

# Miscibility and crystallization behavior of biodegradable blends of two aliphatic polyesters. Poly(3-hydroxybutyrate-*co*-hydroxyvalerate) and poly( $\epsilon$ -caprolactone)

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## Abstract

Biodegradable polymer blends of poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) and poly( $\epsilon$ -caprolactone) (PCL) blends were prepared with the ratio of PHBV/PCL ranging from 80/20–20/80 by co-dissolving the two polyesters in chloroform and casting the mixture. Differential scanning calorimetry (DSC) and optical microscopy (OM) were used to investigate the miscibility and crystallization of PHBV/PCL blends. Experimental results indicated that PHBV showed no miscibility with PCL for PHBV/PCL blends as evidenced by the existence of unchanged composition independent glass transition temperature and the biphasic melt. Crystallization of PHBV and PCL was studied with DSC and analyzed by the Avrami equation by using two-step crystallization in the PHBV/PCL blends. The crystallization rate of PHBV at 70 °C decreased with the increase of PCL in the blends, while the crystallization mechanism did not change. In the case of the isothermal crystallization of PCL at 42 °C, the crystallization rate increased with the addition of PHBV, and the crystallization mechanism changed, too, indicating that the crystallization of PHBV at 70 °C had an apparent influence on the crystallization of PCL at 42 °C.

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**Keywords:** Poly(3-hydroxybutyrate-*co*-hydroxyvalerate)/poly( $\epsilon$ -caprolactone) blends; Miscibility; Crystallization

## 1. Introduction

Biodegradable polymers have received considerable attention due to their potential applications in the fields related to environmental protection and ecology in the last two decades. There are mainly two types of biodegradable polymers according to the difference in the preparation methods. One is the biosynthetic polymers, such as bacterial poly(hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV). PHB is probably the most extensively studied biodegradable thermoplastic polymer. However, practical application of PHB has often been limited by its brittleness and narrow processing window. Therefore, blending of PHB with other polymers has been often reported in literature.

Miscible blends have been prepared by mixing PHB with poly(vinyl acetate), poly(epichlorohydrin), poly(vinyl phenol), poly(vinylidene fluoride), poly(ethylene oxide) and poly(vinylidene chloride-*co*-acrylonitrile) [1–6]. On the other hand, PHB was known to be immiscible with poly( $\epsilon$ -caprolactone), poly(cyclohexyl methacrylate), poly(hydroxyoctanoate), high molecular weight poly(L-lactide) and poly(methylene oxide) [7–11]. Recently, Di Lorenzo et al. and Ha et al. reviewed the miscibility, properties and biodegradability of blends containing either PHB or PHBV, respectively [12,13]. The other is the chemosynthetic polymers, such as the linear aliphatic polyesters. Poly( $\epsilon$ -caprolactone) (PCL) is just one of them. PCL has received extensive investigation. PCL is reported to be immiscible with PHB, and PEO [14–15]. On the other hand, PCL is found to be miscible with poly(vinyl phenol), bisphenol-A polycarbonate, and phenoxy [16–18]. Recently, Eastmond reviewed the polymer blends based on PCL [19].

Binary crystalline polymer blends have received much less attention than fully amorphous or amorphous/crystalline systems. Only a small number of works have been reported

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on the miscible polymer blends of two crystalline polymers with different chemical structures, which may be of considerable technological interest and offer the possibility of investigating crystallization and morphological behavior related to blend miscibility [20–22]. On the other hand, it is also possible to determine how the crystallinity of one component affects the morphology, crystallization and mechanical properties of the other in the case of binary immiscible blends of two crystalline polymers [23–25].

In previous works, the miscibility and crystallization behavior of PBSU/PCL and PHBV/PBSU blends were studied by DSC and POM [26,27]. Both PBSU/PCL and PHBV/PBSU blends were biodegradable crystalline/crystalline polymer blends. It was found that PBSU/PCL and PHBV/PCL blends were immiscible as evidenced by the composition independent glass transition temperature and the biphasic melt. Furthermore, the crystallization of one component was influenced apparently by the other component.

