

Binary blends of microbial poly(3-hydroxybutyrate) with polymethacrylates

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Blends of bacterial poly(3-hydroxybutyrate) (PHB) with poly(methyl methacrylate) (PMMA) and poly(cyclohexyl methacrylate) (PCHMA) were prepared by melt compounding followed by quenching to room temperature. PHB/PMMA blends containing up to 20 wt% PHB are single-phase amorphous glasses with a composition dependent glass transition temperature (T_g). When the concentration of PHB exceeds 20 wt%, partially crystalline pure PHB coexists with a constant-composition PHB/PMMA (20/80) mixture, which represents the solubility limit of PHB in PMMA. In such blends crystallization of PHB, both isothermally from the melt and with heating from the rubbery state, is retarded by increasing amounts of PMMA in the blend. PHB shows no miscibility at all with PCHMA. In the PHB/PCHMA blends, two phases, consisting of the pure polymer components, are present over the whole composition range and PHB crystallization is unaffected by the presence of the methacrylate polymer.

(Keywords: poly(3-hydroxybutyrate); polymethacrylates; binary blends)

INTRODUCTION

Poly(3-hydroxyalkanoates) (PHA) are isotactic, high-molecular-weight polyesters produced by a wide range of micro-organisms as intracellular carbon and energy reserve materials^{1,2}. Using the bacterium *Alcaligenes eutrophus*, the homopolymer poly(3-hydroxybutyrate) (PHB) and random copolymers containing the 3-hydroxybutyrate and 3-hydroxyvalerate units (PHBV) have been produced on an industrial scale by ICI (UK). These commercially available biopolymers have attracted much attention for use in agricultural, marine and medical applications²⁻⁴. The main advantages of such thermoplastic polymers are biocompatibility and biodegradability. Degradation of PHAs occurs both *in vivo* through hydrolysis of the ester linkage, and in an accelerated fashion in the environment, due to the intervention of extracellular enzymes produced by micro-organisms present in soil and water. In order to improve the physical properties, and in particular to decrease the brittleness of highly crystalline microbial PHB, blending with a second polymeric component has been attempted by a number of investigators. A wide variety of polymers have been considered as components in binary blends with PHAs, including hydrocarbon polymers⁵, polysaccharides⁶, aliphatic synthetic polyesters^{7,8}, poly(ethylene oxide) (PEO)⁹, poly(vinyl acetate) (PVAC)^{7,10}, chlorinated polymers¹¹, and cellulose derivatives^{12,13}. Only a few of the blends investigated have been reported to be truly miscible, namely those with PEO⁹, PVAC^{7,10} and some of the cellulose esters^{12,13}.

This paper investigates the compatibility of blends of PHB with poly(methyl methacrylate) and poly(cyclohexyl methacrylate). Evidence of miscibility has been investigated by means of differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (d.m.t.a.), as well as through isothermal crystallization experiments.

EXPERIMENTAL

Materials

Poly(3-hydroxybutyrate) (PHB) (BXGV9, $M_n = 350\,000$, $M_w = 1\,140\,000$) was kindly supplied by ICI Biological Products (UK). Poly(methyl methacrylate) (PMMA) and poly(cyclohexyl methacrylate) (PCHMA) were commercial products purchased from the Aldrich Chemical Company.

Preparation of blends

For each composition, weighed amounts of the two blend components were mixed in the heated cup of a miniature mixing/injection-moulding machine. In order to minimize the thermal degradation of PHB, the temperature was kept at the lowest possible value that injection moulding could be carried out (195°C). After mixing for 3 min the blends were injection moulded in the form of small bars ($30 \times 7.5 \times 1.5 \text{ mm}^3$), quenched in an ice-water mixture and allowed to age at room temperature for at least 21 days before testing. The pure polymers were also melt processed under the same conditions. Blend compositions are indicated throughout this work as weight ratios of PHB/PMMA or PHB/PCHMA.

