Mechanical properties of polyhydroxybutyrate–hydroxybutyrate–hydroxyvalerate copolymer blends

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Blends of polyhydroxybutyrate and its copolymers with hydroxyvalerate have been prepared. Under certain conditions of composition and temperature these blends can phase separate. It is shown that for freshly prepared samples, crystallization from a biphasic, rather than a homogeneous, melt leads to improvement in yield and fracture properties. However, during storage at room temperature, an ageing process occurs and the improvement in properties is largely lost.

1. Introduction

Polyhydroxybutyrate (PHB) and copolymers of hydroxybutyrate and hydroxyvalerate (PHB/HV) are naturally occurring thermoplastics produced by bacteria as energy-storage granules. The polymers are currently being produced in large quantities by Zeneca Bio Products and Fine Chemicals and are marketed under the trade name BIOPOL. There are many potential uses for these materials due to their unique combination of properties; in particular, the polymers are both melt processable and biodegradable. We have studied the physical properties of both PHB [1] and the copolymers [2].

The polymers, and particularly the homopolymer, PHB, tend to be somewhat brittle, limiting the range of possible uses [3], for example, limitations in the medical application of PHB due to its ageing are discussed elsewhere [4]. This brittleness tends to develop during storage at room temperature, a process which has become known as ageing of the polymers [5]. During ageing, the modulus increases while the extension to break decreases. Various attempts to explain the ageing process have been made (see, for example [6]), and some attempts have been made to understand the low strength and extension to break in the homopolymer [7]. However, to date, no truly satisfactory explanation for the ageing process has been accepted, nor is the low strength of the homopolymer properly understood.

One approach to improve mechanical properties of brittle polymers is to use rubber toughening; by adding a dispersed phase of a soft rubbery material it is often possible to make large improvements in the fracture toughness of otherwise brittle materials; the best known example is probably toughened polystyrene [8]. Some attempts to blend rubbers with PHB to achieve a similar improvement have been made with limited success [9]. In polyethylenes it is well known that some linear low-density polyethylenes (LLDPEs) have significantly higher low-temper-

ature toughness than other polyethylenes. One possible explanation which has been proposed for this increase in toughness [10], is that these LLDPEs are bimodal and are liable to phase separate in the melt into linear-rich and branch-rich phases which form a special, tough, "phase morphology" on crystallization.

In two previous papers [11, 12], we have demonstrated that blends of PHB with PHB/HV, and those of different PHB/HVs can display liquid phase separation (LLPS), under certain conditions of blend composition and temperature. The region of LLPS is only observed provided there is a difference in HV content between the two components of the blend of at least 8 mol % HV (this figure is for extruded samples; for statically mixed samples a greater difference in HV content is required before LLPS is observed). The general form of the phase diagrams for these blends are very similar to those for blends of linear and branched polyethylenes (LPE/BPE blends). These blends have been shown to behave similarly to LLDPEs in certain ranges of composition and branch content of the BPE [13]. There is some evidence that samples crystallized from a biphasic melt can display a higher fracture toughness than blends crystallized from a mixed melt. Accordingly, by analogy with the polyethylene systems, it may be possible to produce 'toughened' PHB/HV systems by crystallizing from phase-separated melts.

This paper reports some preliminary investigations into the mechanical properties of PHB/HV blend systems. In the PHB/HV systems we must take note of the ageing effects described above and make measurements on both freshly prepared and fully aged samples. We decided that for an initial survey we would not measure fracture toughness, but rather simply concentrate on the tensile modulus, the extension to break, and the yield and fracture stresses. It will become apparent that while there is some improvement in the yield and fracture stresses in freshly prepared samples which had been crystallized from

biphasic melts, this improvement is largely lost in the ageing process.

2. Experimental procedure

2.1. Sample preparation

Three polymers were used in this study, a PHB homopolymer code name GO8, and two PHB/HV copolymers, codes PO29 and PO31; details of the molecular weights and HV contents of these three materials are given in Table 1. Blends of GO8 with both PO29 and PO31 with a range of compositions were prepared by mixing in the melt at 160 °C in a single screw extruder, 1% boron nitride was added as a nucleating agent to the blends containing PO31 [14]. The pelleted blends were then moulded in a hot press to form the sheets from which samples for mechanical testing were cut. Some samples were stored in a freezer in order to prevent any ageing: these are referred to as fresh or unaged samples. Other samples were left at room temperature for at least 5 weeks before testing: these are referred to as aged samples.

2.2. Mechanical tests

All the mechanical tests were carried out using an Instron screw driven tensometer. The tests were performed on samples with a gauge length of 12 mm at a strain rate of $8 \times 10^{-4} s^{-1}$. The tensile modulus was taken as the secant modulus at a strain of 0.1%, the tensile strength quoted refers to the engineering stress at failure and the yield strain is taken as the strain at the maximum recorded load. At least six measurements were taken in each case and the mean values are shown in the figures; the error bars in the data for the tensile strength represent the range of the data. The results for the moduli and yield strain showed very little variation, so the data are shown in the figures with no error bars.