In this manuscript, the miscibility and crystallization behavior of PHBV/PCL blends were investigated by DSC and OM based on the previous works of PBSU/PCL and PHBV/PBSU blends. Both of the components are crystalline and biodegradable. The aim of this work is to investigate the miscibility and crystallization of crystalline/crystalline biodegradable polymer blends. Such polymer blends are of great interest since they not only provide the possibility of investigating crystallization and morphological behavior related to blend miscibility but also have potential practical application in industrial fields.

## 2. Experimental

PHBV ( $M_w=454,000$ ,  $M_n=153,000$  and HV%=14) and PCL ( $M_w=14,300$ ,  $M_n=6100$ ) were purchased from Aldrich Chemical Company Inc. and Scientific Polymer Products, Inc. (Ontario, NY), respectively. PHBV/PCL blends were prepared with mutual solvent chloroform. The solution of both polymers (0.02 g/ml) was cast on a petri dish at room temperature. The solvent was allowed to evaporate in a controlled air stream for 1 day and the resulting films were further dried in vacuum at 50 °C for 3 days. In this way, blends were prepared with various compositions ranging from 80/20–20/80 in weight ratio, the first number referring to PHBV.

Thermal analysis was performed using a TA Instruments differential scanning calorimetry 2910 with a Thermal Analyst 2000. The glass transition temperatures and melting point temperatures of the melt-quenched PHBV/PCL blends were measured at a heating rate of 20 °C/min. The samples were first annealed at 200 °C for 3 min to destroy any thermal history and subsequently quenched into liquid nitrogen.

Two different procedures were employed to study the crystallization behavior of PHBV/PCL blends. The samples were quenched to 70 °C to crystallize PHBV for some time until the completion of the crystallization of PHBV after being held at 200 °C for 3 min to destroy any thermal history, and then quenched to 42 °C to crystallize PCL. The above mentioned isothermal crystallization conditions consist of

the following two steps, namely, the isothermal crystallization of the PHBV phase at 70 °C from the melt, and the isothermal crystallization of the PCL at 42 °C from the liquid phase in the presence of previously crystallized PHBV. In the case of the crystallization of PHBV at 70 °C, PCL was still in the melt since the crystallization temperature 70 °C is above the melting point of PCL. However, in the case of the crystallization of PCL at 42 °C, PCL must crystallize in the presence of the PHBV crystals formed previously at 70 °C. The presence of the PHBV crystals is expected to have an influence on the crystallization nucleation and growth of PCL.

## 3. Results and discussion

### 3.1. Study of miscibility of PHBV/PCL blends based on the glass transition temperature by DSC

It is well known that binary polymer blends can usually be prepared by two methods. One is to blend the two components by melt blending. The other is to blend the two components through solution casting method by using a cosolvent. However, one of the biggest disadvantages of biodegradable polymers is their thermal stability. The biodegradable polymers may undergo decomposition more or less during melt blending process. Therefore, PHBV/PCL blends were prepared by using solution casting method in this manuscript.

Miscibility between the two components plays an important role on the morphology, thermal properties, mechanical properties and biodegradability for the PHBV/PCL blends. It is well known that binary polymer blends can usually be classified into three types in terms of the miscibility between the two components. They are completely miscible, partially miscible and completely immiscible polymer blends. The easiest method to study the miscibility of binary polymer blends is to measure the  $T_g$  of the blends if the difference in the  $T_g$ s of the two components is not less than 20 °C. The two components are completely miscible polymer blends if polymer blends exhibit one single composition-dependent  $T_g$ . The two components are completely immiscible polymer blends if polymer blends exhibit two composition-independent  $T_g$ s close to those of neat components. The two components are partially miscible polymer blends if polymer blends exhibit two composition-dependent  $T_g$ s which locate between those of neat components.

