

DEVELOPMENT OF BLEND FILMS OF POLY(3-HYDROXY)BUTYRATE AND CELULOSE TRIACETATE: THERMAL AND CRYSTALLINE PROPERTIES

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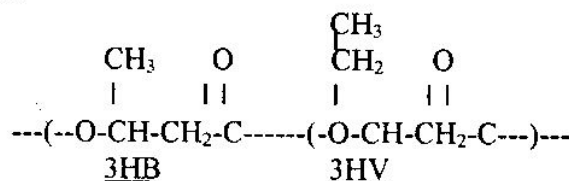
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Abstract

Derivative polysaccharide, cellulose triacetate (CTAc) is blended to the combination of poly-hydroxybutyrate and its copolymer polyhydroxyvalerate (PHB-PHV) as the internal plasticiser. The blend films were analyzed by differential scanning calorimetry and X-ray diffraction. The DSC method shows the miscibility of this blend by a single peak of glass transition temperature and a decrease in the melting point. By using a certain composition in mixing, the product shows lower crystallinity than plain PHB. The combination of such properties of these new blends will put PHB as a potentially new source of biopolymer material with a better processability window.

Introduction

Optically active poly-D-(-) (3-hydroxybutyrate) or PHB is a polyester produced via biosynthesis by bacterial fermentation. It accumulates in a variety of bacteria as an energy source. One of the important characteristics of a bacterial polyester is in being thermoplastic with biodegradable properties. As a thermoplastic it is suitable for biomedical applications or as a source of small-molecule specialty chemicals (Marchessault, 1984; Holmes, 1985). The molecular structure of PHB and its copolyester P(3HV) as:



have recently attracted industrial attention as large-scale biotechnological products. An optically active polymer of poly-3-hydroxybutyric acid (PHB) is a thermoplastic material with very high crystallinity and a melting temperature around 180 °C. PHB has special biodegradable and biocompatible properties. The thin PHB films show good resistance to water vapour but the drawbacks are its high degree of crystallization and brittleness especially in the phase below its glass transition temperature (Howells, 1982). PHB can be extruded and injection moulded providing

care is taken to minimize melt temperatures and residence time. It is melt unstable and degrades to crotonic acid if kept for a relatively long time at temperatures of only a few degrees above its melting point (Grassie et. al.,1984). Thus PHB suffers two limitations in its use: a very narrow processability window, and a low impact resistance. Some research had been done to modify these limitations by blending PHB with other synthetic (Abellar & Martuscelli, 1988) and natural polymers (Yasin et. al.,1989). PHB shows miscibility with functional polymers such as Nylon, polyethylene oxide and other polysaccharides. From these considerations, the aim of the research is to find another suitable polymers to be mixed with PHB to obtain new PHB-based materials with improved processability and impact resistance.

Materials and Methods

MATERIALS

The PHB sample used in the study was supplied by Aldrich Chemical Company. It is commercial grade synthesized by the continuous fermentation of a glucose utilizing mutant of *Alcaligenes eutrophus*. The PHV used is also obtained from Aldrich Chemical Co. It was produced from copolymerization of PHB with pentanoic acid in the medium under specific conditions. The content of hydroxyvalerate (HV) is 20%. Cellulose triacetate is soluble in tetrachlorometane aqueous, analytical grade 99% with boiling point at 61.2 °C.

Table 1 Molecular characteristics, source and code of PHB, PHV and CTAc

Polymer	Source	Code	Molecular mass
Poly-D(-)(3-hydroxybutyrate)	Aldrich Chem. Co.	PHB	279000 ^a
Poly-D(-)(3-hydroxyvalerate)	Aldrich Chem. Co.	PHV	670000 ^a
Cellulose triacetate	Fluka-AG	CTAc	72000-74000 ^b

^a By g.p.c. in chloroform at 30 °C

^b By intrinsic viscosity at 30 °C in water

EXPERIMENTAL SET-UP AND PROCEDURE

Preparation of blends.