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Experimental methods

Dynamic mechanical measurements were performed with a dynamic mechanical thermal analyser (Polymer Laboratories Ltd), operated in the dual cantilever bending mode, at a frequency of 3 Hz and a heating rate of 3 deg min⁻¹, over the temperature range from -150 to 150°C. Calorimetric (d.s.c.) measurements were carried out by means of a Dupont 9900 thermal analyser, with the temperature scale being calibrated by using high-purity standards. After preliminary heating to 200°C in order to remove the effects of any previous thermal history of the sample, followed by a rapid quench to -80°C, d.s.c. scans were carried out at a heating rate of 20 deg min⁻¹ over the range from -80 to 200°C. The melting temperature (T_m) was taken as the peak temperature of the melting endotherm while the glass transition temperature (T_g) was taken as the inflection point of the specific heat increment at the glass transition. When crystallization was observed during the heating scan, the crystallization temperature (T_c) was taken as the temperature of the main exothermal peak.

Measurements of the isothermal radial growth rate of PHB spherulites were carried out with a Zeiss Axioscop polarizing optical microscope, equipped with a Linkham TH 600 hot stage. Isothermal crystallization measurements were performed on thin slices of the injection moulded sample, which were inserted between two microscope cover-glasses and subjected to a five-stage thermal programme: (i) heating in the microscope hot stage at a rate of 20 deg min⁻¹ to 180°C; (ii) isothermal treatment for 1 min, during which time the melt was squeezed into a film by means of a small pressure applied to the upper glass; (iii) heating at a rate of 10 deg min⁻¹ to 200°C; (iv) quenching to the crystallization temperature (T_c) by means of a N₂ gas flow (cooling rate > 250 deg min⁻¹) and; (v) isothermal treatment at the selected T_c . The whole procedure was carried out without removing the sample from the hot stage. A videocamera, attached to the microscope through the Linkham VTO232 interface, allowed real-time measurements of the spherulite dimensions, after calibration with a micrometric reticule. A new sample was used for each crystallization measurement.

RESULTS AND DISCUSSION

PHB/PMMA blends

Figure 1 shows the d.s.c. thermograms of PMMA and its blends with PHB contents up to 30 wt%. Over this composition range, an endothermal baseline shift associated with the glass transition is observed for all of the samples. With an increasing PHB content in the blend, the transition is seen to broaden quite markedly on the low temperature side. This behaviour is particularly evident in blend (30/70), where the transition spans ~100°C. However, the high temperature side of the specific heat step is quite well-defined and has been indicated in Figure 1 by drawing the intersection of the tangent to the specific heat increment with the baseline above T_g . While the intersection temperature decreases with increasing PHB content up to 20 wt%, it remains constant upon further increases (e.g. blend (30/70)).

The d.s.c. thermograms of blends with PHB contents greater than 30 wt% (Figure 2) show a glass transition at a temperature identical to the T_g of pure PHB,

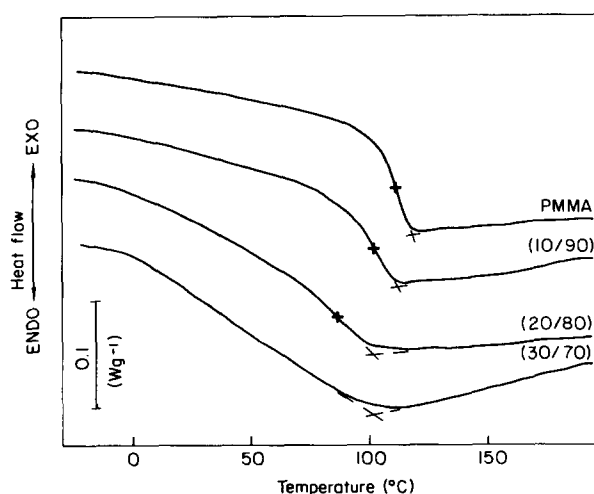


Figure 1 D.s.c. thermograms of PMMA and various PHB/PMMA blends after melt quenching; T_g s are indicated by crosses on the curves

