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Miscibility, crystallization and morphology of poly(β-hydroxybutyrate)/poly(*d,l*-lactide) blends

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The miscibility, crystallization and morphology of poly(β-hydroxybutyrate) (PHB)/poly(*d,l*-lactide) (PLA) blends were investigated by means of differential scanning calorimetry, polarizing optical microscopy and scanning electron microscopy studies. The results indicated that PHB/PLA blends prepared by casting a film from a common solvent at room temperature were immiscible over the range of compositions studied, while the melt-blended sample prepared at high temperature showed some evidence of greater miscibility. The crystallization of PHB in the blends was affected by the level of addition of PLA. The thermal history caused a depression of the melting point and a decrease in the crystallinity of PHB in the blends. Compared with plain PHB, the blends exhibited a certain improvement in mechanical properties.

(Keywords: biodegradable; poly(β-hydroxybutyrate); poly(*d,l*-lactide))

INTRODUCTION

Poly(β-hydroxybutyrate) (PHB) is a thermoplastic polyester produced via biosynthesis by bacterial fermentation[1]. Being biocompatible and biodegradable, PHB is potentially useful in biomedical materials such as bioabsorbable surgical sutures, matrices for drug delivery systems and the like. However, PHB is a highly crystalline polyester with a melting point of around 180°C, is very brittle and has a very low biodegradation rate[2]. In general, the level of crystallinity and melting point can be reduced by incorporating other hydroxyalkanoate units into the PHB chains[3], such as β-hydroxyvalerate (HV) units to form P(HB-*co*-HV) copolymers via fermentation[4]; however, there are restrictions on the carbon sources, the kinds of bacteria and the biochemical mechanisms of biosynthesis. Thus the poor processability still limits the uses of such polymers[5].

Blending of polymers is an effective alternative way to acquire new materials with desired properties. Recently, some efforts have been made to tailor the processability and the impact properties of PHB using a second polymer[6–12]. Poly(*d,l*-lactide) (PLA) is well known as an amorphous, biodegradable polyester with a fast degradation rate[13]. This paper focuses on PHB/PLA blends to investigate their miscibility, crystallization and morphology and to find out the effect of the PLA component on the crystallinity and melting point of PHB, and the mechanical properties and biodegradation behaviour of the blend.

EXPERIMENTAL

Materials

The PHB sample used in the present paper was supplied by Chengdu Institute of Biology, Academia Sinica, and was synthesized by bacterial fermentation using methanol as the carbon source. Its average molecular weight determined by viscosity measurement was 3×10^5. Poly(*d,l*-lactide) (PLA) was synthesized by the ring-opening polymerization of *d,l*-lactide using an $AlBui_3/H_2O/H_3PO_4$ complex catalyst. The PLA sample had an $\bar{M}_n$ of 4.3×10^4 and an $\bar{M}_w/\bar{M}_n$ of 1.9, as measured by gel permeation chromatography (g.p.c.) in THF.

Preparation of blends

Blends were prepared by dissolving the polymeric binary mixtures in chloroform (3% w/v) and casting films, unless stated otherwise. The solvent was evaporated at room temperature, and then the films were vacuum dried for 24 h.

Differential scanning calorimetry (d.s.c.) studies

D.s.c. was used to study the miscibility of the blends and the influence of the composition and thermal history on quantities such as the crystallinity, melting point and crystallization temperature of PHB. A Perkin–Elmer DSC-7 apparatus equipped with a Perkin–Elmer 3700 data station was used. The glass transition temperatures (T_g) of plain polymers and blends were obtained by heating samples first to 200°C and then rapidly cooling to −60°C.

The films obtained by casting were heated from −60°C to 200°C. The melting temperatures (T_m) and the

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crystallinities were determined from the d.s.c. endothermic peaks. After 1 min at 200°C the samples were cooled down to −60°C, and the crystallization exotherms and the crystallization temperatures (T_c) were registered. Finally, the samples were heated up to 200°C, and the melting point and crystallinity of PHB in the blends after this thermal treatment were again measured. A scan rate of 20°C min^{-1} was used throughout.

