

The fractionated crystallization phenomenon in poly(3-hydroxybutyrate)/poly(ethylene oxide) blends

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Differential scanning calorimetry and scanning electron microscopy were used to investigate the phenomenon of 'fractionated crystallization' exhibited in poly-D(-)(3-hydroxybutyrate)/poly(ethylene oxide) (PHB/PEO) blends. PHB and PEO, both crystallizable polymers, are compatible in the melt, where only one homogeneous phase is formed. However, complex phase separation takes place during subsequent crystallization: in particular, under non-isothermal conditions, after PHB crystallization, the PEO phase can give rise to fractionated crystallization, as it can crystallize in two steps at different supercoolings. It was observed that this phenomenon depends mainly on the crystallization conditions, the previous thermal history and the crystallization rate used to crystallize the PHB phase. The two different exothermic peaks relative to PEO crystallization were attributed to a homogeneous (high supercooling) and a heterogeneous (low supercooling) nucleation mode respectively. The addition of a nucleating agent, saccharin, supported such a hypothesis. These foreign particles act as heterogeneous nuclei, thus allowing the PEO phase to crystallize completely at lower supercooling according to a heterogeneous mode of nucleation.

(Keywords: poly-D(-)(3-hydroxybutyrate); poly(ethylene oxide); blend nucleation; fractionated crystallization; thermal behaviour; phase structure)

INTRODUCTION

Poly-D(-)(3-hydroxybutyrate) (PHB) is an optically active saturated aliphatic polyester found in small amounts in a wide variety of micro-organisms, where it acts as an energy and carbon storage product¹. Under controlled conditions, it can be advantageously produced by bacterial fermentation².

PHB has attracted much attention owing to its biodegradability and biocompatibility. Being a thermoplastic polymer, PHB can be processed like other thermoplastic materials. However, it may suffer thermal degradation when kept for a relatively long time at temperatures above its melting point.

Owing to its bacterial origin, PHB is a very pure polymer. This high purity leads to the presence of very few heterogeneous nuclei, which makes PHB an advantageous polymer for nucleation studies. PHB shows different modes of primary nucleation according to the crystallization conditions³. It is shown that in the pure melt PHB may present homogeneous nucleation phenomena, while on adding foreign particles (e.g. saccharin) the nucleation becomes completely heterogeneous.

Poly-D(-)(3-hydroxybutyrate)/poly(ethylene oxide) (PHB/PEO) blends, the two components being miscible in the amorphous state, offer the advantage of a lower equilibrium melting temperature; this results in a processability window shifted towards lower temperatures with respect to plain PHB⁴.

In previous papers^{4,5} we have investigated the thermal behaviour, phase structure and crystallization of PHB/PEO blends. PHB/PEO blends show a single glass transition temperature and a depression of both the equilibrium melting temperature and the growth rate of PHB spherulites. These results indicate that PEO and PHB are miscible in the melt. Moreover, we also observed a complex mode of crystallization of the PEO phase, when it takes place after complete isothermal crystallization of PHB (which happens at crystallization temperatures higher than the PEO melting point). D.s.c. experiments have shown that, after isothermal crystallization of PHB, at temperatures where the PEO phase is still in the liquid state ($T > 70^\circ\text{C}$), subsequent cooling (to -100°C) shows the presence in the thermograms of two exothermic crystallization peaks, both related to the PEO phase. Moreover it was found that the relative area ratio of these peaks (whose maxima are located at $\approx 40^\circ\text{C}$ and $\approx -20^\circ\text{C}$ respectively) turns out to be influenced by the composition of the blends⁵.

The present paper reports further results concerning the phase structure development during isothermal and non-isothermal crystallization of PHB/PEO blends from the melt. More precisely, it concentrates on the origin of the phenomenon, called 'fractionated crystallization', that PEO seems to exhibit when it crystallizes from PHB/PEO blends. This phenomenon, observed so far only in the case of a few immiscible blends⁶, consists of a blend component crystallizing in more than one step at different supercoolings.

Our investigations were undertaken with the aim of establishing the type of PHB nucleation in PHB/

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Table 1 Molecular characteristics, source and code of PHB and PEO

Polymer	Source	Code	Relative molecular mass
Poly(3-hydroxybutyrate)	ICI (UK)	PHB	279 000 ^a
Poly(ethylene oxide)	Fluka AG	PEO	20 000 ^b

^a By g.p.c. in chloroform at 30°C

^b By intrinsic viscosity at 30°C in water

Table 2 Composition and code of PHB/PEO blends investigated

Blend composition PHB/PEO (wt ratio)	Code
100/0	PHB
80/20	PHB 80
60/40	PHB 60
40/60	PHB 40
20/80	PHB 20

PEO blends and its influence on the following PEO crystallization process.

