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Crystallization and morphology of poly(ethylene succinate) and poly(*β*-hydroxybutyrate) blends

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Summary

The melting and crystallization behavior of poly(ß-hydroxybutyrate) (PHB) and poly(ethylene succinate) blends has been studied by differential scanning calorimetry and optical microscopy. The results indicate that PHB and PES are miscible in the melt. Consequently the blend exhibits a depression of the melting temperature of both PHB and PES. In addition, a depression of the equilibrium melting temperature of PHB is observed. The Flory-Huggins interaction parameter (χ_{12}), obtained from melting point depression data, is composition dependent, and its value is always negative. Isothermal crystallization in the miscible blend system PES/PHB is examined by polarized optical microscope. The presence of the PES component gives a wide variety of morphologies. The spherulites exhibit a banded structure and the band spacing decreases with increase PES content.

INTRODUCTION

Poly(ß-hydroxybutyrate) (PHB) is an optically active polymer of D-(-)3-hydroxybutyric acid produced by a variety of microorganisms as an intracellular carbon and energy reserves.[1-3] PHB is a biodegradable and biocompatible thermoplastic polymer of high melting temperature (180 °C) and crystallinity. PHB has attracted much attention as an environmentally degradable resin to be used for agricultural, marine, and medical applications.4 One of the limitations of PHB for these applications is its brittleness and narrow processing window. In the literature a significant number of studies on blending PHB with other polymers to decrease the brittleness and melting point are reported.[4-8] PHB is known to be miscible with poly(methylmethacrylate),[9, 10] poly(epichlorohydrin), [11. 12] poly(ethylene oxide), [5, 13] poly(ß-hydroxybutyrate)-co-(ß-hydroxyvalerate). [14-16] poly(vinyl phenol), [17] poly(vinyl acetate),[7] and poly(vinylidene flouride).[18]

Poly(ethylene succinate) (PES) is an aliphatic, semicrystalline polyester and well-defined melting point around 105 °C. [19] The blends of PES with polycarbonate show a single glass transition temperature and a depression of the melting temperature. [20] Blends of PES with poly(butylene succinate)[21] is useful as biodegradable films and fibers. Furthermore, PES is also used to synthesize composites with good injection moldability.[20, 21] However, no attention has been paid to the blending of PES and PHB. The present work focuses on the characterization of the state of miscibility in binary blends of PES and PHB, by using differential scanning calorimetry (DSC) and polarized optical microscope.

EXPERIMENTAL

Materials

The bacterial PHB (number average molecular weight , Mn, = 358,000 and polydispersity = 2.8) sample was purchased from Aldrich, and its melting temperature is 172 ° C. Th poly(ethylene succinate) was purchased from Aldrich, and its glass transition temperature (Tg) and melting temperature are -1 and 108 °C, respectively. Both materials were used as received.

Blend Preparation

PES/PHB blends were prepared by melt mixing in a Haake high shear blender at 190 °C and 50 RPM for 3 minutes. Blends with weight ratios of 80//20, 60/40, 40/60 and 20/80 PES/PHB were prepared by molding under mild pressure at 190 °C in a carver press.

Thermal Analysis

Differential scanning calorimetry (DSC) was carried out for PES/PHB binary blends and isothermally crystallized samples with a 910-DSC apparatus equipped with a thermal analysis station TA-2000. The measurements were performed on a ca. 10 mg samples at a heating rate of 20 °C/min. The instrument was calibrated with an indium standard. First the samples were heated from 25 to 200 °C. The melting temperature (T_m) of the PES and PHB phase was determined from the DSC thermograms. After 1 min at 200 °C the samples were cooled down to room temperature (the cooling run) and the non-isothermal crystallization exotherms recorded. From this it was possible to derive the Tc of PES and PHB. Finally the samples were heated to 200 °C, then quenched to suitable isothermal crystallization temperature. The samples were allowed to crystallize under such conditions for 3 h and quenched to room temperature and reheated from room temperature to their melting transition. Peak melting endotherms were then recorded for each crystallization temperature and blend composition so as to carry out the Hoffman-Weeks analysis for each material. The maximum of the endothermic transition and the minimum of the exothermic transition were taken as the melting temperature and crystallization temperature, respectively.

