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Nucleation of poly(hydroxy butyrate) by epitaxy on nitrogen-containing compounds

S. J. ORGAN, P. J. BARHAM
H. H. Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL, UK

Ammonium chloride (NH_4Cl) is shown to be an effective nucleating agent for poly(hydroxy butyrate) (PHB). However, NH_4Cl only acts as a nucleant when it is in the face centred cubic (fcc) crystal modification. The fcc form of NH_4Cl has a lattice match with PHB; thus it appears that there is some epitaxial growth of PHB crystals on to NH_4Cl. Several more nitrogen-containing compounds that possess a similar lattice match have been investigated and these all show some nucleating effect.

1. Introduction

Poly-3-hydroxybutyrate (PHB) is a thermoplastic polyester produced by bacterial fermentation [1]. Copolymers of hydroxybutyrate with hydroxyvalerate (PHB/HV) have recently become commercially available (ICI "Biopol") and are attracting interest due to their biodegradable and biocompatible properties [2]. PHB and PHB/HV may be melt processed using conventional techniques and typically produce highly crystalline materials. However, extremely low nucleation densities in the pure polymers [3, 4] make processing times prohibitively slow and lead to weak, brittle materials [5]. To reduce crystallization times and improve mechanical properties it is necessary to identify heterogeneous nucleating agents capable of increasing nucleation densities without compromising the "natural" status of PHB/HV. Very few effective nucleating agents are known.

Although there are many reports of studies of the effectiveness of nucleating agents for various polymers in the literature [6–13] these are usually concerned with the measurement of the change in crystallization rate on addition of the nucleant. In a few cases [3, 7, 8] specific nucleation mechanisms are proposed and discussed. Such mechanisms can be divided into two general categories: chemical and physical nucleation. Chemical nucleation occurs when the nucleant either reacts with the polymer itself or forms a new compound that interacts with the polymer [6–8]. The enhanced rate of nucleation arises from the high nucleation rate of the modified polymer. Physical nucleation occurs when the interaction between the polymer and the nucleant surface is of a purely physical nature [3, 9–12]. Examples include the adsorption of molecules at the nucleant surface, the reduction in entropy of the polymer melt due to exclusion of parts of the molecule near the surface and the epitaxial growth of polymer crystals on to the nucleant [3, 9]. The assignment of nucleation mechanisms is made particularly difficult by the need for small nucleating particles (which have a high specific surface area) in practical applications. To identify the nucleation mechanism it is usually necessary to use large nucleating particles where the interface is easily observed.

The purpose of this paper is to report the discovery of a class of nucleating agents for PHB. Our work has suggested that nitrogen-containing compounds with a suitable lattice parameter are potential nucleants for PHB. We arrived at this conclusion through the discovery that ammonium chloride is a particularly effective nucleant. NH_4Cl nucleates only when in the face centred cubic (fcc) crystal form, in which the lattice parameter is closely related to a PHB crystal dimension. Further experiments have shown that other nitrogen-containing compounds with similar lattice parameters act as nucleating agents, with varying degrees of effectiveness. The efficiency of ammonium chloride as a nucleating agent is comparable with that of compounds in current commercial use. It has the added advantages of being cheap, readily available and easily dispersed from aqueous solution. Degradation rates are also likely to be enhanced by the presence of ammonium chloride.

2. Experimental procedure

All the experiments described here were performed using a PHB homopolymer with $M_w = 407\,200$ and $M_n = 235\,300$, measured by gel permeation chromatography. The effectiveness of nucleation was measured by recording the crystallization during cooling of PHB containing 1% additive in a Perkin–Elmer DSC7 differential scanning calorimeter (DSC). Samples of a few milligrams were sealed into DSC pans, heated to 200 °C and held for 2 min to melt completely, then cooled at 20 °C min^{-1} to room temperature. The approximate temperature at which crystallization commenced (the onset temperature), the peak position of the crystallization exotherm (the peak temperature) and the half-width of the peak were measured in each case. Results will be shown for pure PHB and for samples containing technical grade (98% pure) NH_4Cl, technical grade NH_4Cl finely dispersed

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by mixing an aqueous solution with PHB single crystals then drying, high-purity (99.999% pure) NH_4Cl, urea, hydrogen peroxide salt of urea and boron nitride. The nucleating action of ammonium chloride was also examined by optical microscopy and transmission electron microscopy (TEM): TEM was performed on replicas of the surface of nucleated samples, which had been etched with methylamine [14].

