Crystallization behaviour of poly(ethylene oxide) from poly(3-hydroxybutyrate)/poly(ethylene oxide) blends: phase structuring, morphology and thermal behaviour

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The influence of composition and thermal history on the phase structure and crystallization processes of poly(D(−)-3-hydroxybutyrate) (PHB) and poly(ethylene oxide) (PEO) blends at temperatures below the melting temperature of PHB has been investigated by differential scanning calorimetry (d.s.c.) and scanning electron microscopy. PHB and PEO, both crystallizable polymers, are compatible in the melt, where only one homogeneous phase is formed. But complex phase separation can take place when PHB crystallizes isothermally in the presence of the one-phase melt blend at temperatures higher than the melting temperature of PEO. During growth of the PHB spherulites, some PEO molecules are trapped in interlamellar regions, forming a homogeneous solution with uncrystallized PHB. Other PEO molecules are probably rejected into interfibrillar regions, forming almost pure PEO domains. Such domains of PEO crystallized on cooling, as shown by d.s.c. and scanning electron micrographs at temperatures between 45 and 35°C, close to the crystallization temperature of pure PEO. On the contrary, the PEO molecules trapped with uncrystallized PHB in interlamellar regions of PHB spherulites can crystallize only after cooling to lower temperatures, between −20 and −30°C. This behaviour is related to the fact that the amorphous PHB/PEO solution has a composition-dependent glass transition temperature higher than that of pure PEO: so the diffusion of PEO molecules is lowered. This complex phase separation is also influenced by the growth rate of PHB spherulites.

(Keywords: poly(D(−)-3-hydroxybutyrate; poly(ethylene oxide); blend; crystallization; phase separation; phase structure; thermal history)

INTRODUCTION

Poly(D(−)-3-hydroxybutyrate) (PHB) is a biosynthetic optically active aliphatic polyester obtained by bacterial fermentation[1–12]. This polymer is highly crystalline, with a melting temperature of about 180°C[13,14]. Moreover, PHB is completely biodegradable and biocompatible[8–12]. PHB is a thermoplastic polymer, and thus it can be processed like other thermoplastic materials. The only problem is represented by the fact that PHB has a rather narrow window of processability, as it may suffer thermal degradation when kept at temperatures higher than T_m.

For these reasons we have started research with the goal of finding polymers compatible in the melt with PHB that when blended with PHB may lower the melting temperature without any deterioration of its end-use properties.

In previous papers[15,16] we investigated the thermal and isothermal crystallization behaviour of binary blends obtained by mixing PHB and poly(ethylene oxide) (PEO). The blends show a single glass transition temperature and a depression of both the equilibrium melting temperature of PHB and the growth rate of spherulites of PHB.

The results on the whole led us to the conclusion that PEO and PHB are compatible in the melt. Moreover, when PHB crystals grow isothermally in equilibrium with homogeneous two-component melt, at T_c, where PEO is in the liquid state, the PEO molecules are likely to be trapped in intraspherulitic regions (interlamellar and/or interfibrillar) where they may form a homogeneous solution with uncrystallized PHB molecules[15,16].

The present paper reports on the results of an investigation aimed at a better understanding of the phase structure of PHB/PEO blends at temperatures below the melting temperature of PHB; in particular when the blend undergoes different thermal treatments and crystallization conditions that also allow the crystallization of PEO molecules.

EXPERIMENTAL

Materials

Samples of PHB were furnished by ICI. The polymer was obtained by the continuous fermentation of a glucose-utilizing mutant of *Alcaligenes eutrophus*[8–12]. The PEO sample used in the present paper was purchased from Fluka AG. The molecular characteristics of PHB and PEO are reported in *Table 1*.

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Table 1 Molecular characteristics, sources and codes of PHB and PEO

Polymer	Source	Code	Relative molecular mass
Poly(D(−)-3-hydroxybutyrate)	ICI (UK)	PHB	$M_n = 279\,000^a$
Poly(ethylene oxide)	Fluka AG	PEO	$M_n = 20\,000^b$

[a] By g.p.c. in chloroform at 30°C[17]

[b] By intrinsic viscosity in water at 30°C[18]

Table 2 Compositions of PHB/PEO blends investigated and their codes

Blend investigated, PHB/PEO (wt ratio)	Code
100/0	PHB
80/20	PHB-80
60/40	PHB-60
40/60	PHB-40
20/80	PHB-20
0/100	PEO

Preparation of 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 composition and the codes of the blends investigated are reported in *Table 2*.