EXPERIMENTAL

Materials

The PHB sample used in the present paper was supplied by ICI. It was synthesized by the continuous fermentation of a glucose-utilizing mutant of *Alcaligenes eutrophus*.

The PEO sample was provided by Fluka AG.

The molecular characteristics of PHB and PEO are shown in Table 1.

Saccharin was used as nucleating agent for PHB.

Preparation of the blends

The PHB/PEO 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 code of the blends investigated are given in Table 2.

The blends containing saccharin were prepared by first dissolving the nucleating agent in methanol and then adding the solution to PHB/PEO blends dissolved in chloroform. The resulting solution was dried under vacuum at 80°C.

Techniques

Calorimetric studies were performed using a Mettler TA-3000 differential scanning calorimeter equipped with a control and programming unit (microprocessor TC-11) and a calorimetric cell DSC-30 operating under a N₂ atmosphere.

Morphological investigations on the spherulitic structure of the blends were carried out by means of a Leitz polarizing optical microscope equipped with a Mettler hot stage (precision ±0.2°C).

Scanning electron microscopy (SEM) analyses were carried out using a Philips 501 SEM on d.s.c. crystallized samples after metallization by means of a Polaron sputtering apparatus with Au-Pd alloy.

RESULTS AND DISCUSSION

Non-isothermal crystallization: calorimetric studies

As described in a previous paper⁵, d.s.c. experiments have shown that the PEO component in PHB/PEO blends, after PHB crystallization, can crystallize in two different steps. In fact, two exothermic peaks, henceforth named the higher-temperature peak (HTP, ≈ 40°C) and the lower-temperature peak (LTP, ≈ -20°C) have been found. These peaks were attributed to the PEO component.

When PHB/PEO blends are cooled non-isothermally from the melt (200°C), the occurrence of three peaks is observed. As an example, the d.s.c. crystallization curve of PHB 60 blend sample is shown in Figure 1. The sample was cooled down by using a scan rate of 6°C min⁻¹. Clearly the peak at highest temperature (≈ 80°C) reflects the heat evolved during the crystallization of the PHB phase, while the remaining two peaks (≈ 40°C and ≈ -20°C) are attributable to the crystallization of the PEO phase.

In order to understand the origin of this fractionated crystallization of PEO, the influence of the crystallization rate of PHB on PEO crystallization was examined by the following d.s.c. experiment.

First the blend films obtained by casting were heated from 25°C to 200°C at 20°C min⁻¹ (first run). After 2 min at 200°C the samples were cooled down to -100°C (crystallization run). Two different cooling rates, 1 and 20°C min⁻¹ respectively, were used for each blend composition. D.s.c. crystallization thermograms of PHB/PEO blends as functions of composition and cooling rate are shown in Figure 2. From the observation of such figures the following points come out:

(i) At lower cooling rate (1°C min⁻¹) and when the content of PEO is less than 60%, the enthalpies related to the lower-temperature peak prevail over those of the higher-temperature peak.

(ii) The intensity of the HTP seems to be dependent on the composition: in fact, it decreases with increase of PHB content.

(iii) At higher cooling rate (20°C min⁻¹), the heat due to the higher-temperature peak prevails over that of the lower-temperature peak for almost all examined compositions. Only in the case of the PHB 80 blend are the two peaks comparable. The lower-temperature peak seems to be dependent also on the composition, as it disappears when the content of PEO is more than 60%.

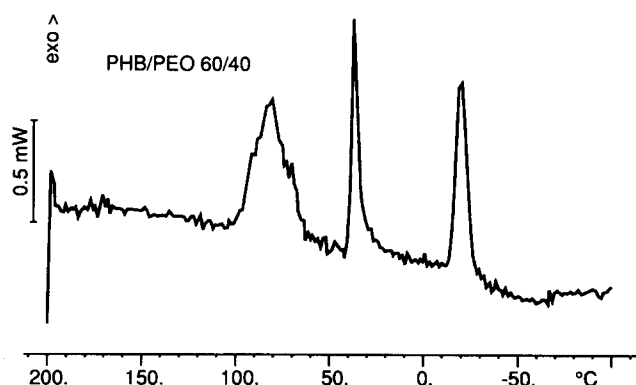


Figure 1. D.s.c. crystallization exotherm of PHB 60. The sample was cooled from 200°C to -100°C at a cooling rate of 6°C min⁻¹

