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Miscibility, crystallization and melting of poly(3-hydroxybutyrate)/poly(L-lactide) blends

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The spherulitic structure, growth rates and melting behaviour of blends of bacterially produced poly(D(−)-3-hydroxybutyrate) (PHB) and poly(L-lactide) (PLLA) were investigated using polarized light microscopy. Results indicated that low-molecular-weight PLLA ($M_n = 1759$) was miscible in the melt over the whole composition range, whereas a blend of high-molecular-weight PLLA ($M_n = 159\,400$) with PHB showed biphasic separation, in accordance with calculations based on Flory–Huggins theory. Two types of spherulite were formed on cooling, relating to the crystallization of PHB and PLLA respectively. In some blends, spherulites of opposite type interpenetrated when the growth fronts met. It is proposed that lamellae belonging to one type of spherulite continued to grow in the interlamellar regions of the other type of spherulite.

Keywords: PHB/PLLA blends; biodegradable polymers; spherulites)

INTRODUCTION

As part of an on-going study of environmentally friendly thermoplastic materials, we have been investigating the properties of bacterially produced poly(D(−)-3-hydroxybutyrate) (PHB) blended with synthetic polymers. The properties of PHB homopolymer have already been documented in several publications (e.g. refs. 1–6). Blends of PHB with non-biodegradable polymers, poly(ethylene oxide), poly(vinyl acetate) (PVAc) and ethylene–propylene rubber, have been investigated by Martuscelli and coworkers[7,8] and Azuma and coworkers[9]. Work on PHB blended with the biodegradable synthetic polymer polycaprolactone has been reported by Gassner and Owen[10], Yasin and Tighe[11] and Yumagai and Doi[12].

The present paper deals with the properties of PHB blended with poly(L-lactide) (PLLA), which is a synthetic polymer commercially obtained either by ring-opening polymerization of lactones or by polycondensation of hydroxycarbonic acids[13]. PLLA degrades by hydrolysis in the presence of water to lactic acid, and is thereby suitable as a resorbable, non-toxic material for surgical use.

The purpose of this work was to investigate the miscibility, crystallization and melting behaviour of blends of PHB and PLLA (*Figure 1*). Apart from being biodegradable and resorbable, the two blend components are very suitable test substances for understanding the physical properties of polymer mixtures.

EXPERIMENTAL

High-purity grade, bacterially produced PHB powder was provided by Zeneca Bioproducts (formerly ICI Biological Products), Billingham, UK (molar mass $M_n = 222\,000, M_w = 794\,000$). The PLLA used was a low-molar-mass powder ($M_n = 1759$; tradename Resomer L104). Some results were also obtained for a higher-molar-mass powder ($M_n = 159\,400, M_w = 416\,6000$; Resomer L209). These samples were supplied by Boehringer-Ingelheim, Ingelheim am Rhein, Germany[13].

Blends were prepared by mixing and sieving the powders before melting them in a press and moulding into films 0.2 mm thick. The films were quenched from the melt and subsequently stored at room temperature. Films containing 0, 10, 25, 50, 75, 90 and 100% PHB were obtained in this way.

Samples cut from these films were investigated in a polarizing microscope (SM-LUX-POL, Zeiss, Wetzlar) equipped with a Mettler hot stage (FP5). The polarizing microscope was used in conjunction with the hot stage to observe the phase structure and to obtain radial growth rates of spherulites and melting-point values. Radial growth rates were obtained by first melting a few milligrams of substance in the hot stage (established by disappearance of birefringence under crossed polars). The sample was then cooled rapidly to the required isothermal crystallization temperature T_c, and the nucleation and growth of spherulites was recorded using a video camera in place of the microscope eyepiece. After crystallization at T_c had taken place, the sample was heated at 10°C min^{-1} and the melting point T_m measured (disappearance of birefringence). This measurement could be made to an accuracy of approximately ±0.2°C.

