Phase separation in blends of poly(hydroxybutyrate) with poly(hydroxybutyrate-*co*-hydroxyvalerate): variation with blend components

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The phase behaviour of a series of blends containing poly(hydroxybutyrate) with poly(hydroxybutyrate-*co*-hydroxyvalerate) or a mixture of two copolymers of differing hydroxyvalerate (HV) content has been investigated using calorimetric methods backed up by morphological observations. Under static conditions, liquid–liquid phase separation (*LLPS*) was found to occur in blends where the relative HV level (i.e. difference in HV between the blend and the component of lowest HV) exceeded about 12%. The region of *LLPS* is asymmetrically placed at the high HV side of the phase diagram and the extent of phase separation increases as the relative HV level between the blend components is increased. Phase separation was promoted by shear. The results are compared with similar behaviour found in blends of linear with branched polyethylene.

(Keywords: poly(hydroxybutyrate); blends; phase separation)

INTRODUCTION

Poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHB/HV) are bacterial polyesters produced in a range of compositions by ICI under the trade name 'Biopol'[1]. Both PHB and PHB/HV can attain high crystallinities: for the relatively low HV copolymers of greatest commercial interest (i.e. with HV levels below about 25%) this is achieved by incorporation of some HV units into the PHB lattice[2,3]. The physical properties of these polymers vary considerably with comonomer content (see, for example, refs 1 and 4) and blending provides a potential method for optimizing mechanical properties without compromising ease of processing. Several studies have been made of the effects of blending PHB or PHB/HV with other, dissimilar, polymers (for example, refs 5–9): blending PHB with its own copolymers offers the additional advantages that cocrystallization is possible between the blend components and the biodegradable and biocompatible characteristics of the homopolymer are preserved. In a recent paper[10], the phase behaviour of a blend system comprising PHB with PHB/HV containing 18.4% of HV units (PHB/18.4%HV) was investigated. A region of liquid–liquid phase separation (*LLPS*) was identified for molten blends containing 13% or more of copolymer. This phase separation could be 'frozen-in' by rapid crystallization and studied using thermal analysis or morphological examination.

The experimental techniques developed for this blend system, described in detail in ref. 10, were adapted from similar methods that have been extensively used to study blends of linear with branched polyethylenes (LPE, BPE)[11,12]. Blends of LPE with BPE are similar to blends of PHB with PHB/HV in that the two blend components have closely related chemical structures, differing only in the number and length of side branches, and are capable of cocrystallization. There are major differences, however, in the crystallization kinetics and in the morphological differences between the two blend components. In both cases the methods developed for studying phase behaviour rely on the assumption that the composition present in the melt is largely preserved during rapid crystallization: in blends of PHB with PHB/HV this assumption is supported by comparison of the results obtained from nucleated and non-nucleated samples of the same blend crystallized under otherwise identical conditions[10]. Given this prerequisite, the phase structure originally present in the melt under particular conditions may be deduced from subsequent studies of melting behaviour or morphology after quenching. For blends of PHB with PHB/HV the crystalline morphologies of the homopolymer and the copolymer, as revealed by methylamine etching[13] and replication, are very similar, and contrast between two different phases in a phase-separated blend is often poor. For this reason analysis of melting behaviour is most useful for such blends. A summary of the complex melting behaviour exhibited by these blends is included in the Experimental section: in brief, the appearance of a double melting peak which is not strongly influenced by changes in heating rate is indicative of a phase-separated structure.

In this paper the results of studies on various blend systems are presented, including both blends of PHB with different PHB/HV copolymers and blends of two copolymers with widely differing HV contents. In some

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cases comparisons were made between blends crystallized under static conditions in the laboratory and samples of identical composition crystallized following shear experienced during extrusion. *LLPS* was found in several cases and was more extensive in blends with a greater difference in HV level between the two components. Shear promoted phase separation, a result with important consequences for the processing of such blends.

EXPERIMENTAL

All the polymers used were kindly supplied by ICI Bio Products and Fine Chemicals. The HV contents, batch numbers, molecular weights and typical melting points of the materials are shown in *Table 1*. Different pairs of polymers were blended together in various proportions — the combinations used and the HV differences between the two constituents are shown in *Table 2*. Mixing was carried out by solution blending in chloroform, with the exception of the extruded samples, which were mixed in powder form prior to extrusion. Where appropriate, nucleation densities were increased by the addition of 1% boron nitride or 2% ammonium chloride.

