Miscibility of Bacterial Poly(3-hydroxybutyrate) with Cellulose Esters

Mariastella Scandola,* Giuseppina Ceccorulli, and Maria Pizzoli

Dipartimento di Chimica "G. Ciamician" della Università di Bologna and Centro di Studio per la Fisica delle Macromolecole del CNR, Via Selmi 2, 40126 Bologna, Italia

ABSTRACT: Blends of bacterial poly(3-hydroxybutyrate) (P(3HB)) with cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) were prepared by melt compounding. P(3HB)/CAB blends containing 5–50% P(3HB) and P(3HB)/CAP blends with 5–60% P(3HB) are transparent, stable homogeneous amorphous glasses, while blends with higher P(3HB) content are partially crystalline. When in the amorphous state, both P(3HB)/CAB and P(3HB)/CAP blends show a glass transition which regularly decreases with increasing P(3HB) content, in excellent agreement with the behavior predicted for totally miscible blends. Both dynamic mechanical (DMTA) and calorimetric (DSC) measurements show that P(3HB) and CAB can crystallize from the blends only at temperatures higher than the composition-dependent T_g. When crystallization is induced by thermal treatments, the melting temperature of the crystalline phase obtained depends on composition, as expected for miscible blends of crystallizable polymers. Besides the strongly composition dependent glass transition, another relaxation is observed, located in proximity to the T_g of P(3HB) and slightly shifting to higher temperature with increasing CAB or CAP content. DSC measurements on melt-quenched blends containing more than 50% P(3HB) indicate contribution of both blend components to this glass transition process, on the basis of the very large specific heat increment observed. It is suggested that the two glass transitions are the manifestation of two mobilization processes coexisting in blends which appear in all respects to be single-phase, homogeneous mixtures.

Introduction

Bacterial poly(3-hydroxybutyrate) (P(3HB)) and related microbial polyesters are currently the focus of intensive fundamental and applied research.[1-3] Biodegradability and biocompatibility are the main merits of these thermoplastic polymers which are mostly used as biomaterials in the medical field, high production cost still preventing wider scale applications. Blending with a second polymeric component can offer opportunities to lower cost and enlarge the range of applicability of these biopolymers, without impairing their desirable properties. To meet this objective, we have explored a range of commercially available cellulose-based materials, suitable to be mixed with bacterial polyesters. Preliminary results[4-6] have shown good compatibility of cellulose derivatives with both P(3HB) and random copolymers containing the 3-hydroxyvalerate co-unit.

In view of potential applications of such materials, the present paper reports a detailed investigation on the thermal and mechanical relaxation properties of blends of P(3HB) with two cellulose esters, cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). Blends obtained through melt mixing over the entire composition range have been examined by means of differential scanning calorimetry and dynamic mechanical spectroscopy. In a forthcoming paper a comprehensive study of the isothermal crystallization of P(3HB) from molten P(3HB)/CAB blends will be reported.

Experimental Section

Bacterial poly(3-hydroxybutyrate) was obtained from Aldrich (MW = 800 000). Cellulose acetate butyrate was an Eastman Kodak product (EAB 500-1, 48% butyryl, 6% acetyl, and 0.7% hydroxyl), while cellulose acetate propionate was produced by Bayer (Cellit PR 900, 45% propyl, 3.5% acetyl, and 1.6% hydroxyl). The molecular weight of the cellulose esters (CAP $\bar{M}_w$ = 2.65 × 10⁵, $\bar{M}_w/\bar{M}_n$ = 2.28; CAB $\bar{M}_w$ = 1.30 × 10⁵, $\bar{M}_w/\bar{M}_n$ = 2.12) was kindly determined by Dr. C. Buchanan (Eastman Chemical Co., Kingsport, TN).

Blends of P(3HB) with CAB or CAP were obtained by melt mixing at 190–235 °C in a miniature mixing/injection molding machine. In order to minimize thermal degradation of P(3HB), the temperature was kept to the lowest possible value allowing injection molding and depended on the blend components (CAP requiring higher values than CAB) and composition, being lower the higher the P(3HB) content. The blends were molded into small bars (30 mm × 7.5 mm × 1.5 mm), quenched in an ice-water mixture and allowed to age at room temperature (22–28 °C) for at least 3 weeks. Specimens of all compositions were transparent immediately after quenching from the melt but, upon room storage, blends containing more than 50–60% P(3HB) turned opaque due to crystallization of P(3HB). The pure blend components were melt-extruded too, following the same procedure.