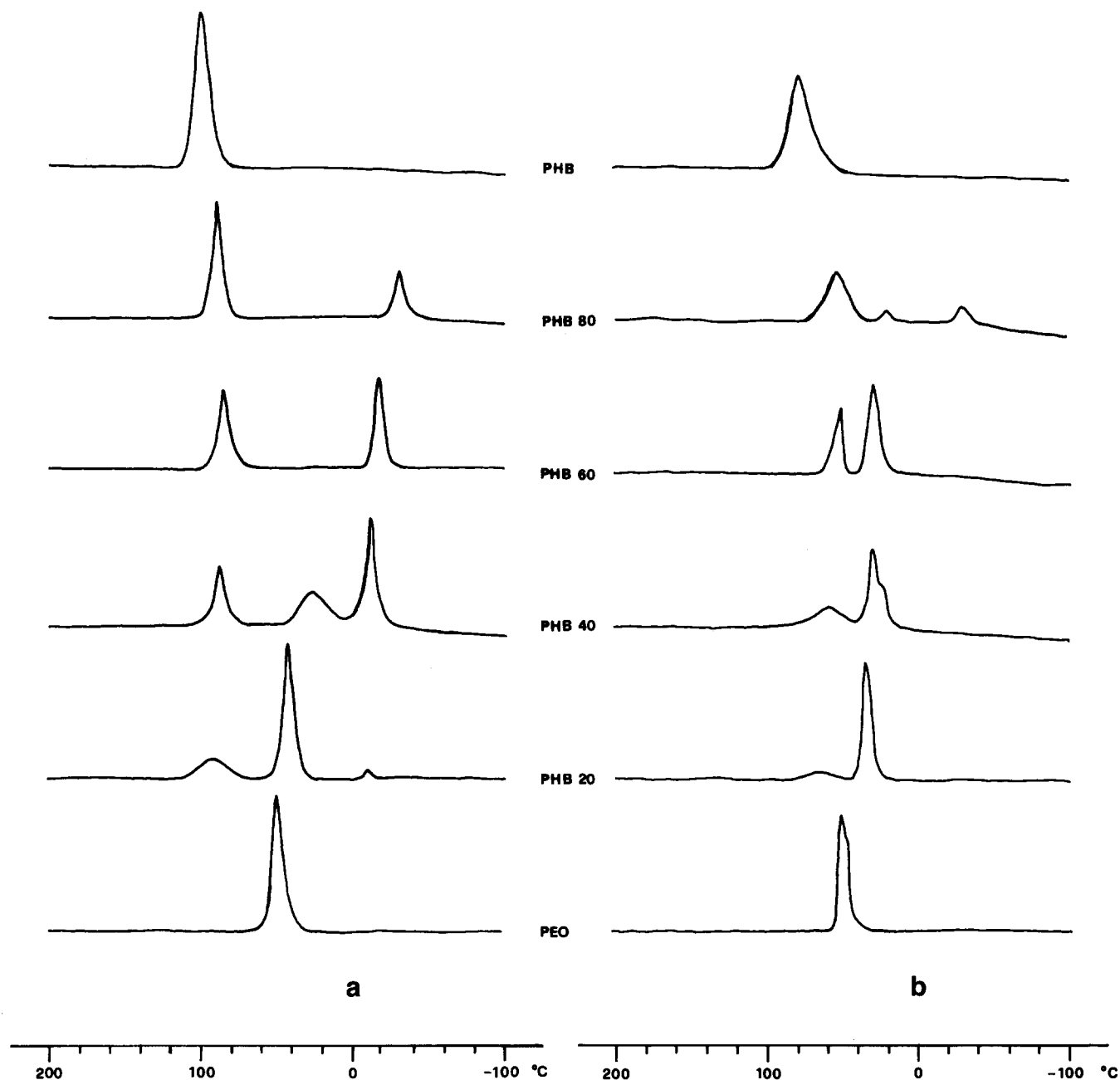


Figure 2 D.s.c. crystallization curves of PHB/PEO blends of different compositions at two different cooling rates: (a) $1^{\circ}\text{C min}^{-1}$ and (b) $20^{\circ}\text{C min}^{-1}$

