                       | 3.8                     |
| 30/70   | -20              | -/48                 | 1.7                      | 35         | 0.8                      | 0.7                       | 2.2                     |
| 20/80   | -9               |                      |                          |            |                          |                           |                         |
| 10/90   | 5                |                      |                          |            |                          |                           |                         |
| 0/100   | 7                |                      |                          |            |                          |                           |                         |

<sup>a</sup>This value was taken from the previous work [23]

temperature. This resulted from the crystallization of PCL in the blends. All the blends were transparent just above the melting point of PCL, which primarily indicated that PCL and OER are miscible in the molten state. The d.s.c. thermograms for quenched PCL/OER blends are shown in Fig. 1 and the results were summarized in Table 1 and Fig. 2. The crystallinity degree ( $X_c$ ) was calculated by the

following equations:

$$X_{c(\text{blend})} = (\Delta H_f - \Delta H_c) / \Delta H_f^\circ \quad (1)$$

$$X_{c(\text{PCL})} = X_{c(\text{blend})} / W_{(\text{PCL})} \quad (2)$$

where  $\Delta H_f^\circ = 136$  J/g is the heat of fusion of 100% crystalline PCL [22].  $\Delta H_f$  is the heat of fusion of polymer blend.  $\Delta H_c$  is the heat of crystallization.

The appearance of a single, composition-dependent  $T_g$  strongly suggests that the blend present a homogeneous amorphous phase, i.e. the two components are miscible in the amorphous state. The  $T_g$  values of the blends as a function of blend compositions are given in Fig. 2 (full circles). Because of the experimental limitation, the glass transition corresponding to the pure PCL and the 80/20 PCL/OER blend cannot be detected. The  $T_g$  value of the pure PCL in Fig. 2 and Table 1 was taken from our previous work [23]. The overall  $T_g$  variation indicates that these polymers are completely miscible at all compositions. In the figure, the broken curve is drawn on the basis of the Fox equation [24] which is given as follows:

$$1/T_{g(\text{blend})} = W_{(\text{OER})}/T_{g(\text{OER})} + W_{(\text{PCL})}/T_{g(\text{PCL})} \quad (3)$$

where  $T_{g(\text{blend})}$  is the glass transition temperature of the blend.  $T_{g(\text{OER})}$  and  $T_{g(\text{PCL})}$  are those of plain OER and PCL, respectively.  $W_{(\text{OER})}$  and  $W_{(\text{PCL})}$  are the weight fractions of OER and PCL, respectively.

From Fig. 2, it is noted that for the 70/30 PCL/OER blend, the  $T_g$  has a remarkably positive deviation from the value predicted by the Fox equation, which is considered to be the result of the high crystallinity of PCL. Because of the crystallization of PCL in the blend, the weight fraction of PCL in the amorphous phase,  $W_{(\text{PCL})}'$ , is not equal to the overall weight fraction of PCL in the blend,  $W_{(\text{PCL})}$ . These quantities are related by Fernandes et al. [25]:

$$W_{(\text{PCL})}' = (W_{(\text{PCL})} - X_{c(\text{blend})}) / (1 - X_{c(\text{blend})}) \quad (4)$$

The open circles in Fig. 2 represent a replot of  $T_g$  value versus the amorphous fraction of PCL, fitting the Fox equation quite well.

Fig. 2 also shows the  $T_c$  and  $T_m$  of the quenched samples

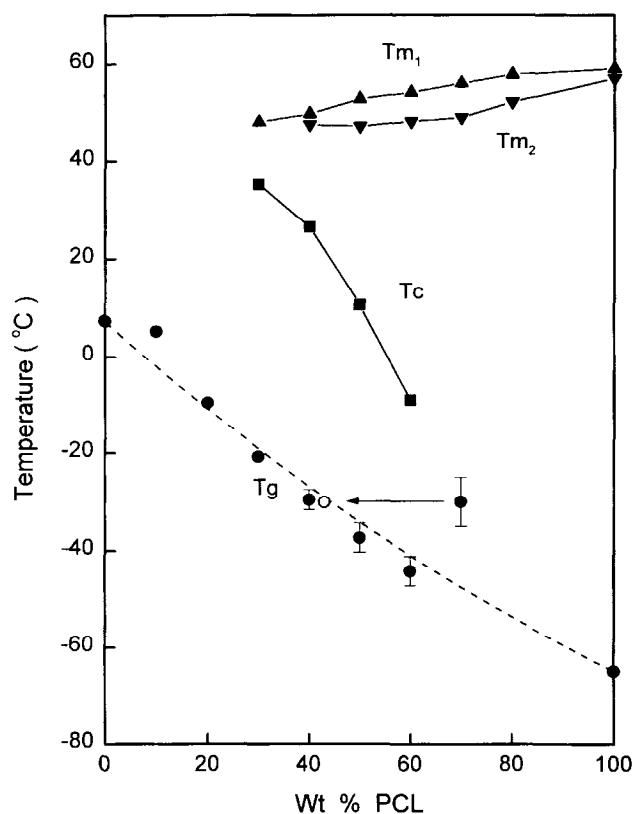


Fig. 2. Thermal properties of PCL/OER quenched samples. (●) Experimental plot of  $T_g$  versus overall blend composition; (○) the plot of  $T_g$  versus calculated amorphous composition, and (---) theoretical curve of  $T_g$  versus composition according to the Fox equation. Also show are:  $T_c$  (■),  $T_{m1}$  (▼) and  $T_{m2}$  (▲) of the PCL/OER blends as functions of blend composition. The  $T_g$  value of the pure PCL was taken from our previous work [23].