The blending of PHB with PHV and CTAc is prepared in the aqueous form using chloroform as solvent. The ratio of PHV as internal plasticiser in the mix is not more than 40% of overall blends. Blends were prepared by slowly casting films from chloroform. The resulting films were dried under vacuum at 80°C until they reached constant weight. The best ratios selected according to the lowest melting point of

blends obtained under optimum conditions. The composition of the blends are investigated and the range of the crystallization temperature (T_c) are explored.

Differential scanning calorimetry and glass transition temperature measurements. Differential scanning calorimetry (DSC-7 Perkin-Elmer) was used to study the influence of blend composition and thermal history on properties such as crystallinity and T_m and T_c of PHB and its blends. First the films obtained by casting were heated from 25 to 200°C (1 run). The T_m of the PHB, PHV and CTAc phase together with the corresponding crystallinity were determined from the d.s.c endotherms. After 1 min at 200 °C the samples were cooled down to room temperature (crystallization run) and the crystallization exotherms were registered. From this it was possible to derive the T_c of PHB, PHV and CTAc. Finally the samples were heated to 200°C (II run). The melting point and the crystallinity of polymers after this thermal history were again measured. A scan rate of 20°C min⁻¹ was used throughout. The glass transition temperature (T_g) of plain polymers and blends was obtained by heating a sample first at 200°C and then rapidly quenched at -100°C. A Mettler TA-3000 apparatus, equipped with programming unit and calorimetric cell that allows temperature from -170 to 600°C was used.

X-ray diffraction.

Wide-angle X-ray diffraction measurements were made and Cu K α radiation ($\lambda = 0.1542$ nm) was used as the source. Thin films (after drying in vacuum oven at 80°C) had been aged for 2 weeks at room temperature to gain stability. The X-ray diffraction patterns were recorded at 27 °C in the range $2\theta = 6-40^\circ$ at scan speed of 1 - 3°/min.

Results and discussion

Thermal analysis.

Non-isothermal crystallization; Calorimetric studies

The d.s.c thermograms of PHB and PHB-PHV/CTAc films as obtained by casting show two distinct endotherms peak when heated from room temperature to 200°C. The higher temperature peak represents the fusion of the CTAc phase while that at lower temperature (around 172°C) is the melting of the PHB phase. The apparent melting temperature (T'_m) of the PHB and CTAc phase (run I) decreases with the increase of the second component content. As far as the T_g is concerned it emerges from d.s.c analysis that PHB-PHV/CTAc blends are characterized by a single T_g intermediate between that of PHB-PHV and CTAc. Moreover, as shown by Table 2, T_g is composition dependent. One of theoretical equations have been used to describe the T_g - composition dependence of polymer/polymer blends is the Fox equation; is written as:

$$1/T_g(\text{blend}) = W(\text{PHB})/T_g(\text{PHB}) + W(\text{CTAc})/T_g(\text{CTAc}) \quad (1)$$

where $T_g(\text{blend})$ is the glass transition temperature of the blend, $T_g(\text{PHB})$ and $T_g(\text{CTAc})$ are those plain polymer and $W(\text{PHB})$ and $W(\text{CTAc})$ are the corresponding weight fractions.

Equation (1) as shown by Table 2, fits the experimental data quite well. The results strongly suggest that PHB and CTAc are compatible in the melt and in the amorphous state.

Table 2 Melting point, (T_m), glass transition temperature (T_g) of plain PHB, PHV and PHB-PHV/CTAc blends from experiment and Fox equation.

PHB-PHV/CTAc	T_m (°C)	T_g (°C)	T_g from Fox equation(°C)
100/0	172.86	-3.44	-3.44
80/20	172.90	-4.29	-4.38
64/36	171.90	-2.38	-3.08
36/64	169.45	-3.68	-2.95
27/73	169.30	-4.66	-3.00
25/75	168.40	-5.45	-3.32
0/100	314.64	48.45	48.45

Isothermal crystallization

Equilibrium melting temperature and melting point depression.