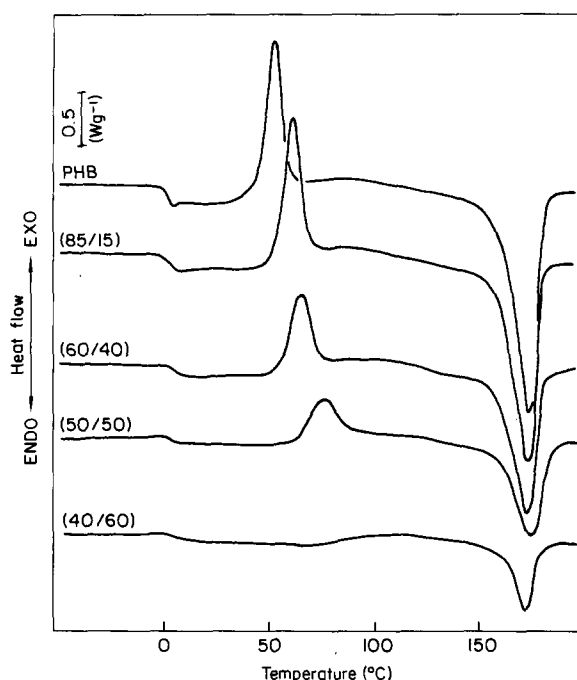


Figure 2 D.s.c. thermograms of PHB and various PHB/PMMA blends after melt quenching

suggesting that an amorphous PHB phase is present in quenched PHB/PMMA blends containing 40 wt% or more of the bacterial polymer component. As commonly observed in melt quenched PHB¹⁴, the glass transition is followed by an exothermal cold crystallization phenomenon, with a main peak that shifts to higher temperatures with an increasing PMMA content in the blend. This behaviour indicates that above T_g the amorphous PHB phase crystallizes in a somehow retarded fashion due to the presence of the methacrylate component. The temperature of the melting endotherm does not change appreciably with composition, with the exception of blend (40/60) where the melting peak is clearly shifted to a lower temperature. In this particular case, crystallization upon heating is barely observable under the experimental conditions that are employed here.

The temperatures of the calorimetric transitions of the PHB/PMMA blends, taken from the curves of Figures 1 and 2, are plotted in Figure 3 as a function of composition; no T_g value is reported for the blend containing 30 wt% PHB, due to the uncertainty in determining T_g from the curve shown in Figure 1. The curve connecting the T_g s of PHB and PMMA in Figure 3 can be represented by the Fox equation¹⁵:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (1)$$

where subscripts 1 and 2 indicate the two component polymers. A number of equations, based on different theoretical grounds, have been proposed to describe the composition dependence of the glass transition in miscible polymer blends¹⁶. However, due to its simple form and to the lack of any adjustable parameters, equation (1) is one of the most commonly used. The fact that the T_g s of the blends containing 10 and 20 wt% PHB follow the predictions of the Fox equation is a good indication that up to values of 20 wt% the blend components form a homogeneous mixture.

The d.s.c. results suggest that blend (20/80) represents a kind of solubility limit of PHB in PMMA in the melt from which the blends have been quenched. In this hypothesis, all of the PHB component exceeding 20 wt%