3. Results

We show in Fig. 1a and b the tensile modulus of the blends as a function of the HV content in the blends; the vertical line marks the boundary between samples crystallized from mixed and phase-separated melts [12]. It can be clearly seen in both blend systems that the modulus decreases with HV content of the blend and increases on ageing. No effect of the phase morphology can be seen. Fig. 2a and b show the tensile strengths of the blends. In the fresh samples, the strength tends to decrease a little with increasing HV

TABLE I Polymers used in this study

Polymer	Weight average molecular weight [a], M_w	HV content (%)
GO8	539 000	0
PO29	732 000	18.4
PO31	424 00	19.7

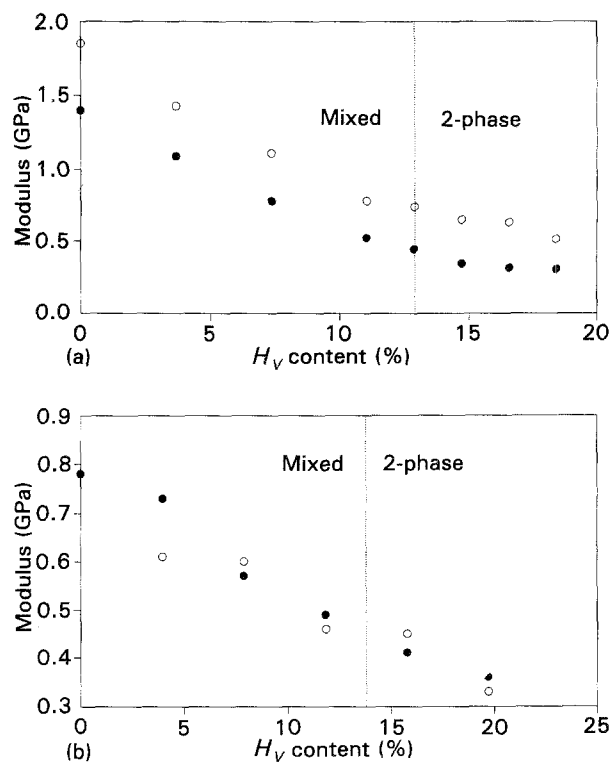[a] All the polymers had polydispersity of ~ 3.

Figure 1 Graphs of tensile modulus of (●) fresh and (o) aged blend samples as a function of overall HV content in the blend. Note: the points at the highest HV content correspond to samples of pure copolymer. (a) Data for blends of GO8 with PO29, and (b) data for blends of GO8 with PO31.
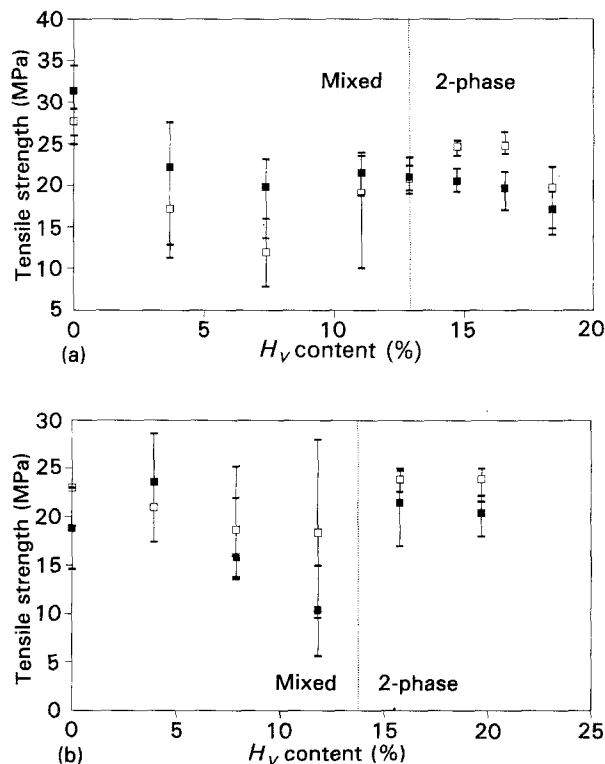

Figure 2 Graphs of tensile strength of (■) fresh and (□) aged blend samples as a function of overall HV content in the blend. Note: the points at the highest HV content correspond to samples of pure copolymer. (a) Data for blends of GO8 with PO29, and (b) data for blends of GO8 with PO31.

content for the samples crystallized from mixed melts, but increase once the HV content is high enough that the melts were phase separated before crystallization. The small improvement in fracture strength is retained

after ageing. Note that in the mixed samples there is a much greater range in the measurements of tensile strength than in the separated ones; this is seen in Fig. 2 by the smaller error bars for the separated samples. Fig. 3a and b show the yield strain; in the fresh samples there is a marked increase in yield strain when the samples are crystallized from a biphasic melt from typically 7% to typically 20%. However, on ageing, the improvement is largely lost; the samples crystallized from a homogeneous melt have yield strains of about 3%, while those crystallized from biphasic melts have yield strains of only about 6%. The effect of ageing on ductility is clearly shown in Fig 4a and b, where the log of the extension to break is shown as a function of the blend composition. In these figures there again appears to be a significant increase in ductility of the fresh samples when they are crystallized from a phase-separated melt; note that the extension to break decreases to a minimum as the HV content of the blends is increased until the blends phase separate when the extension to break increases rapidly. However, once again most of this large improvement is lost on ageing.