Polarized Optical Microscope

The morphology of PHB spherulites was performed on a thin films using a Nikon polarized optical microscope (Optiphot-Pol) equipped with a Mettler hot stage (FP82). Blend samples were sandwiched between microscope cover glasses, melted at 190 °C for 1 min and then rapidly cooled to the crysallization temperature (Tc = 100 °C). Polarized optical micrographs of the spherulitic morphologies were recorded at Tc.

RESULTS AND DISCUSSION

The observed melting temperature (T_m) of PES and PHB in blend system *versus* weight percent (wt%) of PES curve is shown in Figure 1. The results show that the melting temperature of PHB and PES are depressed systematically by increasing the second component content. The T_m of PHB decreases from 174 °C for pure PHB to 162 °C for a blend containing 80 wt% PES. The T_m of PES decreases from 108 °C for pure PES to 95 °C for a blend containing 80 wt% PHB. On blending semicrystalline polymers with other polymers, a decrease in melting temperature is indicative of miscibility of the polymers in the amorphous state. The behavior of the PHB and PES melting temperatures in the blends suggests miscibility of these polymers.

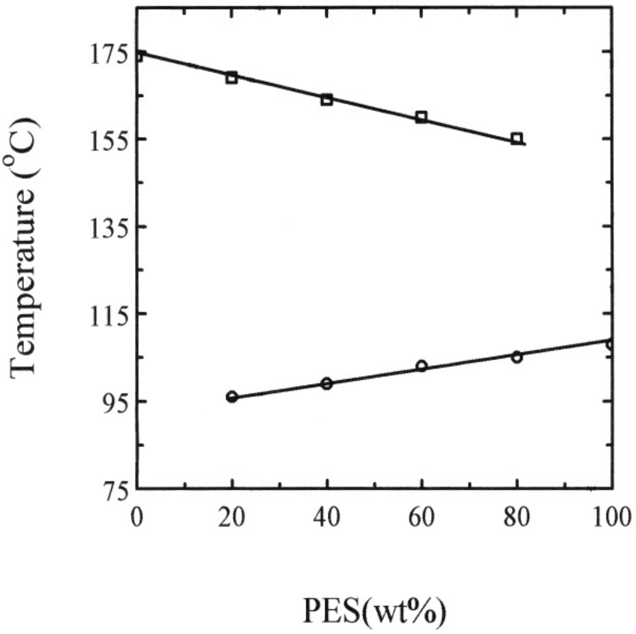

Fig. 1. Phase diagram of PES/PHB blends. (□) T_m PHB; (O) T_m PES.

The decrease in crystallization rate of PHB and PES in blends is also observed in the non-isothermal crystallization process during the cooling run. The non-isothermal crystallization process shows the presence of two exothermic peaks corresponding to the crystallization of PHB and PES. Figure 2 summarizes the Tc data as a function of blend composition. It can be seen that the Tc is composition dependent and the Tc of the two polymers is sharply depressed by the presence of the second component. Similar results were found in PEO/PHB[5], PEO/PMMA[22] and PVF_2/PMMA[23] blend systems. The decrease of Tc of both PHB and PES with the amorphous content is related to the depression of the spherulite growth rate due to the mutual dilution effect of the two polymers.

It is well known that the melting behavior of crystalline polymers depends on the conditions under which they have been crystallized. Several crystallization temperatures ranging between 100 and 135°C for 3 h are selected for the PES/PHB blend samples. The observed melting points (T_m) of PHB as measured by DSC are plotted versus crystallization temperature (Hoffman-Weeks approach[24]) in Figure 3 and extrapolated to the line where T_m = Tc to obtain the equilibrium melting points of an infinitely large crystals ($T°_m$). As observed, a good linear correlation between T_m and Tc is obtained. The increase in T_m with Tc is a consequence of the more perfect crystals grown at lower supercooling. The equilibrium melting points for PHB as a function of composition are given in Table 1. The equilibrium melting temperature of pure PHB determined here agrees quite well with the previously reported value.[5,17]

