Blends of bacterial and synthetic poly(β-hydroxybutyrate): effect of tacticity on melting behaviour

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(Received 15 November 1991)

Co-crystallization of bacterial and partially isotactic poly(β-hydroxybutyrate) (PHB) was studied by d.s.c. Measurements were made on solvent-cast films and rapidly co-precipitated powders. When the latter technique is used for partially isotactic PHB blended with bacterial PHB, a single melting point was observed at all compositions, which is intermediate between those of the two components. Synthetic atactic PHB was incompatible with the bacterial material but at compositions above 60 wt% atactic PHB a significant drop in melting point of the bacterial PHB was observed. Since both bacterial and synthetic PHB are biodegradable it is concluded that synthetic/bacterial PHB blends can be an attractive alternative to conventional blending involving non-biodegradable polymers.

(Keywords: poly(β-hydroxybutyrate); synthetic; blends; isomorphism; tacticity; biodegradable)

Introduction

Bacterial poly(β-hydroxybutyrate) (PHB) is notable for its properties as a fully biodegradable yet highly crystalline thermoplastic, biosynthesized by a variety of bacteria as an intracellular storage material[1,2].

In the context of usable thermoplastics, the brittleness of PHB limits its use[3]. One solution to this problem has been the development of the random copolymer system poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate) (PHB/V). This material, which is produced commercially by ICI through a fermentation process employing *Alcaligenes eutrophus*[4], exhibits a wide range of physical properties including high extension to break and toughness. Over the composition range of 0–30 mol% hydroxyvalerate (HV), this system is isomorphic[5,6] which assures the maintenance of crystallinity at all compositions.

An attractive solution to the limitations of the PHB homopolymer is through blending with a second polymer. Indeed PHB has been shown to be miscible with poly(ethylene oxide)[7], poly(vinyl acetate)[8], as well as poly(vinylidene fluoride)[9] and poly(vinyl chloride)[10,11]. An alternative approach, which we have investigated, is to blend the naturally occurring bacterial PHB with the synthetic analogues[12,13]. While the former is a highly crystalline polymer with an isotactic configuration, the synthetic version can be prepared with a variety of crystallinities and tacticities, ranging from isotactic and crystalline to atactic and amorphous[14,15]. Furthermore, synthetic PHB of moderate tacticity is biodegradable[16,17]. Hence the blend should retain this property.

It has been shown that bacterial PHB can be blended with PHB/V of 8% HV content by rapid precipitation yielding a single sharp melting endotherm[13]. Although there has not yet been any work done on the mechanical properties of such blends, these results indicated that isomorphic systems such as PHB and PHB/V form strongly interacting blends without loss of crystallinity.

In this communication we present some of our results obtained for the blending of bacterial PHB with synthetic atactic (amorphous) PHB and partially isotactic (semicrystalline) PHB.

Experimental

Bacterial PHB was obtained from Malborough Biopolymers (Billingham, UK) and had a viscosity-average molecular weight of 473 000 as measured in chloroform using values of the Mark–Houwink coefficients reported earlier[18].

The synthetic atactic PHB was supplied by Polysar Rubber Corporation, Sarnia, Ontario and was prepared from racemic β-butyrolactone using $ZnEt_2/H_2O$ catalyst[15,19–21]. The atactic nature of the polymer was confirmed by the presence of two ^{13}C carbonyl peaks of roughly equal intensity in the solution n.m.r. spectrum[15]. Wide-angle X-ray diffraction failed to reveal the presence of crystallinity in the atactic sample. The atactic polymer had a tacky, rubbery feel and a viscosity-average molecular weight of 23 000.

Blends of bacterial PHB with synthetic atactic PHB were prepared from 1% solutions of the two components in chloroform, filtering the resultant solutions onto glass slides, and allowing the solvent to evaporate over the course of ~12 h. Resultant films were then dried under vacuum for 1 day at room temperature. Films were typically 100 μm thick and were allowed to sit at room temperature for 1 week prior to testing to ensure the attainment of equilibrium crystallinity[22].