as functions of blend composition. Neither crystallization exotherm nor fusion endotherm is observed in the blends with 80 wt% OER or more, indicating that PCL in these blends exhibits no tendency to crystallize during the quenching and the heating. For the blend containing 70 wt% PCL or more, no crystallization exotherm is observed, since the crystallization of PCL was sufficiently rapid to occur completely during the quenching. However, the blends with 30–70 wt% PCL show distinct crystallization exotherms. The  $T_c$  increases with increase of OER content, indicating progressively more difficult crystallization of PCL in the blends. This is because an increase in the  $T_g$  of the blends with OER content lowered the molecular mobility and hence reduced the crystallization rate of PCL in the blends. This result further supports the idea that OER is miscible with PCL over the entire composition range in the melt.

The melting process of PCL in the blends exhibits two  $T_m$  values as shown in Figs 1 and 2. It is interesting to see that the difference between the two  $T_m$  values reaches its largest at 70 wt% PCL content, then gradually decreases with decrease of PCL content. The phenomenon of melting point depression can be seen for both of the  $T_m$  values. We noticed that there was only one  $T_m$  for the as-cast samples. Thus, it is believed that the double melting point phenomenon is the overall results of imperfect crystallization of PCL during the quenching and the melting and re-crystallization of PCL during heating.

The values of  $X_{c(PCL)}$  obtained for the PCL/OER blends are plotted in Fig. 3 as functions of blend composition. It can be seen that  $X_{c(PCL)}$  values for the as-cast samples are all

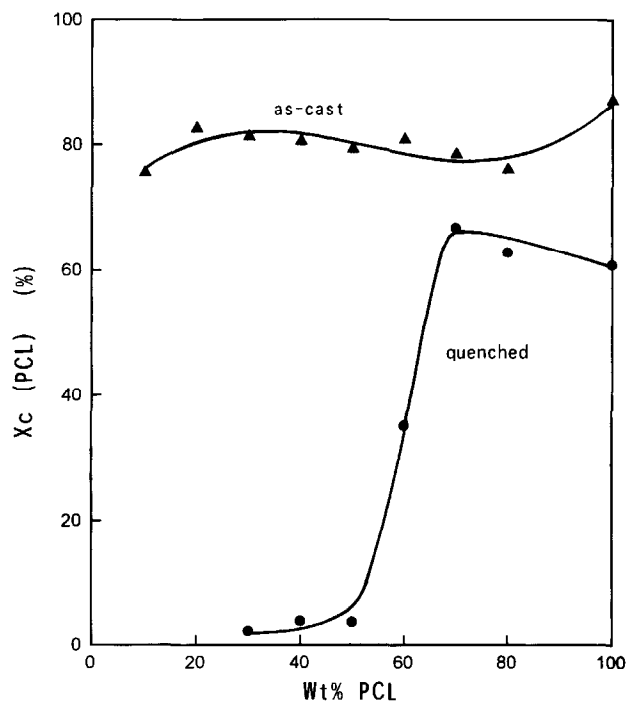


Fig. 3.  $X_{c(PCL)}$  versus PCL weight fraction of PCL/OER blends. (▲) As-cast samples; (●) quenched samples.

higher than those for the quenched samples. For the quenched samples,  $X_{c(PCL)}$  shows a maximum at 70 wt% PCL, then sharply decreases with decreasing PCL content. However, for the as-cast samples,  $X_{c(PCL)}$  has little variation from 10 to 100 wt% PCL. This result indicates that quenching process has great hindrance to the crystallization of the PCL/OER blends, and that the crystallization for the as-cast samples is more complete than that of the quenched samples.

It was reported [26,27] that PCL with its ester groups is an excellent proton-accepting polymer which makes the hydrogen-bonding interaction possible in blends of PCL with a proton donor polymer. Because OER is terminated with  $\alpha$ -propylene-glycol, the hydroxyl groups in OER can play an important role in the miscibility of PCL/OER blends.