3. Results and discussion

Fig. 1 compares DSC thermograms showing crystallization during cooling of pure PHB and PHB containing 1% NH_4Cl in various forms. The corresponding onset temperatures, peak temperatures and peak half-widths are listed in Table I. Large crystals of technical grade NH_4Cl (Fig. 1b) nucleate the PHB reasonably well when compared to the polymer with no additives (Fig. 1a), as evidenced by higher onset and peak temperatures and a narrower peak half-width. A dramatic improvement in nucleation efficiency is obtained if the nucleant is finely dispersed by evaporation from aqueous solution (Fig. 1c). However, when extremely pure NH_4Cl is used there is virtually no nucleating effect (Fig. 1d). This somewhat surprising result can be explained by considering the small exotherm seen in some of the DSC traces at around 170 °C. The exotherm arises from a phase transition in NH_4Cl, from an fcc structure above 184 °C to a body centred cubic (bcc) structure below.

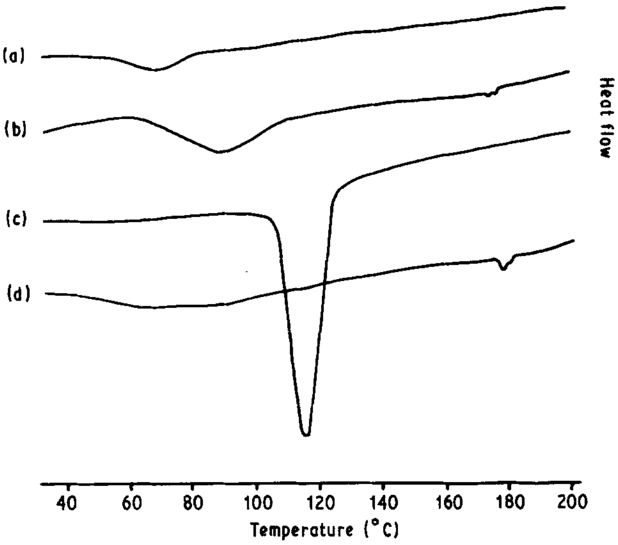


Figure 1 Normalized DSC thermograms showing crystallization during cooling of (a) PHB, (b) PHB + 1 % technical grade NH_4Cl crystals, (c) PHB + 1 % well dispersed NH_4Cl, (d) PHB + 1 % pure NH_4Cl crystals.

TABLE I Influence of 1% additive on crystallization of PHB during cooling measured by DSC

Additive	Onset temperature (°C)	Peak temperature (°C)	Peak half width (°C)
None	85	63	34
Tech NH_4Cl	107	90	21
Dispersed NH_4Cl	109	101	10
Pure NH_4Cl	105	72	52
Urea	83	68	24
H_2O_2 urea	84	72	19

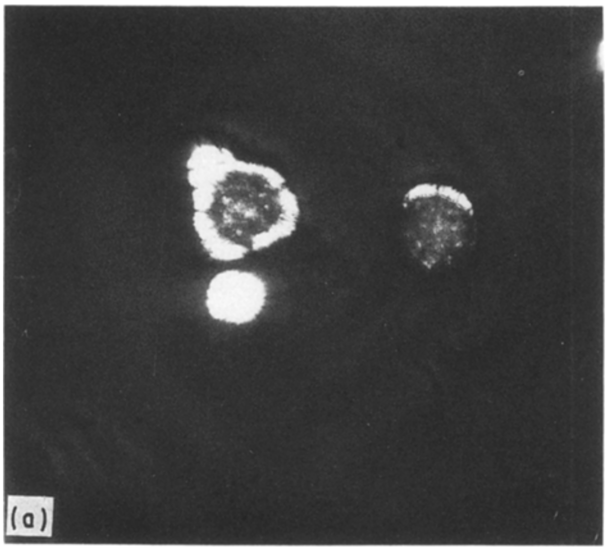
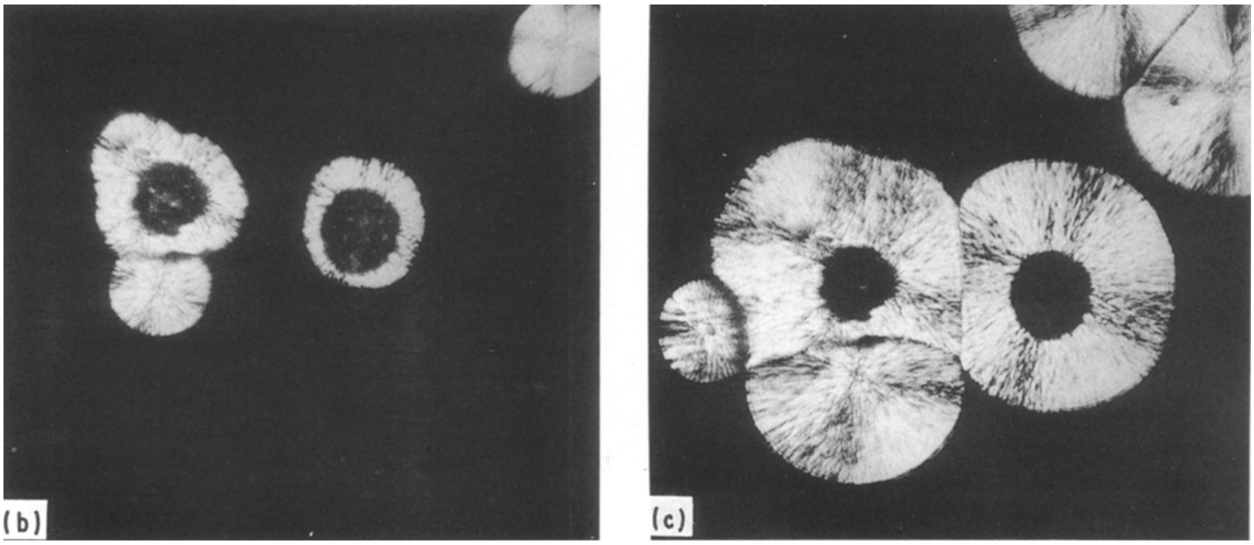