Differential scanning calorimetry was performed with a DSC DuPont 9900 thermal analyzer, calibrated with high-purity standards. After a first scan up to 220 °C, carried out to provide the same thermal history for all samples, followed by rapid quenching to –80 °C, the DSC curves were recorded at a heating rate of 20 deg/min and showed good reproducibility in subsequent thermal scans. The glass transition temperature (T_g) was taken as the inflection point of the specific heat increment. The melting temperature (T_m) and crystallization temperature (T_c) were taken as the peak values of the respective endo- and exothermal phenomena in the DSC curve. In the presence of multiple endotherms, the highest peak temperature was taken as T_m.

Although, as-supplied CAP and CAB powders showed a small melting endotherm in the first scan (ΔH_m = 1.32 J/g and T_m = 190 °C for CAP; ΔH_m = 26.4 J/g and T_m = 188 °C for CAB), no evidence of crystallinity was found in the first scan of melt-extruded CAB and CAP samples.

The dynamic storage modulus E', loss modulus E'', and mechanical loss tangent tan δ were measured with a DMTA (Polymer Laboratories) operated in the dual cantilever bending mode at a frequency of 3 Hz and a heating rate of 3 deg/min.

Results and Discussion

Figure 1 compares the DSC curves of the pure blend components CAB, CAP, and P(3HB) after quenching from the melt. Only a glass-to-rubber transition is evident in the case of the cellulose esters, which occurs at 103 °C (Δc_p = 0.30 J/(g K)) and 145 °C (Δc_p = 0.33 J/(g K)) for CAB and CAP, respectively. Correspondingly, dynamic mechanical measurements carried out on room-stored
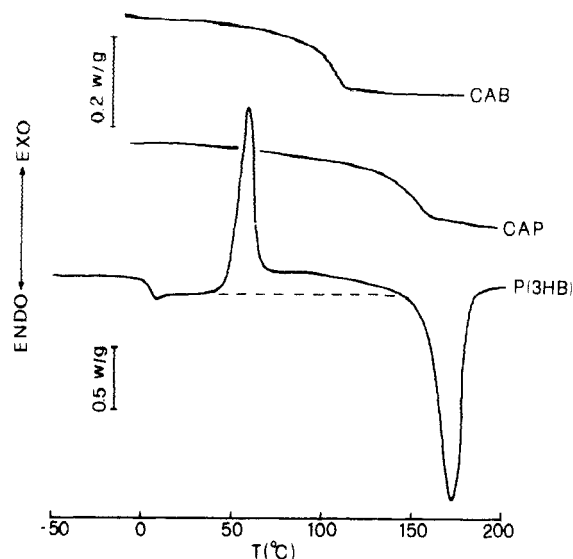
Figure 1. Calorimetric curves of CAB, CAP, and P(3HB) after melt quenching.

samples show a very intense glass transition relaxation, as expected for totally amorphous polymers, at 114 °C (CAB) and 153 °C (CAP).

As regards the bacterial polyester, rapid cooling from the melt freezes P(3HB) macromolecules in the amorphous state[7] and, on subsequent heating, the DSC curve shows the glass transition (T_g = 4.5 °C) followed by cold crystallization (main peak at T_c = 57 °C) and melting (T_m = 175 °C). Since T_g lies slightly below room temperature, on storage after melt extrusion P(3HB) can crystallize. This is confirmed by DMTA measurements which show a very weak tan δ peak and a modest modulus drop in correspondence with the glass transition, due to the presence of a conspicuous P(3HB) crystalline fraction.

It turns out therefore that, after melt processing and room-temperature storage, the phase behavior of the pure components of the blends is different: the two cellulose esters are single-phase amorphous glasses, while the bacterial polyester also contains a crystalline fraction.

Blends of P(3HB) with both CAB and CAP, spanning the whole composition range, have been subjected to calorimetric and dynamic mechanical measurements. Figure 2 shows the viscoelastic spectrum of P(3HB)/CAP blends containing 10–60% P(3HB), together with the curve of pure CAP as a reference. Up to 50% P(3HB), the tan δ curves show a primary relaxation peak associated with the glass-to-rubber transition of the blend which progressively shifts to lower temperature with increasing P(3HB) concentration. The glass transition process broadens, and a new dissipation region appears on the left-hand side of the main relaxation peak, in the temperature range where the glass transition of P(3HB) is found in dynamic mechanical measurements.[7] Concomitant to the growth of this loss process, the storage modulus E' shows a new stepwise decrease, whose magnitude increases with increasing P(3HB) content. In the composition range considered (0–50% P(3HB)), the blends are undoubtedly amorphous, the absence of crystallinity being attested by values of E' lower than 10 MPa in the rubbery region.