Table 3 Temperatures of the maxima $T_{c,HTP}$ and $T_{c,LTP}$ and apparent enthalpies of crystallization ΔH_{HTP}^* and ΔH_{LTP}^* for PHB/PEO blends following slow non-isothermal crystallization (cooling rate = $1^{\circ}\text{C min}^{-1}$)

PHB/PEO	ΔH_{PHB}^* (J g^{-1})	$T_{c,PHB}$ ($^{\circ}\text{C}$)	ΔH_{HTP}^* (J g^{-1})	$T_{c,HTP}$ ($^{\circ}\text{C}$)	ΔH_{LTP}^* (J g^{-1})	$T_{c,LTP}$ ($^{\circ}\text{C}$)	ΔH_{PEO}^* (J g^{-1})
100/0	70	101	—	—	—	—	—
80/20	68	91	no peak	—	64	-25	64
60/40	71	85	no peak	—	94	-21	94
40/60	69	89	64	24	51	-17	105
20/80	58	93	115	42	5	-11	120
0/100	—	—	131	50	—	—	131

Table 4 Temperatures of the maxima $T_{c,HTP}$ and $T_{c,LTP}$ and apparent enthalpies of crystallization ΔH_{HTP}^* and ΔH_{LTP}^* for PHB/PEO blends following fast non-isothermal crystallization (cooling rate = $20^{\circ}\text{C min}^{-1}$)

PHB/PEO	ΔH_{PHB}^* (J g^{-1})	$T_{c,PHB}$ ($^{\circ}\text{C}$)	ΔH_{HTP}^* (J g^{-1})	$T_{c,HTP}$ ($^{\circ}\text{C}$)	ΔH_{LTP}^* (J g^{-1})	$T_{c,LTP}$ ($^{\circ}\text{C}$)	ΔH_{PEO}^* (J g^{-1})
100/0	56	81	—	—	—	—	—
80/20	45	53	14	20	23	-25	37
60/40	52	51	97	31	no peak	—	97
40/60	30	58	103	31	no peak	—	103
20/80	19	62	124	37	no peak	—	124
0/100	—	—	126	46	—	—	126

In Tables 3 and 4 the apparent enthalpies ΔH^* and the temperatures T_c corresponding to the maxima of the crystallization peaks in the d.s.c. thermograms obtained at the two different scan rates ($1^{\circ}\text{C min}^{-1}$ for Table 3 and $20^{\circ}\text{C min}^{-1}$ for Table 4) are reported. From the data it

emerges that the values of ΔH_{PHB}^* corresponding to the PHB phase decrease with both the increase of the PEO percentage and the cooling rate. The total ΔH_{PEO}^* ($\Delta H_{HTP}^* + \Delta H_{LTP}^*$) of the PEO phase, although undergoing a decrease with increase of PHB content, seems to be

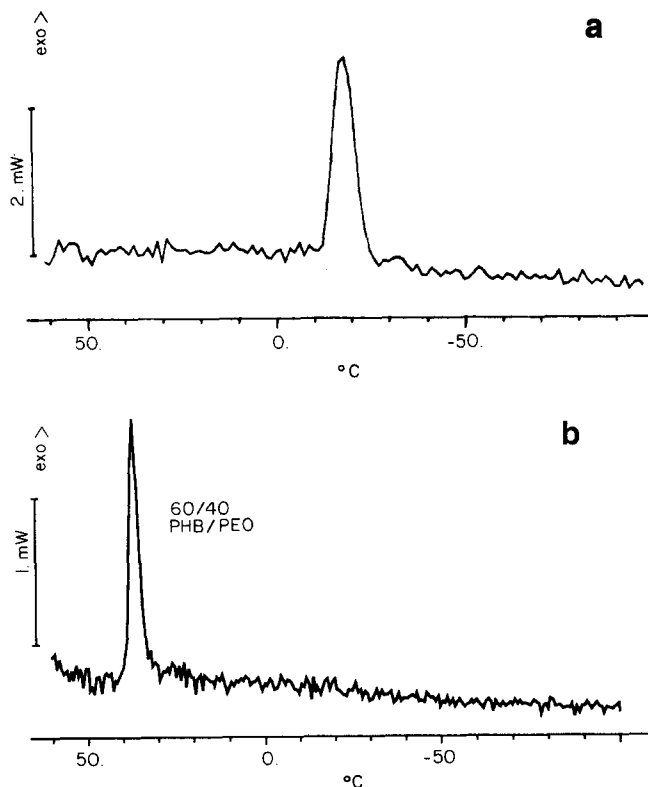


Figure 3 D.s.c. crystallization curves of the PEO component in PHB 60 blend. (a) The sample was cooled at $1^{\circ}\text{C min}^{-1}$ after a non-isothermal crystallization of PHB component at $1^{\circ}\text{C min}^{-1}$. (b) The sample was cooled at $1^{\circ}\text{C min}^{-1}$ after a non-isothermal crystallization of PHB at $20^{\circ}\text{C min}^{-1}$

less influenced by the crystallization rate. Moreover, the temperature corresponding to the maximum of the HTP increases with increase of PEO content at both the cooling rates examined. The maximum of the LTP obtained at $1^{\circ}\text{C min}^{-1}$ exhibits with composition the same trend as the HTP.

