Crystallization and thermal behaviour of poly(D(−) 3-hydroxybutyrate)/poly(epichlorohydrin) blends

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Atactic poly(epichlorohydrin) (PECH) was blended in a wide range of ratios with poly(D(−)3-hydroxybutyrate) (PHB) isolated from *Alcaligenes eutrophus* cultures. The crystallization and thermal behaviour of PHB/PECH blends were analysed by d.s.c. and microscopy. All blends show a single glass transition temperature, whose value is dependent on composition, in good agreement with the theoretical values calculated by the Fox equation. The influence of blend composition on the overall crystallization rate and on the spherulite growth rate suggests that the two components form a miscible blend in the amorphous phase. The equilibrium melting temperature decreases with blending; the negative value of the χ_{12} parameter of the PHB/PECH system suggests that the two components can form a miscible mixture which is thermodynamically stable above the equilibrium melting temperature. The reorganization phenomenon of PHB crystals after first melting was also observed.

(Keywords: poly(D(−)3-hydroxybutyrate); poly(epichlorohydrin); blends; glass transition; spherulitic growth; crystallization kinetics; melting behaviour)

INTRODUCTION

Poly(D(−) 3-hydroxybutyrate) (PHB) is a bacterial aliphatic polyester produced by many types of micro-organisms. It was first isolated by Lemoigne about 60 years ago[1].

The miscibility of PHB and poly(ethylene oxide) (PEO), studied by Avella and Martuscelli[2], showed that the components (both crystallizable) are miscible in the melt. Thus the blend exhibits a single glass transition temperature (T_g) and a depression of the equilibrium melting temperature (T_m°) as well as of the radial growth rate (g) of PHB spherulites. After crystallization, the phase structure of the solid blend is characterized by the fact that during the growth of PHB spherulites the PEO molecules diffuse away from the crystallization front to interlamellar and/or interfibrillar regions. Thus, in such regions a homogeneous solution of uncrystallized molecules of PHB and PEO is probably formed.

In another paper[3] the influence of molecular structure and characteristics of an uncrystallized second component, such as poly(vinyl acetate) (PVAc), on the miscibility, crystallization and thermal behaviour of blends based on PHB has been investigated. These blends show a single glass transition and a drastic depression of the T_m° of PHB. The final conclusion was that PHB and PVAc are miscible. Investigations on the morphology, crystallization and thermal behaviour of blends of PHB with ethylene–propylene rubber were also reported[3]. In this case, immiscibility of the two components in the melt was demonstrated.

The present paper reports the results of an investigation concerning the crystallization, thermal behaviour and morphology of blends obtained by mixing PHB with an uncrystallizable rubbery component, namely atactic PECH, i.e. poly(oxy-2-chloromethyl-ethylene).

EXPERIMENTAL

The molecular characteristics and the source of the polymers used are reported in *Table 1*. PHB was a semicrystalline powder isolated from *Alcaligenes eutrophus* cultures. PECH was purified by centrifugation and filtration using dilute dichloromethane solution.

The binary blends were prepared by solution casting from dichloromethane and then drying under vacuum at 80°C to constant weight. Blends with weight ratios of

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Table 1 Characteristics of the polymers employed

Polymer	Source	Molecular mass (M_w)	T_g (K)
PHB	ICI	150 000	277
PECH	Aldrich	700 000	253

80/20, 60/40, 40/60 and 20/80 PHB/PECH were prepared.

The morphology and the g values of PHB spherulites were studied on thin films using an optical polarizing microscope with an automatic hot stage (Mettler model FP 82), controlled by a Mettler FP80 control processor. Blend samples were sandwiched between microscope cover glasses, melted at 458 K for 1 min and then rapidly cooled to the crystallization temperature (T_c). The radius of the growing spherulites was measured as a function of time by taking photomicrographs at known time intervals.

The time and temperature of melting treatment before crystallization were rigorously controlled, and their influence on nucleation phenomena considered[4]. The overall kinetics of crystallization and the thermal properties of the PHB homopolymer and blends were analysed by d.s.c. using a Perkin Elmer DSC-4 with a Perkin-Elmer 3600 data station. The samples were melted at 458 K for 1 min, then rapidly cooled to the desired T_c; the rate of heat evolution during the isothermal crystallization was recorded as a function of time. The baseline correction and the elaborations of exothermal data were carried out using the Perkin-Elmer TADS (DSC-4 kinetics software kit no. 0419-0332). The weight fraction, X_t, of the material crystallized at time t was calculated using the relation:

$$X_t = \int_0^t \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t \bigg/ \int_0^\infty \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t \qquad (1)$$

where the first integral is the heat generated at time t and the second is the total heat when crystallization is complete.