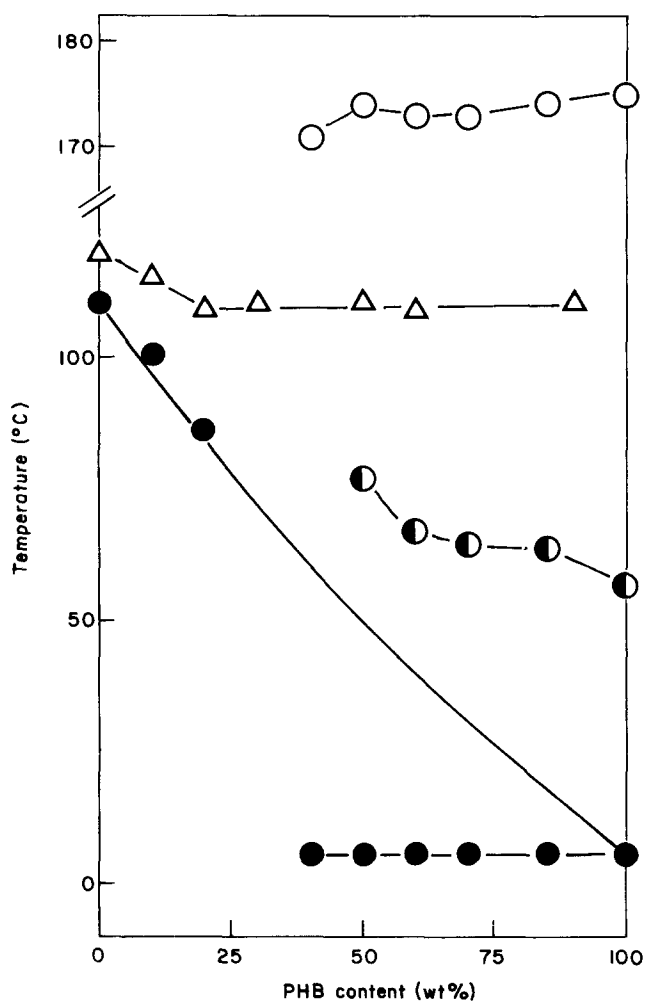


Figure 3 Temperature of the transitions of various PHB/PMMA blends, as a function of the PHB content, using data obtained from the d.s.c. curves shown in Figures 1 and 2: (●) glass transition; (○) crystallization and; (△) melting. Also shown are: (△) glass transition values obtained by d.m.t.a. measurements and; (—) curve representing the Fox equation (see text for details)

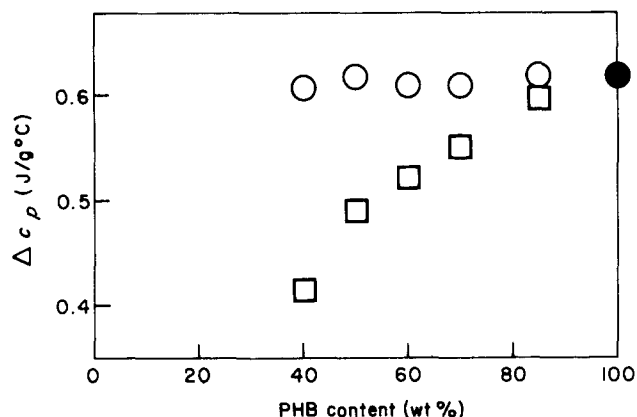


Figure 4 Specific heat increment values at the glass transitions of PHB/PMMA blends as a function of the PHB content (see text)

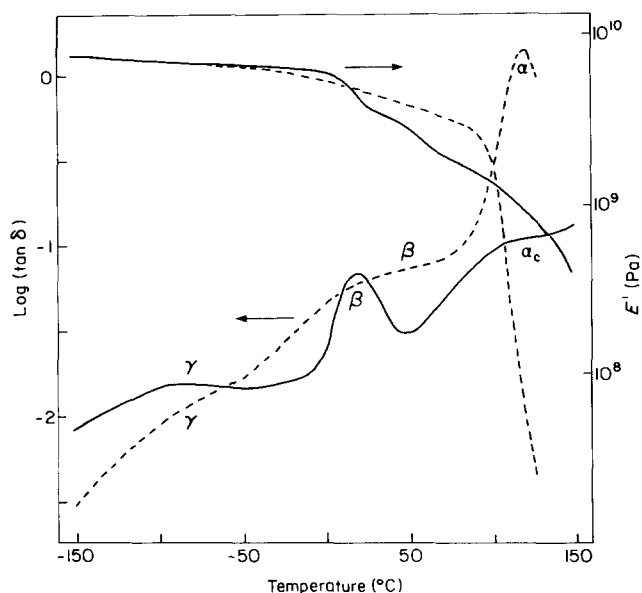


Figure 5 Dynamic mechanical spectra of: (—) PHB and; (---) PMMA

should be present as a pure phase, in equilibrium with a constant composition (i.e. 20/80) mixture. In fact, Figure 2 clearly shows that blends containing more than 30 wt% PHB have a constant glass transition temperature, whose quantification can be used to test the solubility limit hypothesis. Figure 4 shows two sets of specific heat increment (Δc_p) values, calculated either by assigning the observed baseline shift to all of the PHB present in the blend (i.e. the overall PHB content) (shown as squares), or by attributing the transition solely to the PHB which exceeds the amount needed to form the postulated (20/80) mixture (shown as circles). The constancy of the Δc_p values obtained according to the latter calculation indirectly attests the existence of the constant composition (i.e. 20/80) mixture.

The glass transition of such a phase, which should occur at $\sim 85^\circ\text{C}$ in blends where PHB exceeds 20 wt%, is not seen in the curves of Figure 2, due to the occurrence of the PHB cold crystallization process in the same temperature region. Conversely, as shown below, dynamic mechanical analysis of blend samples which have been stored at room temperature easily reveals the (20/80) amorphous mixed phase, free from any interfering crystallization phenomena.