In the present work the difference in the  $T_g$ s between neat PHBV (around  $-1$  °C) and neat PCL (around  $-65$  °C) is more than 60 °C. Therefore, the miscibility of PHBV/PCL blends can be investigated by the determination of  $T_g$ . DSC measurements were performed to characterize the melt-quenched PHBV/PCL blends. However, it should be noted here that the crystallization rate of PCL was very fast during the cooling process from the melt to the amorphous phase. The crystallinity of PCL formed during the cooling process must have a significant negative influence on the accuracy of the measured value of the  $T_g$ . In order to avoid or diminish to the least extent such a negative influence on the accurate measurement of the value of the  $T_g$ , the samples were

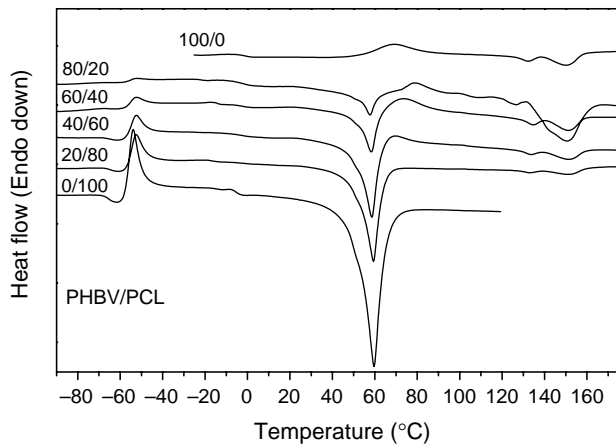


Fig. 1. DSC traces of PHBV/PCL blends after melt quenching at a heating rate of 20 °C/min.

quenched directly into liquid nitrogen as quickly as possible after they were melted at 200 °C for 3 min with a hot stage to destroy any thermal history. Then the samples were transferred to the DSC cell, which had been set at around -100 °C in advance, as quickly as possible to measure the  $T_g$  of the PHBV/PCL blends at a heating rate of 20 °C/min.

Fig. 1 shows the DSC traces of PHBV/PCL blends. Neat PHBV exhibited a glass transition at -1 °C, an exothermic cold crystallization peak at 69 °C, and two endothermic melting peaks at 132 and 150 °C, respectively. Neat PCL exhibited a  $T_g$  at around -66 °C, an exothermic cold crystallization peak at around -54 °C, and a  $T_m$  at around 60 °C. In the PHBV/PCL blends, a  $T_g$  at around -66 °C, which was close to that of neat PCL, can be found for 20/80 and 40/60 blends, while it could not be determined accurately for 80/20 and 60/40 blends. On the other hand, a  $T_g$  at around -1 °C, which was close to that of neat PHBV, could be found for 80/20, 60/40 and 40/60 blends. The cold crystallization peak temperature of PCL in the blends was almost composition-independent, indicating that the addition of PHBV did not have a significant influence on the cold crystallization of PCL in

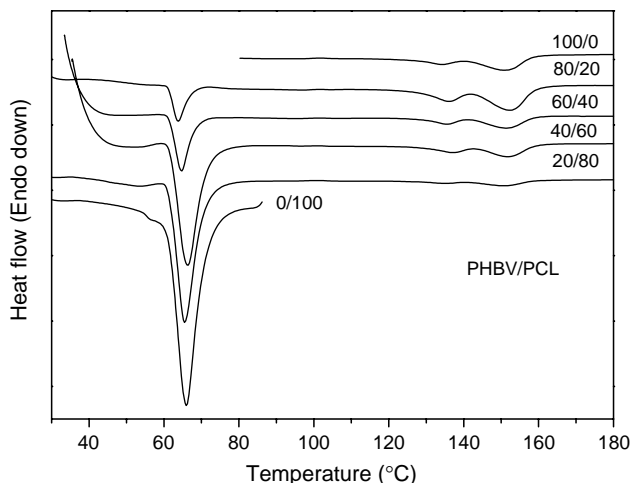


Fig. 2. DSC traces of the as cast PHBV/PCL blends at a heating rate of 20 °C/min.