After crystallization the samples were heated to the melting point at a scanning rate of 10 K min^{-1}. The observed melting temperature (T'_m) was obtained from the maximum of the first endothermic peak.

The T_gs were determined by heating the quenched samples from 213 to 463 K at different scanning rates of 20 and 40 K min^{-1}. The T_g values were taken at the midpoint of the transition and corrected for the error generated by the scanning rate. Pure PHB and the blends were quenched directly in the differential scanning calorimeter (cooled with liquid N_2), taking the samples from 458 to 213 K in ~2 min. This treatment was sufficient to ensure completely amorphous samples.

Gallium and indium standard samples were employed to determine the thermal lag due to the scanning rate and to calibrate the heat of transition.

RESULTS AND DISCUSSION

Glass transition temperatures

Blends of PHB and PECH always exhibit a single T_g, with numerical values dependent on composition. After quenching, the pure PHB and blends are completely amorphous, and the appearance of a single glass transition suggests the presence of a single homogeneous amorphous phase, i.e. that the two components are miscible. The dependence of T_g on composition is shown in *Figure 1*. The solid curve was calculated using the theoretical Fox relation[5]:

$$\frac{1}{T_g} = \frac{W_{\mathrm{PHB}}}{T_{g,\mathrm{PHB}}} + \frac{W_{\mathrm{PECH}}}{T_{g,\mathrm{PECH}}} \qquad (2)$$

where W_{PHB} and $T_{g,\mathrm{PHB}}$, and W_{PECH} and $T_{g,\mathrm{PECH}}$ are the weight fractions and the glass transition temperatures of PHB and PECH, respectively. The experimental points reported in *Figure 1* show good agreement with the theoretical Fox values.

Morphology and spherulite growth rate

Thin films of pure PHB and blends, when observed under the optical polarizing microscope during isothermal crystallization, show birefringent spherulitic structures. After crystallization the samples appear to be completely filled with impinged spherulites for all the PECH concentrations studied. The spherulite dimension, at constant T_c, decreases with increasing concentration of non-crystallizable component. The absence of separate PECH domains in the intraspherulitic regions and in the interspherulitic contact zones suggests that the uncrystallizable component is incorporated in the interlamellar or interfibrillar regions of the PHB spherulites. The spherulite radius, R, increases linearly with time for all blend compositions and T_cs investigated. For all samples, g was calculated at different T_cs as $g = \mathrm{d}R/\mathrm{d}t$.

Values of g *versus* T_c, for different PECH fractions, are reported in *Figure 2*. For a given T_c, by increasing the PECH content, the g values of the blends decrease.

The experimental growth rate data were analysed according to the polymer–diluent theory[6–8]. The equation describing the growth rate of spherulites of a crystallizable polymer in a single-phase melt containing a second polymer acting as a diluent assumes the following form:

$$\ln g - \ln \phi_2 + \frac{U^*}{R(T_c - T_\infty)} - \frac{0.2T^\circ_m \ln \phi_2}{\Delta T} = \alpha_1 = \ln g_0 - \frac{\Delta G_c}{T_c \Delta T f} \qquad (3)$$

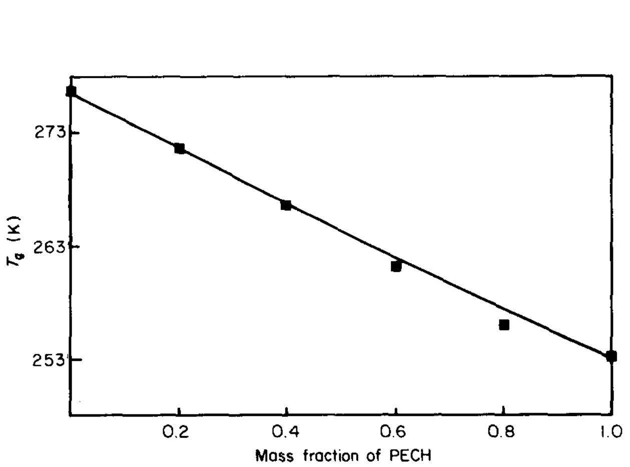

Figure 1 Glass transition temperature (T_g) *versus* composition of PHB/PECH blends. (■) Experimental points; the solid curve was calculated using the Fox equation [equation (4)]