Samples were crystallized either in d.s.c. pans or in thin films pressed between glass cover slips. They were subjected to a thermal history which typically involved melting at T_m (190 or 200°C), annealing at T_a (between 120 and 180°C) then crystallization at T_c (60, 100 or 120°C). Crystallization was carried out either in a microscope hot stage (Mettler or Linkam) or in the d.s.c. itself. Nucleated samples were left for 1 h at T_c, which allows ample time for complete crystallization. Unnucleated samples were left for several days at T_c. After crystallization a few milligrams of each sample were heated in a Perkin Elmer DSC7 and the position and size of all melting endotherms recorded. In most cases a heating rate of 20°C min^{-1} was used, but representative samples were also run at other rates, so that the influence of heating rate on the melting trace could be assessed.

The morphologies of some samples were investigated by etching the surface with methylamine to reveal the underlying lamellar structure. Samples were suspended in a 33% solution of methylamine in methylated spirit, held at 30°C, for 15 min. After washing, surface replicas were made and examined in a Phillips 301 transmission electron microscope.

Table 1 Polymers used for blend studies

Polymer	Batch	HV content (%)	Molecular weight	Melting point (°C) ($T_c = 100$°C)
PHB	G08	0	539 000	171
PHB/3.8%HV	P022	3.8	611 000	159
PHB/8.1%HV	P037	8.1	494 000	154
PHB/19.7%HV	P031	19.7	424 000	145
PHB/22.3%HV	P024	22.3	476 000	143

Table 2 Polymer combinations used to make blends

Blend	Blend components	Difference in HV (%)
A	PHB:PHB/8.1%HV	8.1
B	PHB/8.1%HV:PHB/19.7%HV	11.6
C	PHB/3.8%HV:PHB/22.3%HV	18.5
D	PHB:PHB/19.7%HV	19.7
E	PHB:PHB/22.3%HV	22.3

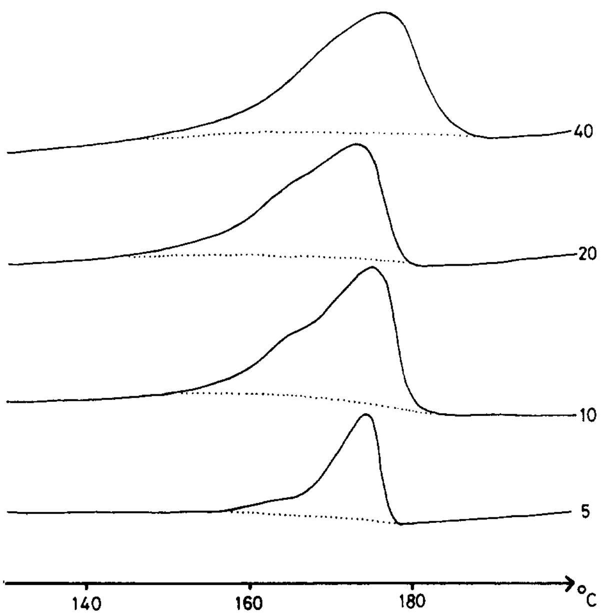

Figure 1 D.s.c. melting endotherms obtained from a blend containing 60% PHB and 40% PHB/19.7%HV at heating rates of 5, 10, 20 and 40°C min^{-1}

For the blends C and E (see *Table 2*), a detailed phase diagram was obtained covering the temperature range 100–200°C. For blends A, B and D only the melt composition present after melting at 190°C was investigated: thus in these cases all samples were nucleated and the annealing stage was omitted from the crystallization procedure. Blends A and D were also crystallized immediately after extrusion to investigate the effect of shear on the results. Extrusion was carried out using a single screw extruder and the molten extrudate was crystallized by passing through a water bath at ~60°C. For highly nucleated samples the nominal crystallization temperature has little effect on the results, since crystallization occurs very rapidly once the melt has cooled to about 100°C.

