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The effect of seeding on the crystallisation of poly(hydroxybutyrate), and co-poly(hydroxybutyrate-co-valerate)

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Abstract

In order to enhance the rate of crystallisation of polyhydroxybutyrate (PHB), and copolyhydroxybutyrate-co-valerate (CHB/HV), the effect of various seeding agents was investigated. Solid mixtures of PHB containing either saccharin or phthalimide, and a blend of CHB/HV with PHB were prepared. The effect of these materials as nucleating agents was compared with a commercial nucleating agent, boron nitride (BN). In assessing the relative seeding abilities, overall crystallisation rate, spherulite development and nucleation density were measured by DSC and optical microscope. FT-IR microscopy was used to determine the solubility of the nucleating agent in the molten polymer. The conclusions are drawn that saccharin and phthalimide are much less effective as nucleating agents than BN. They are comparatively soluble in molten PHB but are rejected from the crystalline PHB. There was little nucleation by saccharin and phthalimide, and whilst small crystallites of saccharin and phthalimide develop within the boundaries of the spherulite much of the material accumulates in the regions between the spherulites. PHB acted as a nucleating agent for CHB/HV although the activity was not found to be superior to BN as the nucleating agent.

Keywords: Poly(hydroxybutyrate); Hot stage microscopy; FT infrared spectroscopy

1. Introduction

The homopolymer, poly(hydroxybutyrate), PHB, and its copolymer with hydroxyvalerate, CHB/HV, are biodegradable engineering polymers with important commercial properties [1]. Although both biological macromolecules are highly stereoregular with a high degree of crystallinity, the crystallisation rate – temperature dependence is not symmetrical with temperature but is skewed to lower temperatures because of an unusually low nucleation density. Crystallisation on rapid cooling in a mould develops at comparatively low temperatures and is subsequently followed by secondary crystallisation on storage at room temperature [2,3]. This leads to embrittlement as the degree of crystallinity increases logarithmically with storage time and there is a corresponding increase in yield stress and decrease in impact strength [1–3]. If these polymers could be crystallised at higher temperatures, a relatively perfect crystal structure would be produced. The resultant embrittlement would then be inhibited and mechanical performance improved [2,4]. Thermal instability is a feature of all the polyhydroxyalkanoates and is seen at temperatures within a few degrees of the melt temperature [5]. The low thermal stability of PHB and CHB/HV therefore makes the long dwell times in the mould, required to obtain a higher degree of crystal perfection, impractical.

Commercially these polymers are produced by a batch fermentation process [1,3] to give extremely pure material, which results in a general absence of heterogeneities that could act as nucleating agents. To achieve crystallisation within the mould, a nucleating agent, usually boron nitride, must be added. However, in order to produce a more environmentally friendly product, alternative nucleating agents have been sought. Nucleation can occur via an enhanced self-seeding mechanism [6,7] and so PHB crystals were added to the copolymer. Mixtures of PHB containing saccharin and phthalimide have also been prepared and the effectiveness of these reagents compared with one another and also with the more conventional nucleating agent, BN. The effect of changing the melt temperature and crystallisation conditions has been detailed in a previous article along with the effect on the spherulite growth rates and nucleation densities [8]. Both saccharin and phthalimide were found to be less effective as nucleating agents than BN. Crystalline PHB promoted the nucleation of CHB/HV without retarding subsequent growth of the spherulites. However its nucleation activity was very sensitive to the melting temperature and if the melting point of PHB was exceeded