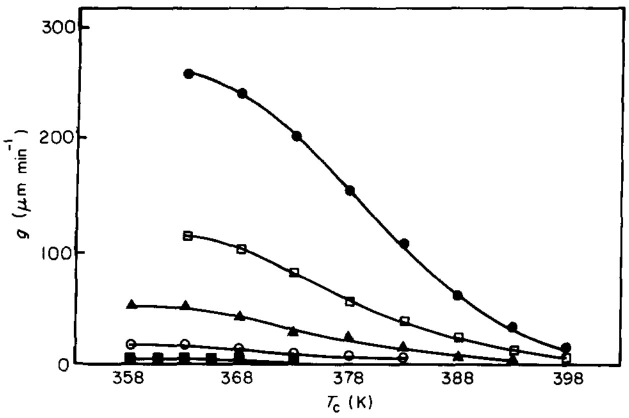

Figure 2 Spherulite radial growth rate (g) *versus* crystallization temperature (T_c) for PHB/PECH blends. PHB (wt%): (●) 100; (□) 80; (▲) 60; (○) 40; (■) 20

where g_0 is the pre-exponential factor that includes all terms that are taken as effectively independent of temperature. The $U^*/R(T_c - T_\infty)$ term contains the contribution of diffusional processes of the crystallizable (PHB) and non-crystallizable (PECH) components to the growth rate. The quantity U^* represents the sum of activation energies for the chain motions in the melt of PHB and PECH molecules, T_∞ ($T_\infty = T_g - C$, where C is a constant) is the temperature below which such motions cease and ϕ_2 is the volume fraction of the uncrystallizable polymer. The term f is a correction factor that takes into account the temperature dependence of the melting enthalpy ΔH and is given empirically by $f = 2T_c/(T_m + T_c)$. The term ΔG_c contains the free energy required to form a nucleus of critical size, the heat of fusion and the T_m.

According to equation (3), the slopes of the straight lines reported in *Figure 3*, are equal to:

$$\Delta G_c = \frac{nb_0\sigma\sigma_e T_m^\circ}{\Delta Hk} \tag{4}$$

where n is a variable changing according to the regime of crystallization[8], b_0 is the distance between two adjacent fold planes, k is the Boltzmann constant, ΔH is the enthalpy of fusion per unit volume, and σ and σ_e are the lateral and folding surface free energies. The procedure for determining ΔG_c involves plotting the left-hand side of equation (3) *versus* $1/T_c\Delta Tf$. Values of $U^* = 10.5$ kJ mol^{-1} and $C = 51.6$ K were chosen to give the best fit least squares lines through the data. The values of ΔG_c calculated from the slopes of the lines in *Figure 3* are reported in *Table 2*. Barham *et al.*[9] found that PHB crystallizes according to regime III at the undercooling used in this study. According to the Hoffman theory[7], $n = 4$ when the crystallization process conforms to regime III.

Unlike the behaviour observed for PHB/PEO[3], the values of ΔG_c decrease with increasing PECH in the blends. Hence, the values of σ_e reported in *Table 2* were calculated using $n = 4$ for the pure PHB and blends. Values of $b_0 = 5.76$ Å (ref. 10) and $\sigma = 0.1b_0\Delta H$ (ref. 11) were used in equation (4). From the results it can be noted that σ_e decreases with increasing PECH content. This behaviour was observed by Martuscelli *et al.*[12] in other miscible blend systems such as PEO/poly(methyl methacrylate).

Isothermal bulk crystallization kinetics

The crystallization isotherms were obtained by plotting X_t *versus* t. The plots for pure PHB and the blends at constant T_c are reported in *Figure 4*. The half-time of crystallization, $t_{0.5}$, obtained from these curves is plotted against T_c values for some blend compositions in *Figure 5*. The trend of these curves indicates that the addition of PECH to PHB also causes a reduction in the overall crystallization rate. It can be observed that for a given T_c, the depression increases with increasing PECH in the blends (see also *Table 3*).