RESULTS

In each of the blend systems studied, the two individual components had well separated melting points, as shown in *Table 1*. When these two components were mixed one of two distinct types of behaviour was usually observed, as found previously for blends of PHB with PHB/18.4%HV[10]. In one case the blend displayed either a single melting peak, or a double peak which was very strongly affected by heating rate. This is illustrated in *Figure 1*, which shows the melting traces obtained from a blend containing 60% PHB and 40% PHB/19.7%HV heated at various rates. For all but the highest heating rate two melting peaks are clearly visible, but the relative areas of the two peaks vary considerably with heating rate. Such behaviour is typical of that often observed in single polymer systems and illustrates the ability of the polymer crystals to rearrange during heating in the d.s.c. to give more perfect material with a higher melting point. The slower the heating rate, the more reorganization can take place: thus the relative area of the higher temperature peak increases with decreasing heating rate, as seen in *Figure 1*. Such annealing effects are less pronounced if the original crystallization temperature is high, as was generally the case in these experiments. The second type of behaviour exhibited by the blends is illustrated in *Figure 2*, which shows melting endotherms obtained at various heating rates from a blend containing 20% PHB and 80% PHB/19.7%HV. Here again there are two distinct melting peaks, but in this case changing the heating rate has very little effect on the relative proportions of the two peaks: *Figure 2* indicates the approximate proportion of the total area appearing in each peak as the heating rate is changed. This latter behaviour has been identified with a two-phase structure[10], each peak corresponding to a separate phase within the sample, while the behaviour shown in *Figure 1* is characteristic of a single-phase sample.

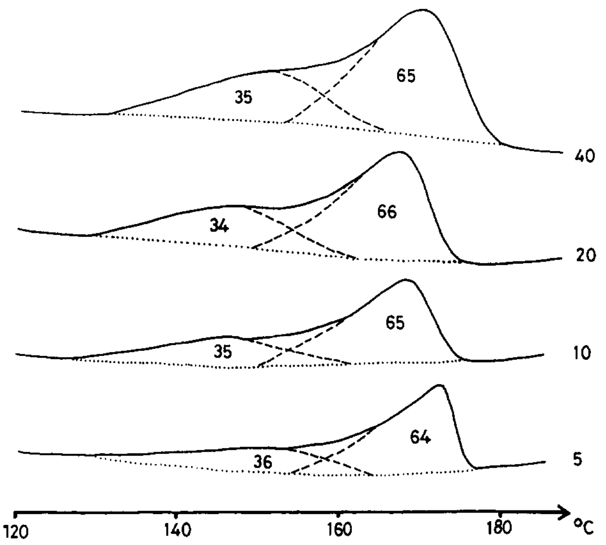

Figure 2 D.s.c. melting endotherms obtained from a blend containing 20% PHB and 80% PHB/19.7%HV at heating rates of 5, 10, 20 and 40°C min^{-1}. The approximate proportion of the total area appearing in each peak is indicated

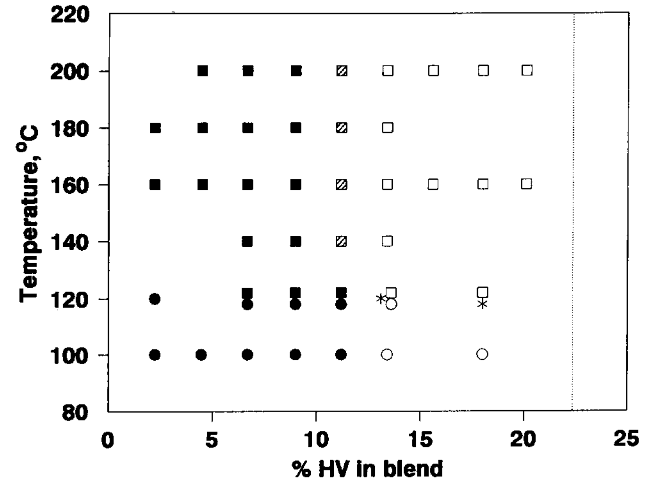

Figure 3 Experimental phase diagram obtained for blends of PHB with PHB/22.3%HV. The dotted line indicates the HV content of the copolymer component. See text for details. ■, Mixed melt; □, two-phase melt; ●, mixed crystals; ○, two-phase crystals; *, crystal/melt

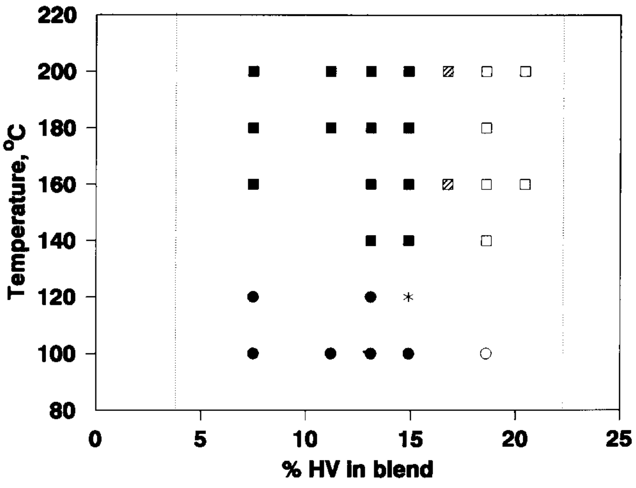

Figure 4 Experimental phase diagram obtained for blends of PHB/3.8%HV with PHB/22.3%HV. The dotted lines indicate the HV contents of the two copolymer components. See text for details. ■, Mixed melt; □, two-phase melt; ●, mixed crystals; ○, two-phase crystals; *, crystal/melt