Although the carbonyl stretch absorption of the ester groups obscures the carbonyl stretch absorption of PCL, the FT-i.r. spectra in the hydroxyl stretching region is more informative, as shown in Fig. 4. For the pure OER, the self-associated hydroxyl band at  $3446\text{ cm}^{-1}$  and the free hydroxyl band at  $3527\text{ cm}^{-1}$  remains invariant for all compositions in the blends. However, the self-associated hydroxyl band at  $3446\text{ cm}^{-1}$  is gradually shifted to the low frequency side, to  $3440\text{ cm}^{-1}$  for 40 wt% PCL in the blend (Curve D), which arises from hydroxyl groups hydrogen bonded to the PCL carbonyl groups. The relative intensity of the hydrogen-bonded hydroxyl band to the

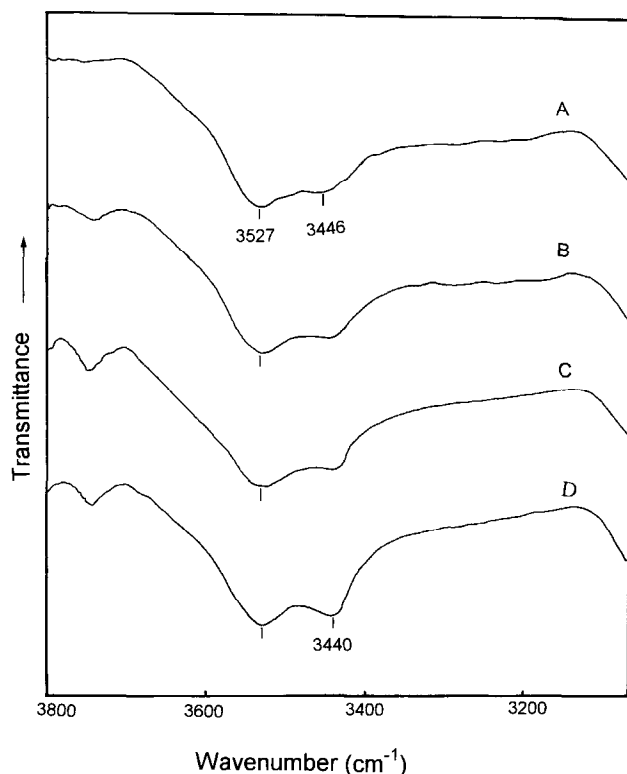


Fig. 4. FT-i.r. spectra in the  $3025\text{--}3800\text{ cm}^{-1}$  region of PCL/OER blends. PCL/OER: (A) 0/100, (B) 10/90, (C) 20/80, and (D) 40/60.

free hydroxyl band is observed to increase with increasing PCL concentration, indicating the gradual increase of the relative percentage of hydrogen bonded hydroxyls in the blends. The frequency difference between the free hydroxyl band and that of hydrogen-bonded species ( $\Delta\nu$ ) is a measure of the average strength of the intermolecular interactions [28]. The above results imply that the average strength of hydrogen bond between the PCL carbonyl groups and the

OER hydroxyl groups ( $\Delta\nu = 87 \text{ cm}^{-1}$ ) seems to be somewhat stronger than that occurring between hydroxyl groups in the pure OER ( $\Delta\nu = 81 \text{ cm}^{-1}$ ). From the analysis of FT-i.r. spectra, it is believed that the hydrogen-bonding interaction is an important driving force to the miscibility of the PCL/OER blends. The entropy contribution to the miscibility of the blends also cannot be neglected owing to the rather low molecular weight of OER.