The dynamic mechanical spectrum of the blend containing 60% P(3HB) (broken line in Figure 2) is quite complex, owing to crystallization of the bacterial polymer above room temperature, during the thermal scan. Crystallization causes an increase of the storage modulus above 65 °C and the appearance of overlapping dispersion regions in the loss factor.
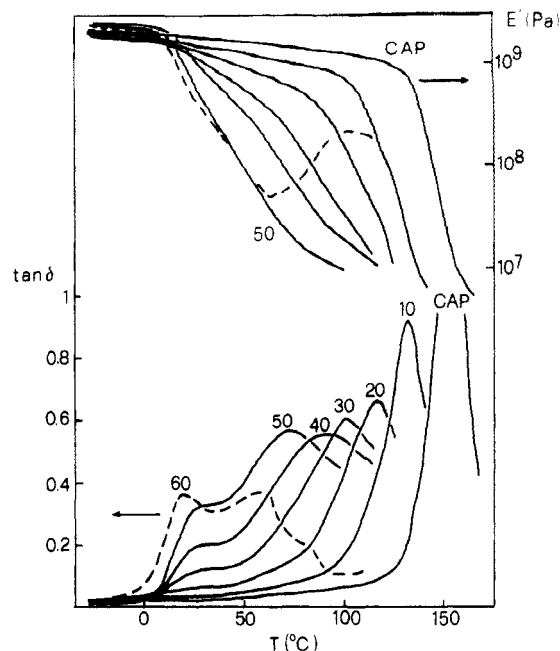

Figure 2. Dynamic mechanical spectra of P(3HB)/CAP blends with different P(3HB) weight percent (number on curves).

Blends with P(3HB) contents higher than 60% partially crystallize upon storage at room temperature, and their viscoelastic spectrum—not shown for the sake of clarity—is characterized by dissipation regions of very low intensity, as commonly found in partially crystalline blends.[8] The presence of crystalline P(3HB) in such blends is confirmed by DSC measurements.

The dynamic mechanical behavior of the P(3HB)/CAB system is analogous to that shown in Figure 2 for P(3HB)/CAP: in the composition range 0–50% P(3HB), the blends are amorphous and show an intense glass transition that shifts to lower temperature with increasing P(3HB) concentration, together with a low-intensity dissipation region at 20–30 °C. When P(3HB) content is higher than 50%, storage at room temperature induces P(3HB) crystallization, resulting in partially crystalline blends.

The calorimetric behavior of both P(3HB)/cellulose ester blends investigated is quite similar and is illustrated for P(3HB)/CAB blends (on different scales for the sake of clarity) in Figures 3 and 4. In the curves of Figure 3 the glass transition of CAB is seen to shift to lower temperatures with increasing P(3HB) content up to 20%. In blends with 25–40% P(3HB) the glass transition region broadens quite markedly on the low-temperature side, the specific heat increases less smoothly, a change of slope seeming to occur in the Δc_p step. Above the glass transition, exo/endothermal phenomena appear in the DSC curves. In Figure 4, blends with 50–84% P(3HB) show a rather well-defined glass transition at temperatures slightly changing with composition, followed by crystallization and melting.

It is worth pointing out that the specific heat increment associated with the glass transitions of Figure 4, which are located in proximity to the T_g of P(3HB), has a practically constant value (0.47 ± 0.02 J/(g K)) comparable with that of pure P(3HB), independent of the amount of P(3HB) present in the blend. This implies that, though the temperature range where such transition is found might suggest the presence of phase-separated P(3HB) undergoing the glass transition, the entity of the phenomenon undoubtedly indicates contribution of both blend components to the process. Quasiconstancy of the Δc_p value,
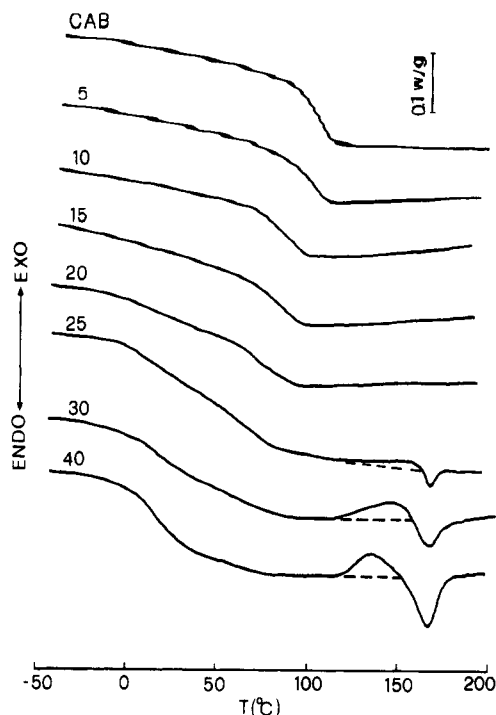
Figure 3. Calorimetric curves of P(3HB)/CAB blends with 0–40% P(3HB) content (number on curves).
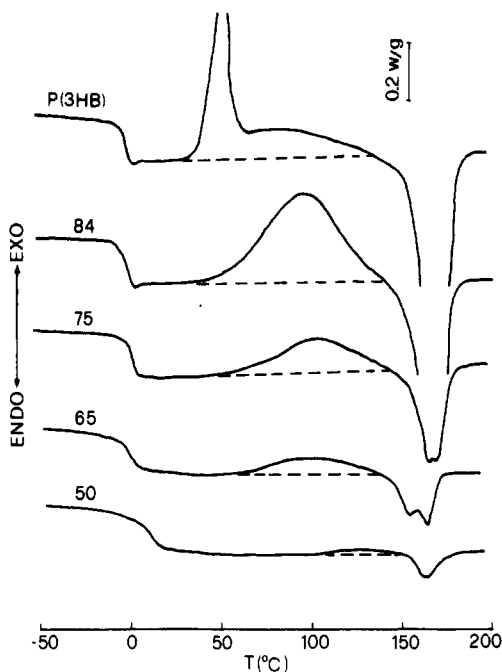