In order to establish the influence of crystallization rate of PHB phase on the fractionated PEO crystallization, the following d.s.c. experiment was performed.

Samples of PHB/PEO blends, after melting, were cooled from 200°C to 60°C at a scan rate of $1^{\circ}\text{C min}^{-1}$ to allow crystallization of PHB. The samples were kept at 60°C for about 2–3 min and afterwards they were cooled to -100°C by using different cooling rates, namely 1 and $20^{\circ}\text{C min}^{-1}$. The crystallization thermogram of the PHB 60 blend, where the cooling rate from 60°C to -100°C is $1^{\circ}\text{C min}^{-1}$, is shown as an example in *Figure 3a*. One should note the presence of only the low-temperature peak (LTP). When the scan rate from 60°C to -100°C was $20^{\circ}\text{C min}^{-1}$, the d.s.c. thermogram

Table 5 Temperatures of the maxima $T_{c,HTP}$ and $T_{c,LTP}$ and apparent enthalpies of crystallization ΔH_{HTP}^* and ΔH_{LTP}^* using a scan rate of $1^{\circ}\text{C min}^{-1}$ for neat PHB 60 blend and by adding saccharin (1 and 2% by weight)

Saccharin (%)	ΔH_{PHB}^* (J g^{-1})	$T_{c,PHB}$ ($^{\circ}\text{C}$)	ΔH_{HTP}^* (J g^{-1})	$T_{c,HTP}$ ($^{\circ}\text{C}$)	ΔH_{LTP}^* (J g^{-1})	$T_{c,LTP}$ ($^{\circ}\text{C}$)
0	71	85	no peak		94	-21
1	90	113	48	50	56	-12
2	92	115	108	49	15	-18

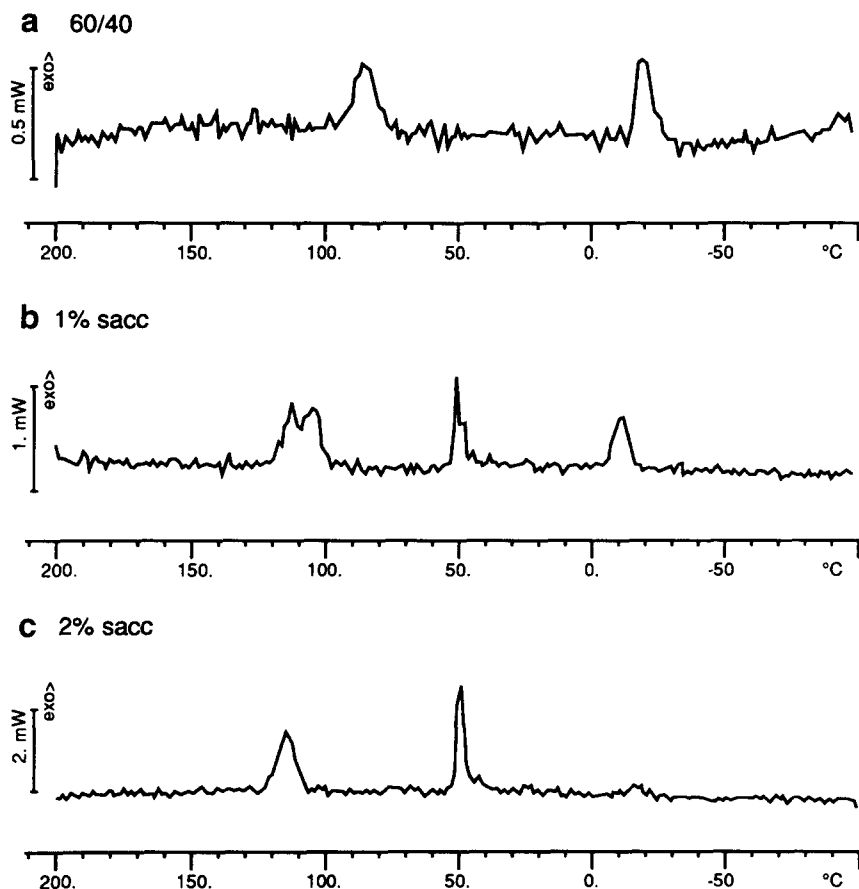


Figure 4 D.s.c. thermograms of PHB 60 blend: (a) neat, (b) with 1% saccharin and (c) with 2% saccharin. The samples were cooled down to -100°C at $1^{\circ}\text{C min}^{-1}$ after melting at 200°C