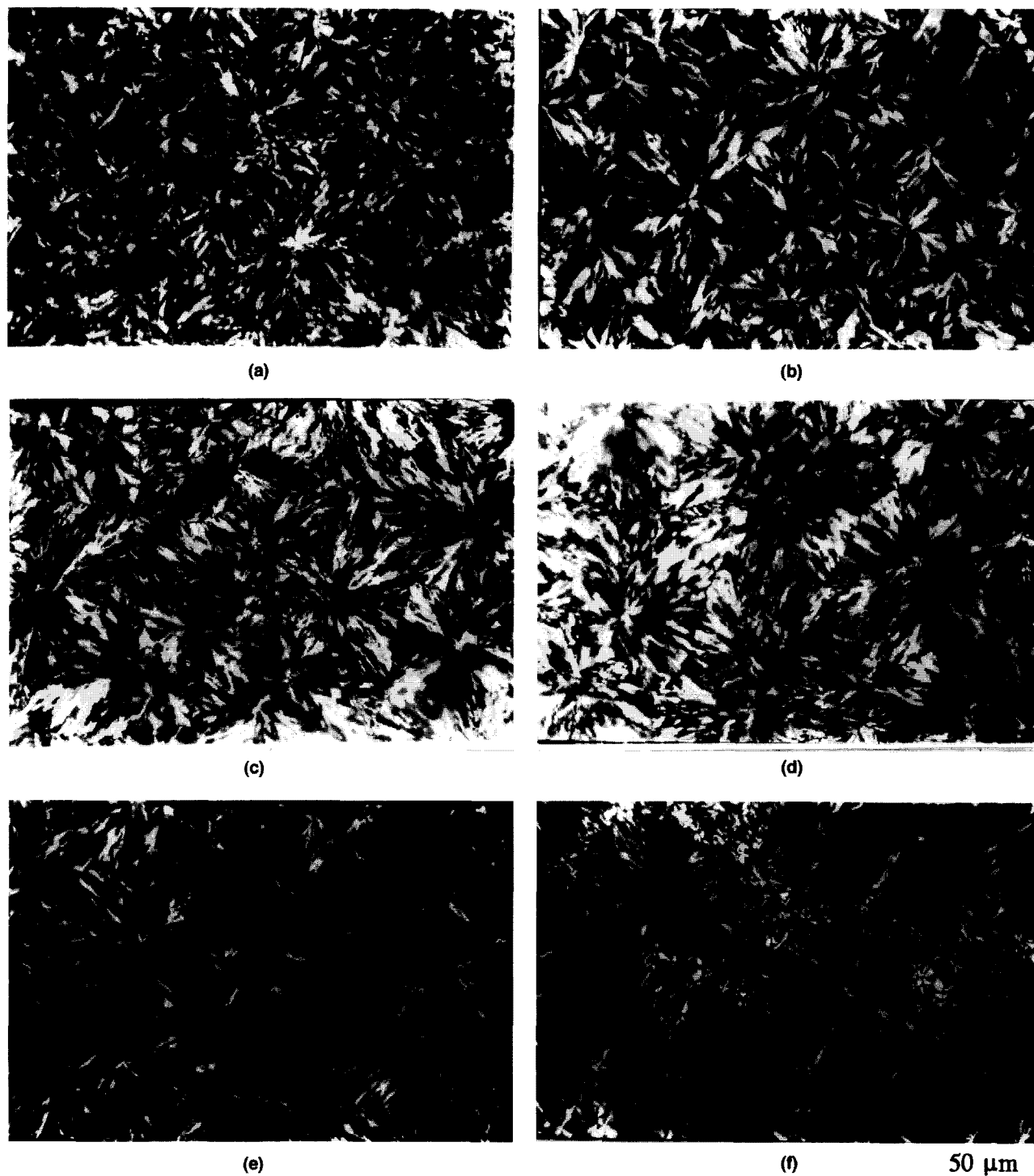


Fig. 5. Optical micrographs of PCL/OER blends crystallized at 39°C. PCL/OER: (a) 80/20, (b) 70/30, (c) 60/40, (d) 40/60, (e) 30/70, and (f) 20/80.

PCL spherulites were observed in the PCL/OER blends with OER content up to 80 wt%. Fig. 5 shows the optical micrographs for the PCL/OER blends crystallized at 39°C. It can be seen from the figure that the blends with PCL content down to 30 wt% are still completely volume-filled with spherulites, and that the size of spherulites increases slightly with decreasing concentration of PCL. It is also interesting to see that the spherulitic morphology appears to remain basically unchanged with OER content up to 70 wt%; i.e. it does not become increasingly more irregular or coarser as usually observed for miscible/crystalline polymer blends. As the molecular weight of OER is rather low, this phenomenon can be considered to be due to the low  $T_g$  (7°C) of OER and the high mobility of OER molecules.

### 3.2. PCL/PER blends

All the PCL/PER blends containing 10 wt% PCL or more were quite opaque at room temperature and did not become clear above the melting point of PCL, indicating that phase separation occurred during crosslinking in these blends. However, the blend with 5 wt% PCL or less was clear, which suggests the homogeneity of the blend. These observations primarily imply that PCL is partially miscible with

crosslinked PER and the phase structures of the PCL/PER blends show composition dependence.

The d.s.c. thermograms of the PCL/PER blends were shown in Fig. 6 and the results were summarized in Fig. 7 and Table 2. The pure PER shows a  $T_g$  at 95°C. For the blends with 5 wt% PCL or less, neither crystallization exotherm nor melting endotherm is observed, this indicates that PCL in these blends exhibits no tendency to crystallize. It is believed that these amorphous blends present homogeneous nature; i.e. these blends are miscible. It should be noticed that the uncured PCL/OER blends with 80 wt% OER or more do not show any crystallization during the quenching and the heating (Fig. 1), whereas the crosslinked blends with PER content up to 90 wt% still remain crystallizable. This result suggests that phase separation could occur in these blends after crosslinking. It is interesting to see that, with increasing PCL content in the PCL/PER blends, the glass transition which is considered to be the segmental movement of PER-rich phase becomes progressively unclear. This phenomenon was considered to be the result of high crystallinity of PCL in the blends. Because of experimental limitations, the glass transition of PCL-rich phase cannot be seen in the d.s.c. thermograms.

No crystallization exotherm was observed for the blends with 40 wt% PCL or more (Figs 6 and 7), indicating that the crystallization of PCL in these blends was rapid enough to occur completely during the quenching. However, the blends containing 10–30 wt% PCL show small crystallization exotherms. The  $T_c$  increases with increase of PER content, indicating progressively more difficult crystallization of PCL. This means that, in the PCL/PER blends, the crosslinked PER phase and the PCL phase are not