The overall kinetic rate constant K_n was calculated for pure PHB and the blends by using the Avrami equation[13]:

$$X_t = 1 - \exp(-K_n t^n) \tag{5}$$

where n is a parameter depending on the geometry of the growing crystals and on the nucleation process. Values of n and K_n were determined, for each T_c, from the slope and the intercept, respectively, of the straight

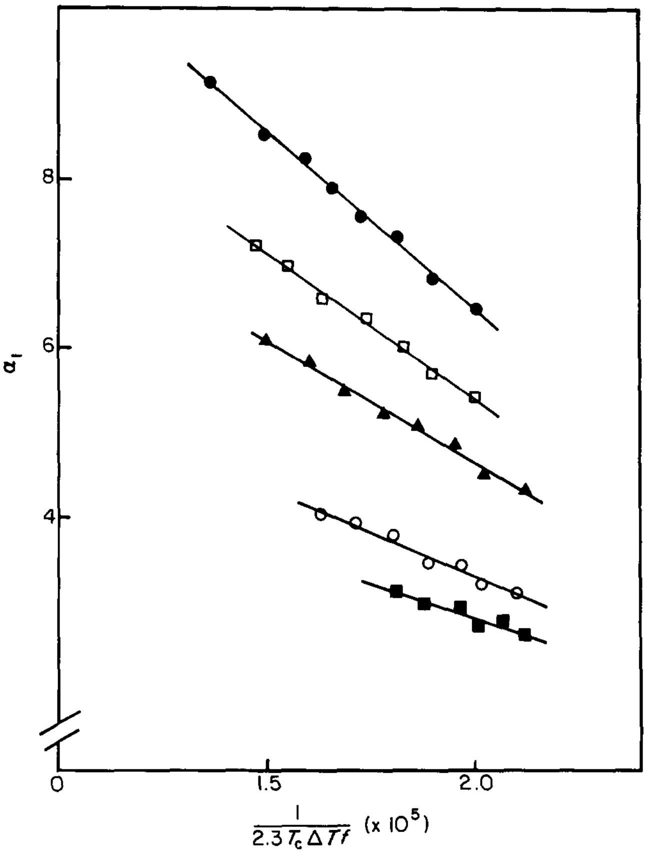

Figure 3 α_l *versus* $1/T_c\Delta Tf$ according to equation (3) for PHB/PECH blends. Symbols as in *Figure 2*

Table 2 Values of ΔG_c and σ_e for pure PHB and PHB/PECH blends

PHB/PECH	$10^{-5}\ \Delta G_c$ (K^2)	σ_e (J cm^{-2}) ($\times 10^7$)
100/0	4.3	96
80/20	3.5	79
60/40	2.9	68
40/60	2.1	49
20/80	1.5	36

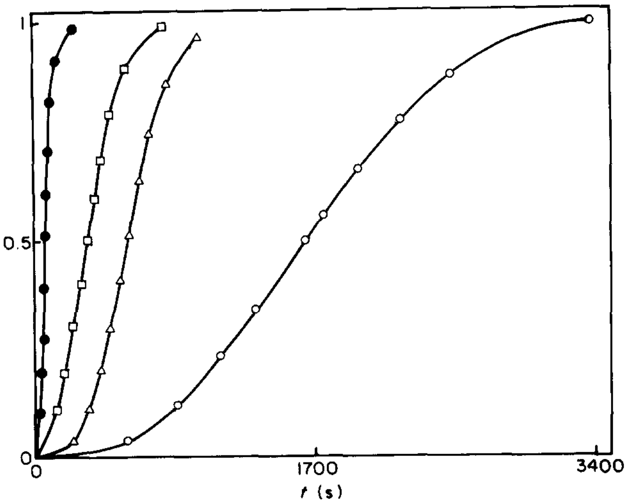

Figure 4 Isothermal curves of crystallization for PHB/PECH blends at $T_c = 373$ K. Symbols as in *Figure 2*

