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Miscibility and tensile properties of poly (β-hydroxybutyrate)–cellulose propionate blends

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Abstract

The phase behaviour, crystallization kinetics and tensile properties of poly(β-hydroxybutyrate)–cellulose propionate (PHB–CP) blends have been investigated using differential scanning calorimetry, optical microscopy and tensile testing measurements. The results show that the blends are miscible as evidenced by the observation of a single composition-dependent glass transition temperature, a depression of the equilibrium melting temperature of PHB, and a decrease in the spherulitic growth rate of the PHB component. Finally, in the study of the tensile properties it is shown that an improvement in the ductility of PHB is brought about by blending with CP.

Keywords: Miscibility; Tensile properties; Phase behaviour

1. Introduction

In recent years there has been much interest in the family of biodegradable polyesters poly(β-hydroxyalkanoates) PHAs. These materials, produced by fermentation, occur as intracellular inclusions within the cytoplasm of many prokaryotic organisms [1]. The most well-known PHA is poly(β-hydroxybutyrate), PHB. This thermoplastic exhibits a high level of crystallinity (60%–70%) and is stereoregular, being fully isotactic in its chain configuration [2]. In contrast, synthetic analogues of bacterial PHB can be produced with a wide range of stereoregularities [3,4], including syndiotactic [5–8] by catalytic ring opening polymerization of β-butyrolactone.

The principal shortcomings of bacterial PHB which limit its usefulness as a thermoplastic material are its thermal instability and brittleness [2]. For these reasons there has been much interest recently in the preparation and characterization of blends based on PHB. For example, bacterial PHB has been blended with poly(vinyl acetate) [9], poly(ethylene oxide) [10], poly(vinyl alcohol) [11], poly(epichlorohydrin) [12], as well as with synthetic PHB [13–15]. In addition, the groups of Scandola [16–19] and Buchanan [20] have investigated blends of PHB with cellulose esters (CEs). These authors reported miscibility in binary blends of PHB with cellulose acetate butyrate (CAB) [16,18,19] and cellulose acetate propionate (CAP) [16,19]. Similarly, blends of the copolymer poly(β-hydroxybutyrate-*co*-hydroxyvalerate) with CAB [17,20] and CAP [17] were observed to be miscible.

In this communication we wish to report our results obtained on the phase behaviour and crystallization kinetics for the binary blend PHB–cellulose propionate (CP). It will be shown that this system exhibits miscibility. Further, some of the unusual trends in the glass transition behaviour for blends of PHB with mixed CEs will be shown to apply also to the present system. It will be demonstrated that addition of CP to PHB is accompanied by a decrease in spherulitic growth rate of the latter. Results pertaining to the tensile properties of the CP–PHB system will also be presented and will show that improvement in the ductility of PHB can be brought about by blending with CP.

2. Experimental

Bacterial PHB was obtained from Marlborough Biopolymers (Billingham, UK). CP was obtained from Scientific Polymer Products (Ontario, New York) and had a degree of substitution of approximately 2.75, as measured by elemental analysis. Molecular weight characterization of

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Table 1
Molecular weight data for PHB and CP samples[a]

Polymer	M_n	M_w	M_w/M_n
PHB	210 000	334 000	1.6
CP	57 000	139 000	2.4

[a]Estimated from gel permeation chromatography using polystyrene standards

the samples was performed by gel permeation chromatography (GPC) in chloroform, using standard polystyrene samples for calibration. The results are presented in Table 1.

Blends of PHB with CP were prepared by casting from chloroform solutions. The resultant films were dried under vacuum at 80°C to constant weight.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC-7 under a nitrogen atmosphere. Approximately 7 mg of sample sealed in an aluminium pan was heated at 10°C min^{-1} from 25°C to 200°C and then quenched rapidly to − 50°C. Subsequently, the sample was heated again at 10°C min to record the glass transition temperature and melting point.

Measurements of spherulitic growth rates by optical microscopy were performed using a small specimen of the solvent-cast blend placed on a microscope slide in a hot stage under a nitrogen atmosphere. The sample was heated to 190°C and held for 1 min. It was then quenched to a preselected crystallization temperature where it was allowed to crystallize isothermally. The growing spherulites were photographed between crossed polars at various time intervals with a camera attached to the microscope. The size of the spherulites as a function of time was measured by comparing with a stage micrometer.