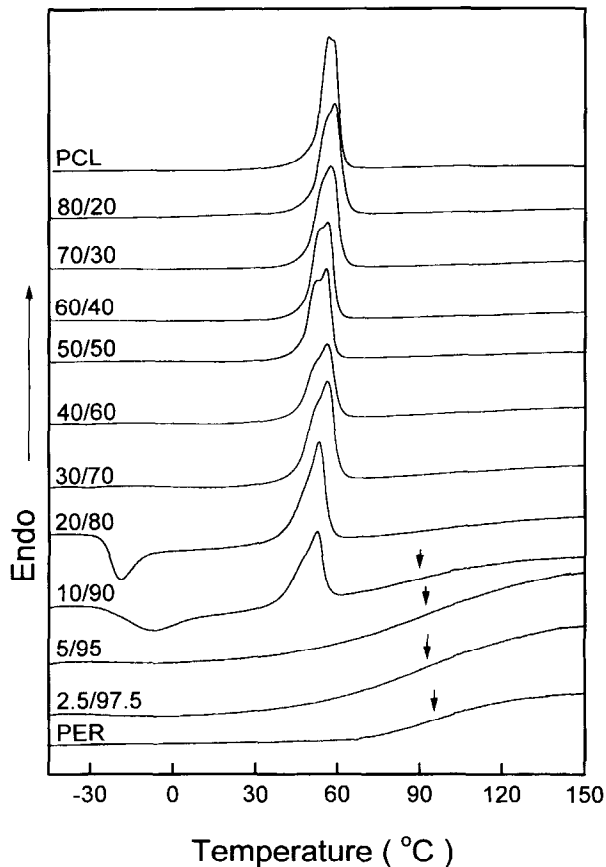


Fig. 6. D.s.c. thermograms of PCL/PER blends. PCL/PER: (A) 0/100, (B) 2.5/97.5, (C) 5/95, (D) 10/90, (E) 20/80, (F) 30/70, (G) 40/60, (H) 50/50, (I) 60/40, (J) 70/30, (K) 80/20, and (L) 100/0.

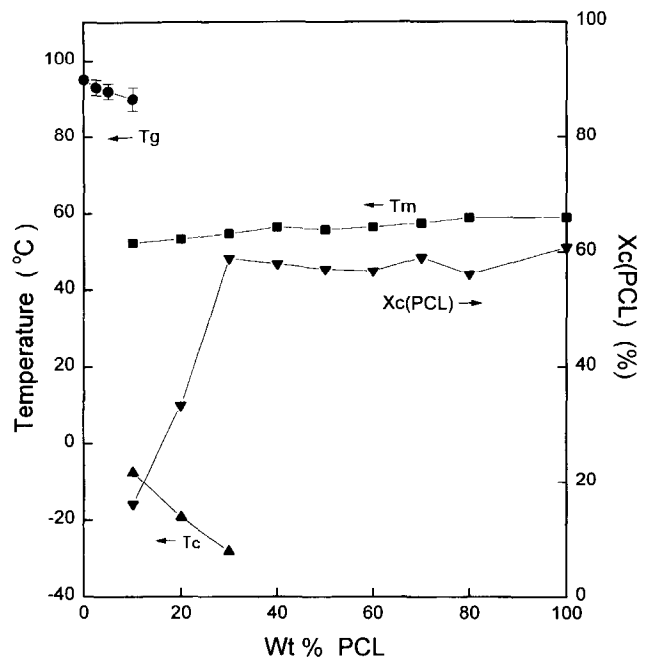


Fig. 7. Composition dependence of  $T_g$  (●),  $T_c$  (▲),  $T_m$  (■) and  $X_{c(PCL)}$  (▼) of the PCL/PER blends.

Table 2  
Thermal properties of PCL/PER blends

| PCL/PER  | $T_g$<br>(°C) | $T_m$<br>(°C) | $\Delta H_f$<br>(J/g blend) | $T_c$<br>(°C) | $\Delta H_c$<br>(J/g blend) | $X_{c(\text{blend})}$<br>(%) | $X_{c(\text{PCL})}$<br>(%) |
|----------|---------------|---------------|-----------------------------|---------------|-----------------------------|------------------------------|----------------------------|
| 100/0    |               | 59            | 82.7                        |               |                             | 60.8                         | 60.8                       |
| 80/20    |               | 58            | 61.0                        |               |                             | 44.8                         | 56.0                       |
| 70/30    |               | 57            | 56.3                        |               |                             | 41.3                         | 59.0                       |
| 60/40    |               | 56            | 46.2                        |               |                             | 34.0                         | 56.6                       |
| 50/50    |               | 55            | 38.7                        |               |                             | 28.5                         | 56.9                       |
| 40/60    |               | 56            | 31.5                        |               |                             | 23.2                         | 57.9                       |
| 30/70    |               | 54            | 25.8                        | -28           | -1.8                        | 17.6                         | 58.8                       |
| 20/80    |               | 53            | 14.4                        | -19           | -5.3                        | 6.7                          | 33.4                       |
| 10/90    | 90            | 53            | 5.5                         | -7            | -3.3                        | 1.6                          | 16.1                       |
| 5/95     | 92            |               |                             |               |                             |                              |                            |
| 2.5/97.5 | 93            |               |                             |               |                             |                              |                            |
| 0/100    | 95            |               |                             |               |                             |                              |                            |

completely separated out from each other; and there is still a small amount of PER in the PCL-rich phase.

