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Miscibility of bacterial poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with ester substituted celluloses

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Summary

Blends of bacterial Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) with cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) were prepared by melt blending. When CAB or CAP content in the blends is ≥ 50%, the blends are stable, homogeneous mixed glasses, characterized by a glass transition that follows the Fox equation. When the cellulose ester content is lower than 50%, PHBV crystallizes upon room storage and the blends are partially crystalline. Besides the strongly composition dependent glass transition, another slightly composition dependent relaxation is observed by both DMTA and DSC measurements in the vicinity of the glass transition of PHBV. It is suggested that both blend components partake in both mobilization processes.

Introduction

Bacterial polyesters have attracted much attention as biodegradable, biocompatible polymers (1-2). Due to high cost, they are presently used mainly as biomaterials for medical applications. Materials that still exhibit useful properties with lower cost may result from blending bacterial poly(3-hydroxyalcanoates), PHAs, with other polymers. Moreover, the blends should keep a degree of biodegradability imparted by the PHA component.

Preliminary results (3-5) indicate that some cellulose esters are compatible with both the homopolymer Poly(3-hydroxybutyrate), P(3HB), and a random copolymer Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV.

This paper investigates the compatibility of PHBV with two cellulose esters, cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP). The effect of composition on the thermal and dynamic mechanical properties of blends obtained through melt mixing is analysed over the entire composition range. Biodegradation studies will be reported elsewhere.

Experimental

Materials

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV, 3HV content 20 mol%, from ^{1}H NMR) was purchased from PolySciences, Inc. Cellulose acetate butyrate, CAB, was an Eastman Kodak product (EAB 500-1: butyryl 48%, acetyl 6%, hydroxyl 0.7%), whereas

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cellulose acetate propionate, CAP, was produced by Bayer (Cellit PR 900: propionyl 45%, acetyl 3.5%, hydroxyl 1.6%).

Blend Preparation

Weighed amounts of the two blend components were mixed in the thermostated cup of a miniature mixing/injection molding machine. The temperature was kept to the lowest possible value allowing injection molding in order to minimize thermal degradation of PHBV; the temperature (190-235°C) depended on the blend components, CAP requiring temperatures higher than CAB, and composition, being lower the higher the PHBV content. Also the melt mixing time (maximum 3 min) was a function of blend composition, being shorter the higher the amount of PHBV. The blends were molded into small bars (30 x 7.5 x 1.5 mm) and allowed to age four weeks at room temperature before testing.

Experimental methods

Dynamic mechanical measurements were performed with a DMTA (Polymer Laboratories Ltd.) operated in the dual cantilever bending mode. The measurement frequency and heating rate were 3Hz and 3 deg/min respectively. The temperature range investigated was -100/200°C. Calorimetric measurements were carried out with a DuPont 9900 Thermal Analyser in the temperature range -80/220 °C, at a heating rate of 20 deg/min. The temperature scale was calibrated with high purity standards. The glass transition temperature (Tg) was taken as the temperature at the midpoint (1/2 Δcp) of the transition. The melting temperature (Tm) was taken as the peak value of the melting endotherm.

Results and discussion

Figure 1 shows the dynamic mechanical spectra of the pure blend components. The dynamic storage modulus E′ and the loss tangent tanδ are reported as a function of temperature for CAB, CAP and

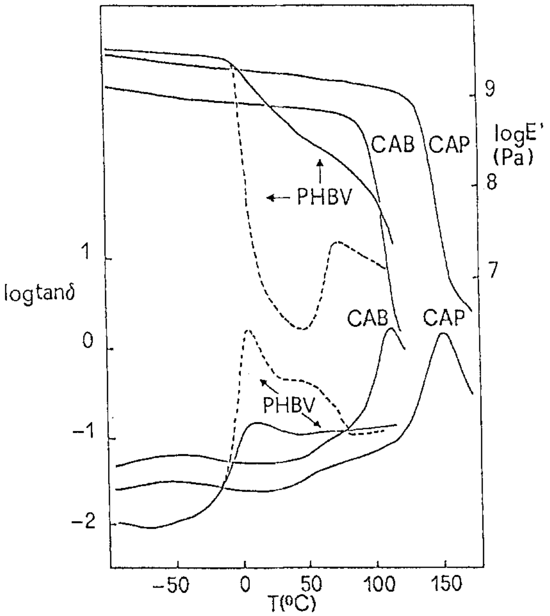


Figure 1. Dynamic mechanical spectra of the pure blend components: (——) room stored PHBV, CAP and CAB. (-----) low temperature stored PHBV.