Polarizing optical microscopy

Studies of the crystallization behaviour and spherulitic morphology of the PHB in the blends were conducted with an Ortholux II POL-BK microscope equipped with a hot stage. The isothermal crystallization behaviour was studied by first bringing the blend samples to 200°C for 1 min. The temperature was then lowered to the desired crystallization temperature (T_c) and PHB allowed to crystallize isothermally.

Scanning electron microscopy (SEM)

SEM was used to examine the phase morphology and the fracture surfaces of the blends. The blend films were first treated with toluene to remove the PLA phase and dried before the SEM study was conducted. The original sample films were torn at liquid nitrogen temperature, then the fracture surfaces were studied by SEM. An AMRAY-1000B microscope was used in these studies. Before observation the samples were coated with a thin layer of gold by vacuum deposition.

Mechanical tensile properties

Stress–strain curves for the films of PHB and its blends were obtained using a Shimadzu DCS testing machine at 20°C. The films were 0.2 mm thick and tested at a stretching speed of 10 mm min^{-1}.

Hydrolytic degradation

Hydrolytic degradation of the pure components and blends was performed at 37°C and pH 7.4 in a potassium dihydrogenphosphate/sodium hydrogenphosphate (KH_2PO_4/Na_2HPO_4) buffer solution. Samples were withdrawn at different time intervals and the water absorption was determined gravimetrically after removing the excess surface water. The water content was expressed as the percentage of water in the dry sample.

RESULTS AND DISCUSSION

Miscibility of the blends

The d.s.c. curves of the blend films obtained by casting show two distinct glass transitions independent of blend composition during the cooling run when samples were rapidly quenched from 200°C. There are minor variations in the glass transition temperatures (T_g) with composition, but most of the T_g values are within experimental error of those for the pure components, the lower T_g and the higher T_g being close to the values observed for pure PLA and pure PHB, respectively (*Table 1*). These results suggest that PHB/PLA blends are immiscible in the amorphous state.

In the d.s.c. heating runs, the thermograms of the blends show a glass transition at about 50°C for the PLA component. It is difficult to recognize the glass transition of the PHB component because of its fast crystallization under the conditions of sample preparation. However, endothermic peaks at almost the same temperature (around 175°C) were registered over the range of compositions studied, as shown in *Table 2*. These results also indicate an immiscible blend.

Table 1 Glass transition temperatures of plain PHB, plain PLA and PHB/PLA blends

Sample code	PHB/PLA composition (w/w)	T_{g1} (°C) Midpoint	T_{g1} (°C) Onset	T_{g2} (°C) Midpoint	T_{g2} (°C) Onset
B10	100/0	1.76	9.6		
B8	80/20	4.45	11.0	45.3	48.3
B6	60/40	0.28	10.3	44.6	54.1
B4	40/60	4.86	10.6	44.1	53.8
B2	20/80	3.27	10.4	44.8	52.2
B0	0/100			52.3[a]	54.9[a]

[a] Obtained from the d.s.c. cooling run at a scan rate of 10°C min^{-1}

Table 2 Melting points and crystallinities of pure PHB and PHB in the blends from the first d.s.c. heating run

Sample code	T_m (°C)	ΔH_f (J g^{-1})	Cr_{blend} (%)	Cr_{PHB} (%)
B10	175.1	82.2	56.3	56.3
B8	175.4	64.2	43.9	54.9
B6	175.0	47.6	32.6	54.3
B4	174.6	31.6	21.6	54.1
B2	174.7	16.5	11.0	55.0

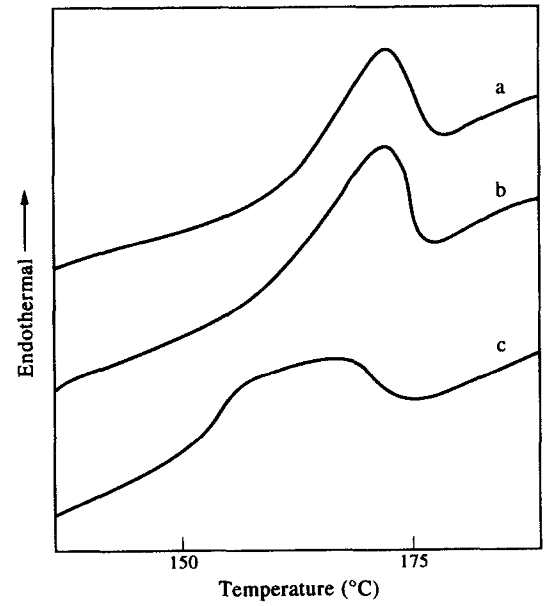

Figure 1 D.s.c. curves of PHB/PLA blends prepared by different methods: (a) 4F; (b) 4P; (c) 4M