Thermal history and determination of phase transitions

Samples of PHB/PEO blends underwent the following thermal history. First, the films obtained directly by casting, sealed in aluminium pans, were heated in a d.s.c. apparatus at 20°C min^{-1} to 190°C and kept at this temperature for about 1 min (run I). Second, the samples were cooled down (50°C min^{-1}) to the desired PHB crystallization temperature and kept at this temperature for a time sufficient to allow complete isothermal crystallization of the PHB phase. Third, the samples were further cooled (10°C min^{-1}) to −100°C in order to promote the crystallization of the PEO phase. Finally, after about 2 min at −100°C the temperature was raised to 230°C by using a scan rate of 20°C min^{-1} (run II).

The glass transition temperatures of the homopolymers and the blends were obtained by heating up the samples first melted at 200°C and then rapidly quenched to −100°C.

A Mettler TA-3000 apparatus was used, which was equipped with a control and programming unit (microprocessor TC-10) and a calorimetric cell DSC-30 that allows temperature scans from −170 to 600°C.

Scanning electron microscopy analysis

The morphological investigations were carried out by using a Philips 501 SEM on d.s.c. crystallized samples after metallization with Au–Pd alloy by means of a Polaron sputtering apparatus.

RESULTS AND DISCUSSION

Thermal and crystallization behaviour

In previous papers[15,16] we have already shown that the run I d.s.c. thermograms of cast film samples of PHB/PEO blends are characterized by the presence of two distinct endothermic peaks (see *Figure 1*). The higher- and lower-temperature peaks are attributed to the melting of PHB and PEO phases, respectively.

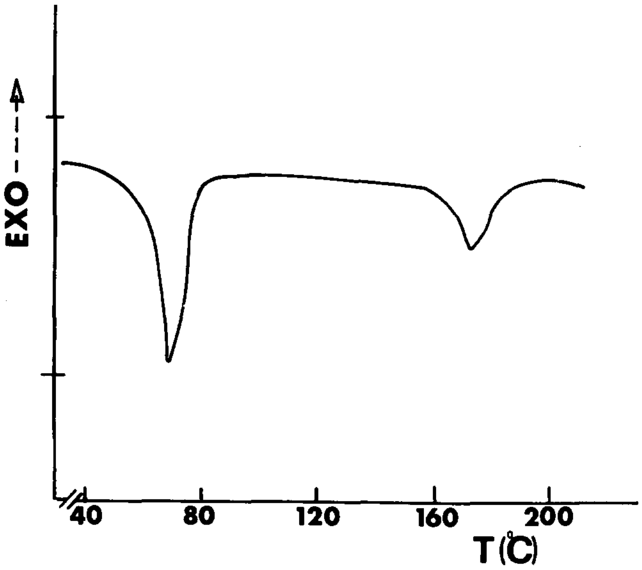

Figure 1 Run I d.s.c. thermogram of a cast sample of PHB/PEO blend

The temperatures of these peaks are composition-dependent, as they change with changes in component content[15,16]. Moreover, the blends show a single composition-dependent glass transition temperature intermediate between that of PHB and PEO. It was found[15,16] that the experimental values are fitted quite well by the Fox equation[19].

The above observations, together with the results of an investigation concerned with the isothermal crystallization behaviour, led the authors to conclude that PHB and PEO are compatible in the melt state[15,16].

The PHB/PEO phase diagram obtained by d.s.c. studies is shown in *Figure 2*.

To assess the level of compatibility between PHB and PEO, and the phase structure after crystallization processes, samples of the blends were subjected to the thermal history described in the 'Experimental' part. After melting, the samples of the blends were rapidly cooled to two different crystallization temperatures (90 and 70°C), at which only the PHB is able to crystallize (T_m(PEO) ≃ 60°C). After a time long enough to permit complete crystallization of PHB, the material was cooled down to −100°C by using a scan rate of 10°C min^{-1}. The corresponding d.s.c. thermograms show two exothermic crystallization peaks (see for example *Figure 3*).

The temperatures of the maxima and the apparent enthalpies of these two peaks are reported in *Table 3* for all blends investigated and for the two crystallization processes investigated.

It is interesting to underline that plain PHB after isothermal crystallization at 70 and 90°C does not show any further exothermic peak when cooled down to −100°C. In the case of neat PEO a single peak at about 44°C is observed.