Using d.s.c. experiments, as outlined above, phase diagrams were obtained over a wide range of conditions for blends of PHB with PHB/22.3%HV (blend E) and PHB/3.8%HV with PHB/22.3%HV (blend C). The results obtained are shown in *Figures 3* and *4* respectively, which are plotted on the same axes to allow easy comparison; the HV contents of the copolymer blend constituents are indicated by dotted vertical lines. Square symbols represent the composition of the melt under the conditions indicated, as deduced from the crystallization behaviour of highly nucleated systems. Hatched symbols indicate conditions where the result obtained was dependent upon the exact crystallization method used, for instance, whether the samples were crystallized in d.s.c. pans or between glass cover slips. The fact that either mixed or separated systems could be obtained in the region of the boundary for *LLPS* emphasizes the non-equilibrium nature of these experiments. The thermal instability of the polymers involved prevents the establishment of true equilibrium so that the results, by necessity, give only a practical guide to the behaviour that is likely to occur under typical working conditions. Circular symbols indicate the composition of unnucleated crystals grown isothermally under the conditions shown, while stars show regions of liquid–solid phase separation (*LSPS*) where HB-rich crystals grow from an otherwise molten sample.

A sample that has undergone *LSPS* will crystallize further on subsequent cooling and this can produce complex melting behaviours. An example of this is shown in *Figure 5*, which compares melting endotherms obtained from two samples of a nucleated blend containing 40% PHB and 60% PHB/22.3%HV. Both samples were melted at 190°C and crystallized at 100°C; the sample represented by curve a was annealed at 140°C before crystallization, while that represented by curve b was annealed at 120°C. The additional peak appearing in curve b arises from crystallization of an HB-rich phase during the annealing stage and is followed by two-phase crystallization very similar to that indicated in curve a. Both the blend systems represented by *Figures 3* and *4* showed *LLPS* over a wide range of temperature for the

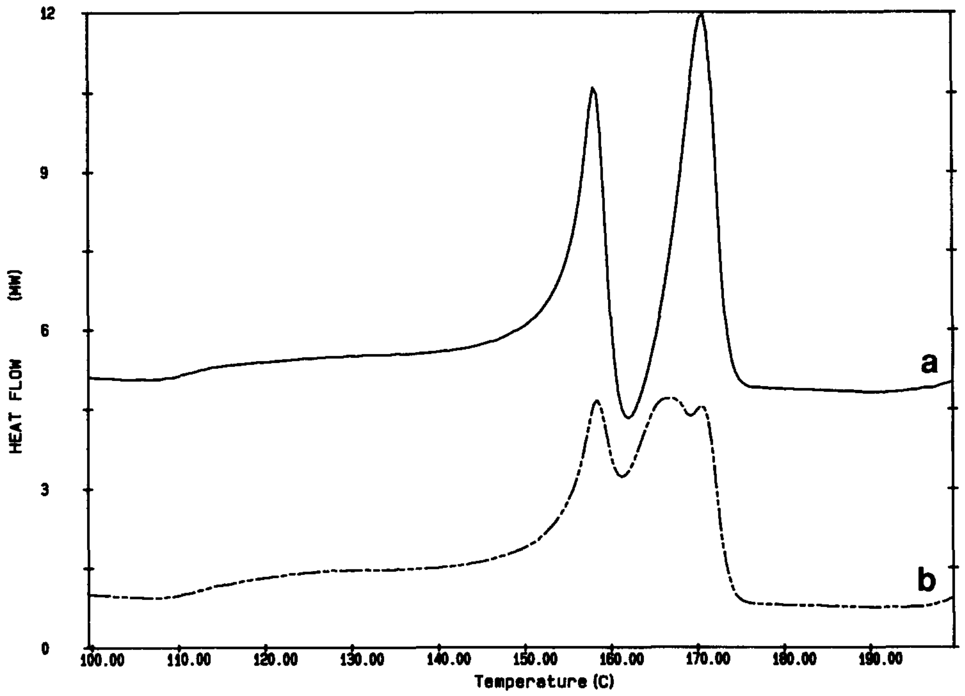

Figure 5 D.s.c. melting endotherms obtained from a blend containing 40% PHB with 60% PHB/22.3%HV. Both samples were melted at 190°C and crystallized at 100°C. In curve a, the sample was annealed at 140°C prior to crystallization; in curve b the annealing temperature was 120°C and the melting behaviour shows evidence of liquid–solid phase separation