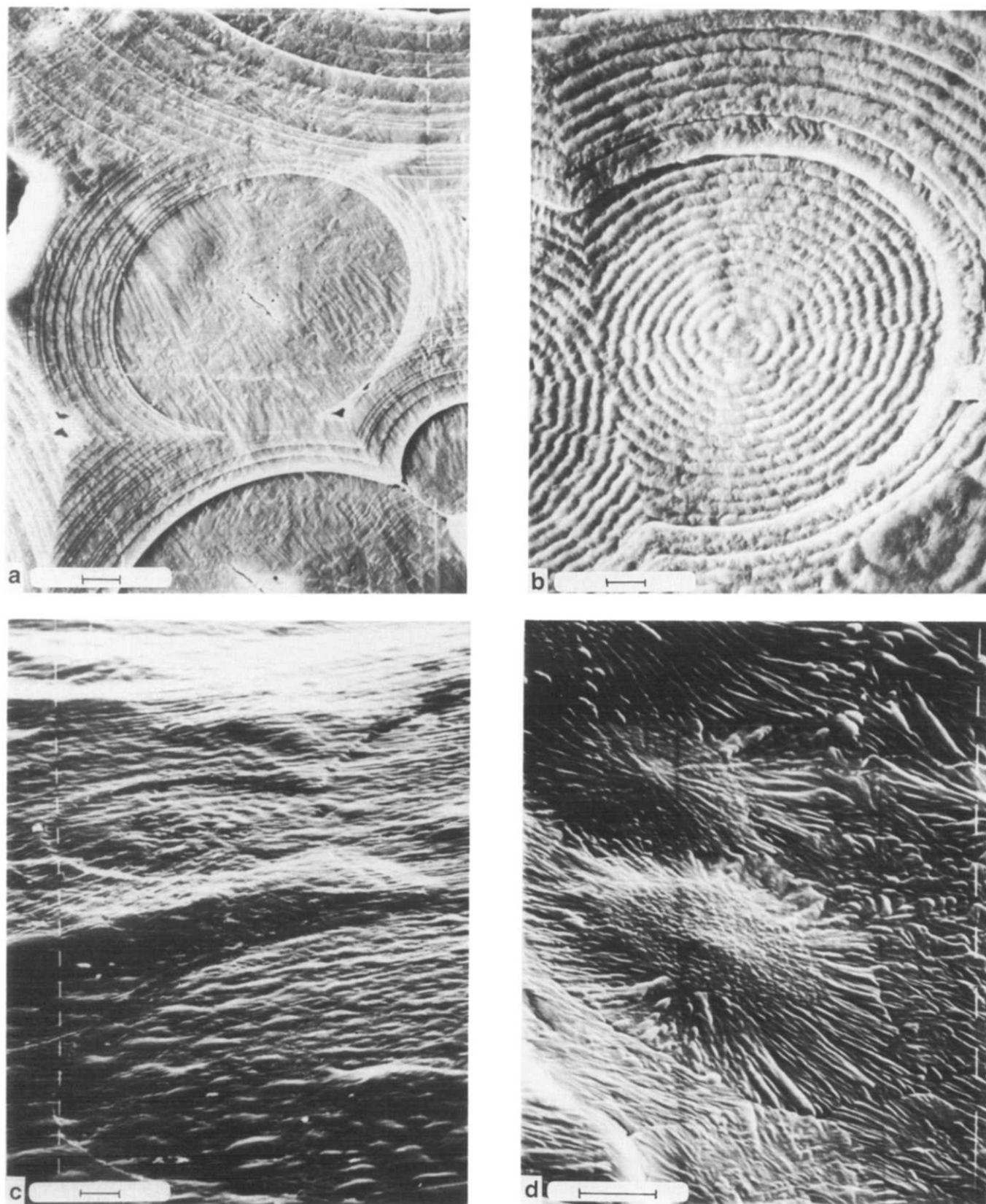


Figure 5 SEM micrographs of samples cooled from the melt to -100°C at $20^{\circ}\text{C min}^{-1}$: (a) PHB 100, (b) PHB 80, (c) PHB 60 and (d) PHB 20 (scale bars represent $30\ \mu\text{m}$)