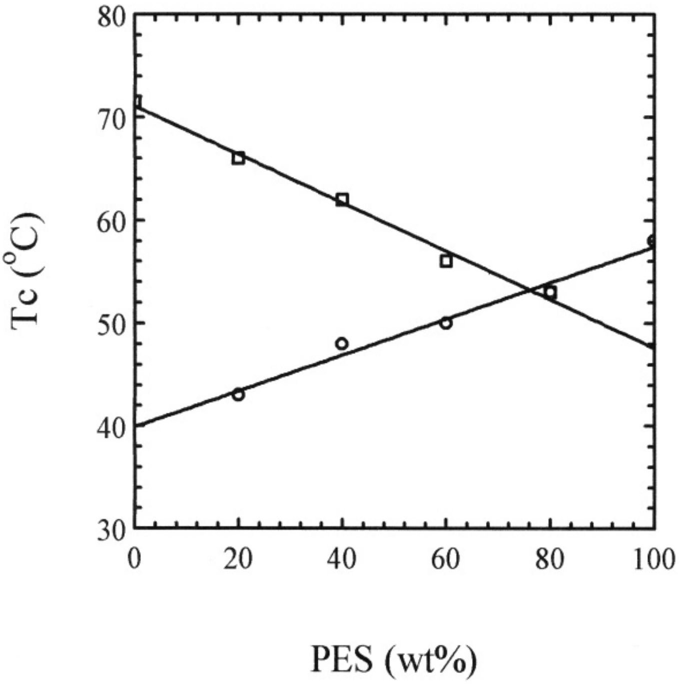

Fig. 2. Non-isothermal DSC crystallization temperature (Tc) of PHB (□) and PES (O) as a function of blend composition

The values of $T°_m$ obtained by this method clearly indicates that the addition of PES causes a drastic depression in the $T°_m$ of PHB. Furthermore, PES is able to act as a diluent for PHB and the two polymers are compatible in the melt phase. The depression of the melting point of the crystalline component of a mixture where the amorphous phase is a miscible blend permits the study of the polymer-polymer interaction parameter. The data obtained in these studies are usually analyzed in Huggins equation to obtain polymer-polymer interaction parameter (χ_{12}).

$$1/T°_{mB} \;-\; 1/T°_m \;=\; -(RV_{c\mu}/\Delta H°_{f\mu}V_{a\mu})\chi_{12}\;\Phi_1^2$$

Where $T°_m$ is the equilibrium melting temperature of pure PHB, $T°_{mB}$ is the equilibrium melting temperature for PHB in blend containing a volume fraction ϕ_1 of PES, $\Delta H°_{f\mu}$ is the heat of fusion of PHB per mole of repeat unit at the equilibrium melting temperature, $V_{c\mu}$ and $V_{a\mu}$ are the molar volumes per repeat unit of crystallizable and amophous polymer, respectively, and R is the universal gas constant.

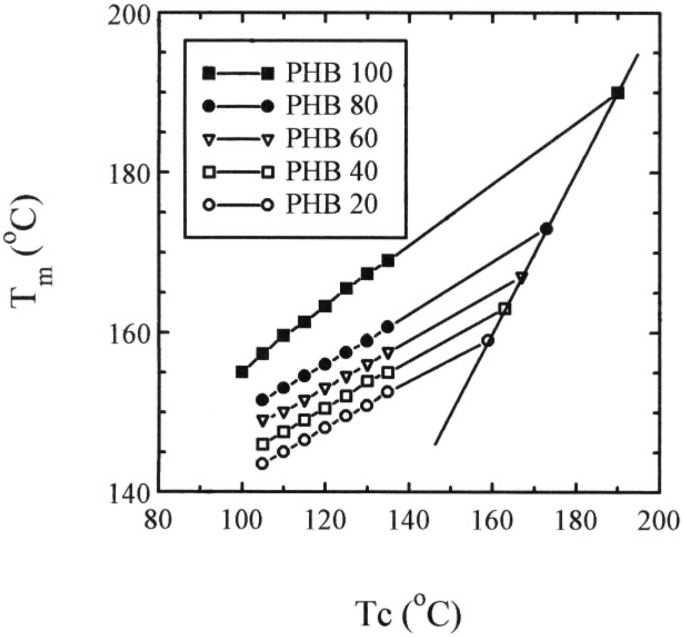

Fig. 3. Hoffman-Weeks plots of PES/PHB blends. The equilibrium melting temperature are obtained by extrapolation to T_m =Tc