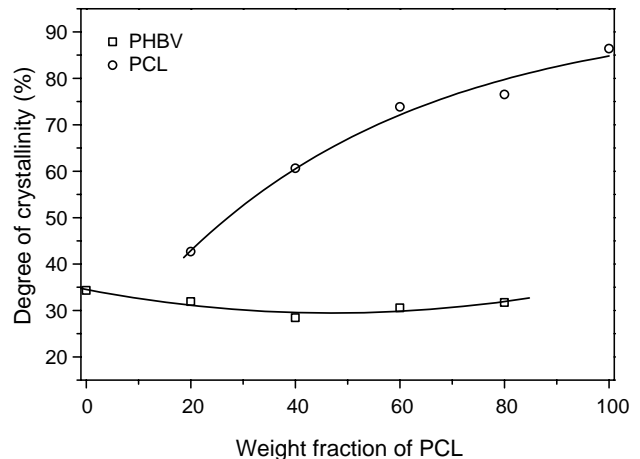


Fig. 3. Degree of crystallinity of PHBV and PCL as a function of blend composition for the as cast PHBV/PCL blends.

the PHBV/PCL blends. However, the cold crystallization of PHBV overlapped with the melting of PCL in the blends. Furthermore, the  $T_m$ s of PHBV and PCL remained almost the same in the blends. All the results mentioned above lead us to the conclusion that PHBV was immiscible with PCL in the blends.

For comparison, we also studied the melting behavior of PHBV/PCL blends for the as cast samples. Fig. 2 shows the melting behavior of PHBV/PCL blends for the as cast samples. The melting endotherm located at low temperature corresponded to the melting of PCL, while the other located at high temperature corresponded to the melting of PHBV. The  $T_m$ s of PHBV and PCL in the blends remained almost the same as those for the neat polymers. On the basis of the heat of fusion of 100% crystalline PHBV (109 J/g) [28] and PCL (136 J/g) [29], the degree of crystallinity of both PHBV and PCL components were calculated from the melting endotherms of the as cast samples and normalized with respect to the composition of each component in the blend.

Fig. 3 summarizes the variation of degree of crystallinity of PHBV and PCL as a function of blend composition. The degree of crystallinity of PHBV remained almost 30–35% and was independent of the blend composition. On the other hand, the degree of crystallinity of neat PCL was around 85%. In the blends, the degree of crystallinity of PCL decreased sharply. For 20/80 blend, the degree of crystallinity of PCL was around 40%, indicating that the presence of high PHBV content had a significant negative influence on the crystallization of PCL in the PHBV/PCL blends.

### 3.2. Isothermal crystallization study by DSC

PHBV and PCL are both semicrystalline biodegradable polyesters, with the  $T_m$  of PHBV higher than that of PCL. The isothermal crystallization of PHBV/PCL blends was also studied by DSC in this work.

As introduced in the experimental section, two-step crystallization was used to study the crystallization of PHBV/PCL blends. The crystallization of PHBV was studied at 70 °C for neat PHBV, 80/20 and 60/40. In the case of the crystallization

of PCL, the crystallization temperature was chosen at 42 °C. PCL crystallized in the presence of PHBV crystals formed at 70 °C.

The well-known Avrami equation is often used to analyze the isothermal crystallization kinetics; it assumes the development of the relative degree of crystallinity with crystallization time  $t$  as

$$1 - X_t = \exp(-kt^n) \quad (1)$$

where  $n$  is the Avrami exponent depending on the nature of nucleation and growth geometry of the crystals, and  $k$  is a composite rate constant involving both nucleation and growth rate parameters [30]. Fig. 4 shows the Avrami plots for the isothermal crystallization of neat and blended PHBV crystallized at 70 °C. The Avrami parameters  $n$  and  $k$  were obtained from the plots of  $\log(-\ln(1-X_t))$  versus  $\log t$  as shown in Fig. 4. The Avrami exponents  $n$  and crystallization rate constants  $k$  of the neat and blended PHBV are listed in Table 1.