remained unchanged, showing only the LTP of PEO. On the contrary, the crystallization thermogram of the PHB 60 blend obtained by first cooling the sample from 200°C to 60°C with a scan rate of $20^{\circ}\text{C min}^{-1}$ and then to -100°C with a scan rate of 1 or $20^{\circ}\text{C min}^{-1}$ shows

only the higher-temperature peak (HTP) of the PEO phase for every cooling rate used (see *Figure 3b*, where the cooling rate is $1^{\circ}\text{C min}^{-1}$).

The above findings can be accounted for by considering the data of *Tables 3* and *4*. From such data it

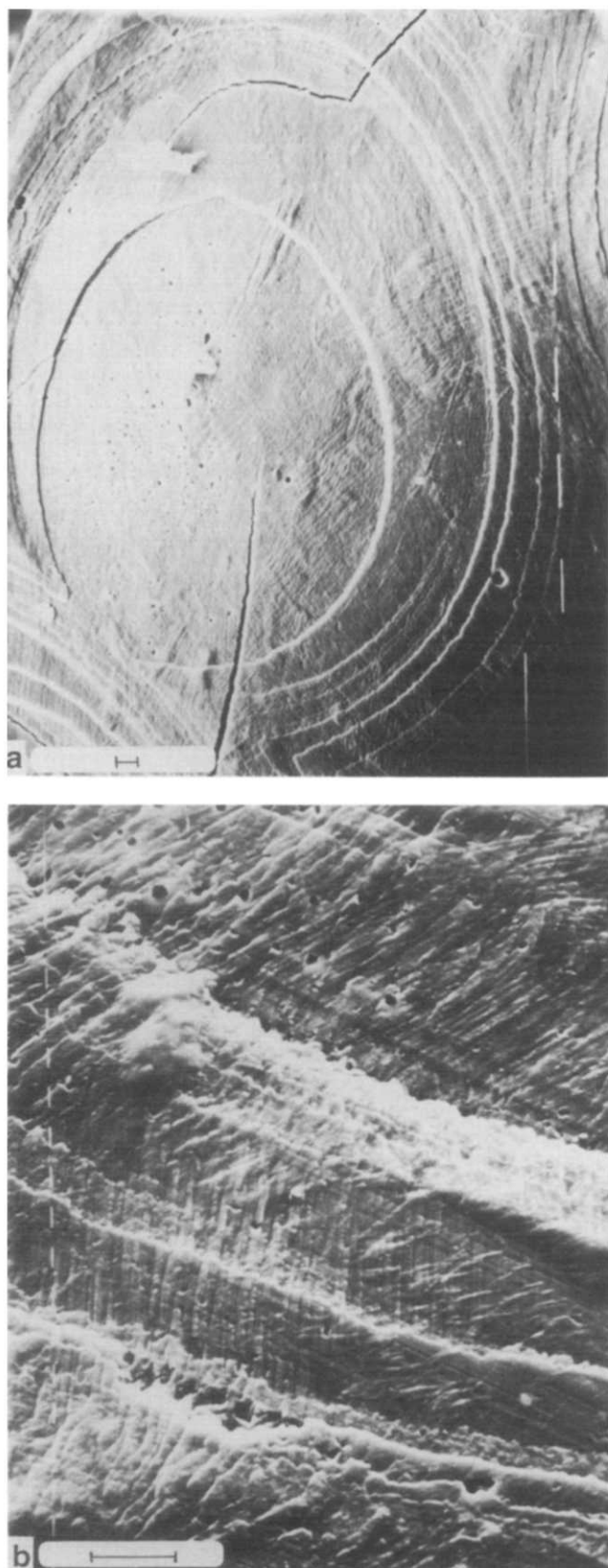


Figure 6 SEM micrographs of samples cooled from the melt to -100°C at $1^{\circ}\text{C min}^{-1}$: (a) PHB 80 and (b) PHB 60 (scale bars represent $50\ \mu\text{m}$)

emerges that the apparent enthalpy of crystallization of PHB is $70\ \text{J g}^{-1}$ for a cooling rate of $1^{\circ}\text{C min}^{-1}$, while for a cooling rate of $20^{\circ}\text{C min}^{-1}$ the value reduced to $56\ \text{J g}^{-1}$. This means that fewer crystals of PHB are formed when the cooling rate is higher. Thus, only some of the heterogeneous particles present in the melt

act as nucleating sites for PHB. Consequently, the remaining heterogeneous particles may contribute to the heterogeneous nucleation mode for PEO.