4. Discussion and conclusion

The results shown in Figs 1–4 show closely similar behaviour for the two blend systems studied; this is not surprising because the copolymers have quite similar HV contents, although they do have different molecular weights and one contains nucleating agents while the other does not. We can readily see that in
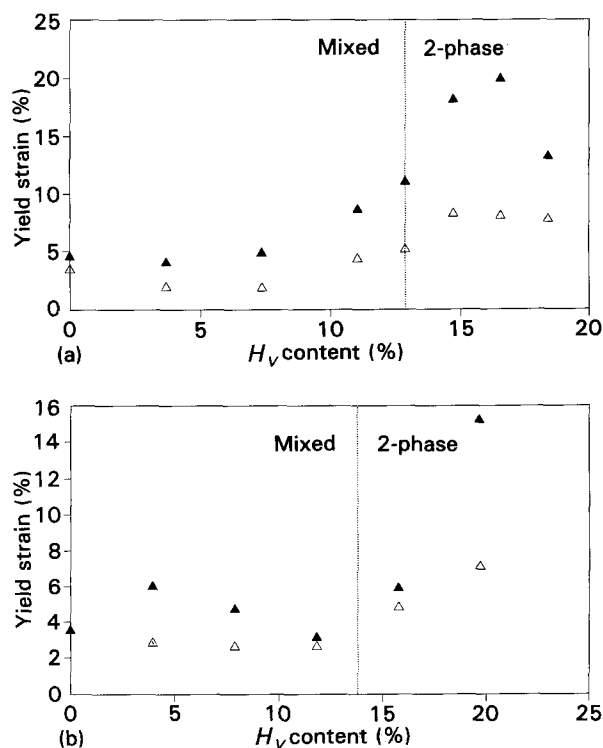
Figure 3 Graphs of yield stress of (▲) fresh and (△) aged blend samples as a function of overall HV content in the blend. *Note*: the points at the highest HV content correspond to samples of pure copolymer. (a) Data for blends of GO8 with PO29, and (b) data for blends of GO8 with PO31.
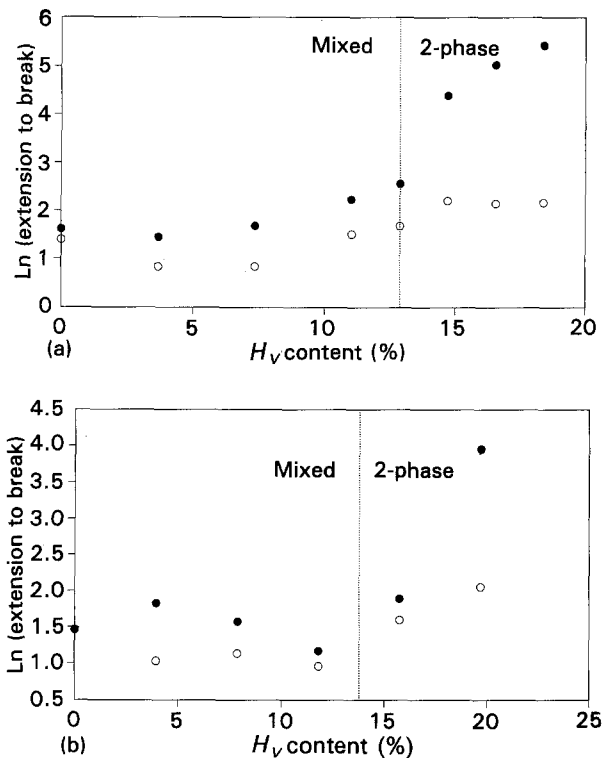
Figure 4 Graphs of extension to break of (●) fresh and (o) aged blend samples as a function of overall HV content in the blend. *Note*: the points at the highest HV content correspond to samples of pure copolymer. (a) Data for blends of GO8 and PO29, and (b) data for blends of GO8 with PO31.

fresh samples the "phase morphology" has a pronounced effect on the yield and fracture of the blends. Blends with a "phase-separated" morphology show a higher ductility than might be expected from extrapolation from the data for samples with a homogeneous uniform morphology. This conclusion is directly comparable with the data for polyethylene systems where it is widely believed that a phase-separated morphology can lead to improved mechanical properties [10, 14]. However, this improvement is largely lost during the ageing process.

We may reasonably conclude that the ageing process dominates the mechanical properties of PHB and PHB/HV copolymers, whether or not they have biphasic morphologies.

Acknowledgements

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