Thermal behaviour and miscibility of poly(3-hydroxybutyrate)/poly(vinyl alcohol) blends

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Thermal behaviour and miscibility of poly(3-hydroxybutyrate) (P(3HB))/poly(vinyl alcohol) (PVA) blend films prepared by casting have been analysed by d.s.c., n.m.r. and density measurements. Blends containing glycerine were also analysed by d.s.c. Melting temperature (T_m) of the P(3HB) crystalline phases decreased as PVA content increased, whereas T_m of the PVA phase remained almost unchanged. The crystallinity of P(3HB) in the blends also decreased with increase of PVA content. These results indicated that the thermal behaviour of the P(3HB) phase was influenced by the existence of PVA. Glycerine had no effect on the thermal properties of the blend, except for depression of T_m of the PVA phase. Miscibility in the amorphous phase of the blend has been analysed by density measurement. If P(3HB) is completely immiscible with PVA, the crystallinity of PVA can be estimated from the crystallinity of P(3HB) and the density of the sample. However, the crystallinities of the PVA phase estimated for some blend samples were greater than unity. This behaviour can be accounted for when these blends are partially miscible in the amorphous phase. In order to investigate the miscibility in detail, we have determined the ^{1}H spin-lattice relaxation times in the laboratory frame (T_1) and in the rotating frame ($T_{1\rho}$). Both T_1 and $T_{1\rho}$ values for the P(3HB) and PVA phases tend to approach those of blend partners with increase of PVA content. That is to say, the increase of PVA content in a blend enhances the miscibility.

(Keywords: poly(3-hydroxybutyrate); poly(vinyl alcohol); blend; miscibility; solid-state high resolution ^{13}C n.m.r.; d.s.c.)

INTRODUCTION

Bacterially synthesized poly(3-hydroxybutyrate) (P(3HB)) is a crystalline polyester of great technological interest, because it is a truly biodegradable and highly biocompatible polymer. This polyester has optical activity, piezoelectricity and gas barrier properties. However, the stiffness and brittleness of P(3HB), due to the relatively high melting temperature and high crystallinity, have limited its use[1–3].

In order to overcome the shortcomings of P(3HB), and to obtain useful new materials based on P(3HB), two approaches have been vigorously studied. One approach is biosynthesizing copolyesters containing hydroxyalkanoate units other than 3HB units. For example, 3HB copolyesters containing 3-hydroxyvalerate[3–6], 4-hydroxybutyrate[7] and 5-hydroxyvalerate[8,9] units can be produced by *Alcaligenes eutrophus*. Poly(3-hydroxyalkanoate)s containing longer side-chains are accumulated in a number of bacteria such as *Pseudomonas oleovorans*[10], *P. putida*[11], *Rhodospillium rubrum*[12], and so on. The composition of monomer unit in these copolyesters can be controlled by using a mixture of different carbon sources in the culture medium. Depending on the chemical and compositional structures of these copolyesters, their physical properties, such as melting points and crystallinity, vary widely.

The second approach is to make miscible blends which consist of P(3HB) and flexible biodegradable polymers or plasticizer of lower molecular weight. It has been found that P(3HB) is miscible with poly(ethylene oxide) (PEO)[13], poly(vinyl acetate) (PVAc)[14], and poly(vinylidene fluoride) (PVDF)[15]. PEO is biodegradable, but PVAc and PVDF are not biodegradable. Thus, P(3HB)/PVAc and P(3HB)/PVDF blends are partially biodegradable materials.

We have attempted to make P(3HB)/PVA blends in order to obtain new biodegradable polymers. Poly(vinyl alcohol) (PVA) is a crystalline polymer which is biodegradable and soluble in water. In comparison with P(3HB), PVA has excellent mechanical properties. When P(3HB) is blended with PVA, significant improvements may be obtained in toughness and ductility.