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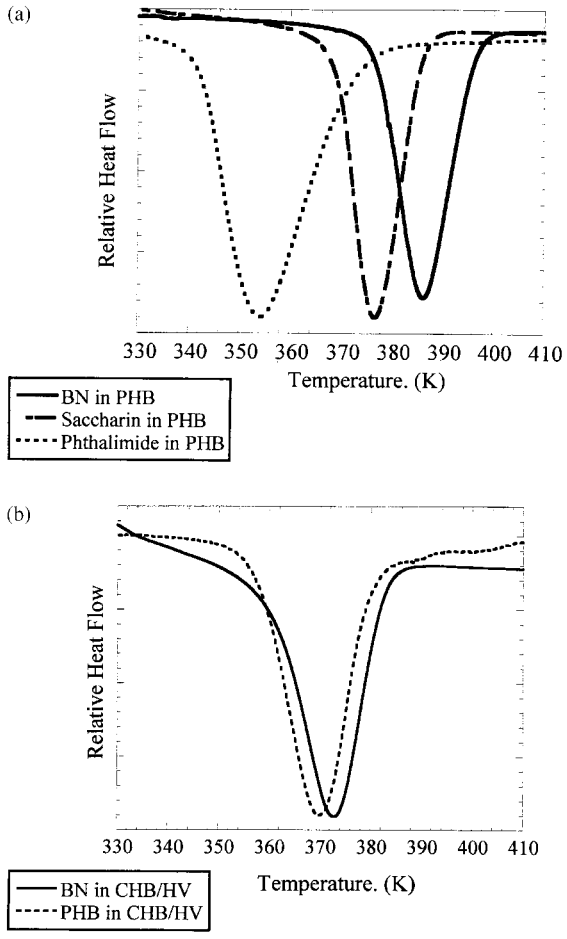

Fig. 1. (a) Variation in the crystallisation onset of PHB blends (b) Variation in the crystallisation onset of CHB/HV blends.

it would no longer nucleate. It is still a viable route to an environmentally friendly product since both polymer and nucleating agent are readily biodegraded.

This article examines the development of crystallinity within each mixture and the relative ability of the additives to nucleate crystallisation.

2. Experimental

Commercial grades of PHB and CHB/HV were supplied by Zeneca Bioproducts as powders and pellets. Saccharin and phthalimide were supplied by Aldrich Chemical Co. Ltd. as fine powders, and were used as received. Mixing was carried out using a Schwabenthan two-roll mill preheated to 463 K. Sheets of the mixtures, 100 × 100 × 1.7 mm^3, were compression moulded on a Moore hydraulic press for 5 min, at 463 K, under a pressure of 10 tonnes. The plaques were quench cooled in ice water to produce an amorphous sheet which was stored below 273 K to prevent crystallisation. PHB, saccharin and phthalimide were each added to the bulk polymer at 1% by weight. These mixtures were compared with the commercial homopolymer and copolymer, supplied by Zeneca Bioproducts with 1% boron nitride, BN, as the nucleating agent.

A Leitz Dialux-Pol polarising light microscope fitted with a Linkam TH600 hot stage was used to view the recrystallisation of the polymers. The temperature was regulated with a Linkam PR600 controller, which controlled temperatures upto 770 ± 0.1 K. Heating rates were between 0.1 and 90 K min^{-1}. Light of constant wavelength was provided with a sodium vapour lamp. The 50-ohm platinum resistor thermometer used was calibrated from the melting point of pure sodium nitrate. The samples were placed in the hot stage sample holder between glass cover slips, fully melted and the development of crystallisation followed on subsequent cooling to the crystallisation temperature.

JEOL 5200 and 5410 scanning electron microscopes were used at 10 keV to view the fracture surfaces of the polymer samples. The specimens were plated with gold to prevent charging up during irradiation with the electron beam.

A Nicolet Magna FT-IR 760 spectrometer was used to measure the infrared spectra on thin film specimens or on samples incorporated into KBr discs in the range 4000–650 cm^{-1}. Between 50 and 100 scans were taken with a resolution of 0.250 or 0.500 cm^{-1}. An IR microscope attachment was used.

A Perkin Elmer DSC, model 2b interfaced and controlled by PC, was used to measure the crystallisation and melting characteristics of circular discs, approximately 10–20 mg, of the polymer, cut from the quenched moulded sheets. The heat flow of the calorimeter was calibrated using the heat of fusion of 99.999% indium, and the temperature calibrated from the melting points of lead, tin, indium and stearic acid. Adjustments were made for thermal lag between the sample and calorimeter.

3. Results and discussion

3.1. Crystallisation rate studies

PHB degrades at temperatures above its melting point [5] and in order to minimise the effect of degradation the seeded mixtures were melted at 460 K for 5 min. This is the shortest period and lowest temperature consistent with complete melting of the sample as determined by the reproducibility of the crystallisation rate at pre-set crystallisation temperatures, T_c. Cooling these melted specimens at 20 K min^{-1} in the DSC separated the relative nucleating abilities of BN, saccharin and phthalimide as indicated by the temperature of the onset of crystallisation and the temperature range over which they crystallised. Fig. 1(a), clearly shows that 1 wt% BN was more effective in nucleating the crystallisation of PHB than the same amount of phthalimide or saccharin. Indeed there was little difference between the crystallisation characteristics of PHB containing 1% phthalimide and PHB alone, suggesting that it had little nucleating ability. When PHB was added to CHB/HV it had a similar effect on the