Table 3 Temperatures of the maxima T_c(HTP) and T_c(LTP) and apparent enthalpies of crystallization ΔH_c^*(HTP) and ΔH_c^*(LTP) corresponding to the d.s.c. high-temperature peak (HTP) and low-temperature peak (LTP) for PHB/PEO blends following the crystallization process described in the text

	$T_c = 70$°C				$T_c = 90$°C			
Blend	T_c(HTP)	T_c(LTP)	ΔH_c^*(HTP)	ΔH_c^*(LTP)	T_c(HTP)	T_c(LTP)	ΔH_c^*(HTP)	ΔH_c^*(LTP)
PHB	–	–	–	–	–	–	–	–
PHB-80	42	−22	50	45	37	−28	20	50
PHB-60	40	−20	75	12	39	−26	60	18
PHB-40	38	−18	132	3	41	−25	128	7
PHB-20	36	–	147	–	40	−23	140	2
PEO	43	–	180	–	44	–	175	–

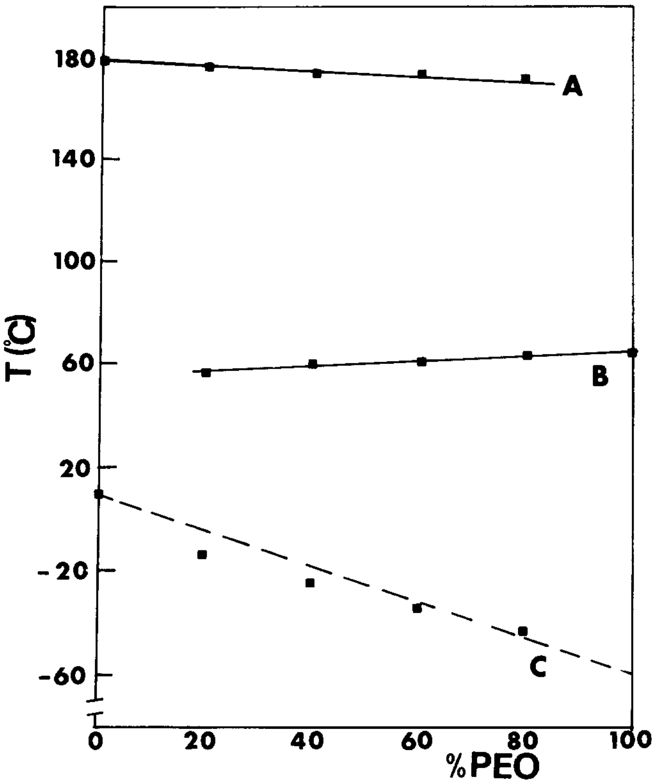

Figure 2 PHB/PEO phase diagram: (A) T'_m(PHB); (B) T'_m(PEO); (C) ■, T_g(expt), ---, T_g(Fox)

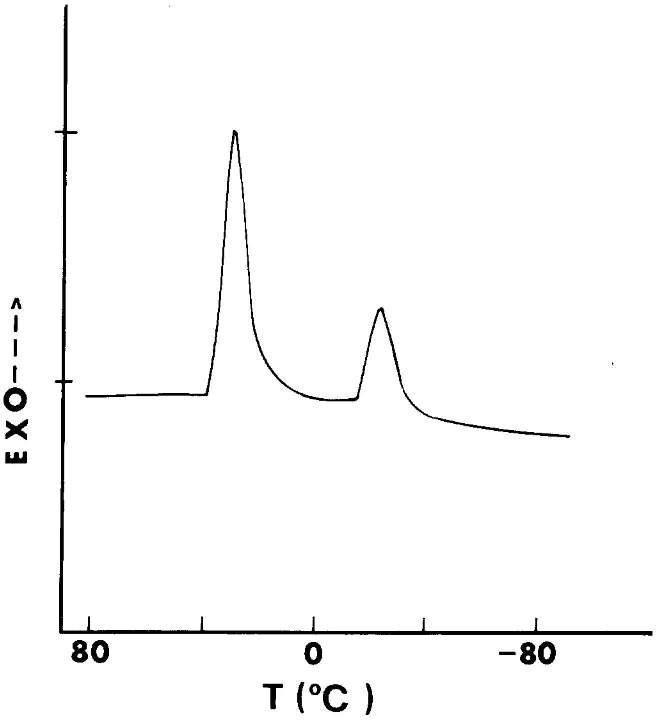

Figure 3 Non-isothermal crystallization d.s.c. thermogram of a PHB/PEO blend sample

From the data of *Table 3* the following emerges:

(1) The temperatures corresponding to the maxima of the higher-temperature peak T_m(HTP) as well as that of the lower-temperature peak T_m(LTP) seem to be composition-dependent.

(2) The apparent enthalpy of crystallization ΔH_c^* as deduced from the area of the peaks is composition-dependent. It can be observed that ΔH_c^*(HTP) increases with PEO content while the opposite is observed for ΔH_c^*(LTP). For the high-temperature peak the values of ΔH_c^* of blends extrapolate very well to the value for neat PEO. It is to be noted that ΔH_c^* values were calculated by referring the peak area only to the overall PEO content in the blend.

(3) The ΔH_c^* are dependent on thermal history too. It can be observed that blends that underwent a PHB crystallization process at 90°C show values of ΔH_c^*(HTP) that are systematically lower especially at high PHB content. The contrary is found for ΔH_c^*(LTP).