Figure 4. Calorimetric curves of P(3HB)/CAB blends with 50–100% P(3HB) content (number on curves).

Figure 5. Melting temperature of P(3HB)/CAB blends as a function of P(3HB) weight fraction w_1.

Figure 6. Dynamic mechanical spectra of selected P(3HB)/CAB blends. P(3HB) weight percent is indicated on curves.

which is higher than calculated assuming additivity ($\Delta c_p = w_1 \Delta c_{p_1} + w_2 \Delta c_{p_2}$), may be attributed to the modest changes of T_g occurring in this composition range, according to the empirical relationship proposed by Boyer[9] which predicts constancy of the product $T_g \Delta c_p$.

The temperature of the melting phenomenon observed in all blends containing more than 20% P(3HB) (see Figures 3 and 4) does not change monotonically with composition. The T_m vs P(3HB) content plot reported in Figure 5 shows a minimum at intermediate compositions; this behavior—peculiar to P(3HB)/CAB blends, not observed in P(3HB)/CAP blends—is typical of binary miscible systems where both components are able to crystallize[8] and indicates the melting point depression of both P(3HB) and CAB due to mixing.
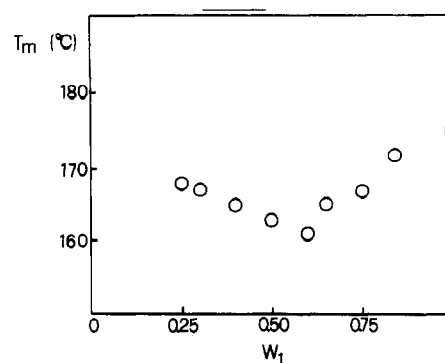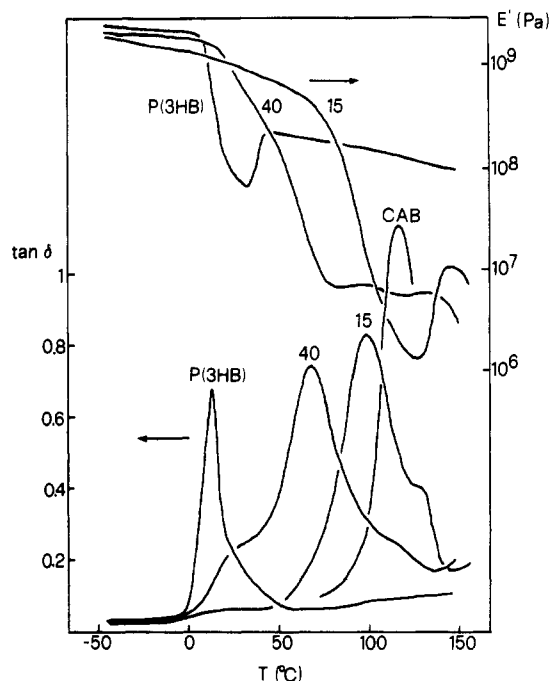
As already pointed out in connection with Figure 1, pure melt-quenched CAB does not show cold crystallization above its T_g. Quite interestingly, the results of Figures 3 and 4 indicate that mixing with P(3HB), which acts as a high molecular weight plasticizer, causes the T_g of the blend to decrease enough to allow rearrangements of the amorphous CAB chains leading to crystallization during the thermal scan. The capability of CAB macromolecules to crystallize in the experimental conditions employed is directly dependent on the width of the T_g/T_m interval. Analogous evidence of crystallization of the cellulose ester due to widening of the T_g/T_m window has been obtained for CAB plasticized with a low molecular weight phthalate plasticizer.