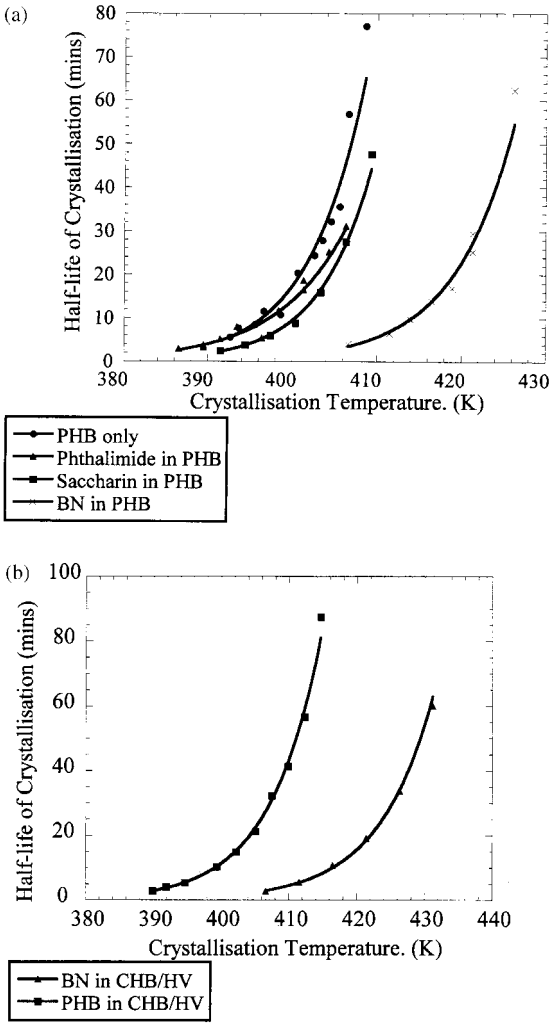

Fig. 2. (a) Variation in the crystallisation half-life of PHB blends (b) Variation in the crystallisation half-life of CHB/HV blends.

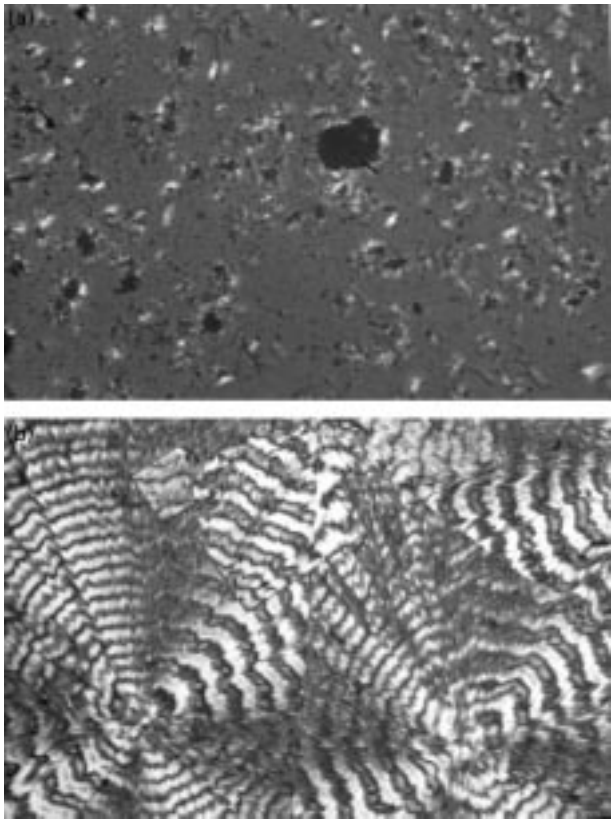

Fig. 3. (a) PHB spherulites developing on CHB/HV crystal fragments (×350) (b) Phthalimide crystals forming in the presence of PHB spherulites, (×350).

onset and temperature range of recrystallisation to that of BN (Fig. 1(b)).