(4) The relative amount of material that crystallizes at lower temperatures decreases with increase of the PEO content in the blends. Such a conclusion is easily drawn by observing the trend of the curve obtained by plotting the ratio $\Delta H_c^*(\mathrm{LTP})/[\Delta H_c^*(\mathrm{LTP}) + \Delta H_c^*(\mathrm{HTP})]$ *versus* PEO percentage (see *Figure 4*).

D.s.c. thermograms obtained by heating the samples, after crystallization of PHB and PEO phase, from −100°C to 230°C (run II) show the presence of two distinct endothermic peaks (see *Figure 5*). The peak at lower temperature is attributed to the melting of PEO phase, while that at higher temperature is due to the melting of PHB phase. As shown by *Figure 6* the T_m of PHB decreases with increasing PEO content. Contrary to this the T_m of PEO seems to show a slight increase with increase of PHB percentage.

The values of the apparent enthalpy of fusion ΔH_m^*(PHB) and ΔH_m^*(PEO) are plotted *versus* PEO percentage in *Figure 7* (ΔH_m^*(PHB) and ΔH_m^*(PEO) have been calculated by referring the peak areas to the PHB and PEO contents in the blends, respectively). From the trend of this plot one concludes that following the thermal history PEO crystals are obtained characterized by a

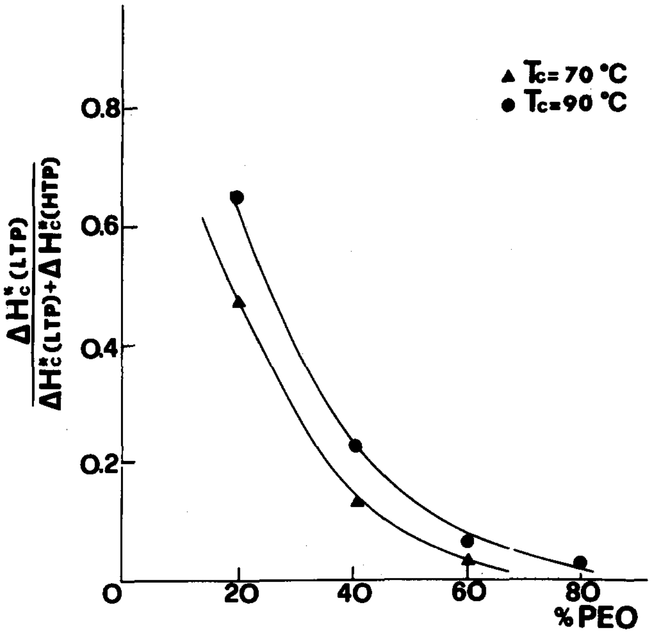

Figure 4 The ratio $\Delta H^*_c(\mathrm{LTP})/[\Delta H^*_c(\mathrm{LTP})+\Delta H^*_c(\mathrm{HTP})]$ *versus* PEO content

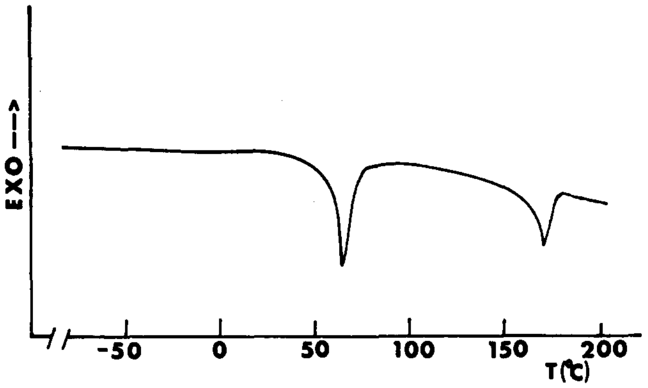

Figure 5 Run II d.s.c. thermogram after PHB and PEO phase crystallization of a PHB-60 blend sample

high degree of order and crystallinity. This indicates that the presence of PHB spherulites interferes positively with the crystallization process of PEO molecules.

As far as ΔH^*_m(PHB) is concerned, it can be observed that the values corresponding to the blends turn out to be slightly lower than that of neat PHB. It must be underlined that the finding of only one endothermic peak corresponding to the melting of PEO in the run II d.s.c. indicates that only one PEO crystalline phase is present after the crystallization process.

Phase structure by optical and scanning electron microscopy

Optical micrographs showing PHB spherulites isothermally crystallized at 90°C from the neat melt and from a homogeneous PHB + PEO melt mixture are shown in *Figure 8*. No apparent phase separation of PEO melt phase is evident. As already stated previously the two polymers are compatible in the melt, and thus at 90°C the PHB spherulites grow in equilibrium with a one-phase melt.