Tensile properties were determined from cut strips of polymer films (25 × 3 nm). A tensile tester manufactured by Katotech was employed at standard conditions (20°C, 65% RH). An initial gauge length of 15 mm and a testing speed of 0.15 mm s^{-1} were used. Stress values were calculated using the initial thickness and width of each strip.

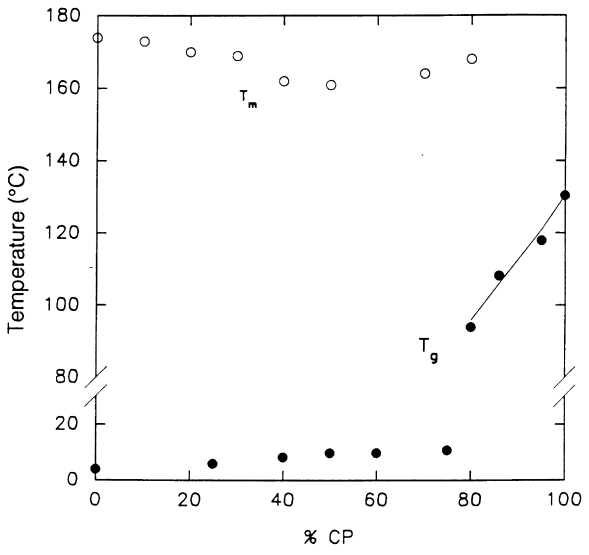

Fig. 1. Variation of melting point T_m and glass transition temperature T_g with composition for the PHB–CP blend system.

3. Results and discussion

3.1. Glass transition temperatures

The variation of T_g with composition for the system PHB–CP is shown in Fig. 1. It is seen that at high levels of CP there is a strong dependence of the measured T_g on composition. The straight line drawn through these data points was calculated using the Flory–Fox equation [21]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}$$

where W denotes weight fraction. It was not possible to fit the T_g behaviour over the entire range of compositions. This equation is the best-known of many which describe the dependence of T_g on composition in miscible blend systems [22–24]. The good agreement between the measured and calculated values indicates that the system is miscible over this composition range. However, as the amount of PHB in the system is increased, the variation of T_g is seen to level off quite noticeably. In fact for CP contents of between 0%–75%, there is a slow but gradual increase in T_g. This overall trend is in agreement with what has been reported previously for blends of PHAs with CEs [17,18].

At first glance the very small variation of T_g with composition for high levels of PHB can be taken as evidence for phase separation in the amorphous zones. However, previous studies have argued quite convincingly that, in fact, these systems are miscible over the entire composition range [17–20]. Rather, the trend in T_g is ascribed to the presence of two mobilization processes in a homogeneous blend [18,20]. As pointed out by Buchanan et al. [20], although the two blend components are miscible in the amorphous phase, they can have quite different segmental mobilities, a reflection of the inherent differences in their respective repeat unit structure. Thus in the case of the PHB–CP system, the apparent break in the T_g–composition curve is a consequence of the T_g behaviour being dominated by the segmental mobility of the PHB component at high to moderate levels of PHB, and that of the CP component at low levels of PHB. Consistent with miscibility in the PHB–CP system at high levels of PHB is the fact that no evidence was found for a second, high-temperature T_g. Further, as will be shown later, these blends exhibit a significant depression in equilibrium melting point for compositions between 0% and 50% CP.