Partially isotactic PHB was prepared by a previously described procedure using alumoxane catalyst[12,14,15].

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0032-3861/92/214647-03

From ^{13}C n.m.r. the isotacticity index was estimated to be 0.42, as defined in terms of the intensities of the carbonyl peaks:

$$\text{Isotacticity index} = (I_h - I_l)/I_h \qquad (1)$$

where I_h is the intensity of the high field carbonyl peak due to isotactic dyads and I_l is the intensity of the low field carbonyl peak due to syndiotactic dyads[15]. The viscosity-average molecular weight was found to be 279 000. Blends of bacterial PHB and partially isotactic PHB were made by co-dissolving the bacterial and synthetic PHB in chloroform (1 wt% solution, total) and precipitating the mixture into an excess of stirred diethyl ether. The characteristics of the three PHB samples used are summarized in *Table 1*.

Differential scanning calorimetry (d.s.c.) measurements on the blends of bacterial PHB and synthetic atactic PHB were performed on a Seiko DSC 120 instrument at a heating rate of 10°C min^{-1}. D.s.c. measurements on the blends of bacterial PHB and partially isotactic PHB were performed on a Perkin Elmer DSC 2b at a heating rate of 20°C min^{-1}. Melting temperatures (T_ms) were taken at the maximum of the melting endotherms.

Results and discussion

D.s.c. results could not be used to obtain information on miscibility of the amorphous regions in this binary system since isotactic bacterial PHB and synthetic PHB of various tacticities have indistinguishable glass transition temperatures (T_gs) of ~4°C. The trend of d.s.c. melting points is illustrated in *Figure 1* for blends of bacterial PHB with synthetic atactic PHB and partially isotactic PHB. There is a small decrease in T_m with atactic PHB content up to a blend composition of ~60 wt% synthetic PHB, followed by a more dramatic drop in melting point for blend compositions above 60 wt%.

In the case of blends containing partially isotactic PHB and bacterial PHB only a single melting point is observed, intermediate between those of the two pure components. Furthermore, the decrease in melting point in the mid range of composition is greater than in the case of atactic PHB blended with bacterial PHB, reflecting the incorporation of the synthetic PHB into the crystalline lattice of bacterial PHB by virtue of isomorphism[23].

The effect of added atactic PHB upon the melting point of bacterial PHB can be ascribed to both morphological and dilution effects. At high levels of atactic material there is a decrease in perfection and/or size of the crystallites of the isotactic component. At low and intermediate levels of atactic material the small drop in T_m is indicative of only a low level of compatibility in the amorphous phase. Preliminary studies using optical microscopy have indicated the presence of volume-filling spherulites of isotactic PHB even at very high (>80 wt%) levels of atactic PHB. This suggests that the atactic component is to be found within the spherulites of the isotactic component. However the exact details of the morphology are unclear at this time. The possibilities include the presence of the atactic component between lamellae of the isotactic PHB, as has been observed for the system poly(ε-caprolactone)/poly(vinyl chloride)[24], or interfibrillar, as in the system atactic polystyrene/isotactic polystyrene[25,26].

Table 1 Characteristics of PHB samples used in blending experiments

Method of synthesis	Isotacticity index^a	M_v (g)^b	T_m (°C)^c	T_g (°C)^c
$ZnEt_2/H_2O$	0	23 000	–	4
$Al(CH_3)_3/H_2O$	0.42	279 000	160	4
Bacterial	1	473 000	177	4

^{a}See equation (1)
^{b}Measured in chloroform
^{c}Measured by d.s.c.