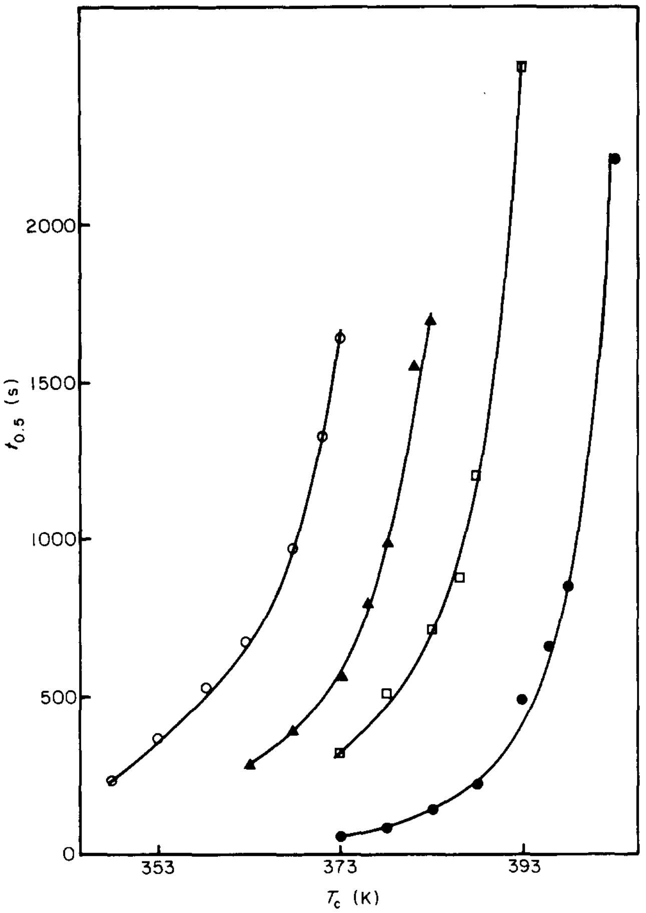

Figure 5 Half-time of crystallization ($t_{0.5}$) *versus* crystallization temperature (T_c) for PHB/PECH blends. Symbols as in *Figure 2*

lines obtained by plotting $\log[-\ln(1-X_t)]$ *versus* $\log t$ (*Figure 6*). The values of n and K_n for the blends investigated are reported in *Table 3* as a function of T_c. The Avrami exponent, n, is non-integral with a value between 2 and 3. Similar anomalous values were also observed by Cimmino *et al.*[8] in the case of PEO/poly(ethyl methacrylate) blends. Contrary to the theoretical prediction[13], in almost all cases the values of n are non-integral. This fact may be accounted for by mixed growth and/or surface nucleation modes and secondary crystallization (this latter process does not seem to occur in our case). Grenier and Prud'homme[14] found that experimental factors such as erroneous determination of the 'zero' time and of the enthalpy of melting of the polymer at a given time can cause n to be non-integral.

Melting behaviour

The d.s.c. curves of pure PHB and the blends, isothermally crystallized, showed two melting peaks, with the peak appearing at the lower temperature corresponding to the melting of the original crystal of the isothermally crystallized sample. The second endothermic

Table 3 Values of $t_{0.5}$, n and K_n, at various T_c values for pure PHB and PHB/PECH blends

PHB/PECH	T_c (K)	$t_{0.5}$ (s)	n	K_n (s^{-n})
100/0	373	60	2.0	1.35×10^{-4}
	378	82	1.9	6.98×10^{-5}
	383	140	2.0	2.32×10^{-5}
	388	228	2.2	8.37×10^{-6}
	393	488	2.1	1.71×10^{-6}
	396	665	2.1	8.97×10^{-7}
	398	850	2.0	4.82×10^{-7}
	401	1302	2.0	2.11×10^{-7}
	403	2216	2.3	7.28×10^{-8}
80/20	373	319	2.2	1.81×10^{-6}
	378	521	2.2	6.05×10^{-7}
	381	605	2.2	4.34×10^{-7}
	383	714	2.2	3.00×10^{-7}
	386	882	2.4	1.87×10^{-7}
	388	1209	2.3	9.26×10^{-8}
	391	1247	2.3	8.64×10^{-8}
	393	2498	2.1	1.84×10^{-8}
60/40	363	280	2.4	4.59×10^{-7}
	368	382	2.5	2.10×10^{-7}
	373	561	2.5	7.93×10^{-8}
	376	796	2.5	3.28×10^{-8}
	378	988	2.5	1.90×10^{-8}
	381	1557	2.5	6.03×10^{-9}
	383	1695	2.7	4.86×10^{-9}
40/60	348	224	2.6	2.13×10^{-7}
	353	360	2.9	5.76×10^{-8}
	358	532	2.6	1.95×10^{-8}
	363	673	3.0	1.02×10^{-8}
	368	960	2.8	3.81×10^{-9}
	371	1320	2.8	1.57×10^{-9}
	373	1636	2.7	8.69×10^{-10}