During the growth of lamellar spherulites it was postulated that the molecules of PEO may be ejected into interlamellar and/or interfibrillar regions, as observed in the case of other miscible crystallizable blends[20,21]. It is highly probable that PEO molecules form a homogeneous phase with uncrystallized PHB molecules or part of them. This is in agreement with the observation that quenched samples show only one glass transition temperature–composition dependence whose

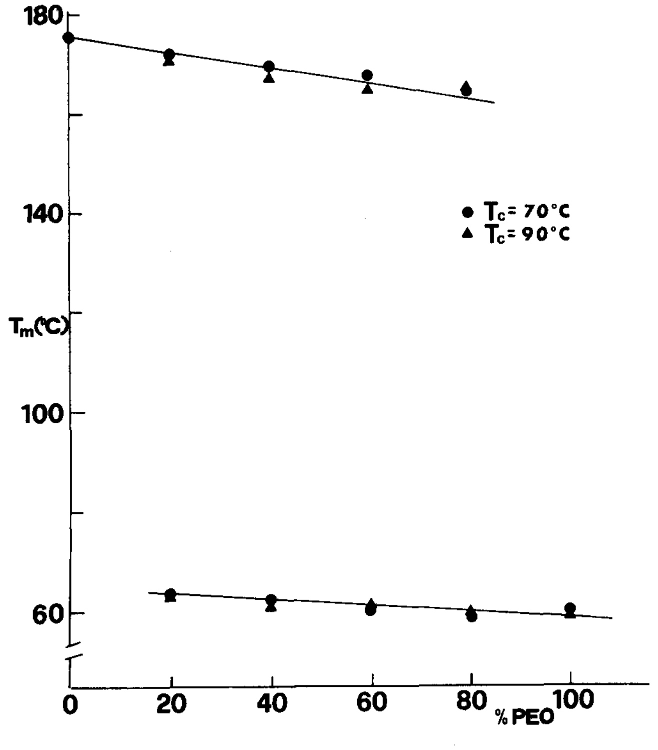

Figure 6 Melting temperatures (T'_m) of PEO and PHB phases after crystallization *versus* PEO content

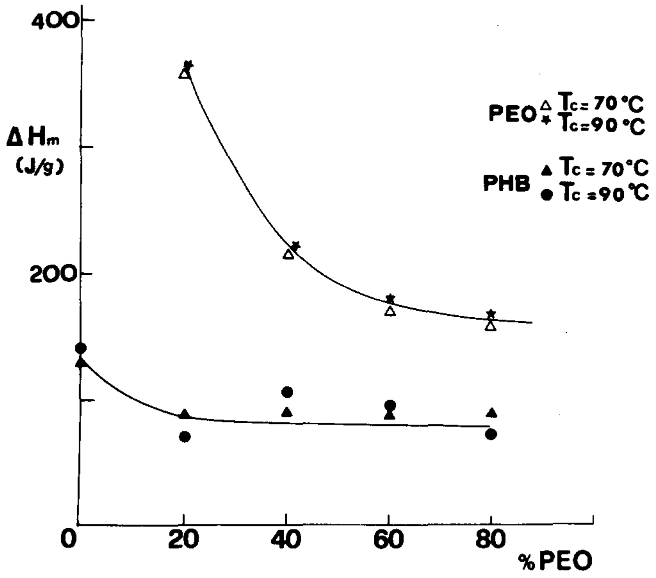

Figure 7 Apparent enthalpies of fusion (ΔH^*_m) of PEO and PHB phases after crystallization *versus* PEO content

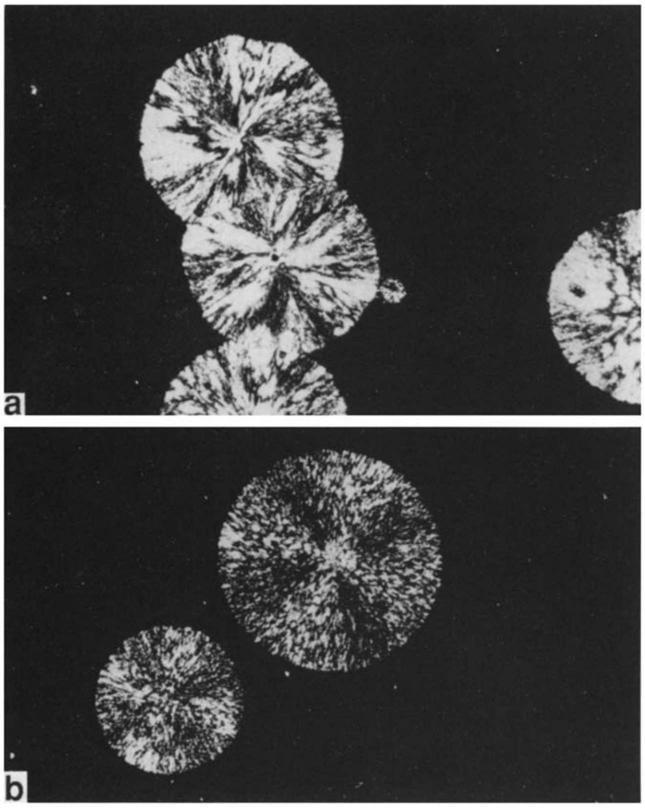

Figure 8 Optical micrographs of PHB spherulites grown isothermally at $T_c = 90°C$: (a) PHB-100; (b) PHB-80