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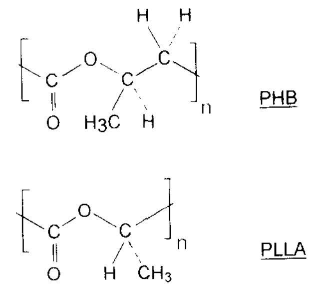

Figure 1 Chemical formulae of PHB and PLLA

RESULTS AND DISCUSSION

Pure components PHB and PLLA

First, measurements were made for pure PHB and PLLA. Owing to the low nucleation density, it was possible to determine the growth rate of individual spherulites conveniently and accurately over a wide range of temperatures before they impinged. *Figure 2a* is a plot of the radial growth rate of PHB spherulites and *Figure 2b* is that for spherulites in low-molecular-weight PLLA as a function of T_c. The data points were fitted here conveniently, but without theoretical justification, to Gaussian curves. A more detailed analysis of PHB growth-rate data in terms of Hoffman's theory[14] can be found in ref. 2. The PLLA spherulites were often dendritic[15,16] and grew much more slowly than the PHB spherulites; they showed a growth-rate maximum of approximately $9\,\mu\mathrm{m\,min^{-1}}$ at $T_c = 105°\mathrm{C}$, whereas PHB spherulites grew at a maximum rate of $230\,\mu\mathrm{m\,min^{-1}}$ at $T_c = 90°\mathrm{C}$.

The sign of bifringence of the spherulites was established in the standard way[16,17], by placing a sensitive-tint retardation plate in the beam at 45° to the directions of the crossed polarizer and analyser. The PHB and PLLA spherulites were found to have opposite sign, which aided considerably in their investigation and identification.

The dependence of melting temperature T_m on crystallization temperature T_c is shown in *Figure 3a* for PHB and *Figure 3b* for low-molecular-weight PLLA. The data for PHB were obtained over a wide T_c range, from 35 to 165°. We found it impossible to extrapolate the results in the usual way to the line $T_m = T_c$, in order to obtain the equilibrium melting point T_m° of PHB, since at low crystallization temperatures the samples recrystallized during heating in the hot stage, so that the measured melting temperatures were too high, whereas for high T_c the results may be too low due, for example, to some thermal degradation of the sample. Avella and Martuscelli[7] have already given T_m° as 194°C using this procedure, a value that is compatible with our results. The extrapolation procedure for PLLA was far less problematical, since recrystallization of PLLA could be neglected during heating in the hot stage. A value of $T_m^\circ = 148.2°\mathrm{C}$ was obtained for the low-molecular-weight PLLA.

Melt structure in blends

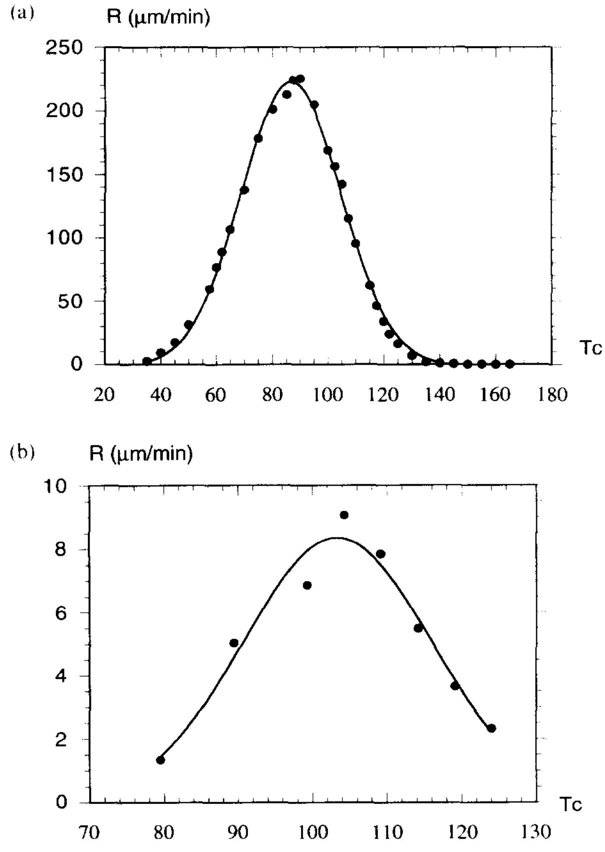

Figure 2 Radial growth rate R of spherulites in (a) PHB and (b) PLLA, as a function of crystallization temperature T_c (°C)

Samples were first melted in the hot stage at 190°C (463 K). The polarizer was then rotated slightly so that the sample appeared in 'bright field'. Provided that the refractive indices of the two components are not the same, it is possible under these conditions of illumination to infer whether the melt is single-phased or biphasic. For all compositions of PHB with low-molecular-weight PLLA we found no evidence of structure indicating phase separation in the melt (at the resolution possible). The same observation was made for blends of PHB with poly(vinyl acetate), which are known to form a homogeneous melt[8]. For PHB blended with high-molecular-weight PLLA, on the other hand, clearly defined biphasic separation was observed, as for the case of PHB–polycaprolactone blends[10].