As far as crystallization of the bacterial polyester is concerned, the curves of Figure 4 clearly show that the crystallization process is retarded by increasing amounts of CAB in the blends. In this case, in fact, the T_g/T_m window narrows with increasing cellulose ester content and P(3HB) crystallization can occur only at increasingly high temperatures.

Crystallization of P(3HB) and CAB from P(3HB)/CAB blends can be evidenced also by dynamic mechanical measurements. Figure 6 shows the relaxation spectra of two selected P(3HB)/CAB blends together with those of the pure blend components. The curve of the bacterial polyester refers to a melt-quenched sample, stored in a
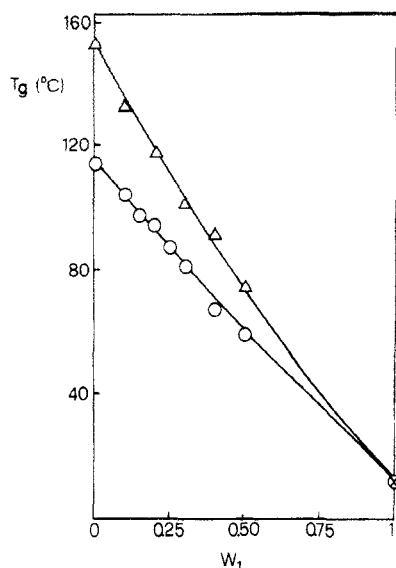
Figure 7. Dynamic mechanical glass transition temperatures of P(3HB)/CAP blends (△) and P(3HB)/CAB blends (O) as a function of P(3HB) weight fraction w_1. Curves: eq 1.

refrigerator prior to measurement to prevent crystallization. It is seen that P(3HB) readily crystallizes above T_g showing a very steep increase of the modulus E' in the range 30/40 °C. In the same experimental conditions CAB does not crystallize above its T_g (modulus curve not shown); however, when 15% P(3HB) is present in the blend, the glass transition temperature is sufficiently depressed to allow CAB crystallization, as revealed by the sudden rise of the storage modulus near 130 °C. If the glass transition further decreases, such as in blend 40P(3HB)/60CAB, two minima appear in the E' curve, indicating crystallization of both polymers, P(3HB) near 80 °C and CAB at about 115 °C. Taking into account that different heating rates are used in dynamic mechanical and calorimetric measurements (3 vs 20 deg/min, respectively), DMTA and DSC results are perfectly consistent.

The glass transition temperature of totally amorphous P(3HB)/CAB and P(3HB)/CAP blends (P(3HB) content 0–50%), is plotted in Figure 7 as a function of composition. The values reported are taken from the dynamic mechanical spectra, due to better definition of the transition temperature from such curves than from DSC. The value for pure P(3HB) refers to the amorphous sample of Figure 6. The curves drawn in Figure 7 correspond to Wood's[10] equation:

$$T_g = (w_1 T_{g_1} + k w_2 T_{g_2})/(w_1 + k w_2) \qquad (1)$$

where w_1, w_2 and T_{g_1}, T_{g_2} are the weight fractions and T_g's of components 1 and 2, respectively, T_g is the glass transition temperature of the blend, and k is an empirical adjustable parameter ($k = 0.70$ and 0.65 for P(3HB)/CAB and P(3HB)/CAP blends respectively). Equation 1 is one of the well-known relationships[10–14] commonly used to describe the T_g–composition dependence in plasticized polymers and in miscible polymer blends.

The fit of eq 1 to the experimental results of Figure 7 is very satisfactory and gives strong evidence in favor of miscibility of both cellulose esters with P(3HB). As a matter of fact, amorphous blends of miscible polymers are expected to show a single T_g intermediate to those of the pure components, with a composition dependence analogous to that plotted in Figure 7. In contrast, the presence of two separate T_g's, invariant with composition, is usually taken as proof of the existence of a miscibility gap or of total immiscibility.[8]

The behavior of the blends examined is quite peculiar in that it seems to share evidence of both miscible and immiscible systems. Besides the strongly composition-dependent glass transition phenomenon typical of homogeneous mixtures, dynamic mechanical results for totally amorphous blends (0–50% P(3HB)) collected in Figures 2 and 6 show the existence of another transition located close to the glass transition of pure P(3HB), whose intensity increases with increasing P(3HB) concentration. A transition in the same temperature range is also revealed by DSC in the composition range where room-stored blends are partially crystalline (P(3HB) content >50%). The results of Figure 4 show that, on quenching of such blends from the melt, an amorphous phase is obtained, whose intense glass transition suggests involvement of both blend components in the process. The transition temperature, determined by both DMTA and DSC, slightly increases with increasing content of cellulose ester (CAB or CAP) in the blend.