compositions with the higher overall HV levels. For PHB with PHB/22.3%HV, *LLPS* sets in when the overall HV level reaches about 11%. For PHB/3.8%HV with PHB/22.3%HV, the overall HV level at the onset of *LLPS* is about 17%; however, if the results are considered instead in terms of difference in HV between the two components then the relative HV level at which *LLPS* occurs is ~13%, very similar to that found in the homopolymer/copolymer system. *Table 3* lists the HV levels at which phase separation would be expected to occur in these blends for a melt temperature of 190°C, giving both actual and relative HV levels for mixtures of two copolymers. *Table 3* also shows the results obtained from blends A, B and D and from the blend of PHB with PHB/18.4%HV (blend F) studied previously[10]. All the results in *Table 3* are derived from nucleated blends melted at 190°C and crystallized at 100°C.

The results summarized in *Table 3* are plotted in *Figure 6*, which shows how the HV level at which phase separation occurs varies with the difference in HV between the blend components: some results have been shifted slightly on the x-axis for clarity. The results from blends comprising mixtures of two copolymers have been plotted in terms of the relative HV level in the blend, i.e. all results have been normalized to reflect the difference in HV level between the two components, rather than the actual overall HV level. In effect, *Figure 6* shows the composition present in the melt at 190°C for a series of blends. In all cases where phase separation was detected, this separation first occurred when the HV level in the blend (relative HV level for copolymer/copolymer systems) reached 11–12%. No *LLPS* was seen in blends where the HV content of the copolymer component (for homopolymer/copolymer blends) or the difference in HV between the two copolymer components (for copolymer/copolymer blends) was less than this critical value. *Figure 7* shows all the results plotted in a different

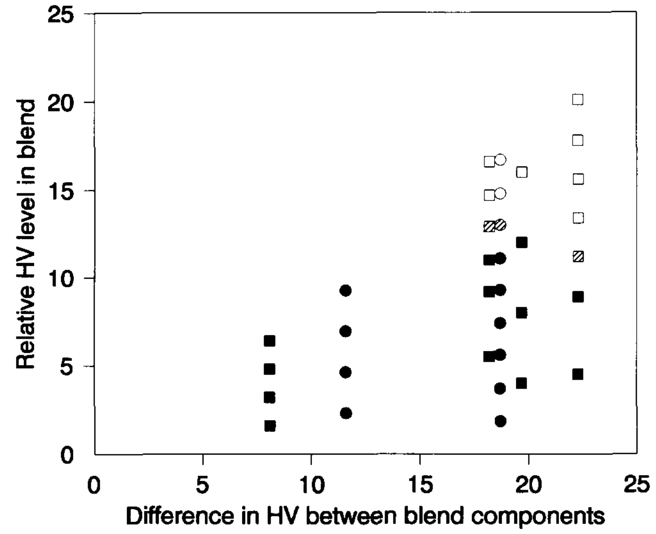

Figure 6 Summary of results obtained from several blend systems for a melt temperature of 190°C. PHB + PHB/HV, mixed (■) and separated (□); PHB/HV + PHB/HV, mixed (●) and separated (○)

Table 3 Approximate position of boundary for liquid–liquid phase separation (*LLPS*)

Blend	Actual HV level at boundary (%HV)	Relative HV level at boundary
A	no *LLPS*	
B	no *LLPS*	
C	16.8 ± 1.3	13.0 ± 1.3
D	14.0 ± 2.0	
E	11.2 ± 2.2	
F[a]	11.0 ± 1.9	