Only a few studies have been reported on blend systems composed of two crystalline polymers, and in most cases the miscibility of the blends is questionable[16–18]. It is very difficult to analyse the miscibility of such blends, because miscibility is a property in the amorphous phase and the existence of the crystalline phase prevents observation of the amorphous phase. For example, it is difficult to observe precise glass transition temperatures (T_gs) of blends with relatively high crystallinity. Thus, it is not easy to judge miscibility of such polymer blends from T_g data. The existence of the crystalline phase increases the apparent T_g.

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In the present paper, thermal behaviour and miscibility of the blend composed of two crystalline polymers, P(3HB) and PVA, were studied by solid-state high resolution ^{13}C n.m.r., d.s.c. and density measurement. Data for the amorphous phase obtained from the density and n.m.r. measurements are independent of those for the crystalline phase. the influence of the blend partner and glycerine upon thermal properties will be discussed.

EXPERIMENTAL

Materials

P(3HB) (M_w 360000) was purchased from Wako Pure Chemical Industries. PVA (degree of polymerization 2000, degree of saponification 99%) was purchased from Nacalai Tesque. P(3HB)/PVA blends were prepared by casting from hexafluoroisopropanol (HFIP), which was kindly donated by Central Glass Co., Ltd. Some blends were cast from HFIP containing glycerine. The resulting films were completely dried under vacuum at 60°C to constant weight. The compositions of the blends investigated in this work are given in *Table 1*.

Differential scanning calorimetry

The d.s.c. thermal data were recorded on a Seiko DSC-20 equipped with an SSC-570 thermal controller. The films were heated from $-50°C$ to 260°C at a heating rate of $10°C\ min^{-1}$. Melting temperature was determined from the peak of a thermogram.

Nuclear magnetic resonance

Solid-state high-resolution ^{13}C n.m.r. spectra were obtained at 67.9 MHz on a Jeol GSX-270 spectrometer equipped with a cross-polarization/magic angle spinning (CP/MAS) accessory. CP/MAS n.m.r. spectra were obtained with a spinning frequency of about 6.0 kHz at room temperature. A contact time of 2 ms and a repetition period of 5 s were used. The ^1H magnetic field was about 50 kHz. Chemical shifts of CP/MAS spectra were referenced to the methyl carbon resonance of external hexamethybenzene (17.4 ppm relative to the signal of tetramethyl silane).

The ^1H spin-lattice relaxation times in the laboratory frame (T_1) and in the rotating frame ($T_{1\rho}$) were determined by $(180°)_x - \tau - (90°)_x$ and $(90°)_x - [90°(\tau)]_y$ pulse sequences, respectively. Overlapping peaks were resolved by using the LAB ONE NMR1 program (New Methods Research, Inc.) for spectral analysis on a Sun-4 workstation.

Table 1 Compositions of PHB/PVA/glycerine blends

	Composition (wt%)		
Sample no.	P(3HB)	PVA	Glycerine
1	100	0	0
2	80	0	20
3	75	25	0
4	60	20	20
5	50	50	0
6	40	40	20
7	25	75	0
8	20	60	20
9	0	100	0
10	0	80	20

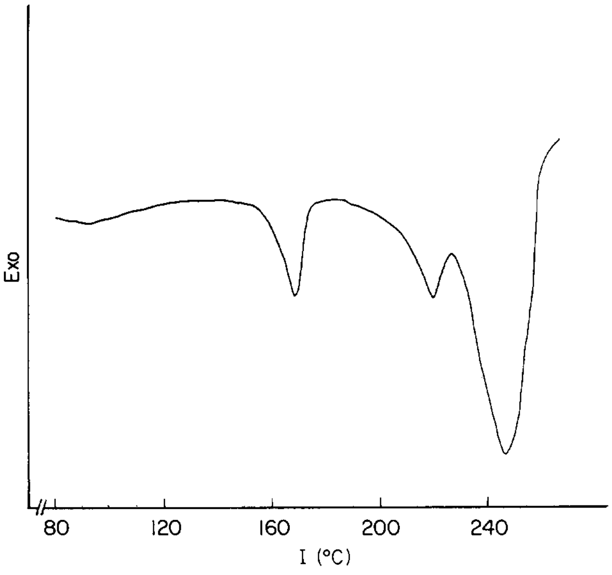

Figure 1 D.s.c. thermogram of P(3HB)/PVA blend sample no. 5

Density measurements

The densities of P(3HB)/PVA blend samples were measured in toluene/carbon tetrachloride at 20°C by the flotation method. The density of each sample was determined as the average of three independent measurements.