A plot of the left-hand side of the equation versus the square of the PES volume fraction (ϕ_1^2) in the blend should give a straight line passing through the origin if χ_{12} is composition independent and the melting point depression in not influenced by morphological effects. In order to calculate the left-hand side, the parameter values used are as follows: $V_{a\mu}$ (= 56.5 cm^3. $Mol.^{-1}$) and $V_{c\mu}$ (= 75 cm^{-3} .$mol.^{-1}$) are the repeat unit molar volume of PES and PHB, respectively, and $\Delta H^\circ_{f\mu}$ (= 3001 cal. $Mol.^{-1}$) [5] is the enthalpy of fusion for completely crystalline PHB.

TABLE 1. Equilibrium melting temperature of PHB, T°_m, and interaction parameter χ_{12}, as a function of blend composition Φ_1.

Blend composition (wt%)	Φ_1	T°_m	χ_{12}
PES/PHB (100/0)	1.0	117	-
PES/PHB (20/80)	0.2	173	- 1.83
PES/PHB (40/60)	0.4	167	- 0.85
PES/PHB (60/40)	0.6	163	- 0.46
PES/PHB (80/20)	0.8	159	-0.29
PES/PHB (0/100)	0.0	190	-

The values of both $V_{a\mu}$ and $V_{c\mu}$ are calculated by using the amorphous density of PES (1.275 g cm^{-3}) and PHB (1.15 g cm^{-3}), respectively. The plot of ($1/T°_{mB}$-1/T°m) versus ϕ_1^2 is shown in Figure 4. The experimental points may be interpolated by a line with an intercept at origin of 8.86 x 10^{-5} and a slope of 1.15 x 10^{-4}. The fact that this line does not pass through the origin can be accounted for by a composition dependence of χ_{12}. The interaction parameter at different blend composition can be obtained from the broken lines in Figure 4.[25] The values of χ_{12} calculated according to this method are given in Table 1 as a function of composition. The value of χ_{12} is negative for all investigated compositions strongly indicates that in the melt, at T_m, PHB and PES are compatible.

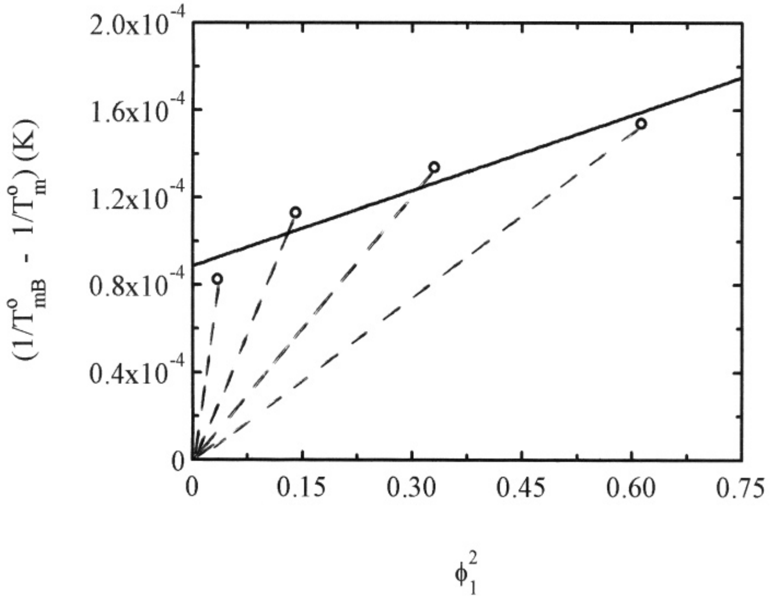

Fig. 4. Plot of ($1/T°_{mB}$ -$1/T°_m$) versus Φ_1^2 following the approach of Nishi and Wang[25].