[a] Blend F is the blend of PHB with PHB/18.4%HV studied in ref. 10

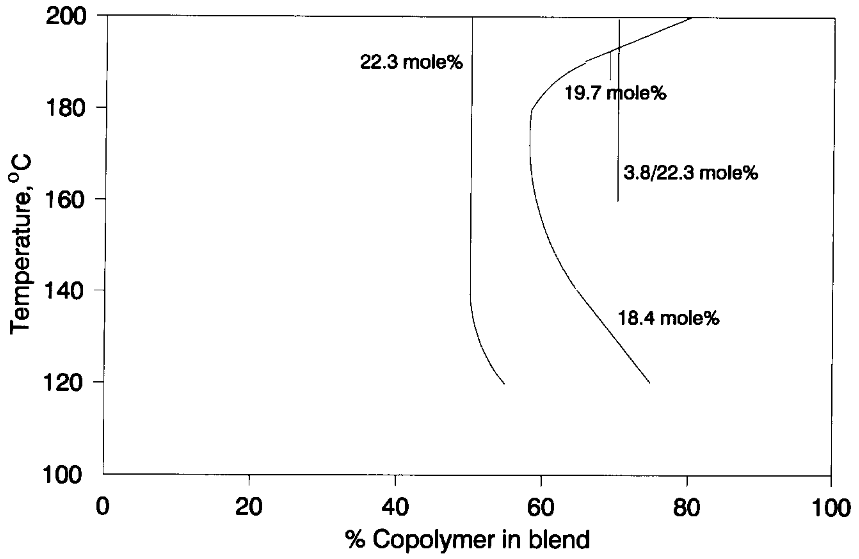

Figure 7 Summary of results showing the approximate position of the boundary for liquid–liquid phase separation in several blend systems in terms of the percentage of each blend component present

format: here the onset of phase separation is shown in terms of the percentage of each blend component present. Plotting the data in this way permits easier comparison with similar results obtained from blends of linear polyethylene with a series of octene copolymers of differing branch content[14], to be discussed below.

Figure 8 shows the effect of shear on the phase behaviour. The results plotted here were obtained from samples of blends A and D which were subjected to shear during extrusion through a single screw extruder. The results are plotted in the same format as those in *Figure 6*, for ease of comparison. In both the blends studied, the application of shear was found to lower the HV level at which *LLPS* occurred. For the blend of PHB with PHB/8.1%HV phase separation occurred in samples containing 80% of the copolymer, whereas none had been seen in any combination in the non-sheared samples. For the blend of PHB with PHB/19.7%HV, phase separation was observed in samples containing 60% or above of copolymer: only the 80% copolymer blend had phase separated in the non-sheared system.

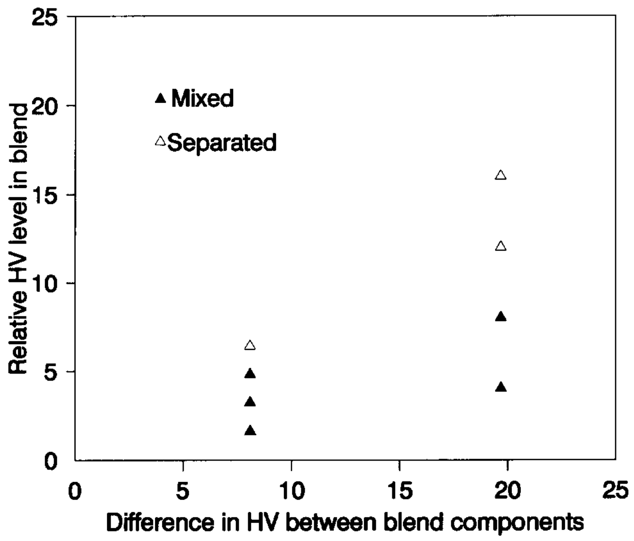

Figure 8 Occurrence of phase separation in sheared blends for a melt temperature of 190°C

The morphologies of crystals grown from PHB and from different PHB/HV copolymers under identical conditions are generally very similar[4]. For unnucleated samples where the spherulites are relatively large, it is often possible to identify differences in band spacing and lamellar arrangement which may be used to distinguish between different blend components — an example of this is given in ref. 10. For highly nucleated samples, the morphological differences are more subtle, but different blend components can still be identified and two-phase structures can be seen. *Figures 9a–d* show surface replicas obtained, respectively, from PHB, PHB/19.7%HV, a mixed blend of 60% PHB with 40% PHB/19.7%HV and a two-phase blend of 20% PHB with 80% PHB/19.7%HV. All samples contain 1% boron nitride and were crystallized at 100°C. For each figure, a general view and a higher magnification inset are given; the scale in each case is the same for all four samples. Comparing *Figures 9a* and *b*, it is apparent that there is a significant difference in lamellar texture between the two samples. The lamellae in the PHB are generally thinner and shorter than those in the copolymer and have a more disordered arrangement. Although the crystals were grown at the same temperature, the equivalent supercooling is higher for the PHB, so that thinner lamellae would be expected in this case. Since the samples are etched and the exact orientation of the lamellae is not known, the observed lamellar spacing bears no direct relationship to the actual crystal thickness; indeed spacings measured from the figures are several times higher than lamellar thicknesses measured by small angle X-ray scattering from similar samples[15]. Nevertheless, qualitative comparisons can prove useful in differentiating between different structures. The mixed blend shown in *Figure 9c* has a uniform morphology, with the distance between lamellae intermediate between that of the two blend components. In contrast, in the blend shown in *Figure 9d* two regions of clearly different morphology can be identified. One region contains shorter, thinner lamellae, while the other consists of longer, broader lamellae with a more regular orientation. These regions an be identified with a PHB-rich and a PHB/HV-rich phase,