RESULTS AND DISCUSSION

Thermal analysis

If a blend system consisting of two crystalline polymers is miscible, co-crystallization[14–16] in a single lattice may occur. However, for almost all pairs of crystalline polymers, the enthalpy of the co-crystallization has a large positive value, whereas the entropy is very small. Thus, co-crystallization is extremely rare. We discuss the miscibility in P(3HB)/PVA blends on the assumption that 3HB and VA units do not co-crystallize.

The d.s.c. thermogram of P(3HB)/PVA sample no. 5 is shown in *Figure 1*. The thermogram of each blend sample has three endotherm peaks. The peaks, which represent the fusion of the P(3HB) crystalline phase, the fusion of the PVA crystalline phase and the decomposition of P(3HB), are positioned at about 170°C, 220°C and 250°C, respectively. The melting temperatures (T_m) of both the P(3HB) and the PVA phases in the blend samples are given in *Table 2* and are plotted against composition in *Figure 2*. The P(3HB) phases in the blend samples with and without glycerine show almost the same T_m values, which decrease as PVA content increases. The T_m values of the PVA phases remain almost unchanged, independent of composition, whereas the blends including glycerine show T_m values of the PVA phase 15°C lower than those without glycerine. It is well known that glycerine usually acts as a plasticizer for PVA. Glycerine, however, should not have a significant effect on the T_m values of P(3HB).

In general, the equilibrium melting temperature, which represents the melting temperature of an infinitely thick lamella, reveals the effect of the blend partner. However, we could not obtain the equilibrium melting temperatures of P(3HB)/PVA blends, because the decomposition of P(3HB) starts before PVA melts completely.

Table 2 Melting temperature (T_m) of P(3HB) and PVA, and phase crystallinity of P(3HB) in blends ($X_c^{P(3HB)}$)

Sample no.	T_m of P(3HB) (°C)	T_m of PVA (°C)	$X_c^{P(3HB)}$ (%)
1	174.3		58
2	170.0		73
3	171.2	221.7	58
4	171.0	209.0	66
5	169.3	219.8	50
6	169.8	210.0	62
7	165.1	220.0	27
8	167.6	206.5	29
9		223.9	
10		208.9	

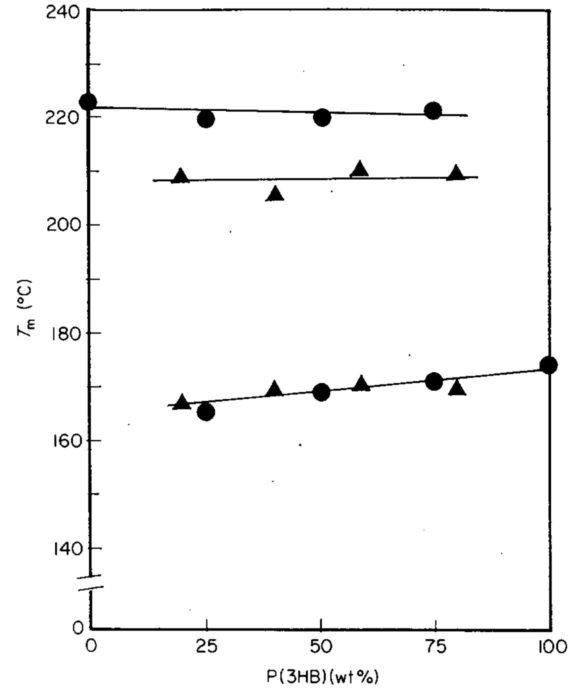

Figure 2 Observed melting temperature of P(3HB) and PVA as a function of PHB content for P(3HB)/PVA (●) and P(3HB)/PVA/glycerine (▲)