The two pure components of the blends under investigation (PHB and PMMA) have rather complex viscoelastic spectra, which are reported in Figure 5.

Partially crystalline PHB, which has been stored at room temperature (solid line), shows a glass transition (β) in the vicinity of room temperature, and a water-related low temperature relaxation (γ), as well as a high temperature process (α_c) involving rearrangements of the crystalline phase¹⁴. The viscoelastic spectrum of PHB is further complicated by strong physical ageing effects¹⁷, which induce both a depression of the glass transition peak intensity and the appearance of a double step in the concomitant modulus drop. In the case of PMMA (shown as the dotted line in Figure 5) three relaxations appear in the viscoelastic spectrum: the glass-to-rubber transition (α), as well as two secondary relaxations in the glassy state, one at low temperature (γ), which is associated with the presence of absorbed water, while the other (β) is attributed to local motions of the side chains¹⁸. Dynamic mechanical measurements have been carried out on PHB/PMMA blends which have been maintained at room temperature for at least 3 weeks after the melt extrusion process. This procedure allows phase separated PHB to crystallize, as confirmed by the first d.s.c. curves that are obtained (not shown), where a melting endotherm is observed in all blends containing more than 20 wt% PHB. The viscoelastic spectrum of such blends is free from any crystallization phenomena in the temperature range where the glass transition relaxation of the mixed (20/80) phase is expected to appear. In fact, the d.m.t.a. curves of the blends (Figure 6) show a very clear glass transition, whose temperature decreases from 120 (pure PMMA) to 109°C (blend with 20 wt% PHB), and then remains practically constant as the PHB content is increased from 20 to 85 wt%. The peak intensity, which reflects the amount of blend material undergoing the transition, gradually decreases over the entire composition range. In curve (c), broadening of the absorption peak on the low temperature side of the curve

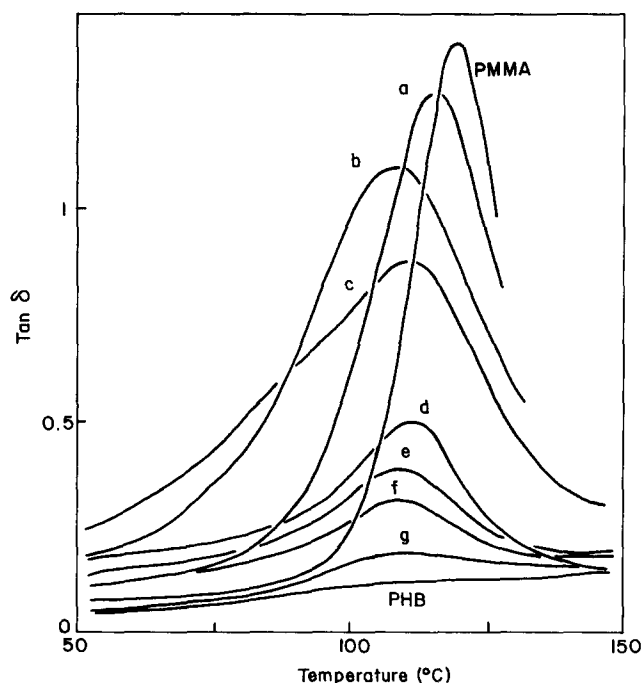


Figure 6 Dynamic mechanical spectra of PHB, PMMA and PHB/PMMA blends: (a) (10/90); (b) (20/80); (c) (30/70); (d) (40/60); (e) (50/50); (f) (60/40) and; (g) (85/15)