The melting point depression of the polymer blend has been achieved until 168.40 °C with 75% CTAc. Composition of CTAc has dominated the chemical properties of blends. CTAc is a derivative polysaccharide with high crystallinity. When blended with PHB-PHV, the reaction has accessed crystallized phase and create a better polarity which enhance the percentage of amorphous area. The T_m of PHB and PHB crystallizes isothermally from its mixtures with CTAc as shown in Table 3.

Table 3 Crystallization temperature (T_c) of PHB and PHBV/CTAc

PHB-PHV/CTAc	T_c (°C)
80/20	35.60
64/36	38.90
36/64	53.00
27/73	-not detected
25/75	-not detected
0/100	70.50

Crystallization of PHB phase, $X_c(\text{PHB})$ and overall blends, $X_{c(\text{blend})}$ can be calculated using this equation:

$$X_{c(\text{PHB})} = \frac{\Delta H^*_{(\text{PHB})}}{\Delta H_{(\text{PHB})}} \quad X_{c(\text{blend})} = \frac{\Delta H^*_{(\text{blend})}}{\Delta H_{(\text{PHB})}}$$

where $\Delta H^*_{(\text{PHB})}$ and $\Delta H^*_{(\text{blend})}$ are the apparent enthalphy per gram PHB and per gram blends, $\Delta H_{(\text{PHB})}$ is the thermodynamic entalphy per gram PHB.

Table 4: Crystallization of blends PHB-PHV/CTAc (X_{cgaulan}) and PHB phase($X_{\text{c PHB}}$) as a function of blend composition

PHB-PHV/CTAc	$X_{\text{c(PHB)}} (\%)$	$X_{\text{c (blend)}} (\%)$
100/0	66	51
80/20	68	57
64/36	79	20
36/64	67	19
27/73	51	15
25/75	55	13
0/100	-	-

Depression in crystallinity phase of PHB-PHV/CTAc blend is observed with the increase in CTAc ratio. These phenomena might be because of any restructured of molecular integrity of crystallinity by addition of the second component. More access of amorphous phase has been achieved in the blend macromolecular structure. Moreover the $X_{\text{c blend}}$ is independent from the chemical properties of second component (CTAc). The decrease is not uniform in the ratio for each blending of the second component until four times less than the initial percentage of crystallinity. This phenomena is influenced by the differences in configuration, structural and chemical properties of PHB-PHV and CTAc to the overall crystallization characteristics of the new blend.

Crystallinity Studies.

PHB plain and PHB-PHV. Figure 1 shows the X-ray diffraction pattern of solution-cast PHB film. The PHB crystal lattice (fiber repeat of 0.596 nm) is observed for the samples with 0 and 30 mol % 3HV. The unit cells of P(3HB) and P(3HV) are orthorombic, $P2_12_12_1$ (D_2^4) with $a = 0.576$ nm, $b = 1.320$ nm, and $c = 0.596$ nm (fiber repeat) for P(3HB) and $a = 0.952$ nm, $b = 1.008$ nm, and $c = 0.556$ nm (fiber repeat) for P(3HV). From Figure 2, there is no clear transformation from the P(3HB) lattice to the P(3HV) lattice only the d spacings (marked *) apparently increases as the 3HV content increases to 30 mol%.

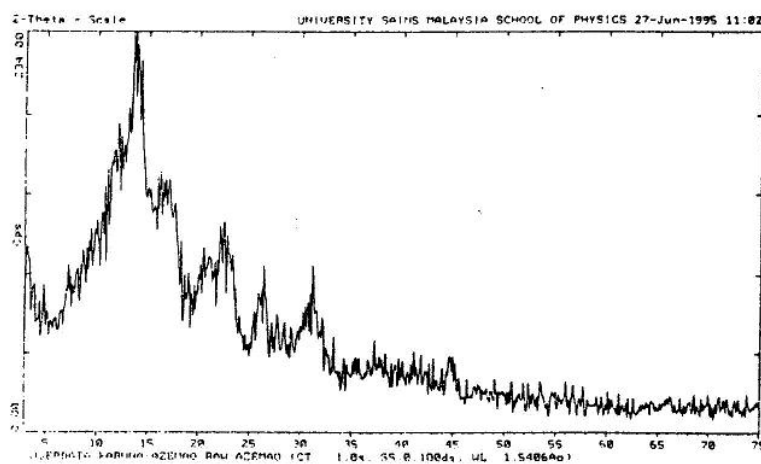


Figure 1. X-ray diffraction patterns of PHB film cast from CHCl_3 solution.