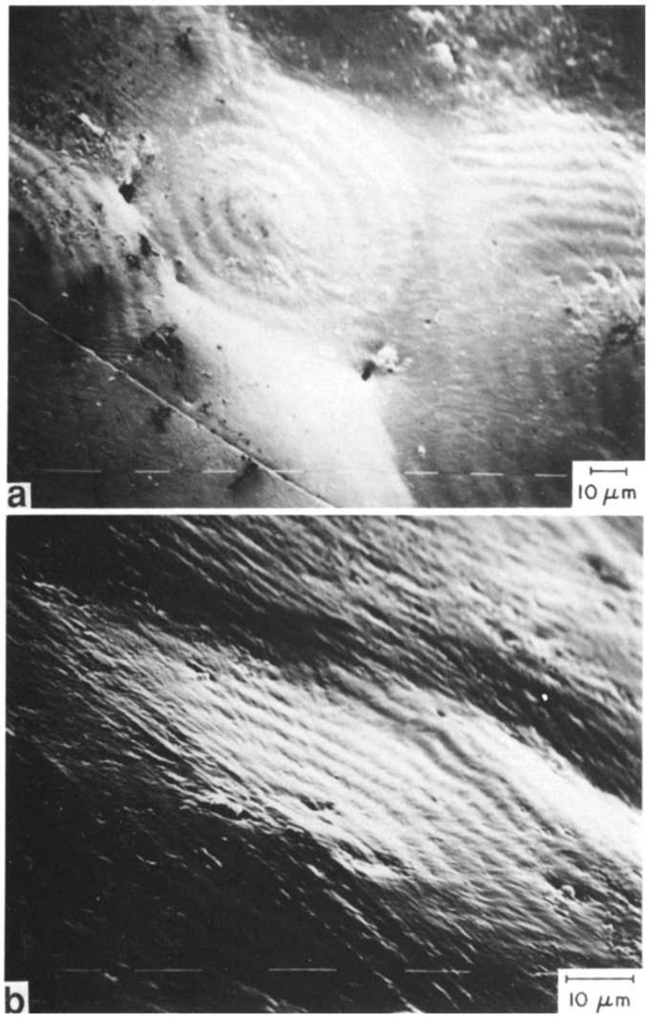

Figure 9 SEM micrographs of PHB-100 blend at two magnifications

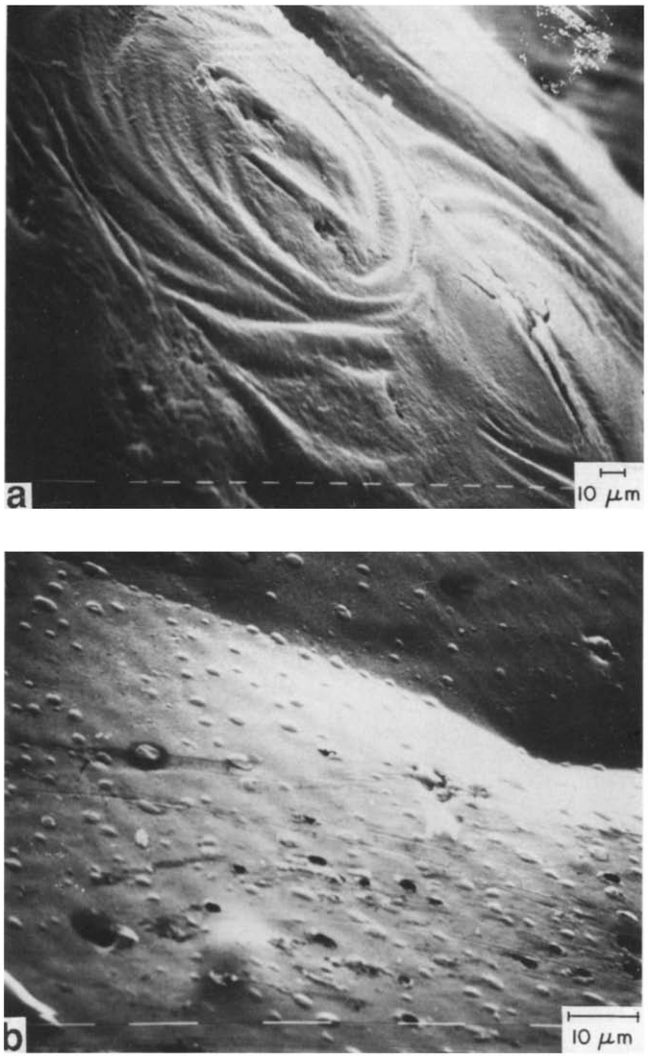

Figure 10 SEM micrographs of PHB-80 blend at two magnifications

values follow the Fox equation[19]. From a SEM investigation on surfaces of samples of neat PHB and of PHB/PEO blends, taken after isothermal crystallization of PHB phase at 90 and 70°C and cooling to room temperature, the presence in intraspherulitic regions of distinct separate domains is clearly shown. Such domains must be related to the crystallization process of PEO phase that occurs at higher temperatures (around 40°C) (see *Figures 9–12*).

Thus during the cooling of PHB/PEO samples from the T_c of PHB to room temperature the PEO crystallizes, giving rise to a phase-separation process that leads to the formation of a distinct solid phase located in PHB intraspherulitic regions.

CONCLUDING REMARKS

From the experimental results reported here combined with those already published by us[15,16], the following conclusions can be made:

At crystallization temperatures higher than the T_m of PEO, the spherulites of PHB grow isothermally in equilibrium with a one-phase melt blend (PHB + PEO). During this process of growth the PEO molecules are mainly ejected into interlamellar and/or interfibrillar