PHBV samples, stored at room temperature for several days after melt extrusion (solid lines). The spectrum of a melt extruded PHBV sample stored in a refrigerator prior to measurement is also shown in Figure 1 (broken line). A very intense glass transition relaxation ($\tan\delta > 1$, modulus drop larger than 2 orders of magnitude) is observed for both CAB and CAP, in the vicinity of 115 and 155°C respectively. For room stored PHBV, on the contrary, the intensity of the loss tangent peak at 10-15 °C is small ($\tan\delta = 0.15$), indicating that a rather modest amorphous fraction undergoes the glass transition; the crystalline phase developed during room storage gives rise to transition broadening, as a consequence of 'physical cross-linking', and to high modulus values above the relaxation. A substantial crystalline fraction (50-60%) is expected in a PHBV containing 20 mol% of 3HB units (6-8).

If crystallization of the copolyester is inhibited by keeping PHBV below its glass transition (broken line), a large relaxation (peak value 6°C) is observed, followed by crystallization during the heating run. This latter process gives rise to a considerable increase of the storage modulus E' and to the appearance of a shoulder on the high temperature side of the $\tan\delta$ peak.

The results of Figure 1 show that, upon storage at room temperature after melt extrusion, the two cellulose esters are in the amorphous glassy state, while PHBV contains both amorphous and crystalline phases.

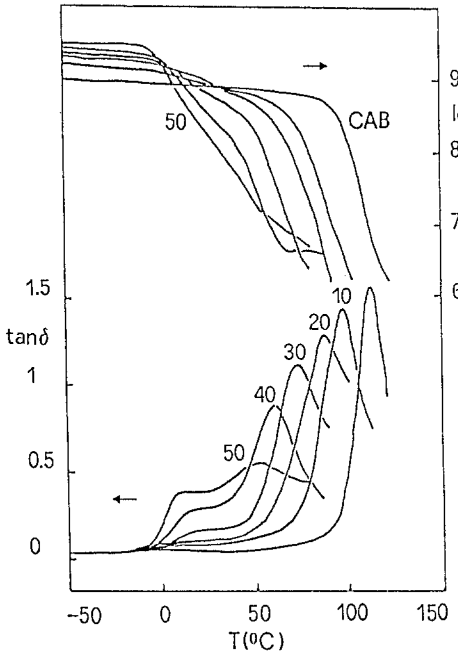
Figure 2 reports the relaxation spectrum of PHBV/CAB blends with PHBV contents up to 50%. A main relaxation process is observed, whose temperature location and intensity decrease regularly with increasing PHBV content in the blend. The dependence on composition of the relaxation peak temperature is shown in Figure 3, where the curve drawn corresponds to Fox equation (9):

$$1/Tg = w_1/Tg_1 + w_2/Tg_2 \qquad [1]$$

w being weight fractions and subscripts 1 and 2 referring to the two component polymers. A number of equations have been proposed to describe the composition dependence of the glass transition of miscible polymer blends (10); the one due to Fox contains no adjustable parameters and is one of the most widely used. The fact that blending with PHBV causes a depression of the glass transition of CAB which follows the Fox equation is good evidence that the blend components are homogeneously mixed over the composition range explored.

In Figure 2 another relaxation is observed, present as a shoulder in the 30PHBV/70CAB blend, which grows larger with increasing PHBV content. Concomitantly, also the storage modulus shows a drop which becomes steeper the higher the PHBV content. The temperature of this relaxation process, which occurs in the range of the glass transition of PHBV, increases with increasing cellulose ester concentration in the blend, as shown in Figure 3.

Results in line with those described above are also found when PHBV is blended with the other cellulose ester (CAP), as shown in the dynamic mechanical spectra of Figure 4. Above the glass transition the elastic modulus is seen to drop to values typical of rubbers (10^6-10^7 Pa), analogous to those observed in Figure 2 for PHBV/CAB blends. This result implies that PHBV crystalliza-