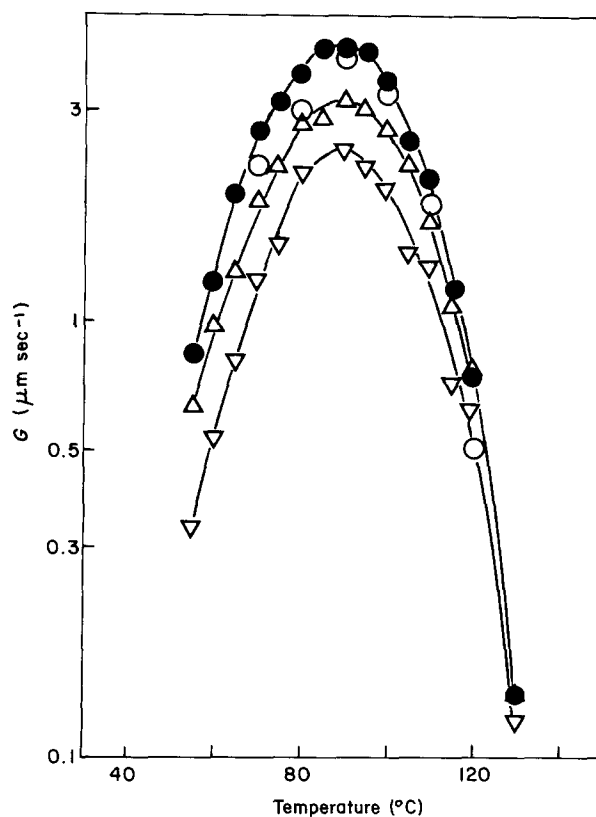


Figure 7 Spherulite growth rate G as a function of crystallization temperature of: (●) pure PHB; (△) PHB/PMMA (85/15) blend; (▽) PHB/PMMA (60/40) blend and; (○) PHB/PCHMA (60/40) blend

is most probably due to minor rearrangements of the crystalline PHB phase.

As expected, and indeed confirmed by d.s.c. experiments, the excess PHB which segregates from PHB/PMMA blends with PHB contents higher than 20 wt% only partially crystallizes upon room temperature storage. Therefore, in such blends three phases can coexist: pure crystalline and pure amorphous PHB, in addition to a mixed amorphous phase with a constant (i.e. 20/80) composition.

It has been pointed out previously (see Figure 2) that when melt quenched PHB/PMMA blends are heated above the T_g , PHB crystallization from the rubbery state is delayed, i.e. it occurs at progressively higher temperatures as the amount of PMMA in the blend is increased. The crystalline PHB phase thus obtained melts at temperatures which are only slightly lower than those observed for the PHB crystals which develop upon heating the pure amorphous polymer (see Figure 3). Further evidence of the inhibiting effect of PMMA on the PHB crystallization can be obtained from isothermal crystallization experiments carried out on molten PHB/PMMA blends. In blends containing up to 40 wt% PMMA, PHB spherulites were seen to grow at all of the crystallization temperatures investigated ($T_c = 55-130^\circ\text{C}$). Since PHB spherulites show a tendency to depart from a spherical shape during growth, which is more marked the higher the PMMA content in the blend, crystallization measurements were interrupted upon appearance of these shape changes. Following this procedure, linear plots of the spherulite radius vs. time were obtained, from which the radial growth rate G was calculated. Figure 7 shows G , as a function of T_c ,

for pure PHB, as well as for blends containing 15 and 40 wt% PMMA. While the temperature at which the maximum crystallization rate is achieved remains the same ($T_c = 90^\circ\text{C}$) for both pure and blended PHB, the G values decrease with increasing PMMA content in the blend. The effect, which is more evident in the low temperature region of the curves, is however less remarkable than that found in totally miscible blends of PHB with cellulose esters^{1,2}, where 20 wt% of the cellulose component decreases the rate of PHB crystallization by one order of magnitude.

Comparison of the isothermal crystallization results of Figure 7 with the d.s.c. curves of Figure 2 shows that crystallization of the bacterial polymer from blends with PMMA is delayed, both when the process is carried out isothermally from the molten state, and also when it occurs dynamically upon heating from the rubbery state. This implies that, although pure phase-separated PHB is available for crystallization in blends where the bacterial polymer exceeds 20 wt%, the coexisting (20/80) mixed phase somehow interferes with the crystallization process.

It is worth noting that in Figure 7 the spherulite growth rate is depressed at all of the T_c s below 110°C , while in the high T_c range (120 – 130°C) no lowering of G is observed. Recalling that the mixed (20/80) phase – whose amount in the blends containing 15 and 40 wt% PMMA is 19 and 50 wt% of the whole blend material, respectively – has a $T_{g,mix}$ of 85°C (from d.s.c.), it is clear that only at $T_c \leq T_{g,mix}$ does the mixed phase delay the crystallization of PHB. On the contrary, at higher crystallization temperatures the mobile, rubbery mixture does not appreciably hinder the crystallization process.