The fact that only the LTP for PEO is observed when the sample is cooled down from 60°C to -100°C at very low scan rate is easily explained by assuming that in such conditions the PHB utilizes most of the heterogeneous particles to crystallize. Then, PEO molecules may crystallize only according to a homogeneous mode of nucleation.

In order to confirm the hypothesis of fractionated crystallization of PEO for the PHB/PEO blends, a typical nucleating agent of PHB, such as saccharin, has been added to PHB/PEO blends and d.s.c. crystallization carried out after melting at 200°C . The crystallization thermograms performed at $1^{\circ}\text{C min}^{-1}$ of the blends obtained by adding 1% and 2% of saccharin to the PHB 60 blend are compared with that of the plain blend in *Figure 4*. The corresponding apparent enthalpies (ΔH^*) and the maximum crystallization temperatures T_c of the peaks as a function of the saccharin percentage are also reported in *Table 5*. The nucleating agent seems to cause a slight increase of the apparent enthalpy and consequently of the crystallinity relative to PHB. Moreover, an enhancement of these parameters for the PEO component was also obtained in the presence of saccharin. From *Figure 4* it emerges that the addition of saccharin increases the HTP/LTP ratio for the sample containing 1% of this nucleating agent and causes the disappearance of the LTP in the case of the sample containing 2% saccharin. This finding confirms the attribution of HTP and LTP to heterogeneous and homogeneous modes of nucleation of PEO respectively. In fact, a percentage of 2% of saccharin seems to be enough to ensure a sufficient amount of heterogeneous nuclei for the nucleation of PHB while still leaving enough heterogeneous nuclei for the PEO component to allow it to crystallize completely at lower supercooling according to a heterogeneous mode of nucleation.

Morphological investigations

Using optical microscopy it was not possible to observe PEO spherulites even in the more PEO-rich blends⁵.

More interesting information can be deduced from SEM micrographs obtained on PHB/PEO samples after crystallization carried out in d.s.c. equipment. The samples examined have been melted and cooled down to -100°C by using scan rates of 1 and $20^{\circ}\text{C min}^{-1}$.

According to the results previously described, the cooling rate used seems also to control the degree of dispersion of PEO in the intraspherulitic region of the PHB phase. In fact, from the observation of *Figure 5*, where the surfaces of rapidly cooled samples using a scan rate of $20^{\circ}\text{C min}^{-1}$ are shown, it emerges that the PEO domains are located in an orderly way in PHB intraspherulitic regions.

Such domains can be related to the crystallization process of PEO that occurs at higher temperatures (HTP) and thus to predominantly heterogeneous nucleation.

On the contrary the morphology of the surfaces of samples slowly crystallized at $1^{\circ}\text{C min}^{-1}$ to -100°C (see *Figure 6*, where the micrographs of PHB 80 and PHB 60 are shown) does not allow the observation of PEO domains, indicating a finer dispersion of PEO. This finding can be supported by the fact that a slower cooling rate produces a homogeneous nucleation at

low temperature ($\approx -20^{\circ}\text{C}$) with a better and finer distribution of PEO particles in the crystallized PHB phase.

Thus it may be concluded that a different phase structure is observed according to the mode of crystallization of the PEO phase.

CONCLUSIONS

From the results reported it is possible to conclude that complex phase separation occurs during the non-isothermal crystallization from the melt of PHB/PEO blends. In particular, during cooling, after PHB crystallization at temperatures where the PEO phase is liquid, subsequent crystallization of the latter gives rise to a fractionated crystallization phenomenon.

It was demonstrated that PEO crystallization can occur in two steps, at different supercoolings, depending on the crystallization conditions, the thermal history and the cooling rate used to crystallize the PHB phase.

These parameters can produce two different modes of nucleation of PEO, homogeneous (at high supercooling) and heterogeneous (at low supercooling), and consequently

different morphologies. In fact, the SEM analysis has shown a different phase structure according to the mode of crystallization of the PEO component.

The global crystallization rate of PHB can also cause the relative amounts of interlamellar and interspherulitic PEO to vary, since it influences the diffusion process of the PEO.

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