We made an estimate of the expected equilibrium phase diagram for the melt of PHB–PLLA blends using the well known Flory–Huggins expression for the free energy of mixing $\Delta G(\mathrm{cal\,cm^{-3}})$:

$$\frac{\Delta G}{RT} = \phi_1\phi_2\chi + \frac{\phi_1 \ln \phi_1}{N_1} + \frac{\phi_2 \ln \phi_2}{N_2} \qquad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of the two blend components, R the gas constant ($\mathrm{cal\,mol^{-1}\,K^{-1}}$), T the absolute temperature (K) and N_1 and N_2 the molar volumes of the two components ($\mathrm{cm^3\,mol^{-1}}$). The interaction parameter χ was obtained via the Hildebrand solubility parameters δ_1 and δ_2 of the two blend components via the relationship:

$$\chi = \frac{V(\delta_1 - \delta_2)^2}{RT} \qquad (2)$$

The solubility parameters were estimated for each component using data given by Van Krevelen[18]. The molar volumes were calculated from the number-average

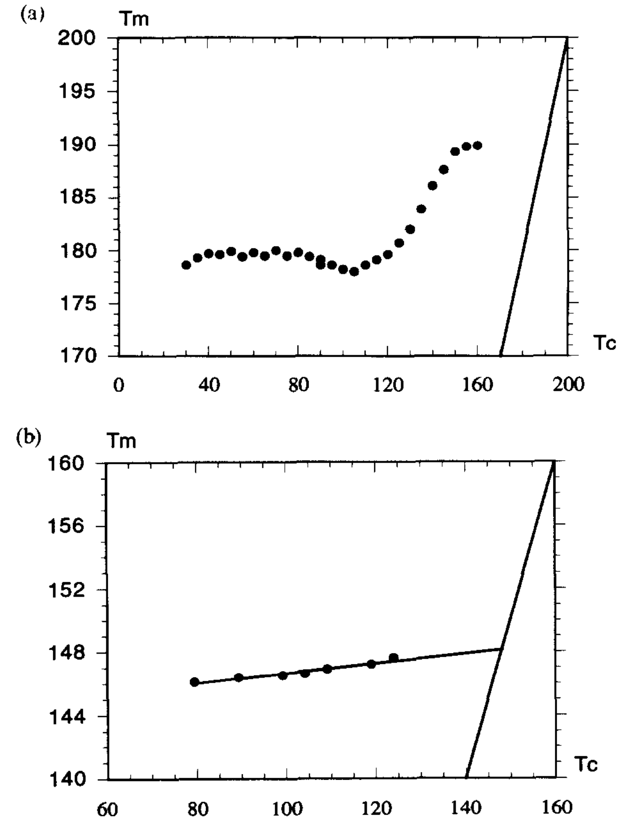

Figure 3 T_m *versus* T_c for (a) PHB and (b) PLLA. The data for PLLA are shown extrapolated to the line $T_m = T_c$

molar masses and the molar volumes of the monomers. Polydispersity was not taken into account. *Figure 4* shows the spinodal ($\partial^2\Delta G/\partial\phi^2 = 0$) calculated in this way for the PHB/low-MW PLLA system. The upper critical solution temperature of around 185 K shows that we expect PHB to be miscible in the melt with low MW PLLA over the whole composition range, as is indeed observed experimentally. (The samples crystallize at temperatures well above this critical temperature, so that biphasic separation in the melt is not observable.) For high MW PLLA the upper critical solution temperature was calculated to be in the region of 5000 K, which means that these blends would always show phase separation in the melt. (The theoretically calculated critical temperature cannot be reached experimentally, since the samples degrade at much lower temperatures.)

Spherulitic growth in blends of PHB and PLLA

The blends of PHB and PLLA (low MW) were rapidly cooled from the melt (at more than $20°\mathrm{C\,min^{-1}}$) to the chosen isothermal crystallization temperature T_c. Crystallization could be conveniently investigated using a T_c of 100°C. After an initiation time of several minutes, two types of spherulite nucleated and grew in the blends, these being characteristic of the spherulites found in pure PHB and pure PLLA respectively. The spherulites were observed under crossed polars with a sensitive-tint plate aligned at 45° to the polarizer[16,17]. *Figure 5* shows two large, banded PHB spherulites with orange sectors 'north-west' and 'south-east', whereas the much smaller, coarsely banded PLLA-type spherulites have their sectors 'north-east' and 'south-west'. From the properties of the retardation plate we deduced that the PHB-type spherulites were positively birefringent, whereas the PLLA-type spherulites were negatively birefringent.