3.2. Melting and crystallization

The PHB–CP blends showed evidence of melting over a wide composition range, as illustrated in Fig. 1 which shows

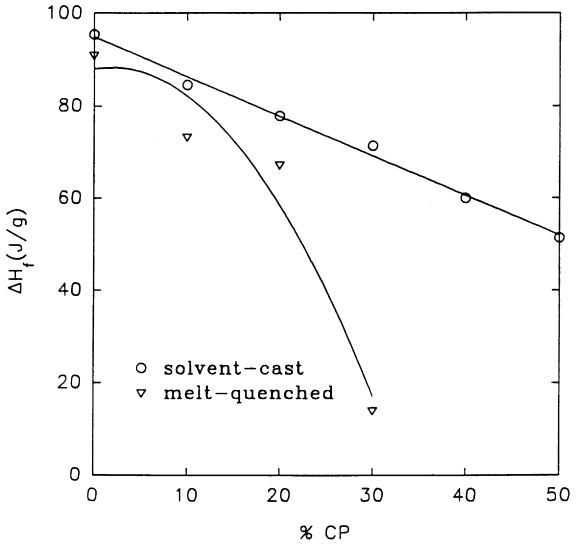

Fig. 2. Enthalpy of fusion versus composition for the PHB–CP blend system.

the variation of melting point, T_m, with composition, following melt quenching. As the level of PHB decreases to 50%, there is a concomitant decrease in T_m. Beyond this point T_m rises again until the level of PHB reaches 20%, after which there is no evidence of a crystalline phase.

The decrease in observed T_m with an increase in CP content is what one would expect for a miscible system. The increase of T_m observed for levels of CP in excess of 50% can be explained by the crystallization of the CP component. This assumption is consistent with what has previously been observed by Scandola et al. [17,18] for the system P(HB-*co*-HV)–CAB. In the present case the suggestion that the CP component in the blend undergoes crystallization is in contrast to the lack of crystallinity for the pure CP component and would result from a widening of the T_g–T_m window as PHB is added to CP [17]. This renders crystallization of the latter possible during the DSC scan. The minimum in the T_m versus composition curve thus probably corresponds to the changeover from CP crystallization to PHB crystallization.

The enthalpy of fusion, ΔH_f, for CP–PHB blends varied with composition as shown in Fig. 2. In the case of solvent-cast blends, the measured ΔH_f decreased in a linear fashion as CP content increased. This result implies that the PHB component attains the same level of crystallinity regardless of the amount of CP present. However, the total level of crystallinity for the blend system decreases linearly as CP is added. Using $\Delta H_f = 146\ J\ g^{-1}$ for 100% crystalline PHB [25], these results suggest a degree of crystallinity of 0.65 for the PHB component in the blend samples. Although not shown for the sake of clarity, the same trend was observed for samples melt-crystallized at 120°C.

The maintenance of a constant level of PHB crystallinity upon blending has been reported previously for the system bacterial–atactic PHB [14]. The implication is that the CP component is behaving simply as a polymeric diluent; hence the PHB chains must disentangle from the CP segments as the process of crystallization proceeds.

In the case of melt-quenched samples, there was a marked decrease in crystallinity as CP was added, as can be seen in Fig. 2. For levels of CP beyond 30%, only very small amounts of crystallinity were detected ($< 10\%$). As will be demonstrated later, this is a result of a retardation of crystallization kinetics upon addition of CP.

The equilibrium melting point, T_m^o, of PHB in the CP–PHB blends was evaluated using the Hoffman–Weeks

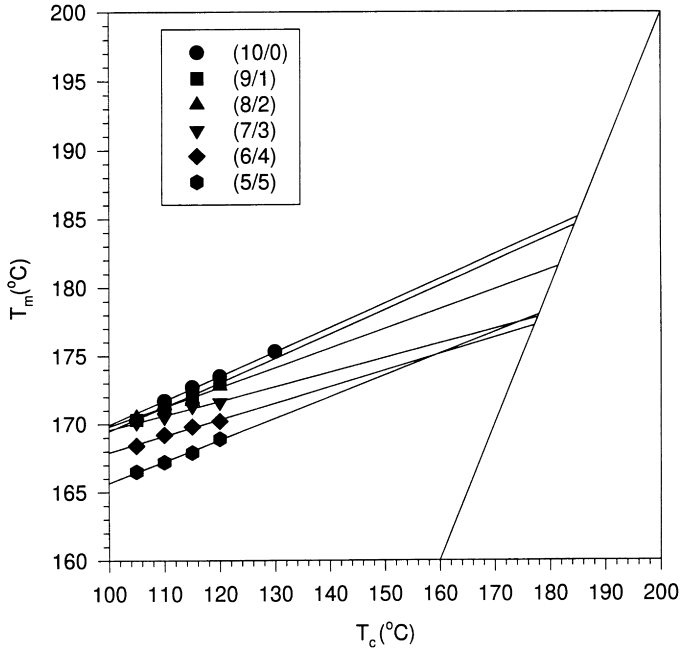

Fig. 3. Hoffman–Weeks plots for the PHB–CP blend system.