Fig. 7 also shows the  $X_{c(\text{PCL})}$  and  $T_m$  as functions of PCL content. With increasing PCL content, the melting point of PCL in the blend is shifted to higher temperature and approaches the  $T_m$  of the pure PCL. The difference in  $T_m$  between the pure PCL and the PCL/PER blend is very small (Fig. 6).  $X_{c(\text{PCL})}$  remains almost invariant as the concentration of PCL decreases down to 30 wt%. However, this quantity decreases sharply with further reduction of PCL. The almost invariant  $T_m$  and  $X_{c(\text{PCL})}$  with decreasing PCL content down to 30 wt% is the result of phase separation of large amount of PCL in the blends. Thus, the conclusion that PCL is partially miscible with PER is reasonable, and a PER-rich phase and a PCL-rich phase exist in the PCL/PER blends.

From the thermodynamic point of view, an increase in molecular weight for either of the components of a miscible blend would decrease the cloud-point temperature. Therefore, the occurrence of even partial miscibility in such polymer blends containing one component with an infinite molecular weight (i.e. highly crosslinked) is surprising and required further comment [16].

Fig. 8 shows the FT-i.r. spectra in the hydroxyl stretching region of the pure PER and the PCL/PER blends at room temperature. For the plain PER, the band at  $3535\text{ cm}^{-1}$  is assigned to the self-association of hydroxyl groups (Curve A). With increase of PCL content, the band at  $3535\text{ cm}^{-1}$  remains invariant and the band at  $3455\text{ cm}^{-1}$  is shifted to lower frequency, to  $3441\text{ cm}^{-1}$  for 40 wt% PCL (Curve D), which arises from hydroxyl groups hydrogen bonded to the PCL carbonyl groups. The relative intensity of the hydrogen-bonded hydroxyl band to the free hydroxyl band increases with increase of PCL content. The average strength of the hydrogen bond between the PCL carbonyl groups and the PER hydroxyl groups ( $\Delta\nu = 94\text{ cm}^{-1}$ ) is obviously stronger than that occurring between the hydroxyl groups in the pure PER ( $\Delta\nu = 80\text{ cm}^{-1}$ ). It is believed that the hydrogen bonding between the PCL and the crosslinked PER is an important driving force to the

partial miscibility of the highly crosslinked PCL/PER blends.

It is also interesting to note that, although the average strength of hydrogen bond between the components of PCL/PER blends is greater than that of PCL/OER blends, the former, without the entropy contribution, is only partially miscible, but the latter is completely miscible. It can be seen, therefore, that the entropy contribution to the miscibility is very important.

Figs 9 and 10 show the optical micrographs for PCL/PER

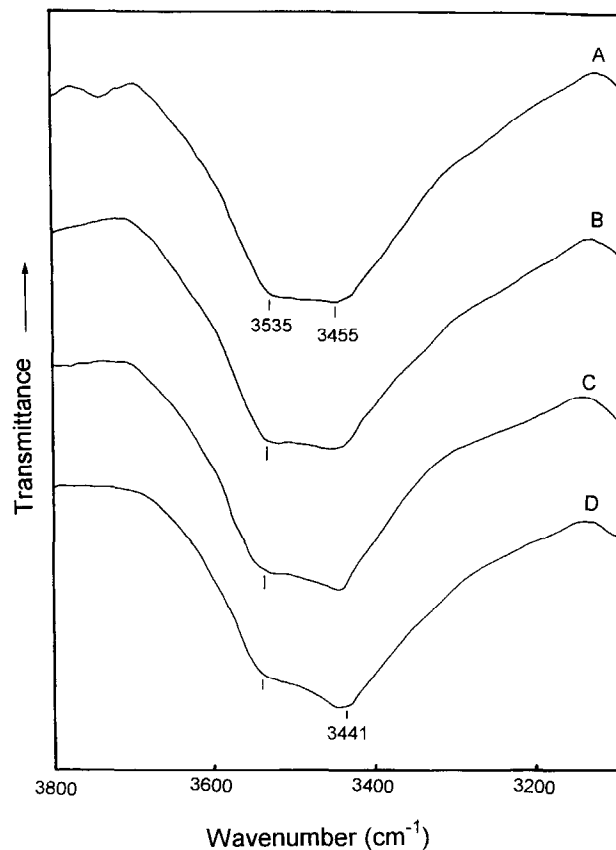


Fig. 8. FT-i.r. spectra in the  $3028\text{--}3800\text{ cm}^{-1}$  region of PCL/PER blends. PCL/PER: (A) 0/100, (B) 10/90, (C) 20/80, and (D) 40/60.