Another three blend samples of 40/60 PHB/PLA were prepared by different processes. Sample 4F was prepared by casting a film from a common solvent. Sample 4P was precipitated with methanol from chloroform solution and dried under vacuum. Sample 4M was melt blended. The blend solution was magnetically stirred and evaporated under reduced pressure, and the residue was maintained at 190°C for 30 min.

D.s.c. traces of the above-mentioned samples are shown in *Figure 1*. There is little difference between 4F and 4P, while a significant difference for 4M is found in

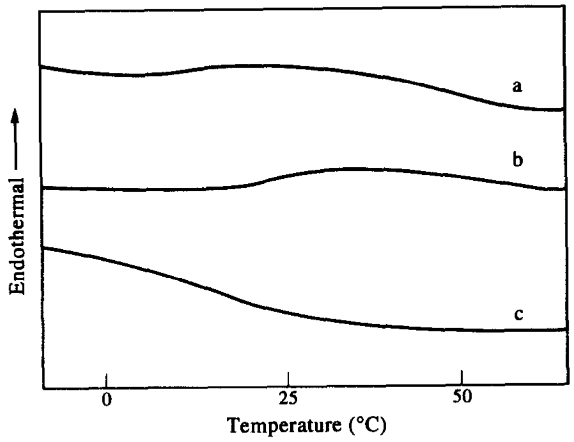

Figure 2 D.s.c. thermograms of PHB/PLA blends from the cooling scan at 50°C min^{-1}: (a) 4F; (b) 4P; (c) 4M

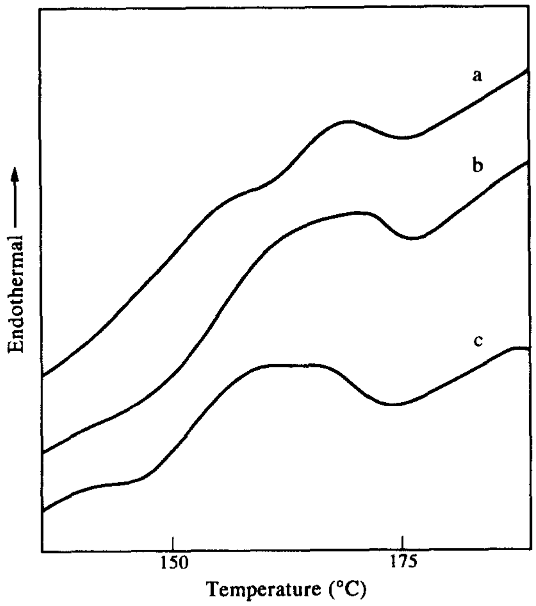

Figure 3 D.s.c. curves of sample 4M from the first (a), second (b) and third (c) heating runs

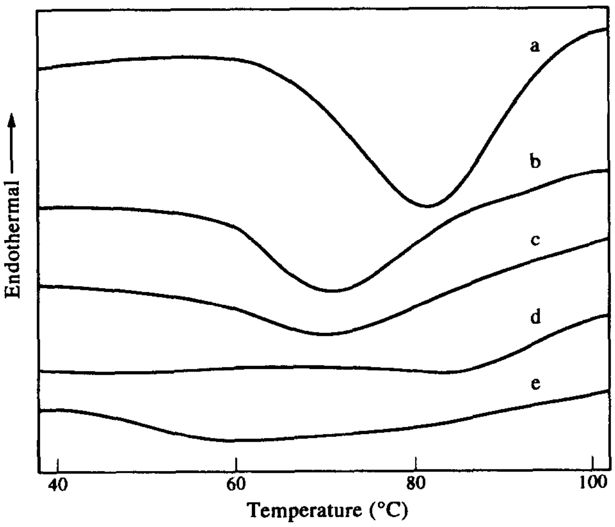

Figure 4 D.s.c. traces of PHB and PHB/PLA blends from the non-isothermal crystallization run: (a) B10; (b) B8; (c) B6; (d) B4; (e) B2