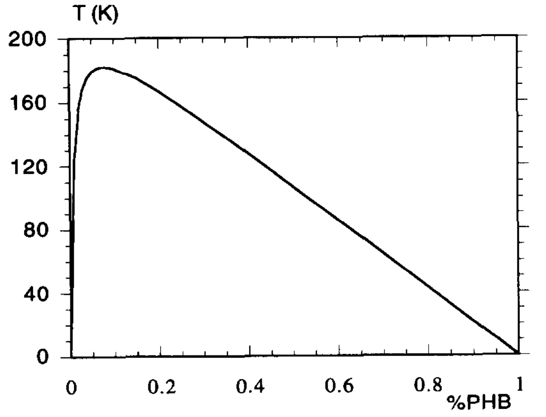

Figure 4 Spinodal curve for PHB–PLLA blends calculated using the Flory–Huggins equation. Parameters used: $N_1 = 2581$, $N_2 = 24.4$, $\delta_1 = 9.40\,(\mathrm{cal\,cm^{-3}})^{1/2}$, $\delta_2 = 9.79\,(\mathrm{cal\,cm^{-3}})^{1/2}$

The radial growth rate of the PHB-type spherulites depended strongly on composition (*Figure 6*), with the rate decreasing with increasing PLLA content. This result is to be expected for a homogeneous melt where the two components are mixed on a molecular scale, i.e. PLLA dilutes the melt and retards the crystallization rate of PHB, since the rate is limited by the amount of PHB being able to diffuse to the growth front. Furthermore, for any temperature and composition, the growth rate was constant, i.e. independent of spherulite radius, suggesting that the PLLA component remained in the interlamellar regions of the PHB spherulites, and was not excluded from these spherulites. Similar observations have been made for PHB–PVAc blends by Greco and Martuscelli[8].

For PHB–PLLA blends containing more than approximately 75% PHB, the PHB-type spherulites grew so quickly that only rarely did PLLA-type spherulites nucleate before the whole sample was filled with PHB spherulites.

For 50% PHB, the crystallization of both types of spherulite could be observed simultaneously, with PHB

Figure 5 Banded spherulites of PHB and PLLA. Scale bar represents 600 μm

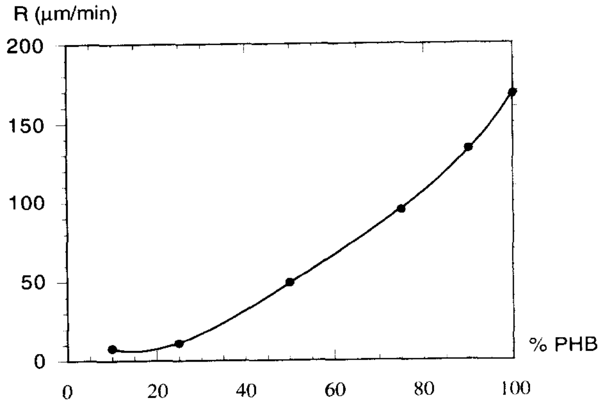

Figure 6 Radical growth rate of PHB-type spherulites in PHB–PLLA blends (crystallization temperature T_c = 100°C)

spherulites generally growing faster than PLLA spherulites. When a PHB spherulite crystallization front reached a PLLA spherulite, instead of growth being arrested, the PHB spherulite penetrated the PLLA spherulite and the crystallization front became distorted. *Figure 7* shows a large banded PHB spherulite growing through smaller PLLA spherulites. Some PLLA spherulites have been completely engulfed by the PHB spherulite. On the other hand, the PLLA spherulites stopped advancing towards the PHB spherulites on contact. Finally, impingement of two PLLA spherulites resulted in growth arrest, and a relatively clear boundary was seen as a line.

All the observations suggest that the PHB spherulites interlock with the PLLA structures, and are not merely advancing over each other as two separate layers. A similar phenomenon has been observed by Galeski and coworkers[19] in poly(oxymethylene) doped with low-molecular-weight poly(oxyethylene), where strong interpenetration of the lamellae of adjacent spherulites of poly(oxymethylene) occurred. In the present work, however, the interpenetration took place between different spherulite species. We propose that the PHB-type spherulites consist of radially directed crystalline lamellar ribbons of virtually pure PHB molecules, with PLLA molecules and some PHB excluded into the amorphous interlamellar regions within the spherulites, and *vice versa* for the PLLA-type spherulites. When different types of spherulite impinge, the PHB crystalline lamellae continue to grow into the PHB-enriched interlamellar regions of the PLLA spherulites. On the other hand, the PLLA crystalline lamellae may be too thick to grow into the PHB interlamellar regions for the 50/50 blend, and hence advance of these spherulites stopped.