The crystallinity of the P(3HB) phase, $X_c^{P(3HB)}$, is obtained according to the relation:

$$X_c^{P(3HB)} = \frac{\Delta H_f}{\Delta H_f^0 W^{P(3HB)}} \tag{1}$$

where ΔH_f^0 and ΔH_f indicate the heat of fusion of completely crystalline P(3HB) and that of the P(3HB) phase in the blend, respectively, and W is the weight fraction of P(3HB) in the blends. The $X_c^{P(3HB)}$ values are given in *Table 2* and are plotted in *Figure 3* against the content of P(3HB) in the blends. The $X_c^{P(3HB)}$ values in the blends without glycerine decrease with increasing PVA content. The PVA crystalline phase may disturb the crystallization of P(3HB). In the case of P(3HB)/PEO blends[13], the crystallinity of the PEO phase decreases with increasing P(3HB) content. This result has been accounted for by assuming that PEO has been trapped in the interlamellar amorphous phase of P(3HB), where the PEO/P(3HB) blend has formed a homogeneous mixture. The $X_c^{P(3HB)}$ in the blends including glycerine also decreases with increasing PVA content. The $X_c^{P(3HB)}$ values in the blends with glycerine are larger than those without. Therefore, glycerine has the effect of increasing the $X_c^{P(3HB)}$.

Evaluation of miscibility density of blend samples

The miscibility of the P(3HB)/PVA blend from density measurements is now considered. Usually, the relationship between the crystallinity and density of a polymer is obtained according to the well known equation:

$$\frac{1}{d} = \frac{X_c}{d_c} + \frac{(1 - X_c)}{d_a} \tag{2}$$

where d is the density of the sample, d_c and d_a are the density of the crystalline and amorphous phases, respectively, and X_c is the crystallinity. If the P(3HB)/PVA blend is completely incompatible, the crystallinity of PVA should be obtained according to the equation:

$$\frac{1}{d} = \left[\frac{X_c^{P(3HB)}}{d_c^{P(3HB)}} + \frac{1 - X_c^{P(3HB)}}{d_a^{P(3HB)}}\right] W + \left[\frac{X_c^{PVA}}{D_c^{PVA}} + \frac{1 - X_c^{PVA}}{d_a^{PVA}}\right](1 - W) \tag{3}$$

where X_i^j and d_i^j represent the crystallinity and the density, respectively, of component j in the i phase. The superscripts c and a express the crystalline and amorphous phases, respectively. The amorphous density of P(3HB) ($d_a^{P(3HB)}$) at 20°C is $1.177\,g\,cm^{-3}$, obtained from extrapolation of dilatometric data[19]. The crystalline density of P(3HB) ($d_c^{P(3HB)}$) is $1.260\,g\,cm^{-3}$, obtained from an X-ray diffraction study[20]. The amorphous and crystalline

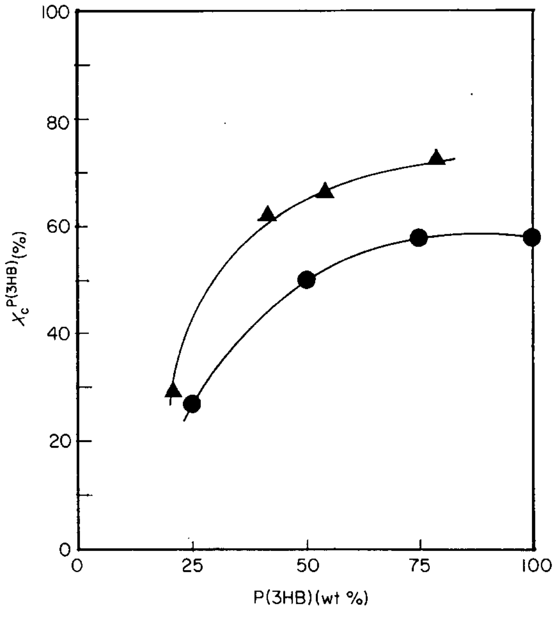

Figure 3 Phase crystallinity of PHB for P(3HB)/PVA (●) and P(3HB)/PVA/glycerine (▲)