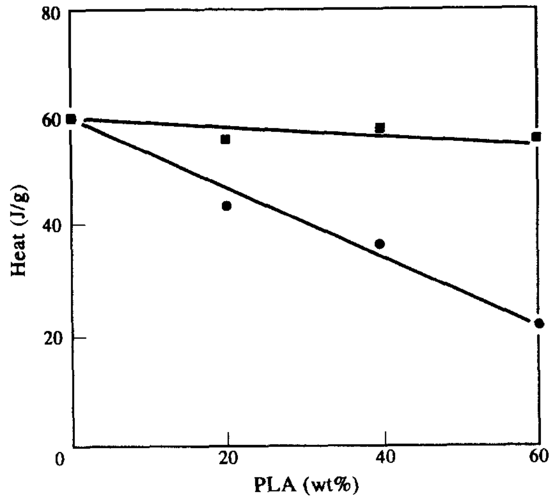

Figure 5 Plots of heat of crystallization ΔH_c (●) and $\Delta H_c/W_{PHB}$ (■) versus PLA content

Table 3 Melting points and crystallinities of pure PHB and PHB in the blends from the second d.s.c. heating run

Sample code	T_m (°C)	ΔH_f ($\mathrm{J\,g^{-1}}$)	Cr_{blend} (%)	Cr_{PHB} (%)
B10	173.0	78.3	53.4	53.4
B8	172.1	61.0	41.8	52.2
B6	171.7	44.5	30.4	50.8
B4	171.5	23.9	16.4	40.9
B2	169.4	12.4	8.49	42.4

the melting point of PHB. Moreover, in the d.s.c. cooling scan at 50°C min^{-1} from 200°C, the curves show that the glass transition temperature of 4M is lower than that of 4F and 4P, and corresponds to that of plain PLA (*Figure 2*). This implies greater miscibility for 4M.

The main cause of these results may be the transesterification of PHB and PLA. Assuming that transesterification takes place between PHB and PLA chains during sample preparation at 190°C, PHB/PLA block copolymers will be produced *in situ*. The copolymers, though limited in amount, will act to compatibilize the two components to improve the PHB/PLA blend miscibility. So, a lower T_m for PHB and a lower T_g for PLA will result.

The thermal treatment also causes other effects, such as degradation of the polymer chains and a change in crystallization kinetics. Both can lead to a lower T_m for PHB. As shown in *Figure 3*, the T_m of PHB in 4M shifts to lower temperature in the second and third d.s.c. heating runs. However, this makes almost no contribution to the blend miscibility.

Melting point and crystallinity of PHB in the blends

The peak melting temperature of PHB remains constant at around 175°C for all the blend ratios investigated, and the phase crystallinity of PHB in the blends shows no change (*Table 2*). The crystallinities of the blends (Cr_{blend}) and of the PHB phase (Cr_{PHB}) can be calculated from