Figure 2 Optical micrographs under crossed polars showing nucleation of PHB by ammonium chloride. (a) $t_c = 3.5$ min, (b) $t_c = 6$ min, (c) $t_c = 13$ min; (a) is underexposed to show nucleation on the top (or botton) surface of the crystals. mag × 20.



This transition is most apparent in the sample containing the purest NH_4Cl (Fig. 1d), slightly smaller when the ammonium chloride is less pure (Fig. 1b) and completely absent in the well-dispersed sample (Fig. 1c) where the crystals are likely to be extremely small. The lattice parameters for the two crystal forms are $d_1 = 0.653$ nm for the fcc and $d_2 = 0.386$ nm for the bcc: the fcc spacing of $2d_1 = 1.31$ nm thus provides a good match for the *b* spacing of 1.32 nm in the PHB lattice. The absence of a phase transition exotherm in Fig. 1c implies that the small crystals of NH_4Cl remain in the fcc form – there are precedents for this in, for example, cobalt. It is likely that impure ammonium chloride may also contain some fcc crystals, which will not be present in the pure sample. Because the nucleating ability of NH_4Cl is related to the amount of fcc crystal present, we propose that the nucleating effect is due to lattice matching between the *b* spacing of PHB and one of the constituents of fcc NH_4Cl. This assumption is supported by observations from optical and electron microscopy.

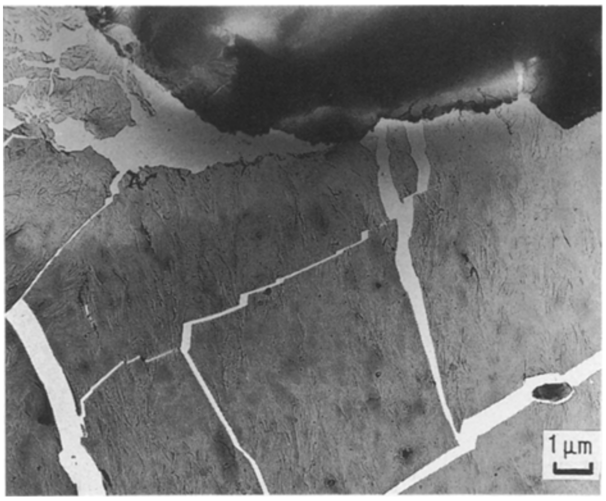


Figure 3 Electron micrograph of a replica of etched PHB showing nucleation along the edge of an NH_4Cl crystal.