Table 3 Density (d) of sample and phase crystallinity of PVA in blend (X_c^{PVA})

Sample no.	$d\,(g\,cm^{-3})$	X_c^{PVA} (%)
3	1.254±0.001	111.6±8.0
5	1.280±0.007	105.9±19.0
7	1.296±0.002	84.0±3.5

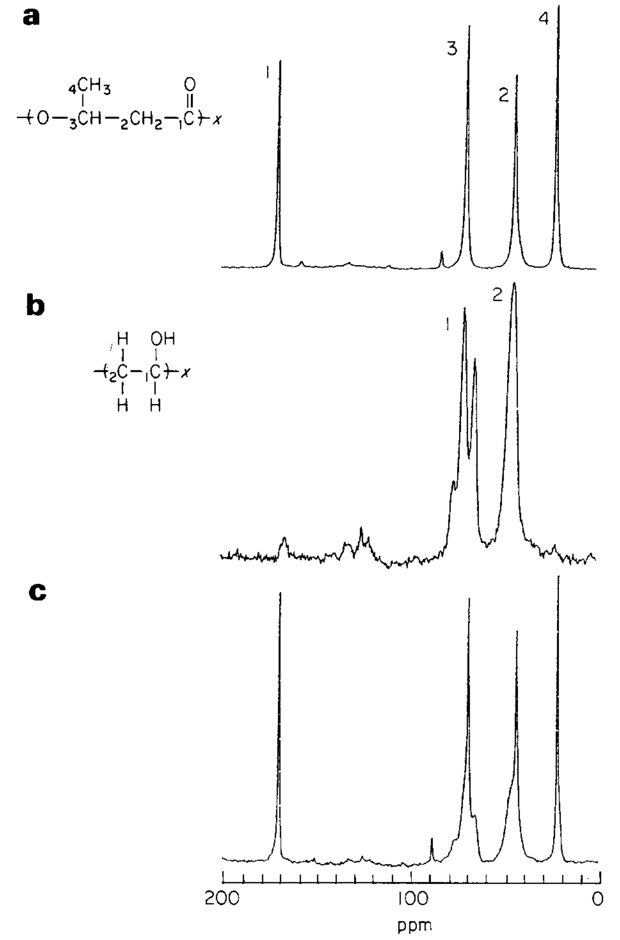

Figure 4 ^{13}C CP/MAS n.m.r. spectra: (a) P(3HB); (b) PVA; (c) 50/50 wt% P(3HB)/PVA blend (sample no. 5)

Table 4 T_1^H and $T_{1\rho}^H$ values of PHB/PVA blends

Sample no.	T_1^H (s) P(3HB)	T_1^H (s) PVA	$T_{1\rho}^H$ (ms) P(3HB)		$T_{1\rho}^H$ (ms) PVA	
1	1.45		6.3	18		
3	1.43	2.6	7.0	18	0.22	3.3
5	1.47	2.1	4.5	15	1.00	5.0
7	1.70	1.8	n.d.[a]	n.d.[a]	1.20	5.0
9		2.7			0.25	3.5

[a] $T_{1\rho}^H$ values cannot be determined because of small peak intensities

densities of PVA are 1.269 g cm^{-3} and 1.345 g cm^{-3}, respectively, from the literature[21]. Densities of samples, shown in *Table 3*, were measured by the flotation method. Phase crystallinities of PVA were obtained from the above data and are given in *Table 3*. Considering that crystallinity must be less than unity, the above assumption that the P(3HB)/PVA blends are completely immiscible should be inappropriate. This blend is, at least, partially compatible in the amorphous phase.