$$Cr_{blend} = (\Delta H_f/\Delta H_f^0) \times 100\%$$

$$Cr_{PHB} = Cr_{blend}/W_{PHB}$$

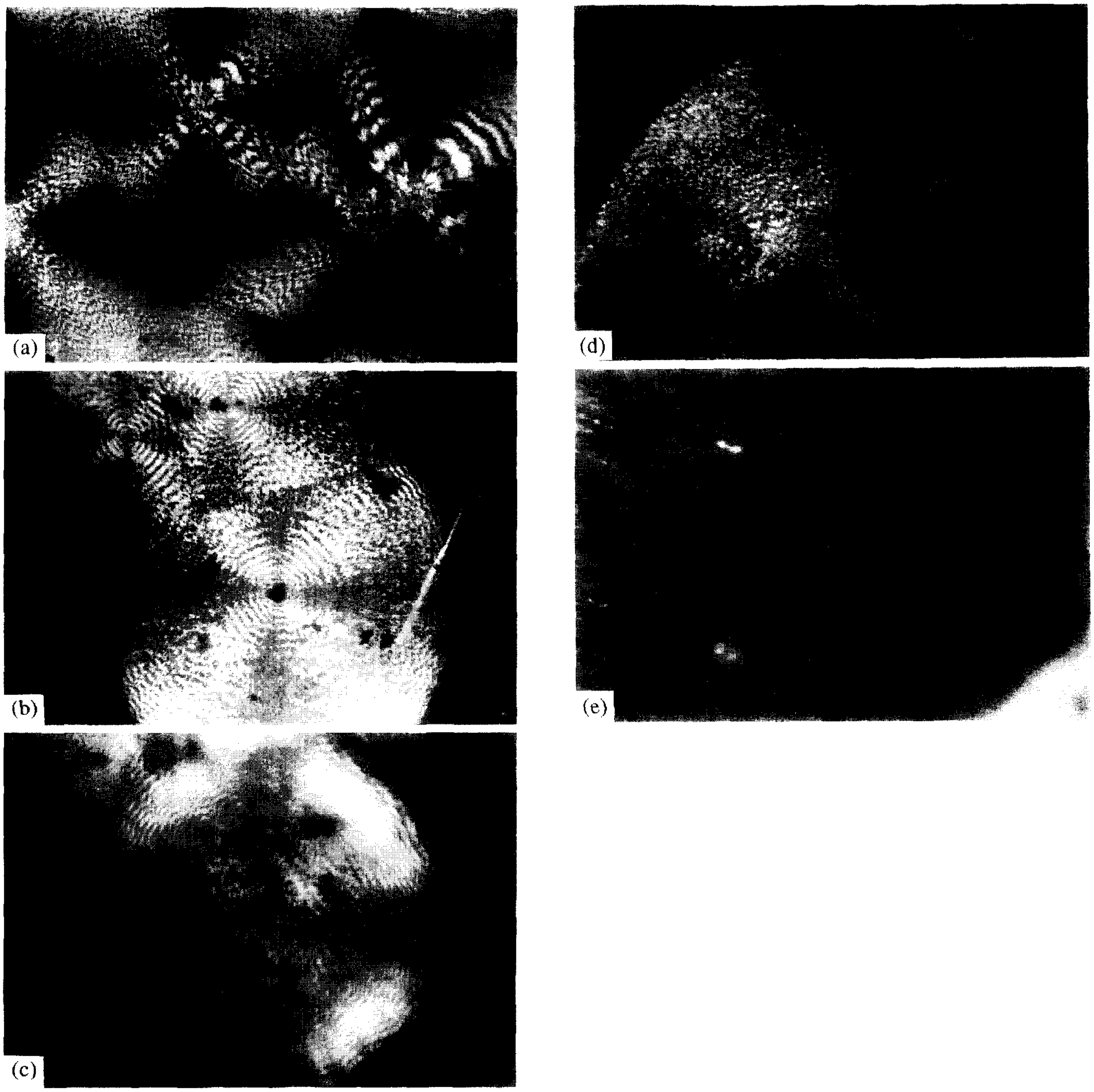

Figure 6 Polarizing optical micrographs (under crossed polars, 2.4 × 32) of PHB and PHB/PLA blends isothermally crystallized at 90°C: (a) B10; (b) B8; (c) B6; (d) B4; (e) B2

where ΔH_f^0 is the thermodynamic enthalpy of fusion per gram of PHB (146.6 J g^{-1}), ΔH_f is the apparent enthalpy of fusion per gram of the blend and W_{PHB} is the weight fraction of PHB in the blend.

That the heating rate in the d.s.c. analysis has an effect on the melting point of PHB implies that the thermal treatment, especially the thermal history, has a major effect on the fusion process. *Table 3* gives the results from the second d.s.c. heating run. Comparing *Table 3* with *Table 2*, we see that samples of the same blend ratio show a depression in melting point and a reduction in phase crystallinity for PHB. Furthermore, T_m and Cr_{PHB} in the second d.s.c. heating run decrease from 173.0°C and 53.4% to 169.4°C and 42.4% with increasing PLA content in the blends. The reductions in T_m and Cr_{PHB}, ΔT_m and ΔCr_{PHB}, calculated by subtracting T_m or Cr_{PHB} in the second d.s.c. heating run from the corresponding value in the first run, show a remarkable increase from 2.1°C and 2.9% to 5.3°C and 12.6% as the PLA content increases from 0% to 80%. These results also come from the effect of amorphous PLA on the crystallization kinetics of PHB in the blends.