It is difficult to reconcile the experimental observations with a macroscale phase separation resulting from the presence of a miscibility gap. In a classical phase separation, two phases with different compositions coexist in equilibrium, giving rise to two glass transitions at the given T_g's: changes of blend composition are expected to affect the relative intensities of the two phenomena but not their temperature location. It is quite clear that the experimental results on the present blends do not enter this kind of picture.

Alternatively, a possible cause of the observed behavior might be sought in the procedure followed to obtain the blends of P(3HB) with the cellulose esters. In principle, it might be hypothesized that melt processing produces inefficient mixing of the blend components or that high temperatures induce chemical reactions. Such conjectures are however ruled out by experimental evidence of identical behavior of P(3HB)/cellulose ester blends prepared by solution mixing and casting at room temperature.

Some results can be found in the literature concerning blends which are defined as "partially miscible" or "on the edge of compatibility" and exhibit two glass transitions, one at constant temperature, the other with a modest, quasi-linear dependence on composition.[15–17] In no case however can the composition-dependent T_g be fitted by equations such as eq 1, which on the contrary very satisfactorily fits the experimental results in Figure 7. All DSC and DMTA evidence collected contributes to indicate that the only phase separation that can occur in P(3HB)/CAB and P(3HB)/CAP blends is segregation of the pure components through crystallization from a homogeneously mixed molten or rubbery phase.

In the past few years binary systems that are completely miscible in the melt but phase separate on cooling due to crystallization of one component, namely blends of poly(vinylidene fluoride) with poly(methyl methacrylate), have been extensively studied.[18–20] They have been shown to contain two amorphous phases, one being a homogeneous mixture of the two polymers, the other the so-called crystal–amorphous interphase constituted only of the crystallizable polymer. The interphase gives rise to a transition at a fixed temperature, whose intensity regularly decreases with increasing content of the second blend component.

If the low-temperature relaxation shown in Figures 2 and 6 arose from the crystal–amorphous interphase of undetectable P(3HB) crystallites, it would be expected to strengthen with increasing crystallinity and to disappear in completely amorphous blends. On the contrary, not
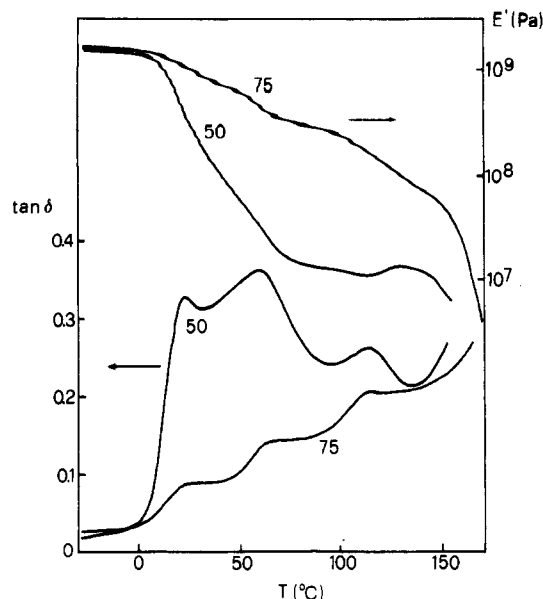
Figure 8. Dynamic mechanical spectra of P(3HB)/CAB blends containing 50 and 75% P(3HB).

only is the relaxation present in blends where the presence of crystallinity can be confidently excluded but its intensity is much larger in amorphous than in partially crystalline blends, as shown in Figure 8 where the relaxation spectra of P(3HB)/CAB blends containing 50 and 75% of bacterial polyester are compared. It is observed that in the amorphous 50/50 blend the magnitude of the relaxation at about 20 °C is 4-fold that of the crystalline blend containing 75% P(3HB). The temperature of the main glass transition relaxation is similar in both blends (about 60 °C), this result being easily rationalized on the basis of a change of composition (with respect to the overall composition) of the amorphous mixed phase in blend 75P-(3HB)/25CAB due to the presence of segregated crystalline P(3HB). An estimate of the amount of crystalline P(3HB) in such a blend, obtained by DSC, allows calculation of the composition of the remaining mixed P(3HB)/CAB phase, which is found to be very close (56% P(3HB)) to that of the other blend reported in Figure 8. The dissipation region observed in the spectra of both blends in the range 100–130 °C is attributable to crystallization processes as well as rearrangements of the crystalline phase occurring during heating.[7]