It could be seen from Table 1 that the average value of the Avrami exponent  $n$  was around 2.5 for the isothermal crystallization of the neat and blended PHBV. The almost unchanged Avrami exponent  $n$  with the addition of PCL indicated that the crystallization mechanism of PHBV was not affected by the presence of PCL in PHBV/PCL blends. The crystallization rate constant  $k$  of PHBV decreased with the addition of PCL, indicating that the addition of PCL retarded the crystallization of PHBV.

The half-life crystallization time  $t_{0.5}$ , the time required to achieve 50% of the final crystallinity of the samples, is an important parameter for the discussion of crystallization kinetics. Usually, the crystallization rate is described as the reciprocal of  $t_{0.5}$ . The value of  $t_{0.5}$  is calculated by the following equation:

$$t_{0.5} = \left( \frac{\ln 2}{k} \right)^{1/n} \quad (2)$$

where  $k$  and  $n$  are the same as in the Avrami equation. The values of  $t_{0.5}$  and  $1/t_{0.5}$  for the neat and blended PHBV were calculated and were also listed in Table 1. The value of  $t_{0.5}$

Table 1  
Crystallization kinetic parameters of PHBV in PHBV/PCL blends at 70 °C

PHBV/PCL	$n$	$k$ (min <sup>-n</sup> )	$t_{0.5}$ (min)	$1/t_{0.5}$ (min <sup>-1</sup> )
100/0	2.58	$1.83 \times 10^{-3}$	9.99	0.100
80/20	2.40	$2.54 \times 10^{-4}$	27.04	$3.70 \times 10^{-2}$
60/40	2.45	$5.90 \times 10^{-5}$	45.98	$2.17 \times 10^{-2}$

increased with the increase of PCL. On the other hand, the value of  $1/t_{0.5}$  decreased with the addition of PCL. The above results indicate that the addition of PCL reduced apparently the crystallization rate of PHBV in the blends. Two possible reasons were proposed to explain the slow-down of the crystallization rate of PHBV after blending with PCL. One is the presence of the PCL suppressed the nucleation of the PHBV in the blends. In other words, the presence of PCL has a negative effect on the primary nucleation of PHBV. The number of heterogeneous primary nuclei of PHBV may decrease with the addition of PCL in the blends because of the migration of heterogeneity from PHBV to PCL. Similar results were also recently reported on the crystallization behavior of PHBV/PBSU blends [27]. Another possible reason of the slow-down of the crystallization rate of PHBV was probably from a physical restriction to the growth of PHBV spherulites by the PCL domains due to the not large phase separation between PCL and PHBV [31]. Therefore, the presence of PCL in the PHBV/PCL blends did not change the crystallization mechanism of PHBV, but reduced the crystallization rate of PHBV in the blends compared with neat PHBV when they crystallized isothermally at 70 °C.

The isothermal crystallization of PCL at 42 °C was also studied by DSC and analyzed by the Avrami equation in PHBV/PCL blends after the samples were held at 70 °C to finish the crystallization of PHBV. Fig. 5 shows the Avrami plots of the neat and blended PCL samples. From the straight lines of the Avrami plots, the Avrami exponent  $n$  and crystallization rate constant  $k$  were obtained and listed in Table 2. Furthermore, the values of  $t_{0.5}$  and  $1/t_{0.5}$  were also calculated and shown in Table 2. The Avrami exponent  $n$  was around 2 for neat PCL while in the blends it was around 2.6,