In a previous study isothermal crystallisation studies were carried out at elevated temperatures (380–410 K) on all three PHB mixtures [8]. The conversion-time curves were analysed in terms of the Avrami equation [9], i.e.,

$$\ln(1 - X_t) = -Zl^n \quad (1)$$

relating the degree of conversion, X_t, at time, t, to a composite rate constant, Z, and a mechanistic parameter, n. The n value was observed to be between 2.5 and 3.0, for the PHB mixtures containing saccharin or BN. The sample containing phthalimide had n values between 2.0 and 2.5. These n values are consistent with the growth of heterogeneously nucleated spherulites with increasing rejection of impurities as the n value dropped [10]. The crystallisation half-lives, $t_{1/2}$, were temperature dependent, see Fig. 2(a), but clearly showed that BN, in crystallising the PHB at the same rate but at higher temperatures, was the most effective nucleating agent followed by saccharin and phthalimide as very poor seconds.

Crystallisation rate studies on the 1% PHB–CHB/HV blends also gave n values between 2.5 and 3.0, similar to that for the copolymer containing 1% BN, and again the PHB was less effective in nucleating the crystallisation, see Fig. 2(b).

The development of crystallisation within the PHB and CHB/HV was followed using a polarised light hot stage microscope. Large spherulites tended to form at higher crystallisation temperatures, close to the melting point, an observation which is consistent with a low nucleation density. Addition of the PHB to the CHB/HV produced a greater number of spherulites that had nucleated from the fragments of crystalline PHB, see Fig. 3(a). The unmelted PHB crystalline fragments were active nucleating agents for the copolymer. However, if the PHB was melted in the blend by heating to higher temperatures then the birefringence of the fragments disappeared, the PHB dissolved in the copolymer melt and enhanced nucleation of the copolymer on cooling was lost.

PHB containing 1% BN crystallised from a very large number of nuclei and produced extremely small spherulites which were unresolvable at the magnifications used. With

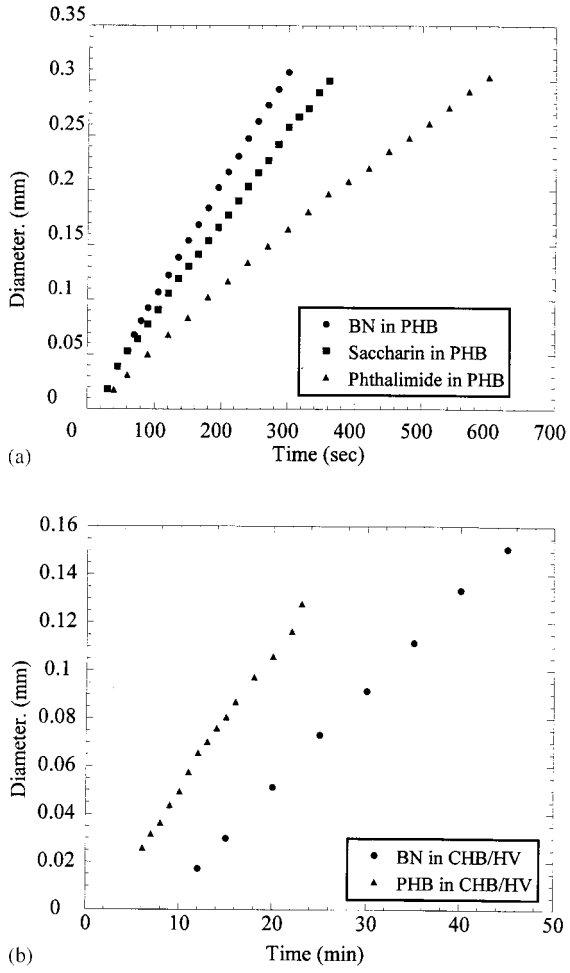

Fig. 4. (a) Radial growth rate of PHB blends (b) Radial growth rate of CHB/HV blends.

the phthalimide and saccharin containing mixtures, only large spherulites were observed on crystallisation from the melt, similar in size to those observed in PHB when there was no nucleating agent present. Thin crystals of phthalimide also formed between the spherulites and the glass cover slips, see Fig. 3(b). There was little evidence that those phthalimide crystals fragments that persisted in the melt acted as nucleation sites on subsequent cooling. The large crystals of phthalimide present on the surface of the spherulites dissolved into the molten polymer on remelting. Saccharin behaved in a similar manner to phthalimide but appeared to be more soluble than phthalimide in PHB.