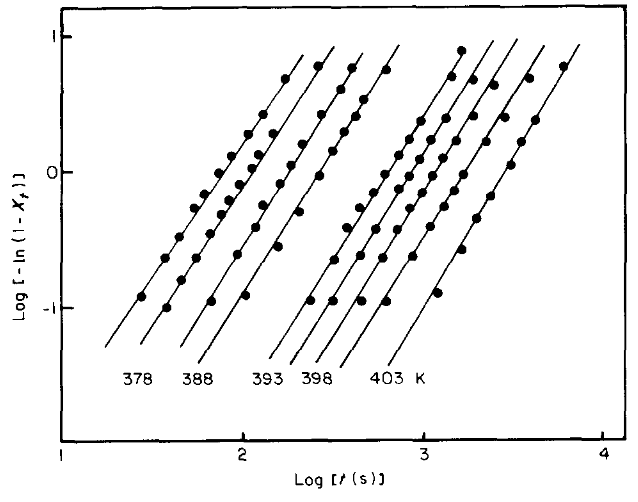

Figure 6 $\text{Log}[-\ln(1-X_t)]$ *versus* $\log t$ according to the Avrami equation [equation (5)] for pure PHB

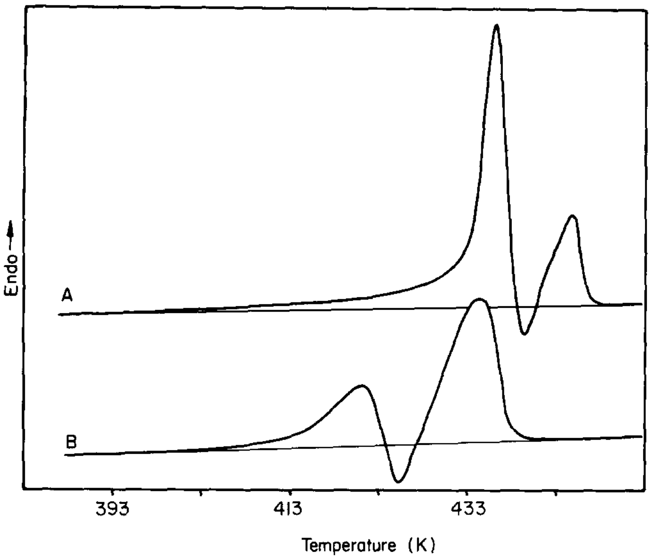

Figure 7 D.s.c. curves of (A) pure PHB and (B) 40/60 PHB/PECH blend, isothermally crystallized at 373 K

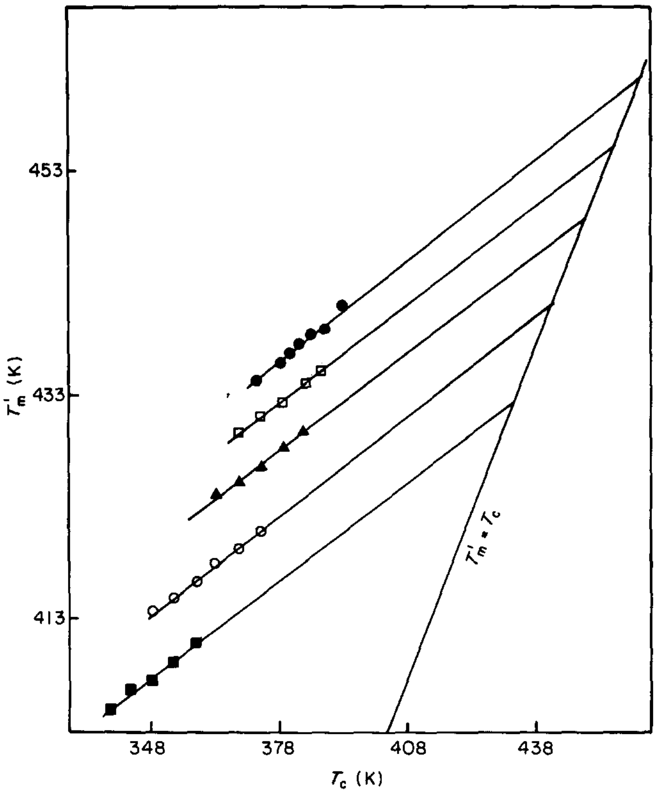

Figure 8 Observed melting temperature (T'_m) of PHB/PECH blends as a function of crystallization temperature (T_c). Symbols as in *Figure 2*