The experimental results so far collected strongly suggest that bacterial P(3HB) yields miscible blends with CAP and CAB. The main points supporting this view are summarized below:

(a) Melt-quenched blends in the composition range 0–50% P(3HB) are characterized by a main glass transition relaxation whose temperature closely follows the predictions of equations describing miscible binary systems, on the assumption of random mixing of the components at a segmental level. (b) In this composition range the blend samples are stable glasses which remain transparent over months of room storage. (c) On heating above room temperature, P(3HB) crystallization occurs only at temperatures that lie above the composition-dependent glass transition of the blend (P(3HB) crystallization is therefore prevented up to mobilization of the mixed amorphous phase). (d) The fact that P(3HB) is seen to crystallize upon room storage in blends with CAP and CAB containing more than 60 and 50% P(3HB), respectively, is a clear indication that the T_g of these blends lies at or below room temperature. (The difference in P(3HB) concentration needed to lower the blend T_g below room temperature

reflects the difference of the cellulose ester T_g's, that of CAP being 40 °C higher than the T_g of CAB.) (e) Further evidence of the existence of a truly mixed phase comes from the observation of crystallization of CAB from mixtures with P(3HB), in conditions where pure CAB does not crystallize. (Crystallization is made possible by lowering of the glass transition temperature, due to mixing with the low-T_g P(3HB) component.) (f) The melting point depression of the crystalline phases formed during heating is the result of mixing which causes a decrease of the chemical potential of CAB and P(3HB).

Additional support to the miscibility issue comes from studies of the rate of isothermal crystallization of P(3HB) from molten P(3HB)/CAB mixtures,[5] showing that the spherulitic growth rate G of the bacterial polyester markedly decreases in the presence of the cellulose ester (20% CAB causes a rate decrease of 1 order of magnitude). This finding can be explained only on the assumption that P(3HB) crystallizes from a mixed phase, where the macromolecules of the two species are intimately intermingled.

Judging from the above considerations, it seems reasonable to conclude that the systems examined exhibit a high level of miscibility in the amorphous state. The only feature that seems contradictory to this interpretation is the presence of the relaxation process located in the vicinity of the glass transition of P(3HB).

In this connection, evidence is growing in the literature[20-22] of unusual relaxation behaviors in miscible systems, investigated using a variety of sensitive experimental techniques. A broadening of the glass transition compared with that of the pure components is usually observed in both miscible polymer blends and plasticized polymers. This broadening is commonly attributed to the presence of local concentration fluctuations which give rise to a distribution of T_g values. Taking into account that different experimental techniques probe different aspects of molecular mobility, increasing information is made available[22-27] regarding the possibility of revealing two mobilization processes with different composition dependencies within binary single-phase mixtures.

As an example, Miller et al.[22] have recently shown that miscible blends of polyisoprene with poly(vinylethylene) exhibit a single glass transition by DSC and ^{1}H NMR, while two composition-dependent glass transition phenomena are revealed by ^{13}C NMR. Despite morphological homogeneity, carbons on the respective polymeric components have been found to undergo the transition to liquidlike mobility at different temperatures resulting in dynamic heterogeneity. The conclusion has been drawn that "very broad glass transitions, or in principle even distinct glass transition temperatures, are not inconsistent with thermodynamic miscibility".

Taking into account the many experimental indications of miscibility for the P(3HB)/CAP and P(3HB)/CAB systems examined in the present work, it can be suggested that the two relaxation processes observed represent two mobilization mechanisms coexisting in a single mixed phase.[28] In this hypothesis, the phenomenon whose composition dependence is shown in Figure 7 would be attributed to the onset of cooperative segmental motions of the cellulose ester under the plasticizing effect of the low-T_g P(3HB) component, while the low-temperature relaxation occurring near the T_g of P(3HB), whose temperature slightly increases with increasing cellulose ester content, would indicate mobilization of P(3HB) under the apparently weak hindering effect of the high-T_g CAB or CAP component.

Conclusions

DSC and dynamic mechanical measurements provide evidence of miscibility of P(3HB) with CAP and CAB. If the P(3HB) content is higher than 50-60%, the bacterial polymer crystallizes from melt-quenched blends upon room storage; on the contrary, when the high-T_g component exceeds 50%, crystallization of P(3HB) is prevented and fully amorphous blends are obtained. In this latter composition range, two mobilization phenomena are observed, the higher temperature one characterized by a T_g-composition dependence well described by eq 1, the other one only slightly composition dependent.