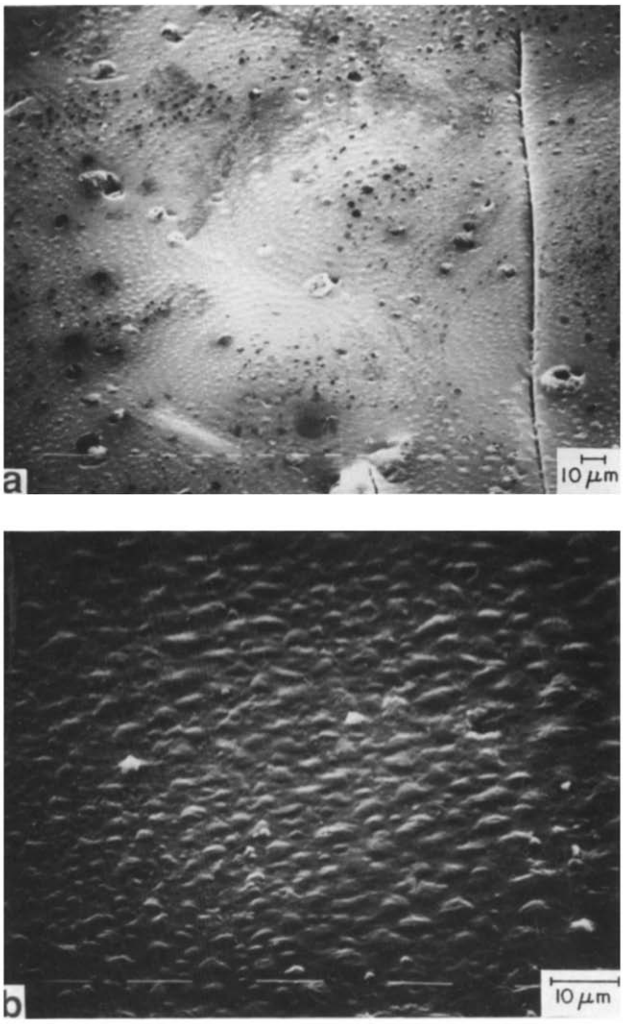

Figure 11 SEM micrographs of PHB-60 blend at two magnifications

The above observation may be accounted for by assuming that, during the growth of PHB spherulites, part of the PEO molecules are trapped in interlamellar regions forming a homogeneous solution with uncrystallized molecules of PHB. This solution is characterized by a glass transition temperature higher than that of neat PEO, and thus the diffusion of PEO molecules will be lowered; moreover, the molecules of PHB will act as a diluent. Both effects will contribute to reducing the rate of crystallization of PEO molecules[22]. Thus the low-temperature d.s.c. exothermic peak must be attributed to the crystallization process of PEO molecules coming mainly from homogeneous PEO + PHB solutions. The high-temperature exothermic peak is to be attributed to the crystallization process of PEO molecules that during isothermal growth of PHB spherulites phase-separate from the melt blend giving rise to the formation of intraspherulitic domains of almost pure PEO. Thus it emerges that after the crystallization of PHB at T_c the system can be characterized by the presence of a liquid PEO + PHB phase and by a phase of almost pure liquid PEO.