Table 2
Equilibrium melting points for the PHB–CP blend system

% PHB	T_m^o (°C)
100	185
90	184
80	182
70	178
60	177
50	178

technique. From Hoffman and Weeks [26] the relationship between the observed melting point T_m and the crystallization temperature T_c is given by:

$$T_m = T_m^o(1 - \frac{1}{\gamma}) + \frac{T_c}{\gamma}$$

where γ is the the ratio of the initial to the final lamellar thicknesses and T_m^o is obtained from a plot of T_m versus T_c by extrapolating the linear data until intersection with the line $T_m = T_c$. The Hoffman–Weeks plots obtained by DSC are shown in Fig. 3 and the values of T_m° are tabulated in Table 2. Despite the scatter evident in Fig. 3, it is clear that the equilibrium melting point of PHB is depressed considerably upon addition of CP. For example, a 50–59 blend depresses T_m^o by 7°C. Such a depression confirms that there is miscibility between the two components in the amorphous zones. Certainly hydrogen-bonding between the residual hydroxyl groups on CP and the carbonyl group of PHB would be expected to enhance miscibility [27].

3.3. Crystallization kinetics

Spherulitic growth rates were measured for the PHB–CP system via optical microscopy. Plots of spherulite radius versus time were linear at all temperatures investigated, as shown in Fig. 4. Hence it can be concluded that CP is being incorporated into the growing PHB spherulites [28]. Scandola et al. [19] have reported non-linear growth rates for blends of PHB with CAB. This behaviour, attributed to simultaneous crystallization of the CAB component, was not observed for our system. However, our DSC results

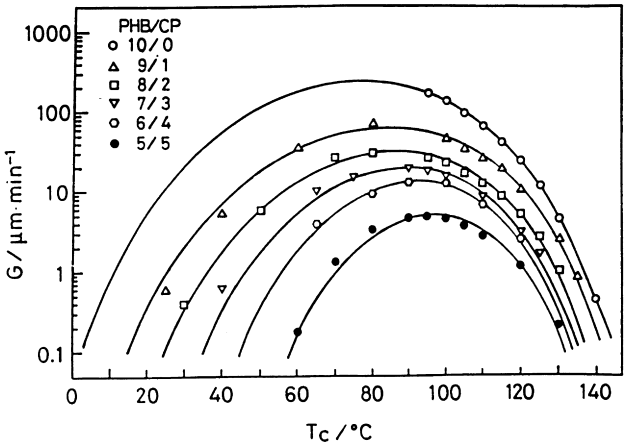

Fig. 5. Spherulitic growth rates of PHB versus temperature for PHB–CP blends of various compositions.

suggest that for high enough levels of CP, crystallization of both components may be a possibility.

The variation of growth rate, G, with temperature for the blend system is illustrated in Fig. 5. To aid in the comparison of data, smooth curves were drawn through the points using the familiar Lauritzen–Hoffman equation and the usual fitting procedure [29]. In the case of pure PHB, a combination of high nucleation density and rapid growth prevented the collection of data below 95°C.

The results in Fig. 5 show that the addition of CP causes a marked reduction in the rate of crystallization of PHB. This is entirely consistent with the addition of a miscible second component, as well as with the results of Scandola et al. on PHB–CE blends [19]. Interestingly, the effect is more pronounced on the low-temperature side of the curves. This could be a reflection of the difficulties with which PHB disentangles from CP chains in the homogeneous melt at lower temperatures, where segmental mobility is restricted.