peak is caused by the melting of the reorganized crystal formed during the heating process[15,16]. In fact, immediately after the first melting peak an exothermic peak is registered (*Figure 7*). The lower T_m depends on the T_c while the higher T_m is almost constant[15].

As shown in *Figure 8*, the T'_m, calculated from d.s.c. curves, for pure PHB and the blends, increases with T_c for a wide range of undercooling. A depression of T'_m for the same T_c is observed for the blends. The magnitude of this effect increases with increasing PECH content. As reported by Barham *et al.*[9] we found a little dispersion of T'_m data for pure PHB and the blends. However, the experimental data may be fitted by the Hoffman–Weeks equation[17]:

$$T'_m = \frac{1}{\gamma} T_c + \left(1 - \frac{1}{\gamma}\right) T^\circ_m \qquad (6)$$

Extrapolation to the line where $T'_m = T_c$ enables the equilibrium melting point to be obtained. The values of T°_m determined by this method are reported in *Table 4*. The accuracy of T°_m was calculated from the standard deviations of the slope and intercept obtained from the linear relationship between T_c and T'_m. In equation (6) $1/\gamma$ assumes values between 0 ($T'_m = T^\circ_m$ for all T_c) and 1 ($T'_m = T_c$). Therefore, the crystals are most stable at $1/\gamma = 0$ and inherently unstable at $1/\gamma = 1$. The $1/\gamma$ values were similar for pure PHB and the blend samples, i.e. independent of composition. The values obtained were ~0.3. It is of interest to note that calorimetric measurements of other polymer crystals[17,19] also yielded comparable values for $1/\gamma$. Such a result indicates that PECH is able to act as a diluent for PHB and that the two polymers are miscible in the melt phase.

According to Flory–Huggins theory, the melting point depression is related to the interaction parameters, χ_{12}, through the following relation[18,19]:

$$-\left[\frac{\Delta H V_1}{R V_2}\left(\frac{1}{T^\circ_{m,b}} - \frac{1}{T^\circ_{m,p}}\right) + \frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)\phi_1\right] = \beta = \chi_{12}\phi_1^2 \qquad (7)$$

Subscripts 1 and 2 represent the non-crystallizable and the crystallizable polymer, respectively, V is the molar volume of the polymer unit at T°_m, ϕ is the volume fraction of the components in the blend, ΔH is the perfect crystal heat of fusion of the crystallizable polymer, m is the degree of polymerization, R is the universal gas constant, and $T^\circ_{m,p}$ and $T^\circ_{m,b}$ are the equilibrium melting temperatures of the pure crystallizable component and of the blend, respectively.

A plot of the left-hand side of equation (7) *versus* ϕ_1^2 should give a straight line passing through the origin if χ_{12} is assumed to be independent of composition. Using the values of T°_m reported in *Table 4*, the plot shown in *Figure 9* is obtained. The following parameter values were used: $\Delta H = 12.6\ \mathrm{kJ\ mol^{-1}}$ (ref. 3); $V_1 = 80\ \mathrm{cm^3\ mol^{-1}}$ (ref. 20); $V_2 = 76\ \mathrm{cm^3\ mol^{-1}}$ (ref. 20); $m_1 = 1742$; $m_2 = 7565$.

The experimental points may be interpolated by a line with an intercept at the origin (β) of 0.0094 and a slope (χ_{12}) of -0.068. The fact that this line does not pass through the origin can be ascribed to the morphological effect and/or to a composition dependence of χ_{12}. By using the same equation (7), Martuscelli *et al.* obtained a value of -0.096 for the PHB/PEO system[2] and a value of -0.073 for the PHB/PVAc system[3].