Crystallization behaviour of PHB in the blends

Figure 4 gives the d.s.c. thermograms obtained from the non-isothermal crystallization d.s.c. runs. Some traces show an exothermic peak corresponding to the crystallization of PHB. The position of T_c is composition dependent, and no such peak for B2 appears in the d.s.c. curve. The heats of crystallization of the blends, ΔH_c

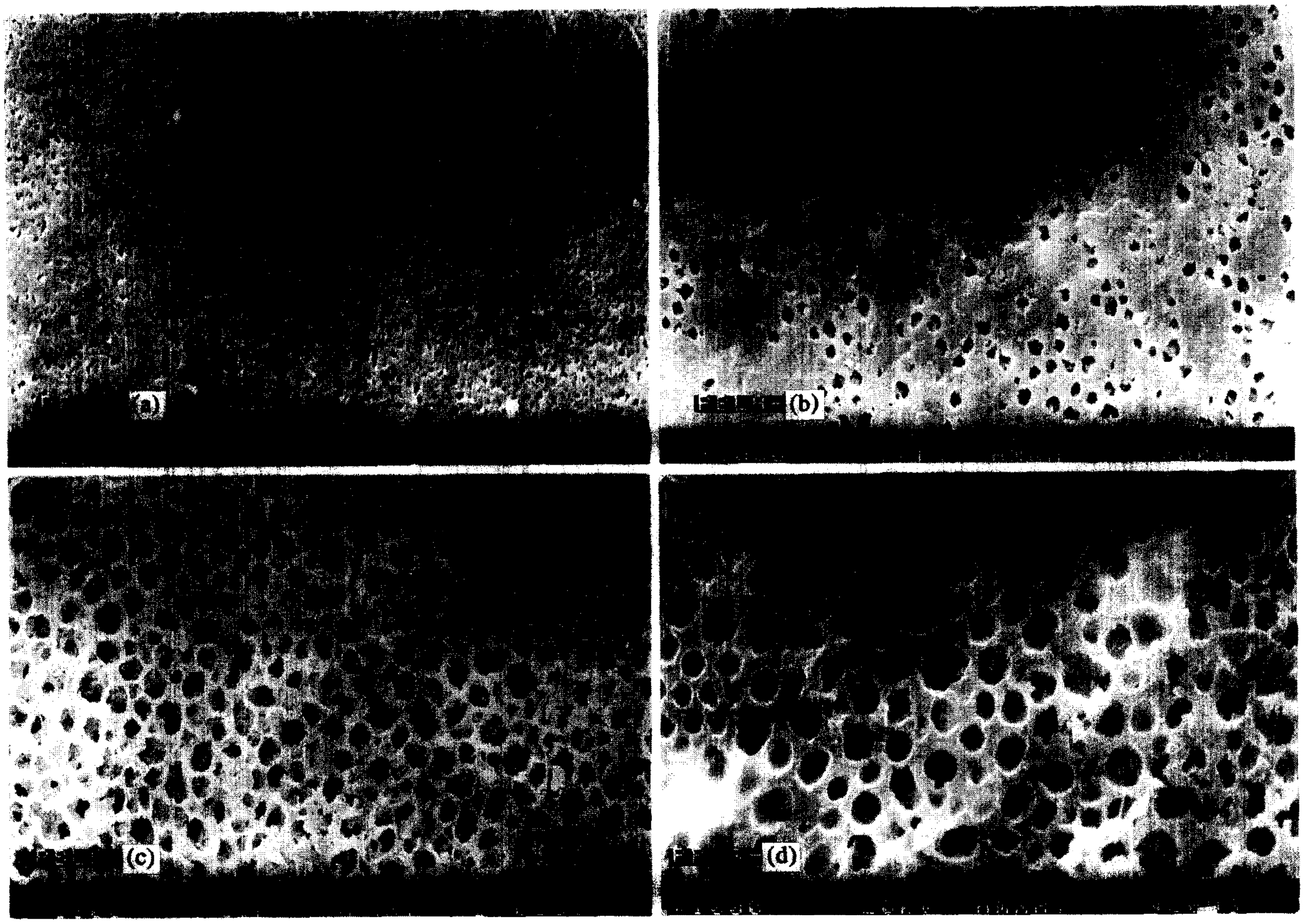

Figure 7 Scanning electron micrographs of PHB/PLA blend films extracted with toluene: (a) B8; (b) B6; (c) B4; (d) B2