Another interesting and related phenomenon occurred for blends containing 25% PHB, where the growth rate of the PHB spherulites was much lower and the birefringent contrast weaker. Several minutes after a PHB spherulite had formed, its sign of birefringence (suddenly) changed from positive to negative (not shown here), indicating that subsequent crystallization of PLLA within the interlamellar regions of the PHB spherulites may have occurred. This is possible because the interlamellar regions are much thicker for this composition than for the 50/50 blend.

Even with a blend containing only 10% PHB, the occasional PHB spherulite was observed together with many PLLA spherulites. In this case, the growth rates of both types of spherulite were approximately equal. *Figure 8* shows the distorted growth front of the PHB spherulite as it penetrated a PLLA spherulite. For this blend composition, the PLLA spherulite could penetrate deeply into the PHB spherulite, since the PHB crystal lamellae were now far enough apart to accommodate PLLA crystal lamellae between them.

Finally, *Figure 9* shows the same region of sample as *Figure 5*, subsequently heated above the melting temperature of the PLLA phase. The PLLA spherulites outside the PHB spherulites have now melted, whereas those inside the PHB spherulites appear to be still present, but with opposite sign of birefringence. We suggest that the birefringent contrast relates to unmelted crystallites of PHB in the interlamellar regions of the PLLA spherulites, the PLLA itself having melted. This observation provides further evidence for interpenetrating spherulite growth.

After crystallization at T_c = 100°C had been completed, samples were heated at a rate of $10°C\,min^{-1}$ and T_m determined for each spherulite type at each blend composition. *Table 1* shows that the T_m of PHB spherulites decreased with increasing PLLA content.

Figure 7 Large banded PHB spherulite growing through smaller PLLA spherulites, in a 50/50 PHB–PLLA blend. Scale bar represents 100 μm

Figure 8 Distorted growth front of a PHB spherulite, in a 10/90 PHB–PLLA blend. Scale bar represents 100 μm

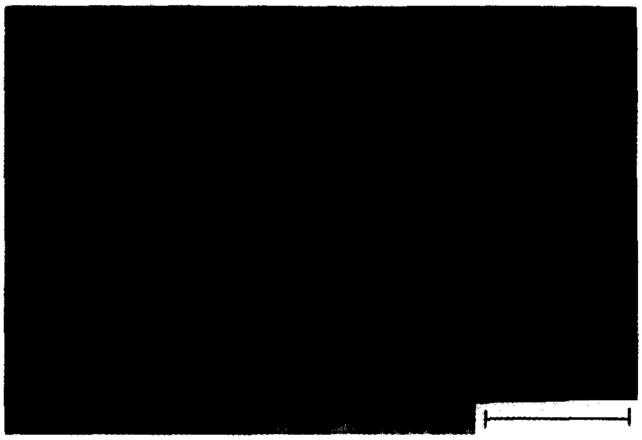

Figure 9 Birefringent contrast due to crystallised PHB within PLLA-type spherulites. Scale bar represents 600 μm

Table 1 Melting temperatures for PHB–PLLA spherulites

PHB (wt%)	100	90	75	50	25	10	0
PHB T_m (°C)	178.7	177.7	176.4	171.7	170.0	166.6	–
PLLA T_m (°C)	–	–	–	151.2	149.6	149.0	147.3

This result suggests that either the PHB lamellae were thinner in the presence of PLLA, or that some PLLA was present in the PHB crystals, acting as defects and hence lowering T_m. However, the increased melting point of PLLA in the presence of PHB indicates that PHB cocrystallized to some extent with PLLA, thereby raising the cohesion of the crystals. These results also add further evidence to indicate that the melt was single-phased.

CONCLUSION

The PHB–PLLA system shows miscibility in the melt for low-molar-mass PLLA and immiscibility for high-molar-mass PLLA, as expected on thermodynamic grounds. For miscible blends, two types of spherulite were observed to nucleate and grow, these being characteristic of pure PHB and PLLA respectively. The different types of spherulite interpenetrated when the growth fronts met. Since the phenomenon of interlocking spherulites could have significant consequences with regard to the mechanical properties of blends, we are now investigating these properties in more detail.

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