The radial growth rates of the PHB spherulites were measured at constant temperature, 393 K in the presence of 1% BN, saccharin and phthalimide. The diameters of the spherulites grew linearly with time only in the case of BN. The rate of growth fell off with time in the presence of the other two materials. This fall off was greater with

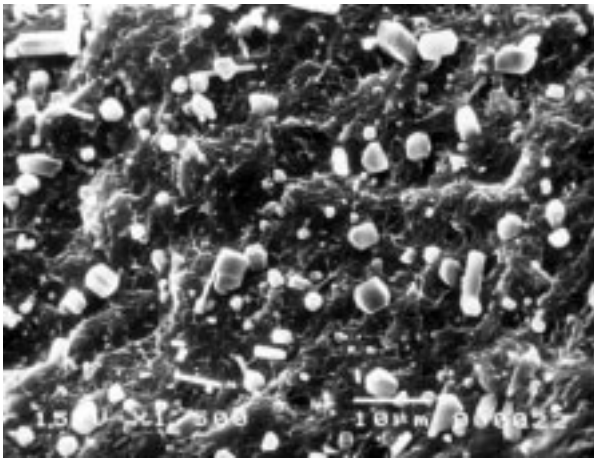

Fig. 5. Brittle fracture surface of PHB in the presence of phthalimide.

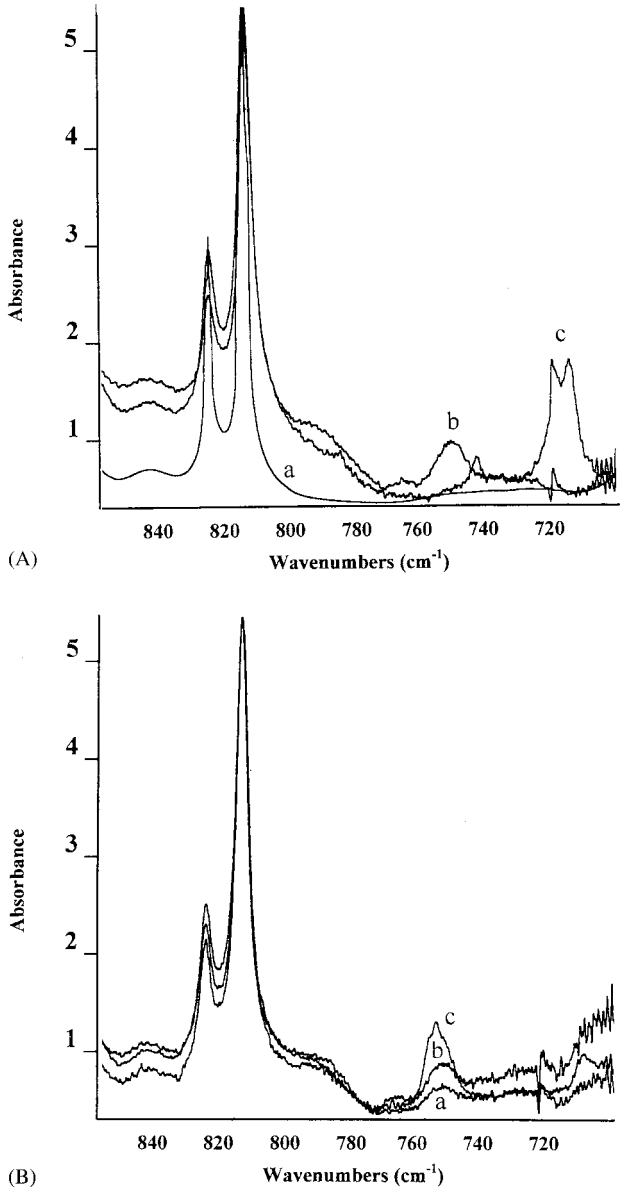

Fig. 6. A. IR spectra of (a) PHB with BN; (b) PHB with saccharin; and (c) PHB with phthalimide. B. IR spectra of different areas around a PHB spherulite in the presence of saccharin: (a) nucleus; (b) mid-radius; and (c) edge.

Table 1
Principal IR absorption bands

Material	Intensity	Position/cm^{-1}	Assignment
Poly(hydroxybutyrate)	strong	840	CH_3 bending
Poly(hydroxybutyrate)	strong	827	CH_2 bending
Saccharin	strong	755	C–H – out of phase
Phthalimide	strong	720	deformation of an ortho
Phthalimide	Medium	747	disubstituted aromatic ring

phthalimide and less with saccharin. The initial rates of growth were similar for all three materials, see Fig. 4(a). The fall off in growth with time was reminiscent of diffusion of impurities retarding growth as discussed by Keith and Padden [11].