The presence of only one endothermic peak related to PEO melting in run II d.s.c. experiments (see *Figure 5*) indicates that the two crystallization processes from pure PEO and from interlamellar and/or interfibrillar intraspherulitic regions, where they may form homogeneous mixtures with uncrystallized PHB molecules.

By cooling down the blend samples from the T_c of PHB to -100°C one promotes the crystallization of PEO molecules. As evidenced by SEM analysis, crystallization gives rise to the formation of well defined PEO spherical domains located in intraspherulitic regions. Such observations represent the first direct evidence of the process of phase separation and crystallization of a blend component from an amorphous state situated in regions that are interconnected by crystalline lamellae of the higher-temperature crystallizable component (PHB).

From the d.s.c. thermograms related to cooling, it emerges that part of the PEO molecules crystallize at a temperature close to that of neat PEO ($\simeq 40$°C) and part at a lower temperature between -20 and -30°C according to blend composition. The relative amount of PEO molecules crystallizing at lower T_c, as measured by the ratio $\alpha = \Delta H_c^*(\mathrm{LTP})/[\Delta H_c^*(\mathrm{LTP}) + \Delta H_c^*(\mathrm{HTP})]$, is strongly dependent on blend composition as well as on thermal history (see *Figure 4*). It can be observed that for a PHB/PEO blend containing 20% (wt/wt) of PEO the value of α turns out to be about 0.47 and 0.65 for samples characterized by a PHB precrystallization temperature of 70 and 90°C respectively. In the case of blend with 60% or more of PEO the value of α reduces to about 0.05.

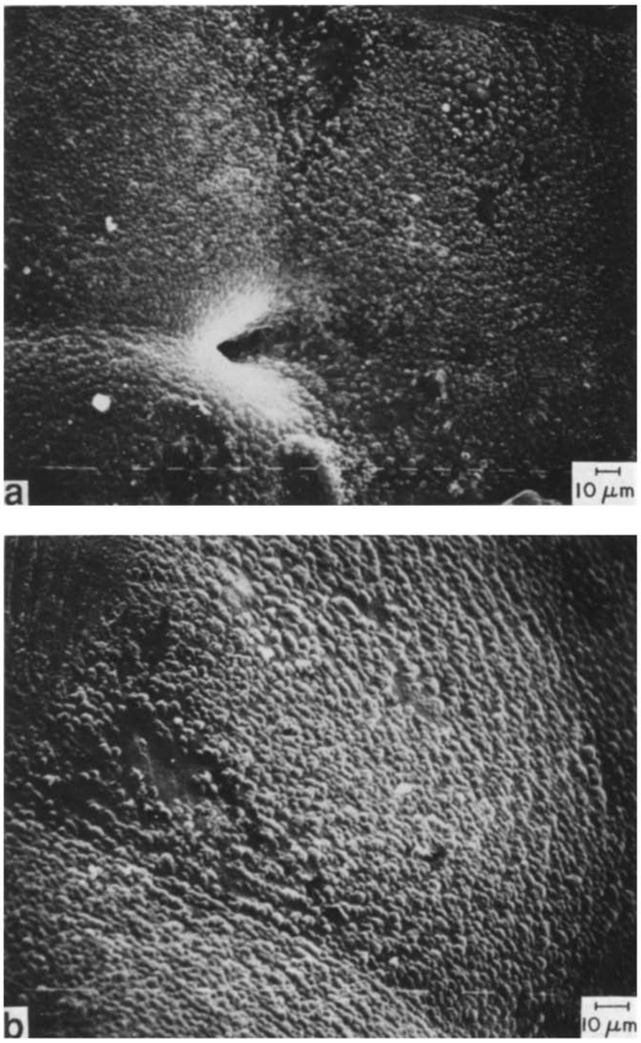

Figure 12 SEM micrographs of PHB-20 blend at two magnifications

melting temperature. Moreover, this fact suggests that no molecular fractionation is active during the blending, PHB crystallization and phase-separation phenomena.

The finding that the fraction of total PEO present as PEO + PHB homogeneous solution is lower at high PEO content is probably accounted for by assuming that the growth rate of PHB spherulites is relatively low[15,16]; thus the PEO molecules may easily diffuse away, having more time to separate from the melt blend.

This observation could indicate that the growth rate of spherulites may play an important role in determining the type of phase structure attained after crystallization for this kind of melt-compatible blend where both components are crystallizable.

It can be concluded that the crystallization conditions and thermal history may drastically influence the phase structuring of a polymer–polymer blend whose components are both crystallizable and compatible in the melt. Work is in progress to study by WAXS, SAXS and SEM the structure and morphology of crystalline PEO phase grown in intraspherulitic regions of precrystallized PHB spherulites.

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