The morphologies of blends crystallized at 100 •C are shown in Figure 5. Polarized optical microscopy observations of the crystallization process indicate that PHB and PES are able to crystallize according to a spherulitic morphology even in the case of the PHB 20 wt% blend. The spherulites exhibit a typical banded structure. The band spacing of PHB spherulites changes with blend composition and decreases with increase in PES content.. Furthermore, the PHB crystal spherulites are always nucleate first for all the blend composition ranges but do not fill the whole sample. Whereas, PES spherulites are observed to develop after an induction period, that is long enough to allow for the PHB spherulites to grow to their fullest

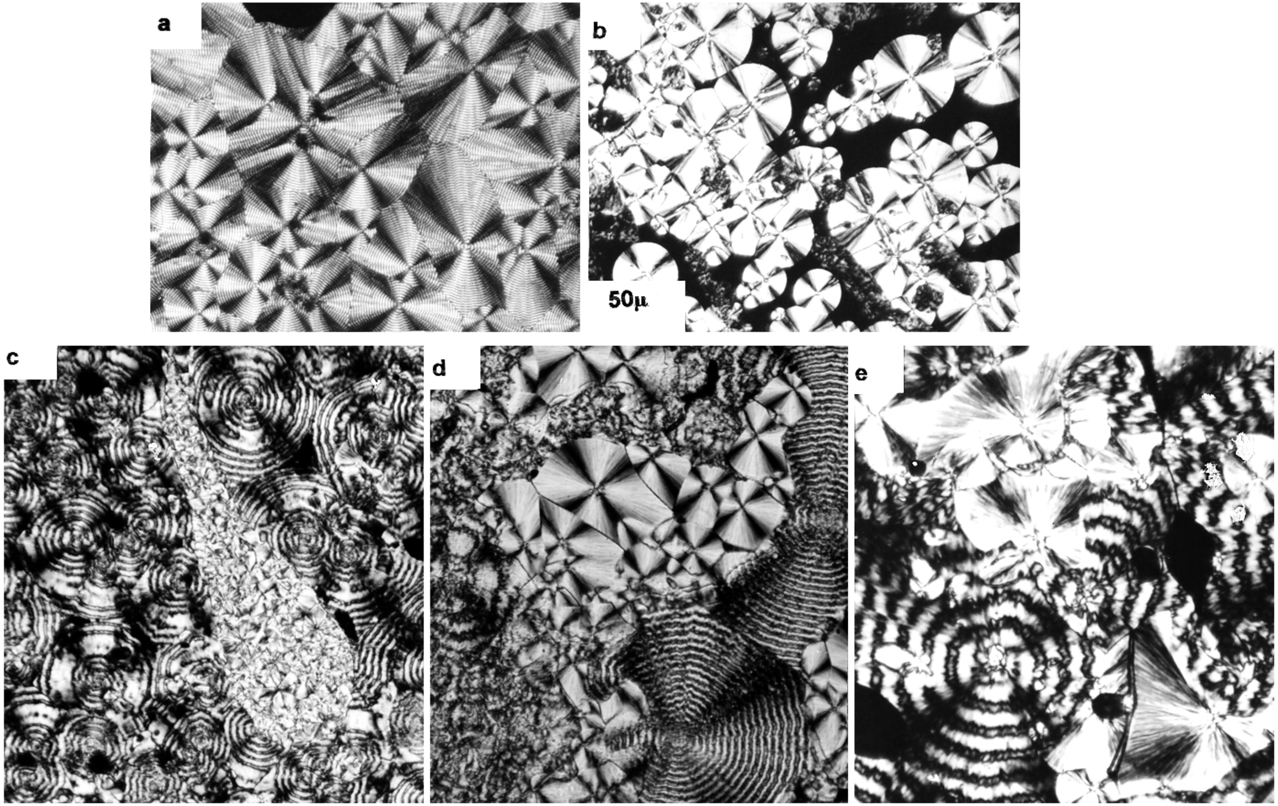

Fig. 5. Polarized optical micrographs ofPES/PHB blends crystallized at 100 °C: a (100/0), b (20/80), c (40/60), d (60/40).

extent. The preliminary results at this crystallization temperature show the existence of a wide variety of morphologies. These complicated morphologies will result from competitive nucleating and growth processes for PHB and PES spherulites. Beside affecting the nucleation and growth rates through the depression of the equilibrium melting temperatures, the blend composition will also control the nature of the interlamellar amorphous material and its composition.

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