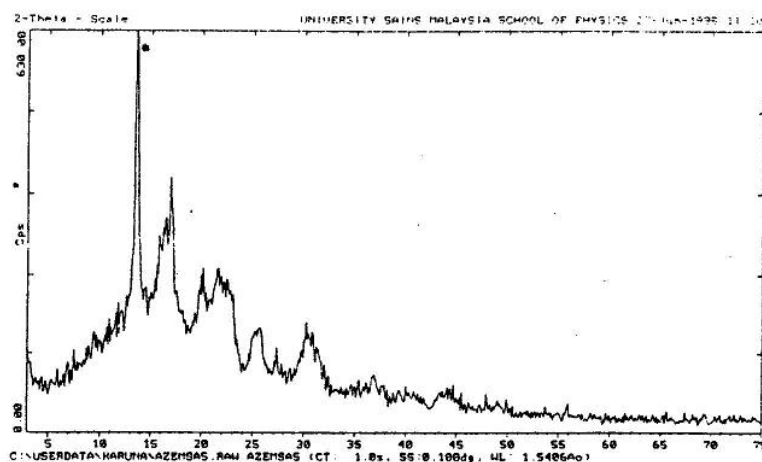


Figure 2. X-ray diffraction patterns of PHB-PHV film cast from CHCl_3 solution.

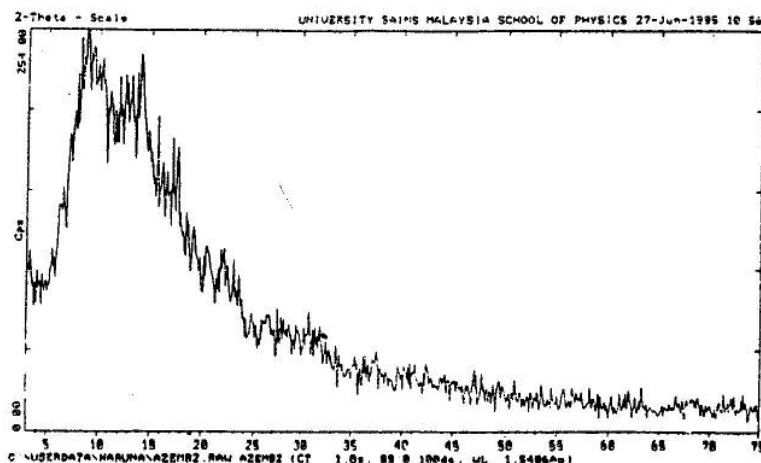


Figure 3. X-ray diffraction patterns of PHB-PHV/CTAc (75%) film cast from CHCl_3 solution.

From previous studies, the transformation from the P(3HB) lattice to the P(3HV) lattice seems to occur at approximately 40 mol% 3HV. The d spacings for sample shows lattice pattern P(3HB) at (020), (110) and (002). The (110) d spacing apparently increases while the (020) and (002) d spacings remain unchanged which means that the ethyl side chains of 3HV units expand the (110) plane of the PHB lattice due to the steric effects.

PHB-PHV/CTAc. Figure 3 shows the diffraction pattern of PHB-PHV/CTAc. It is the basic pattern of PHB-PHV but with less peaks of crystallinity including loss of the peak of the d spacing(110). These changes indicate that crystallinity decreases as the content of CTAc unit is added and increased.

Conclusion

The blending of P(3HB-co-3HV) with cellulose triacetate (CTAc) are compatible in the melt state. Consequently the blend exhibits a single T_g and depression of the T_m values of PHB. There is a good potential to lower down the processing temperature of PHB. From the crystallinity studies, it can be concluded that some kind of molecular interaction must be present in that blending which is likely to involve the functional groups of the PHB and CTAc that changes the blend properties.

Acknowledgement

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