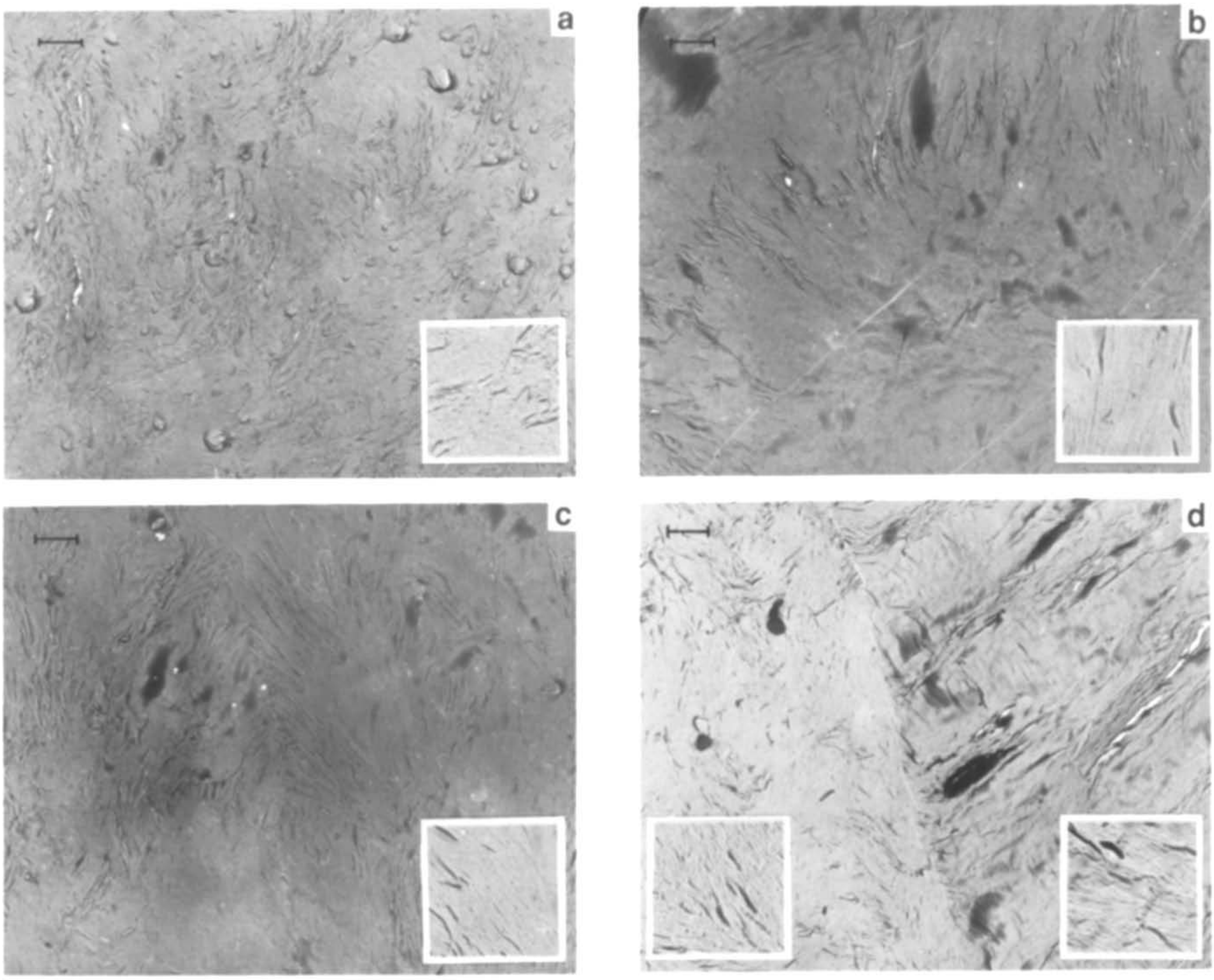

Figure 9 Electron micrographs taken from replicas of etched samples showing typical lamellar morphologies obtained under different conditions: (a) PHB; (b) PHB/19.7%HV; (c) mixed blend of 60% PHB with 40% PHB/19.7%HV; (d) two-phase blend of 20% PHB with 80% PHB/19.7%HV. All samples are nucleated with boron nitride. Scale bars = 1 μm

respectively. Morphological investigations provide useful corroboration of results obtained by d.s.c. but were never used alone to determine phase behaviour.