Table 4 Mechanical tensile properties of PHB and the 60/40 PHB/PLA blend

Sample code	Modulus E (kg mm^{-2})	Stress at break σ_b (kg mm^{-2})	Elongation at break ϵ_b (%)
B10	366	8.7	3.7
B6	274	6.5	27.7

and $\Delta H_c/W_{PHB}$, are plotted against PLA content in *Figure 5*. The values of ΔH_c and $\Delta H_c/W_{PHB}$ are dependent on the blend composition. The results indicate that the amorphous PLA component shows a remarkable effect on the crystallization of PHB in the blends, especially when its content is relatively high.

Polarizing optical microscopy observation of the isothermal crystallization of PHB in the blends leads to a similar conclusion. The morphologies of PHB and the PHB/PLA blends crystallized isothermally at 90°C are depicted in *Figure 6*. The figure shows that PHB is able to crystallize with a spherulitic morphology even in the case of the 40/60 PHB/PLA blend. However, the rate of growth of PHB spherulites decreases with the addition of the amorphous PLA component. When the PLA content reached 80%, the sample (B2) did not crystallize, even after a long time. These results give an explanation of *Table 3*.

Morphology of PHB/PLA blends

Scanning electron microscopic evaluation was carried out on toluene-extracted samples to discern the microstructure of PHB in the blends: the micrographs are illustrated in *Figure 7*. Toluene is a good solvent for PLA but a poor one for PHB; thus, we could selectively remove the PLA phase from the blends and observe the remaining morphology. It was found that the blends consist of a two-phase morphology, and the size of the PLA phase becomes larger as the PLA content increases.

Mechanical properties

The overall effects of the addition of amorphous PLA on the PHB tensile properties are a reduction in modulus (E) and stress at break (σ_b) and an enhancement of the elongation at break (ϵ_b). As shown in *Table 4*, the ϵ_b of the 60/40 PHB/PLA blend is almost eight times that of plain PHB.

Fracture surface studies of blend films gave similar results. The sample films were torn at liquid nitrogen temperature and then studied by SEM. As shown in *Figure 8*, the fracture surface of plain PHB displays the features of a very brittle material. The PHB/PLA blends show quite different morphologies compared to PHB as more amorphous PLA is introduced into the system. The fracture surface of PHB is drastically modified after adding the second phase, and the blends are expected to have better fracture toughness.

Hydrolytic degradation

The hydrolytic degradation of PHB and the blend films was carried out at 37°C in a pH 7.4 buffer solution, and evaluated from the level of water absorption. The degradation behaviour of crystalline PHB in the blends