The equation derived by Kwei and Frisch[21] for non-infinite molecular weight polymers allows the

Table 4 T°_m values for pure PHB and PHB/PECH blends

PHB/PECH	T°_m (K)
100/0	461 ± 3
80/20	455 ± 2
60/40	449 ± 2
40/60	441 ± 1
20/80	432 ± 2

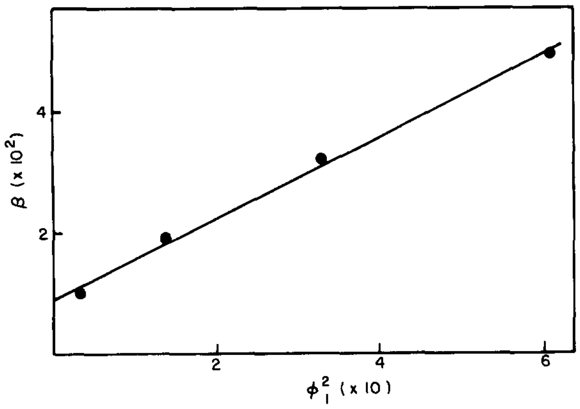

Figure 9 β *versus* ϕ_1^2 according to equation (7) for PHB/PECH blends

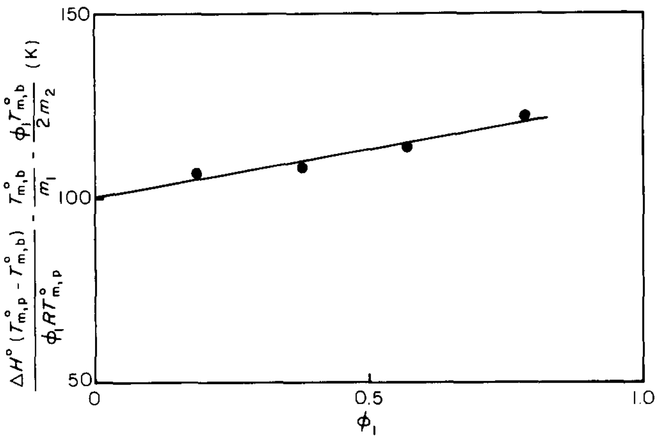

Figure 10 Application of the Kwei–Frisch equation on melting temperature depression for PHB/PECH blends. The left-hand side of equation (8) is plotted *versus* ϕ_1

Table 5 Data from the Kwei–Frisch equation [equation (8)]

PHB/PECH	C/R	$\chi_{12}T^{\circ}_{\mathrm{m,b}}\phi_1$	χ_{12} at T°_{m}
100/0	101	0	−0.054
80/20	101	−4.50	−0.055
60/40	101	−9.22	−0.056
40/60	101	−14.19	−0.057
20/80	101	−19.43	−0.058

proportionality constant for the morphological contributions, C, and χ_{12} to be calculated:

$$\frac{\Delta H^{\circ}(T^{\circ}_{\mathrm{m,p}} - T^{\circ}_{\mathrm{m,b}})}{\phi_1 R T^{\circ}_{\mathrm{m,p}}} - \frac{T^{\circ}_{\mathrm{m,b}}}{m_1} - \frac{\phi_1 T^{\circ}_{\mathrm{m,b}}}{2m_2} = \frac{C}{R} - \chi_{12}T^{\circ}_{\mathrm{m,b}}\phi_1 \tag{8}$$

Plotting the left-hand side of equation (8) *versus* ϕ_1 should yield a straight line where the intercept at the origin is C/R and the slope is $-\chi_{12}T^{\circ}_{\mathrm{m,b}}$.

The results are shown in *Figure 10*. From this, one determines a value of 200 for C and a value of −0.054 for χ_{12}. The χ_{12} value depends on composition and its value is similar to that derived from the Flory–Huggins equation. By comparing the two terms on the right-hand side of equation (8), one finds that C/R is greater than the term $\chi_{12}T^{\circ}_{\mathrm{m,b}}\phi_1$, and thus it may be concluded that morphological effects strongly influence the melting point depression of PHB/PECH blends (see *Table 5*).

CONCLUSIONS

Miscibility in the melt between PHB and PECH is confirmed by the detection of a single T_g and by the influence of PECH on the spherulitic growth rate and on the overall crystallization rate. The depression of T°_{m} appeared to be strongly influenced by morphological effects.

All results seem to indicate that after crystallization the PECH molecules are rejected in the interlamellar or interfibrillar regions of PHB spherulites, where they form a homogeneous mixture with uncrystallized PHB molecules.

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