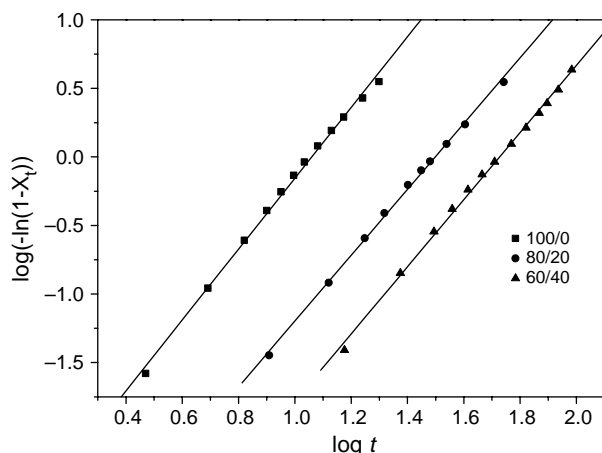


Fig. 4. Avrami plots of PHBV isothermally crystallized at 70 °C for PHBV/PCL blends.

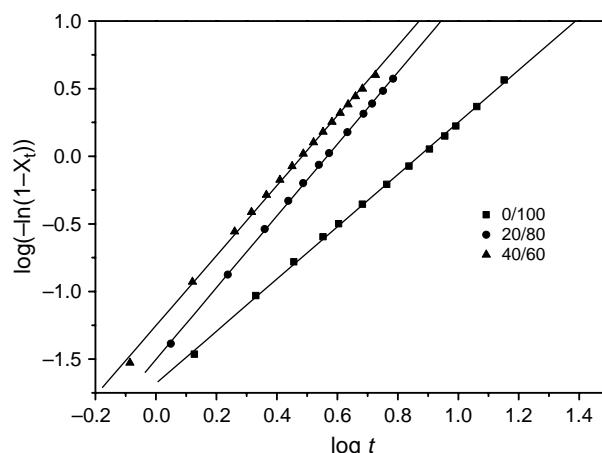


Fig. 5. Avrami plots of PCL isothermally crystallized at 42 °C for PHBV/PCL blends.

Table 2  
Crystallization kinetic parameters of PCL in PHBV/PCL blends at 42 °C

PHBV/PCL	<i>n</i>	<i>K</i> (min <sup>-<i>n</i></sup> )	<i>t</i> <sub>0.5</sub> (min)	1/ <i>t</i> <sub>0.5</sub> (min <sup>-1</sup> )
0/100	1.93	2.09 × 10 <sup>-2</sup>	6.14	1.63 × 10 <sup>-1</sup>
20/80	2.66	3.14 × 10 <sup>-2</sup>	3.21	3.12 × 10 <sup>-1</sup>
40/60	2.58	5.60 × 10 <sup>-2</sup>	2.65	3.72 × 10 <sup>-1</sup>

indicating that the presence of PHBV crystals changed the crystallization mechanism of PCL in the blends. Meanwhile, from the values of *t*<sub>0.5</sub> and 1/*t*<sub>0.5</sub> it could be concluded that the crystallization rate of PCL increased with the increase of PHBV in the blends. PHBV and PBSU were both crystalline polymers. From the above studies, PHBV and PBSU were immiscible. In the case of PHBV crystallization at 70 °C, PHBV crystallized in the presence of the phase separated melt of PCL. However, in the case of PCL crystallization at 42 °C, PCL must crystallize in the presence of PHBV crystals formed previously at 70 °C. The presence of the PHBV crystals may have two different influences on the crystallization of PCL. One is the possible positive effect on the nucleation of PCL spherulites. The other is the possible negative effect on the crystal growth of PCL spherulites. The increase of the crystallization rate of PCL might arise from the competition between the two opposite effects. The positive effect of the presence of the PHBV crystals on the nucleation of PCL spherulites seems to play a dominant role during the crystallization of PCL. Such two-step crystallization of PHBV/PCL blends was also studied by optical microscopy shown in the next section, which might provide some further information on the effect of the crystals of PHBV on the crystallization of PCL. Therefore, the crystallization rate of PCL increased in the blends. Conclusively, the addition of PHBV in the PHBV/PCL blends not only changed the crystallization mechanism of PCL but also increased the crystallization rate of PCL.