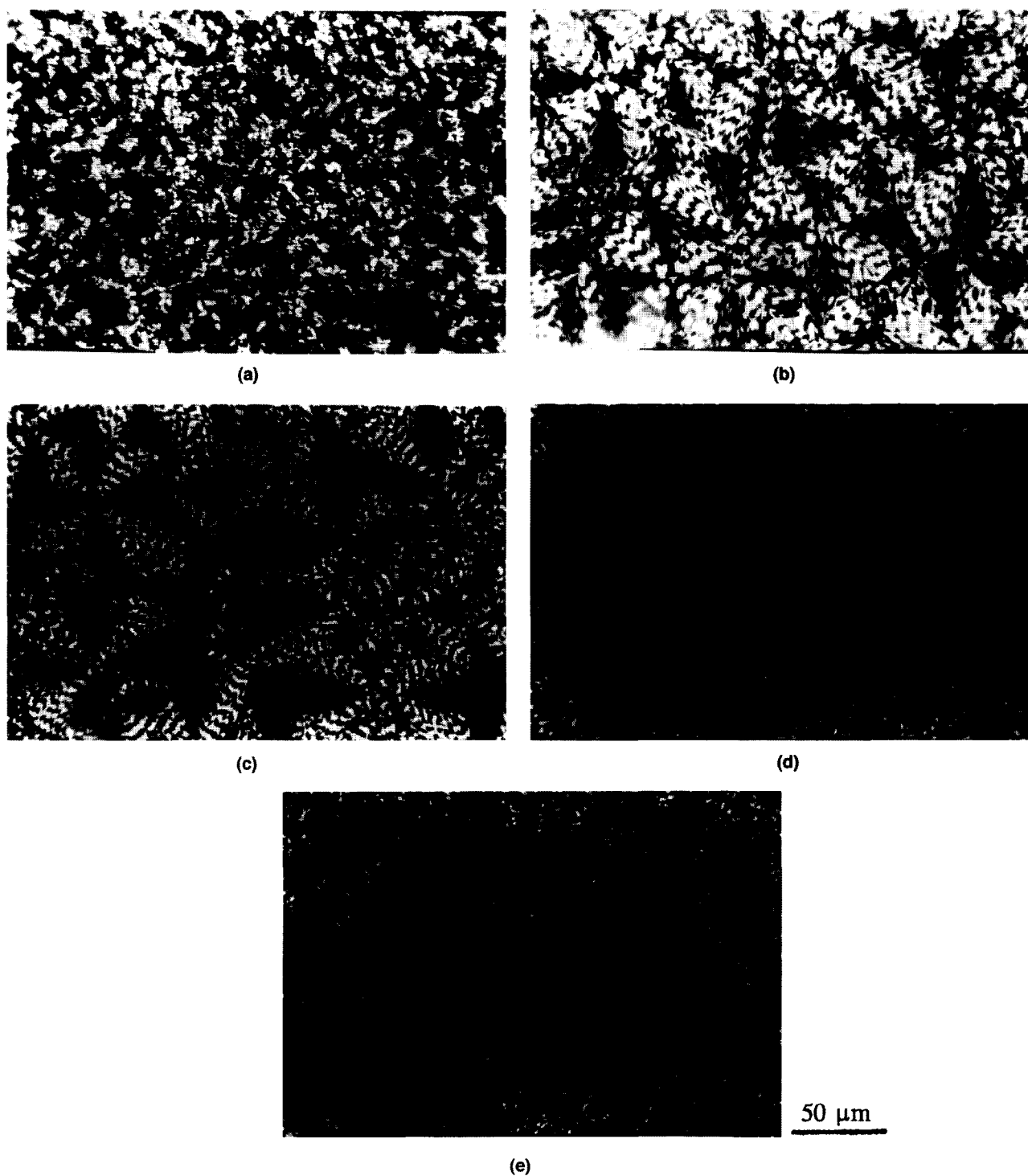


Fig. 9. Optical micrographs of PCL/PER blends crystallized at 39°C. PCL/PER: (a) 100/0, (b) 80/20, (c) 70/30, (d) 60/40, and (e) 50/50.

blends crystallized at 39 and 44°C, respectively. Birefringent spherulites with a 'Maltese cross' truncated by impingement were observed. A distinct pattern of extinction rings, which was absent in pure PCL and uncured PCL/OER blends, is apparent in the blends. Furthermore, it can be seen that the texture of the spherulites becomes increasingly open, coarser and more irregular with increasing content of PER. The ring-banded spherulites crystallized at 44°C

are still apparent in the blends with PCL down to 40 wt%. It is known that the formation of ring-banded spherulites normally depends on the rate of growth [29]. Ring-banded spherulites are formed at a slow growth rate and at a temperature near the melting point [29,30]. Figs 9 and 10 also show the influence of crystallization temperature on the morphology of PCL spherulites in PCL/PER blends, which indicates that raising the crystallization temperature