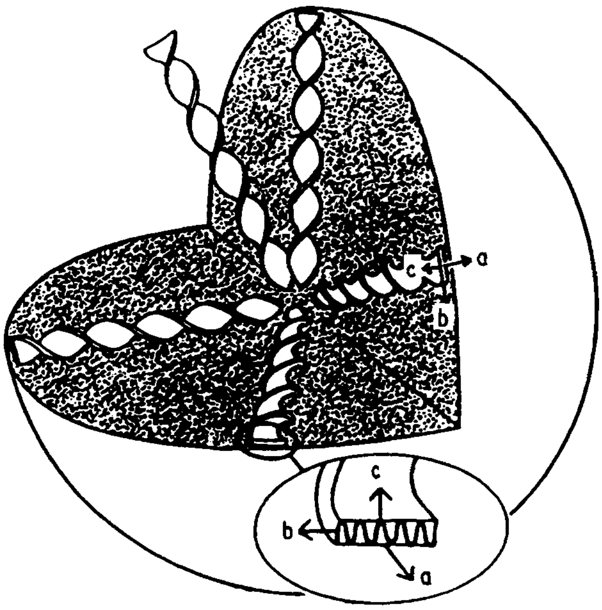


Figure 4 Schematc diagram showing the orientation of the different crystal axes within spherulites of PHB.

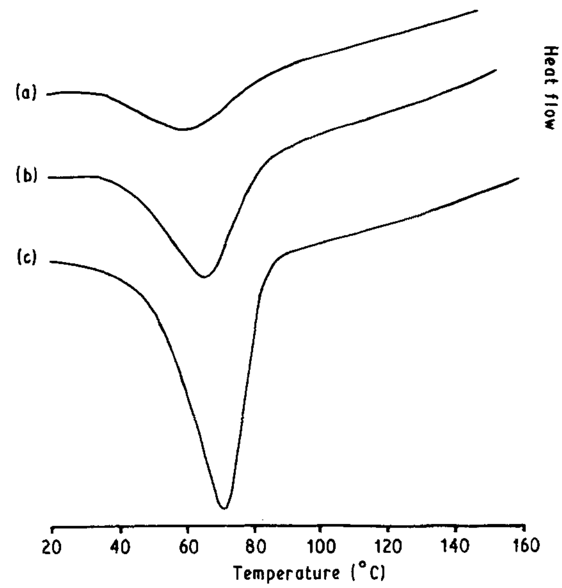


Figure 5 Normalized DSC thermograms showing crystallization during cooling of (a) PHB, (b) PHB+1 % urea, (c) PHB+1 % hydrogen peroxide salt of urea.

Fig. 2 shows a low HV content copolymer growing around some large crystals of NH_4Cl at 110 °C, viewed between crossed polars. Growth has occurred fairly evenly all around the crystals and the appearance of the spherulites is consistent with lamellae growing radially from each point on the surface. This is shown more clearly in Fig. 3, which is a replica from an etched sample of PHB containing large crystals of ammonium chloride. Lamellae are evenly spaced along the edge of the crystal, growing at right angles to it. The orientation of the PHB lattice within a spherulite is shown in Fig. 4 for reference.

To test further the hypothesis that nucleation by ammonium chloride is due to lattice matching and to identify the particular species involved, other compounds were examined for a similar match. Boron nitride, a known nucleant for PHB, provides a good example, having a hexagonal structure with a *c* spacing of 0.669 nm. Nucleation by saccharin is also thought to involve lattice matching [3], although the particular face involved has not been clearly established [13]. Because all these compounds contain nitrogen, we decided to look at other compounds with a suitable lattice parameter to see whether the effect was general. Fig. 5 shows crystallization endotherms obtained during cooling of PHB and PHB containing 1% urea and the hydrogen peroxide salt of urea. Corresponding values of the onset temperature, the peak temperature and the peak half-width are shown in Table I. The hydrogen peroxide salt of urea, with $a = 0.686$ nm, does act as a nucleant (Fig. 5c) while the effect is much reduced with urea (Fig. 5b) which, although possessing a very similar nitrogen-containing structure, does not contain a suitable lattice match. Potassium bromide, which with $d = 0.659$ nm provides an almost perfect match for PHB, shows no nucleating effect at all.

4. Conclusion

A group of nucleants has been identified for PHB; all contain nitrogen in their chemical structure and possess a lattice parameter that closely matches half the *b* spacing in PHB (1.32 nm). The most notable amongst these compounds is ammonium chloride, which in its face centred cubic form has a lattice spacing of 0.653 nm – almost half that of PHB. Pure ammonium chloride undergoes a phase transition to the body centred cubic form on cooling through 184 °C, but this is thought to be suppressed by producing very small crystals or by including impurities in the lattice. The nucleating efficiency of ammonium chloride is comparable with other additives in current commercial use, with the added advantages of being cheap, readily available and non-toxic. The presence of ammonium chloride is also thought to aid biodegradability.

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