On heating blends immediately after melt-quenching, crystallization of P(3HB), as well as of CAB in P(3HB)/CAB blends, is observed only above the composition-dependent T_g of the blend. The crystalline phase formed during heating melts at a temperature that follows the T_m-composition behavior typical of miscible systems.

Finally, attention is called to potentially interesting consequences of the results of the present work. It has been shown that a variety of morphologically different situations can be obtained in blends of bacterial P(3HB) with cellulose esters. This can be achieved, for example, through heat treatments above the composition-dependent T_g of the blend. Owing to the recognized relevance of morphology to the much discussed issue of polymer biodegradability, the way is opened to the development of materials whose biodegradation rate is regulated through ad hoc induced phase behavior and morphology. Investigations along these lines are in progress.

References and Notes

(1) Holmes, P. A. In *Developments in Crystalline Polymers*; Bassett, D. C., Ed.; Elsevier: New York, 1988; Vol. 2.

(2) Anderson, A. J.; Dawes, E. A. *Microbiol. Rev.* 1990, 54, 450.

(3) Doi, Y. *Microbial Polyesters*; VCH Publishers Inc.: New York, 1990.

(4) Scandola, M.; Ceccorulli, G.; Pizzoli, M. *Biomateriali* 1991, 5, 115.

(5) Ceccorulli, G.; Pizzoli, M.; Scandola, M. *Book of Abstracts—Cellulose 91*; New Orleans, 1991; p 273.

(6) Gilmore, D. F.; Lotti, N.; Lenz, R. W.; Fuller, R. C.; Scandola, M. *Book Abstr.—Int. Sci. Workshop Biodegrad. Polym., 2nd* 1991, 74.

(7) Scandola, M.; Pizzoli, M.; Ceccorulli, G.; Cesaro, A.; Paoletti, S.; Navarini, L. *Int. J. Biol. Macromol.* 1988, 10, 373.

(8) Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978; Vol. 1.

(9) Boyer, R. F. *J. Polym. Sci., Polym. Symp.* 1975, 50, 189.

(10) Wood, L. A. *J. Polym. Sci.* 1958, 28, 319.

(11) Fox, T. G. *Bull. Am. Phys. Soc.* 1956, 1, 123.

(12) Kelley, F. N.; Bueche, F. *J. Polym. Sci.* 1961, 50, 549.

(13) Gordon, J. M.; Rouse, G. B.; Gibbs, J. H.; Risen, W. M., Jr. *J. Chem. Phys.* 1977, 66, 4971.

(14) Couchman, P. R.; Karasz, F. E. *Macromolecules* 1978, 11, 117.

(15) Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* 1978, 11, 150.

(16) Wang, L. F.; Pearce, E. M.; Kwey, T. K. *Polymer* 1991, 32, 249.

(17) Nassar, T. R.; Paul, D. R.; Barlow, J. W. *J. Appl. Polym. Sci.* 1979, 23, 85.

(18) Hahn, B.; Wendorff, J.; Yoon, D. Y. *Macromolecules* 1985, 18, 718.

(19) Hahn, B. R.; Hermann-Schonherr, O.; Wendorff, J. H. *Polymer* 1987, 28, 201.

(20) Ando, Y.; Yoon, D. Y. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* 1988, 29, 381.

(21) Runt, J. P.; Barron, C. A.; Zhang, X.; Kumar, S. K. *Macromolecules* 1991, 24, 3468.

(22) Miller, J. B.; McGrath, K. J.; Roland, C. M.; Trask, C. A.; Garroway, A. N. *Macromolecules* 1990, 23, 4543.

(23) Kambour, R. P.; Carbeck, J. D.; Nachlis, W. L. *J. Non-Cryst. Solids* 1991, 131-133, 563.

(24) Hains, P. J.; Williams, G. *Polymer* 1975, 16, 725.

(25) Plazek, D. J.; Riande, E.; Markovitz, H.; Raghupathi, N. *J. Polym. Sci., Polym. Phys. Ed.* 1979, 17, 2189.

(26) Ceccorulli, G.; Pizzoli, M.; Scandola, M. *Polymer* 1987, 28, 2077.

(27) Pizzoli, M.; Scandola, M.; Ceccorulli, G. *Eur. Polym. J.* 1987, 23, 843.

(28) In a private communication, Dr. Buchanan (Eastman Chemical Co.) kindly made us aware of his results on cellulose acetate butyrate/poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (CAB/PHBV) blends. He too concludes that in miscible CAB/PHBV blends two mobilization processes occur: ^{13}C NMR measurements reveal vastly different mobilities of CAB and PHBV (50/50 blend) even in the molten state (185 °C).