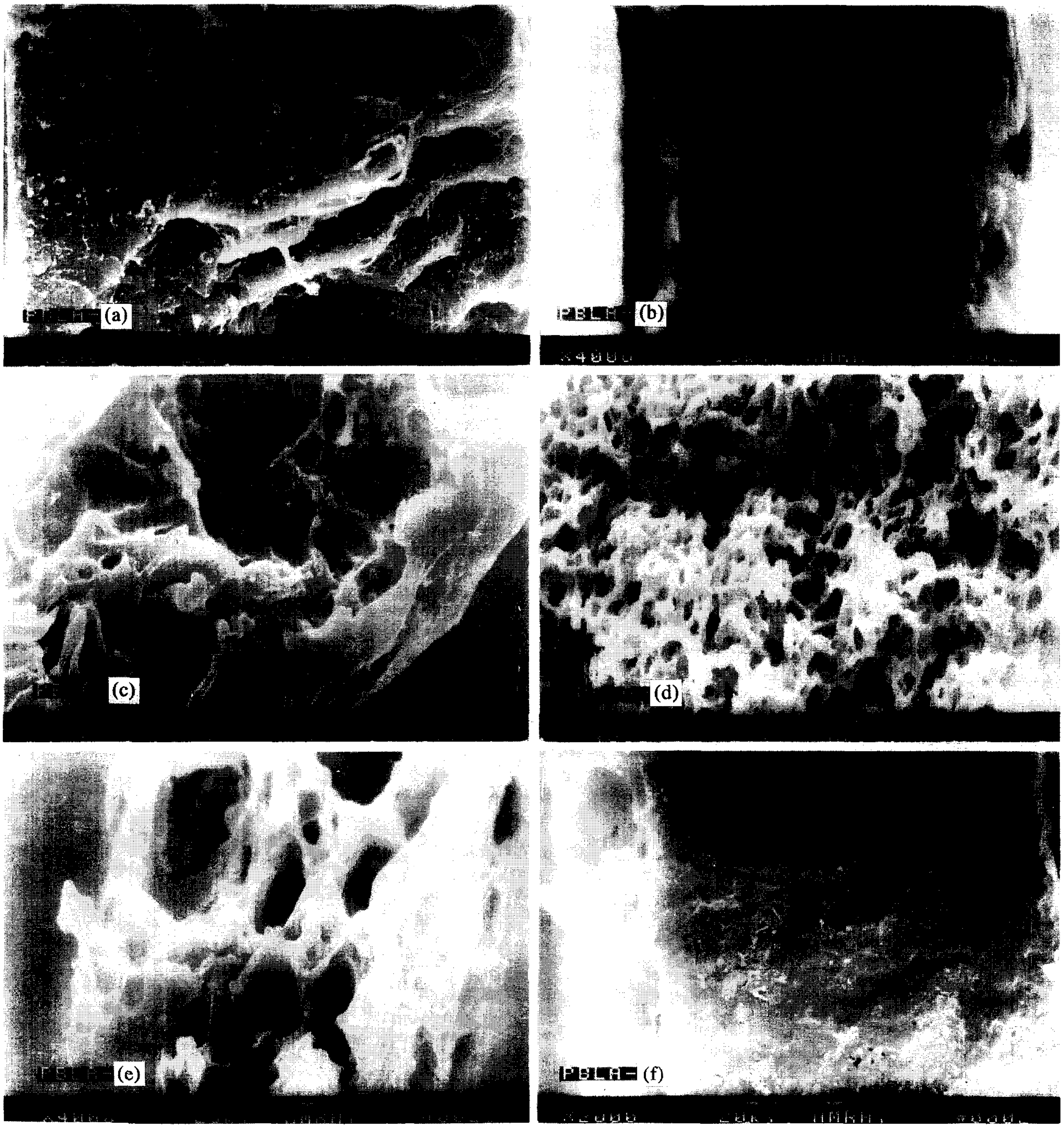

Figure 8 Scanning electron micrographs of fracture surfaces: (a) B0; (b) B10; (c) B8; (d) B6; (e) B4; (f) B2

was markedly influenced by the amorphous component. The two-phase nature of the blends resulted in a higher water absorption than shown by pure PHB. The water contents of pure PHB and the 50/50 PHB/PLA blend after 2, 10 and 35 days of hydrolytic degradation were 14%, 19% and 23.5% and 19.5%, 25% and 27.5%, respectively. The blend films are more hydrophilic than PHB, so faster hydrolytic degradation would be expected.

CONCLUSIONS

From the above discussion, it is possible to conclude that PHB and PLA are immiscible in the amorphous state. The blends exhibit two glass transitions corresponding to the glass transitions of plain PHB and PLA. The melting point and phase crystallinity of PHB are independent of blend composition. Thermal treatment causes changes in T_m and Cr_{PHB}. The sample prepared at high temperature exhibits some evidence of greater miscibility, possibly because of transesterification between PHB and PLA chains. The crystallization of PHB in the blends is affected by the addition of amorphous PLA; when the PLA content reaches at least 80%, no spherulitic morphology is observed. The change in the crystallization kinetics of PHB in the blends results in a decrease in T_m and Cr_{PHB} and an increase in ΔT_m and ΔCr_{PHB} with increasing PLA content for the second d.s.c. run. As expected, the mechanical properties of PHB can be modified by adding amorphous PLA, and hydrolytic degradation is accelerated by the quickly degraded PLA component. The blend morphologies have a two-phase nature and the nature of the crystallization of PHB in the blends is affected by the PLA content. We can conclude that by the means employed in this work, a series of materials with different mechanical properties and hydrolytic rates suitable for biomedical applications might be obtained.

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