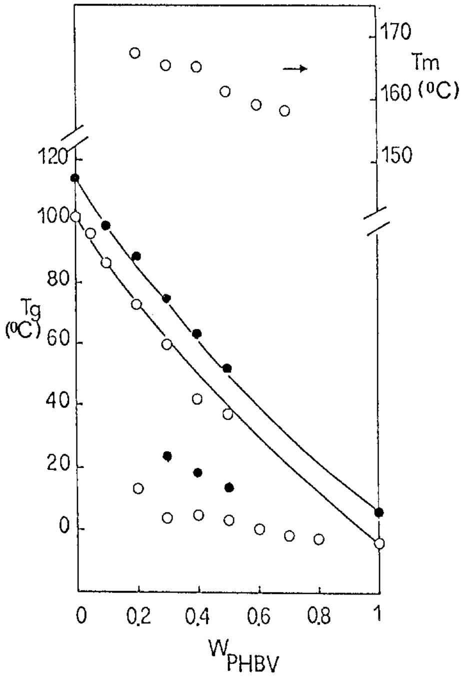
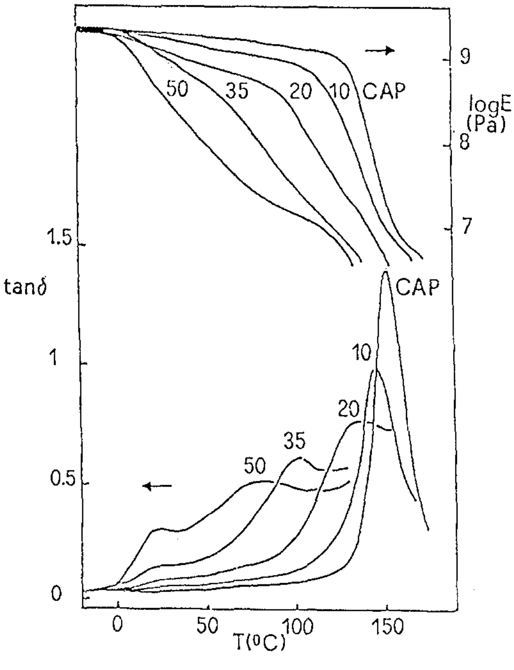


Figure 2. Dynamic mechanical spectra of PHBV/CAB blends; number on curves: PHBV content in weight%.

Figure 3. Glass transition temperature and melting point from DSC (○) and peak temperature of the glass transition relaxation from DMTA (●) as a function of composition for PHBV/CAB blends.

tion is totally inhibited by the presence of 50% or more of the cellulose ester component. In this composition range, samples obtained by melt blending are transparent and no trace of crystallinity is observed even after months of blend storage at room temperature. Only when PHBV exceeds 50% does crystallinity develop with time in both PHBV/CAB and PHBV/CAP systems, and the blend samples turn opaque.

The blends have been subjected to calorimetric measurements. Figure 5 shows the DSC curves of PHBV/CAB blends with different composition together with the curves of the pure blend components. The thermograms are relative to samples pre-heated at 20 deg/min up to 220°C, to cancel any differences in thermal history, and rapidly quenched to -80°C. A single endothermal baseline shift indicative of the blend glass transition is observed for PHBV contents 5 and 10%. The curve for blend 20PHBV/80CAB shows two distinct glass transition phenomena, while in blends where the amount of PHBV is 30-50% the two transitions are so close that the upper one appears as a change of slope rather than a further step in the specific heat increment. When the PHBV content is equal or higher than 60% a single glass transition at low temperature is detectable. At a first sight, due to the temperature location of such a transition, the presence of phase separated amorphous PHBV might be inferred. However, the specific heat increment (Δcp) associated with this transition is much larger than expected on the basis of the PHBV present in each



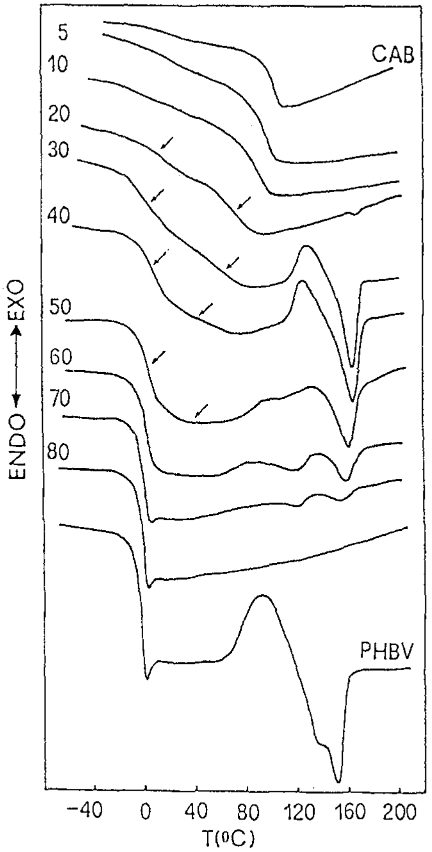


Figure 4. Dynamic mechanical spectra of PHBV/CAP blends; number on curves: PHBV content in weight%.