The spherulitic radial growth rates were also measured for the copolymer blend but no reduction in rate was observed on addition of PHB and there was no retardation with time, see Fig. 4(b).

3.2. Microstructural analysis

The crystalline samples of the mixtures were broken at liquid nitrogen temperatures to produce brittle fracture surfaces for analysis. Fracturing at this temperature leads to no deformation and does the least damage to the morphology. Both saccharin and phthalimide containing PHB showed similar features with widely dispersed crystals protruding from the surface of the polymer, see Fig. 5. There was no evidence of strong interaction between the matrix and the phthalimide crystals and no evidence of primary nucleation of the spherulites from the large number of such crystals. This suggests that they formed at a later stage to the development of the PHB spherulitic structure.

Selective area analysis of thin films of the crystalline polymer mixtures was carried out on the FT-IR microscope, from which it was possible to determine local composition within the boundary of the spherulites. Different absorption bands in the region 870–700 cm^{-1} characteristic of PHB, saccharin and phthalimide (because of the C–H deformation), see Table 1, were used to determine local concentrations within the spherulites. The system was calibrated from the spectra of the 1% mixtures, using Lambert's and Beer's laws for which:

$$\log(I_0/I) = \varepsilon c l \tag{2}$$

where I_0 and I are the incident and transmitted intensities respectively, ε is the molar extinction coefficient, c the concentration and l the path length.

Analysis of the concentration of each component in different areas of the same sample was carried out. The distances between the areas under examination were small and the films are uniform as regards overall thickness and concentration. Accordingly I_0, c and l were considered to be constant throughout the analysis, and equation 2 can be rearranged thus;

$$\text{Ratio of absorption} = \frac{(\varepsilon_1 c_1)}{(\varepsilon_2 c_2)} \tag{3}$$

where ε_1 and c_1 relate to the polymer and ε_2 and c_2 relate to the nucleating agent. Using a spectrum of the sample as a whole, the ratio of ε_1 to ε_2 was calculated. Fig. 6 shows the spectra of PHB, and PHB containing 1% of saccharin and phthalimide, respectively. Values for the ratio of ε_1 to ε_2 are shown in Table 2. From the ratio of the intensities of the phthalimide and saccharin peaks to those owing to PHB alone the change in concentration of the phthalimide and saccharin within the spherulite was determined. Fig. 6(B) shows the relative absorption patterns for selected areas within the spherulites for the saccharin containing material. From this it was apparent that both saccharin and phthalimide were being excluded from the growing polymer crystallites and accumulated at the interface between the spherulite boundary and the melt. The relative concentrations of the constituents are summarised in Table 2.

Table 2
Concentration of nucleating agent within the spherulites

Nucleating agent	$\varepsilon_1/\varepsilon_2$	wt.%			
		Bulk	Nucleus	Mid radius	Intersection
Saccharin	12.0	1.0	0.4	0.7	1.6
Phthalimide	70.1	1.0	0.6	0.7	2.7

These observations confirm that there is limited accommodation of the saccharin or phthalimide within the spherulite boundary with most being driven ahead of the growth front. The lower proportion of saccharin than phthalimide found at the intersection of the spherulites is because of its greater solubility in molten PHB. Analysis of the spherulites during the growth of the spherulite was not possible since a hot stage attachment was not available for the IR microscope.

4. Conclusions

BN, phthalimide and saccharin have different nucleating abilities for crystallising PHB. BN is the most effective while phthalimide and saccharin are less effective. Phthalimide and saccharin both appear to be soluble in the melt but

are less so in the crystalline regions. During crystallisation any excess material, not accommodated in the amorphous regions, is driven ahead of the spherulite growth front and crystallises out when the solubility exceeds the relevant threshold. The mixtures form a complex-phase system with the phthalimide or saccharin at the intersection of the polymer spherulites. The samples consist predominantly of a small number of large spherulites.

There was less variation in the nucleating ability of PHB and BN in CHB/HV. BN was more effective than PHB but the temperatures at onset of recrystallisation were similar and there was no decline in growth rates over time.

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