Nuclear magnetic resonance

Figure 4 shows the 67.9 MHz ^{13}C n.m.r. spectra of P(3HB), PVA and blend sample no. 5. The splitting of the methine carbon resonance of PVA is thought to be caused by both intramolecular and intermolecular hydrogen bonds[22]. In a blend of two crystalline polymers, the crystalline and amorphous phases of each component have, in general, different characteristic T_1^H values. The apparent relaxation times (T_1^H, $T_{1\rho}^H$), however, are modified by spin diffusion among protons. In the blend mixed closely at the molecular level, domains should have the same apparent relaxation time. Thus, T_1^H measurement makes it possible to estimate the degree of miscibility of polymer blends at a time scale of T_1^H (several tens of nanometres). If the sizes of two contacting domains are small enough for effective spin diffusion, these domains have the same T_1^H values. When their sizes are larger, each domain has different T_1^H values.

The T_1^H values of the samples were measured. Each homo-P(3HB) and homo-PVA has a single T_1^H value. This indicates that the crystalline and amorphous phases of both homo-PHB and homo-PVA have a sufficiently small domain size for spin diffusion of the T_1^H time scale. The T_1^H decay curves of the samples were not single exponential, and thus were practically reproduced on the assumption of a biexponential decay. The estimated T_1^H values are shown in *Table 4*. The two T_1^H values of sample no. 3 corresponded to those of homo-P(3HB) and homo-PVA. This indicates that sample no. 3 in the solid state consists of homo-P(3HB) domain and homo-PVA domain, whose sizes are larger than the effective size for homogeneous spin diffusion. However, the two T_1^H values of samples no. 5 and no. 7 did not correspond to those of homo-P(3HB) and homo-PVA. In particular, the two T_1^H values of sample no. 7 were almost the same. This indicates that the structure of sample no. 7 is homogeneous within several tens of nanometres.

The measurements of $T_{1\rho}^H$ provide information about the compositional homogeneity of blends on a molecular scale (several nanometres). That is to say, $T_{1\rho}^H$ measurement scales are smaller than those of T_1^H, so we can determine the miscibilities of blends on a molecular scale by $T_{1\rho}^H$ measurement. $T_{1\rho}^H$ data for methine carbons of the blend samples are shown in *Table 4*. Both homo-P(3HB) and homo-PVA have two $T_{1\rho}^H$ values which probably correspond to crystalline and amorphous phases. The $T_{1\rho}^H$ decay curves of the blend samples were practically reproduced on the assumption of four exponential decays, because both P(3HB) and PVA fractions in blends are thought to have two $T_{1\rho}^H$ values. The $T_{1\rho}$ values of sample no. 3 are almost the same as those of homo-P(3HB) and homo-PVA. This indicates that the P(3HB) phase and PVA phase exist individually at $T_{1\rho}^H$ time scales. The domain sizes of both crystalline and amorphous phases in the respective polymers are larger than the molecular scale. However, in samples no. 5 and no. 7, $T_{1\rho}^H$ values of the P(3HB) and PVA phases approach the values of the blend partners. This suggests that the compatibilities are enhanced on a molecular scale as PVA content increases. This tendency corresponds to the results of T_1^H measurements.

CONCLUSIONS

The thermal behaviour and miscibility for P(3HB)/PVA blends cast from solution were studied by d.s.c. and solid-state ^{13}C n.m.r. Both the melting temperature and the crystallinity of the P(3HB) phase in the blends show composition dependence. In particular, the crystallinity of sample no. 7 decreases to 0.27 from 0.58 for 100% P(3HB). The melting temperature of the PVA phase remains almost unchanged.

The degree of miscibility for P(3HB)/PVA blends is found to be composition dependent. Measurements of T_1^{H} and $T_{1\rho}^{\mathrm{H}}$ indicated that miscibilities between P(3HB) and PVA are enhanced with increasing PVA content.

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