DISCUSSION

Liquid–liquid phase separation has been found to occur in several blends of PHB with PHB/HV, or of two copolymers, where the difference in HV between the two blend components is fairly high. The region of phase separation is placed asymmetrically on the phase diagram in the region of highest HV content, typically occurring where the relative HV level in the blend exceeds about 12%. A further area of mixing must, by necessity, occur as the composition of the blend approaches that of pure copolymer. Such a region was not observed under the experimental conditions employed here, implying that the position of this boundary lies very close to the copolymer end of the phase diagram. The position determined experimentally for the lower HV boundary for *LLPS* depends to a small extent on the exact experimental conditions employed, which emphasizes the non-equilibrium nature of the results. The phase behaviour observed is very similar to that found in blends of LPE with BPE, where it has also been possible to demonstrate the existence of both upper and lower critical temperatures for phase separation. For the blend systems studied here, no evidence for an upper critical temperature was found in the experimental range investigated, although in a previous study of PHB blended with PHB/18.4%HV such behaviour had been observed[10], as indicated in *Figure 7*. The possibility of a lower critical temperature is suggested from the results from blend E, shown in *Figures 3* and *7*, by the curving round of the boundary at 120°C. This feature has also been observed previously in PHB with PHB/18.4%HV[10].

The extent of the region of *LLPS* varies according to the HV contents of the blend components, as summarized in *Figures 6* and *7*. From these results it is clear that the amount of phase separation is influenced by the *difference* in HV content between the two blend components, rather than the overall HV level. For blends of homopolymer with a copolymer there appears to be an increase in the extent of phase separation as the HV level of the copolymer component is increased, i.e. increasing the branch content favours phase separation. This is in contrast to results obtained from blends of an LPE with a series of octene copolymers of differing branch content[14], where for blends containing copolymers with between 2 and 8 mol% of octene units the region of phase separation became smaller as the octene content of the copolymer increased.

A qualitative scheme has recently been proposed to model theoretically the occurrence of *LLPS* in blends of homopolymers with their branched copolymers[16]. The simple model proposed introduces the concept of an asymmetric extra term in the free energy of mixing of the blend components. This extra term, which could be of either an attractive or a repulsive nature, can account for all the major features of the phase separation that have been reported. One possible source for such an asymmetric extra free energy term could arise from a non-linear apportionment of the specific volume on mixing of the blend components. The origin of such an effect can be qualitatively envisaged by considering the free volume associated with a branched copolymer: spaces may exist in the copolymer melt which are too small to accomodate another branched chain but which can be filled by a linear chain. Thus the addition of a small amount of linear material may lead to an initial increase in density. Conversely, if the branches of the copolymer can themselves fill any spaces, then the addition of some linear molecules may decrease the density. Either effect could lead to an asymmetric extra free energy term as proposed.

Application of shear to a molten blend of PHB with PHB/HV, in this case by extrusion, promotes phase separation. The boundary for the onset of *LLPS* is shifted to lower HV levels on the phase diagram and in some cases phase separation may be induced where none had occurred under static conditions. This result has important practical significance since most commercial processes would involve shear, often at much higher levels than that produced in the single screw extruder used here. The effect on the phase behaviour of further increasing the amount of shear is at present unknown. Phase separation during processing could cause practical difficulties. However, preliminary measurements, to be reported elsewhere[17], suggest that the resultant mechanical properties may be enhanced by a phase-separated structure due to a 'rubber toughening' type mechanism, and therefore for some applications deliberate promotion of phase separation could be an option.

CONCLUSION

Phase separation in blends of PHB with PHB/HV or of mixtures of copolymers has been investigated using calorimetric methods backed up by morphological observations. Liquid–liquid phase separation was detected by using highly nucleated samples in which crystallization occurs sufficiently rapidly that the composition of the melt is reflected in the resultant crystal structure. *LLPS* was found in several blends: in samples crystallized under static conditions, phase separation occurred when the relative HV level in the blend (i.e. the difference in HV between the blend and the component of lowest HV) exceeded about 12%. When samples were subjected to shear by extrusion, the position of the boundary was lowered. The results are one example of what appears to be a general behaviour in blends of linear polymers with closely related branched compounds, studied most notably in blends of linear and branched polyethylenes[11,12,14]. Phase separation in blends of PHB with PHB/HV or of different copolymers could have important practical consequences for the processing of these materials.

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