### 3.3. Preliminary optical microscopy study

Optical microscopy was also used to study the miscibility and crystallization behavior of PHBV/PCL blends. Provided that the refractive indices of the two components are not the same, it is possible to infer whether the melt is single-phased or biphasic. If PHBV is miscible with PCL, the single-phased melt should be observed. Otherwise, if PHBV is immiscible with PCL, the biphasic melt should be observed. PHBV/PCL blends samples were first melted at 200 °C and then were observed by optical microscopy. For all the compositions studied, biphasic separation was observed, indicating that PHBV was not miscible with PCL in the melt. As an example, shown in Fig. 6 are the phase separation and crystallization of PHBV and PCL for 60/40 blend observed by OM. Fig. 6(a) shows the banded spherulites of PHBV, which were crystallized at 70 °C from the crystal-free melt with the dark PCL melt dispersed in. On cooling the sample to a low temperature 40 °C, PCL could also crystallize and coexist with the PHBV crystals. Fig. 6(b) shows the bright crystals of PCL, which were

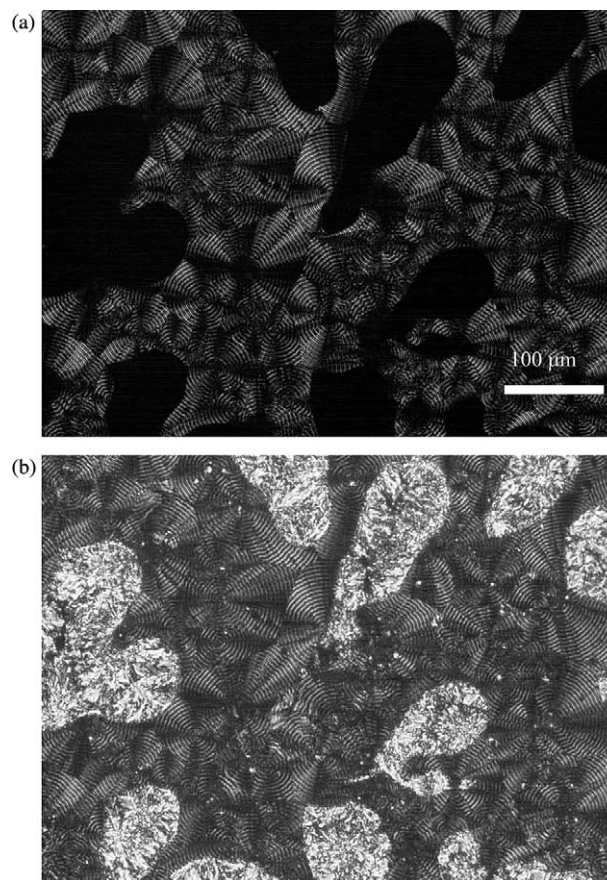


Fig. 6. Optical micrographs (same magnification, bar = 100 μm) of PHBV/PCL blends; (a) 60/40 blend at 70 °C and (b) 60/40 blend at 40 °C.

crystallized at 42 °C in the presence of the PHBV spherulites formed at 70 °C. The PCL crystals were brighter than the PHBV spherulites. It should also be noted that the crystallization of PCL blended with PHBV was faster than that of neat PCL due to the possible nucleation induced by the presence of PHBV crystals.

## 4. Conclusions

The miscibility of PHBV/PCL blends was investigated by DSC and OM. PHBV was found to show no miscibility with PBSU at all from the independence of the glass transition temperature and the phase separated melt. The isothermal crystallization of PHBV/PCL blends were studied using two-step crystallization process, the high melting point component PHBV at 70 °C and the low melting point component PCL at 42 °C. The crystallization rate of PHBV decreased with the increase of PCL in the blends while the crystallization mechanism did not change. The crystallization rate of PCL in the blends increased with increasing the PHBV content, indicating that the presence of the PHBV crystals formed at 70 °C earlier had a positive influence on the crystallization of PCL. Furthermore, the crystallization mechanism of PCL in the blends was different from that of neat PCL.

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