3.4. Tensile properties

The tensile behaviour of the CP–PHB system is illustrated in Fig. 6 for solvent-cast samples. It can be seen that PHB, as previously reported [2], is brittle, breaking at

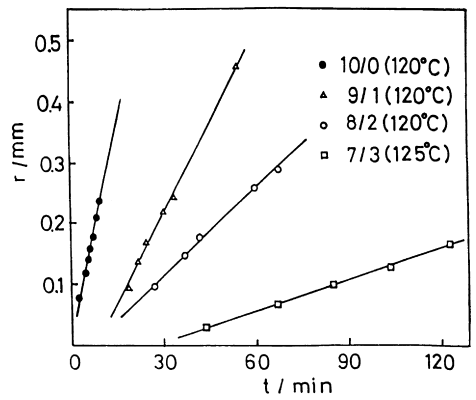

Fig. 4. Spherulitic radius versus time for the PHB–CP blend system.

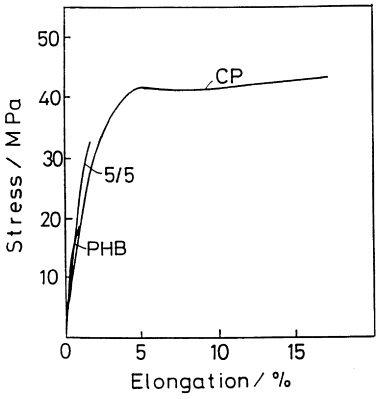

Fig. 6. Stress–strain curves for solvent-cast PHB, CP and 5–5 blend films.

an elongation of only 3%. CP, on the other hand, can be elongated to about 17%, which is beyond the yield point. A 50–50 blend of the two exhibits tensile behaviour which is intermediate between that of the two constituent polymers. This is consistent with a simple dilution effect of the CP.

The tensile behaviour of melt-quenched samples is illustrated in Fig. 7. The traces corresponding to the pure polymers are essentially identical to the case of solvent-cast samples. Quite remarkable, however, is the behaviour of the 50–50 blend, which demonstrates a significant increase in ductility as compared with the constituent polymers. An elongation of greater than 90% could be achieved. Such an increase in ductility is commonly found in semicrystalline–amorphous polymer blends [30]. This result is typically due to the decrease in crystallinity exhibited by the blend.

The brittleness of PHB has been linked to the development of radial and circumferential cracks within spherulites [31]. Since the crystallinity of PHB is largely suppressed in the melt-quenched samples, the tensile behaviour is presumably dictated by the amorphous zones. As pointed out previously, the effect of the amorphous zones on the tensile properties of a semicrystalline system is analogous to the effect of rubber reinforcement in polyolefins [32] (e.g. high-impact polystyrene).

4. Summary and conclusions

In the present communication, results have been presented pertaining to the PHB–CP blend system. Specifically it has been shown that the system is miscible over the entire composition range, as demonstrated by the detection of a single glass transition temperature which is composition-dependent, as well as a depression in the equilibrium melting point of PHB. It has also been shown that the addition of CP does not affect the level of crystallinity attained by the PHB component. Finally, a marked reduction in the rate of crystallization of PHB upon addition of CP has been demonstrated.

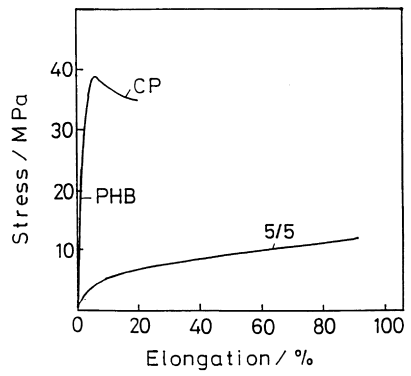

Fig. 7. Stress–strain curves for melt-quenched samples.

Much of the work in the area of PHB-based blends is motivated by the limitations of this biopolyester for possible thermoplastic applications. Within this context blends of PHB with CEs offer the possibility of circumventing some of these difficulties with only kinetic compromises on the biodegradability of the cellulose polymer. This shortfall could probably be rendered minor if a lower DS cellulose propionate were used.

As shown by the present data, as well as previously published work, these blends exhibit a depression of melting point which could alleviate problems associated with melt-instability. It has been demonstrated that addition of CP to PHB could be a viable approach to reducing the brittleness associated with the latter.

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