Figure 5. DSC curves of PHBV/CAB blends, after quenching from the melt; number on curves: PHBV content in weight%.

blend; conversely, the experimental value well compares with that calculated assuming Δcp additivity. It follows that both blend components contribute to the low temperature glass transition of blends containing 60-80% PHBV.
The temperature location of the calorimetric Tg's (from Figure 5) are plotted in Figure 3 as a function of composition. The solid line represents again equation [1], which is seen to fit satisfactorily the DSC data relative to the strongly composition dependent upper glass transition. It turns out very clearly that this is the same relaxation phenomenon that has been evidenced by dynamic mechanical analysis and that it represents the glass-to-rubber transition of mixed amorphous PHBV/CAB blends.
In the DSC curves of Figure 5 pure PHBV is seen to crystallize during the thermal scan, in agreement with the DMTA results of Figure 1. The DSC curves also show that blending with 20% CAB completely hinders PHBV crystallization on heating, as seen from the curve of blend 80PHBV/20CAB which is featureless at T > 0°C.

The endo-/exothermal phenomenon which appears in the DSC curves of blends with 30 to 70% PHBV can be explained in terms of crystallization and melting of CAB, though the cellulose ester in the pure state is not seen to crystallize and melt. The intensity of the exo-/endothermal phenomenon increases at first (30-40% PHBV) then decreases and is barely detectable in blend 70PHBV/30CAB. The observed behaviour is the result of two opposing effects which appear with increasing PHBV content: on one hand a decrease of the blend Tg widens the Tg/Tm window, promoting CAB crystallization (mobilization and consequent rearrangement of the macromolecules into 3-dimensional order can occur at decreasing temperatures); on the other hand, the concomitant decrease of CAB content in the blend lowers the amount of material which can crystallize. Up to 40% PHBV, the first effect prevails; then it is the amount of CAB present in the blend which dictates the entity of the crystallization and melting phenomena observed.

The peak value of the melting endotherm (Tm), taken from the curves of Figure 5, is plotted in Figure 3. For blends containing 60 and 70% PHBV, which show multiple endotherms, the higher peak temperature is reported. As expected for the melting temperature of a crystallizable polymer in a compatible blend system (10), Tm is seen to decrease rather regularly with increasing concentration of the second blend component. No Tm data are reported in Figure 3 for pure CAB nor for blends with low PHBV contents, since only when the window between Tg and Tm is wide enough crystallization of CAB can occur in the experimental conditions employed.

Conclusions

In blends with PHBV contents up to 50%, evidence indicating miscibility of the bacterial polymer with CAB and CAP can be summarized as follows: a) the blend Tg decreases with increasing PHBV concentration according to the equation proposed by Fox for miscible systems; b) crystallization of CAB from the rubbery state above the blend glass transition confirms that the low Tg component (PHBV) acts as a high molecular weight plasticizer towards the cellulose ester.

In blends where PHBV concentration is higher than 50%, PHBV crystallinity develops upon room storage and the blends are no more single-phase systems. However, the DSC results on melt quenched blends seem to indicate that in the melt the blends are miscible over the entire range of compositions. The only phase separation that is observed in the blends investigated is segregation through crystallization of pure components from the homogeneous blend mixture, a process which is possible only at temperatures higher than the blend Tg.

The experimental evidence presently collected on the two PHBV/cellulose ester systems closely agrees with the results of an investigation on compatibility of blends of the same cellulose derivatives with the bacterial homopolymer poly(3-hydroxybutyrate), reported in a separate paper (11). In this latter work the miscibility issue is thoroughly discussed and it is concluded that evidence of two mobilization processes in the blends, one strongly composition dependent at higher temperature, the other less influenced by composition at lower temperature, does not indicate incompatibility of the system. The observed phenomena are instead the experimental evidence of dynamic heterogeneity in morphologically homogeneous polymer blends. A similar suggestion has been put forward recently by Miller et al. (12) on the basis of ^{13}C NMR results on poly(isoprene)/poly(vinylethylene) blends.

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