PHB/PCHMA blends

No evidence of compatibility is obtained by either calorimetric or dynamic mechanical measurements on PHB/PCHMA blends: all of the compositions that were examined showed two glass transitions, with constant temperatures that corresponded to that of the pure blend components. As an example, Figure 8 compares the d.s.c.

curves of the pure polymers (using different scales to allow for the large crystallization and melting peaks of PHB) with that of blend (20/80) (using the same scale as PCHMA), after quenching from the melt. The blend shows two glass transition temperatures, at 6 and 107°C , and the associated specific heat increments, compared with those of the pure components, unambiguously indicate an independent contribution of each component to the corresponding glass transition process. The d.s.c. curve of the blend also shows exo- and endothermic peaks corresponding to crystallization and melting of PHB. Attention is drawn to the remarkable differences between the calorimetric response of this immiscible blend and the corresponding PHB/PMMA (20/80) blend shown in Figure 1, where a single glass transition, intermediate to that of the pure components, is the only thermal event that is observed.

All of the PHB/PCHMA blends investigated show d.s.c. curves analogous to that reported in Figure 8 for the (20/80) blend, the only difference being the relative intensity of the observed thermal phenomena, which, as expected, change according to composition. In no case was retardation of the crystallization process observed, as is found in the other blend system. Moreover, despite the obvious difficulties in measuring spherulite growth from a macroscopically biphasic melt, it was found that PHB crystallizes from its blends with PCHMA at a constant rate, which was independent of blend composition. As an example, Figure 7 reports G vs. T_c for the blend containing 40 wt% PCHMA, whose behaviour, contrary to the corresponding PHB/PMMA blend, approximately matches that of pure PHB.

CONCLUSIONS

The binary blends of microbial PHB with two types of methacrylate polymer have shown poor compatibility: 20% by weight is the solubility limit of PHB in blends with PMMA, while no miscibility at all is found in the PHB/PCHMA blends. In the former blends, all of the PMMA is involved in a fixed composition (20/80) mixture, while excess PHB, with respect to that entering such a mixture, segregates and partly crystallizes. A decrease of the rate of isothermal crystallization of PHB from the melt has been observed at all crystallization temperatures lower than the T_g of the (20/80) mixed phase. Investigations on blends with different compositions have shown that the higher the content of glassy mixture in the blend the larger is the delaying effect on isothermal PHB crystallization. In addition, the development of a crystalline PHB phase from the rubbery state (produced by heating quenched PHB/PMMA blends) has been found to be increasingly inhibited as the amount of PMMA in the blend is raised, i.e. by the higher amounts of the (20/80) mixture interfering with the crystallization process.

It may be concluded that while PHB/PCHMA blends form a biphasic system over the whole composition range, with the phases consisting of the two pure polymers, in contrast, PHB/PMMA blends form a homogeneous mixture in the range 0–20 wt% PHB. At higher levels of PHB content in the PHB/PMMA blends a (20/80) mixture coexists with a pure partially crystalline PHB phase, whose properties are somehow affected by the coexisting mixed amorphous phase.

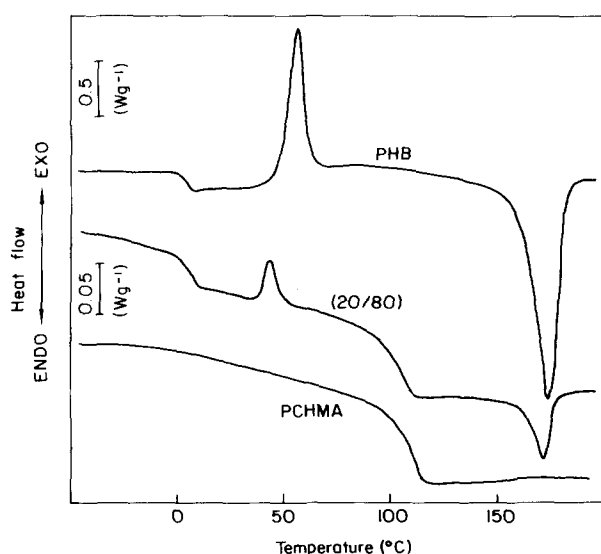


Figure 8 D.s.c. thermograms of PHB, PCHMA and PHB/PCHMA (20/80) blend, after melt quenching

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