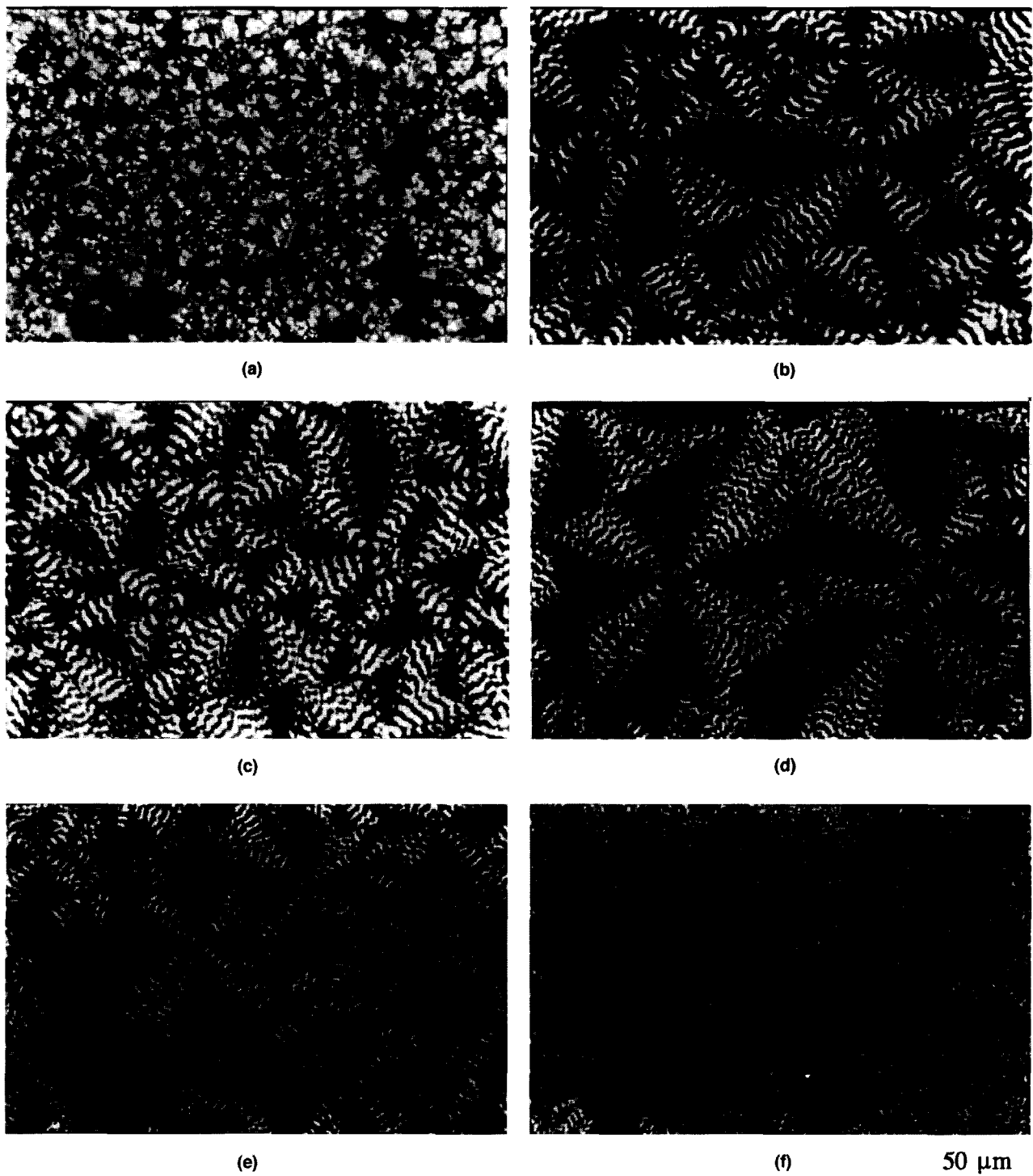


Fig. 10. Optical micrographs of PCL/PER blends crystallized at 44°C. PCL/PER: (a) 100/0, (b) 80/20, (c) 70/30, (d) 60/40, (e) 50/50, and (f) 40/60.

favours the formation of ring-banded spherulites. According to Keith et al. [31], the twisted crystallization results from stress building up during crystallization, which probably occurs within disordered fold surfaces of polymer crystals. Although visible signs of phase separation have been observed in PCL/PER blends with 10 wt% PCL or more, PCL and PER are partially miscible as we have discussed previously. In the PCL-rich phase, PCL is miscible with a

small concentration of PER, which can be considered as a polymer diluent. Keith et al. [31] indicated that adsorption of the diluent on crystal boundaries (growth face and fold surfaces of lamellae) underlies the formation of the ring-banded spherulites. Similarly, in the partially miscible PCL/PER blends, the rejection of a small amount of PER in the PCL-rich phase from crystalline lamellae to inter-lamellar amorphous region may give rise to stress on the

lamellar surface and result in twisting of lamellae during crystallization.

#### 4. Conclusion

PCL and OER are miscible in the amorphous state, as shown by the single composition-dependent  $T_g$ . PCL is partially miscible with crosslinked PER, and a PER-rich phase and a PCL-rich phase exist in the PCL/PER blends. The melting point and the crystallinity of PCL in PCL/PER blends with 30 wt% PCL or more approach those of the pure PCL. FT-i.r. studies revealed that a hydrogen-bonding interaction exists between the components of both the PCL/OER blends and the PCL/PER blends, which plays an important role in the miscibility of the systems. Only birefringent spherulites can be seen in the uncured PCL/OER blends, whereas, except the birefringent spherulites with a 'Maltese cross', a distinct pattern of extinction rings is apparent in the crosslinked PCL/PER blends.

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