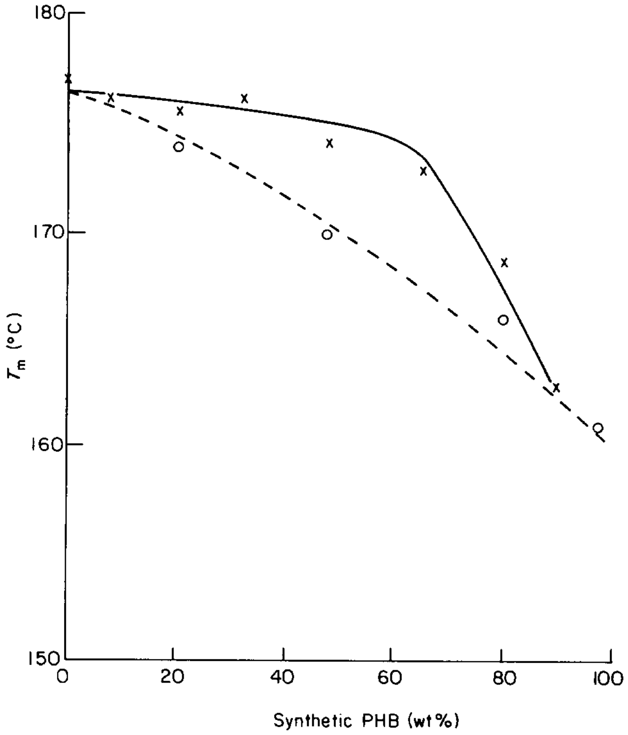

Figure 1 D.s.c. melting points of blends of bacterial PHB with synthetic atactic PHB (×) and partially isotactic PHB (○)

The trend in melting points for the blends of bacterial and partially isotactic PHB suggests that the two components are co-crystallizing and that inclusion is essentially complete. However, it was necessary to rapidly co-precipitate the two components from a non-solvent in order to obtain compatibility as evidenced by the presence of one melting endotherm. Slow evaporation of the solvent at room temperature led to the presence of two distinct melting endotherms, one for each crystalline phase. These results suggest that non-equilibrium crystallization conditions are necessary to obtain compatibility in this case. This is consistent with the results of Yang *et al.*[27] in their study of blends of high density and low density polyethylene. As was pointed out by Albert *et al.*[28], phase behaviour is highly sensitive to parameters such as blend preparation technique and molecular weight effects. For example, the work of Patterson and co-workers[29,30] showed that the role of solvent in the preparation of polymer blends is more than just the reduction of unfavourable interactions between polymer segments of different type. In fact it was shown that a small difference in solvent–polymer interactions ($X_{12} \neq X_{13}$) can have a large effect on polymer compatibility. We conclude that in the case of bacterial and partially isotactic PHB blends isomorphism can be invoked as miscibility-enhancing and leads to a strongly interacting system.

In the case of isotactic (bacterial) and atactic (synthetic) PHB, the conformational irregularity of the latter is an important factor in rendering the two components almost completely immiscible. Furthermore, attempts at bringing about rapid crystallization by co-precipitation into a non-solvent did not yield a change in melting point and hence there was no apparent change in phase behaviour. The same was true of melt pressing the solvent-cast films. In the absence of strong interactions between the two components such as hydrogen bonding, and the inability of the atactic component to co-crystallize with the isotactic component (in contrast to partially isotactic PHB), it is apparent that there is no mechanism for the two components to associate to any significant extent.

The results presented here indicate that blending of synthetic and bacterial PHB is a promising route towards improving the physical characteristics of bacterial PHB. Since it has been shown that the synthetic analogues are biodegradable[16,17], as is bacterial PHB, the synthetic/bacterial PHB system is an attractive alternative to conventional blending techniques involving non-biodegradable synthetic polymers. In a subsequent paper we will present a detailed study of blends of atactic and bacterial PHB, in order to further elucidate the morphology of the system.

Acknowledgements

We are grateful to Dr Steven Bloembergen, Polysar Rubber Corporation, Sarnia, Ontario for providing the synthetic atactic PHB. This work was supported by the Natural Sciences and Engineering Research Council of Canada, Xexox Corporation and Fonds Pour La Formation De Chercheurs Et L'Aide à La Recherche (FCAR).

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