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The observation of rapid surface growth during the crystallization of polyhydroxybutyrate

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ABSTRACT

A two stage growth during isothermal cold crystallization of PHB has been observed in the temperature range 5–40 °C when a free surface is present. This growth has been investigated with optical and atomic force microscopy both in-situ and ex-situ. Initially, crystal growth is observed to be composed of lamellae oriented approximately flat-on relative to the free surface. At later stages of growth there can be a change to a distinctly different form of crystal growth that is composed of edge-on lamellae which grow at a substantially higher crystallization rate. This change in growth rate at constant temperature gives rise to curved interfaces between the slower growing flat-on growth and the faster growing edge-on growth. Several possible explanations for this change in growth rate are put forward.

1. Introduction

Crystal morphology can greatly influence the mechanical and optical properties of any crystalline material [1,2]. In the case of semi-crystalline polymer materials it is the morphology of the typical polycrystalline aggregate, the spherulite, composed of individual plate-like lamellae, which affects the physical and mechanical properties of the final polymer material. It should be expected that crystallization behaviour will differ between that in the bulk, and that at surfaces and interfaces. Hence it is important that the crystallization process and conditions that give rise to changes in the crystalline morphology of polymers, especially in relation to surfaces, is well understood so that materials with the desired physical properties can be produced repeatedly and effectively.

Poly(3-hydroxybutyrate) (PHB), a member of the polyhydroxyalkanoates (PHA) family, is a biologically synthesized polyester that has been investigated as a possible biodegradable alternative to more common thermoplastics [3,4]. However due to the high crystallinity and low glass transition temperature of this polymer it generally produces stiff and brittle materials [5]. One environment where PHB and PHAs in general are being utilised is for medical applications and tissue engineering in particular [3]. This material offers a good candidate for the study of some aspects of polymer crystallization due to properties such as a low homogeneous nucleation rate while displaying little heterogeneous nucleation [6]. For this reason, spherulites in samples of PHB can usually be followed over quite large distances during their growth. This, coupled with the fact that crystallization rates are accessible by a number of in-situ observation techniques including atomic force microscopy (AFM) where the capture of a single image can take several minutes, make PHB (and its copolymers [7]) an ideal system to follow the growth of polymer crystals. In addition, the easily accessible glass transition and melt temperatures mean that crystal growth through a whole range of undercoolings can be followed without large temperature gradients between sample and equipment.

Here the crystallization behaviour of PHB is studied with particular focus on crystallization at the free surface of thick (>1 μm) supported films and how this differs from crystallization in the bulk. This thickness is selected so that the films thickness is greater than either the lamellar thickness or the radius of gyration for a molecule of the polymer. It is expected that surface behaviour will differ from that in the bulk [8] and previous experimental [9–11] and simulation [12] work has provided evidence for differences between molecular dynamics, and hence crystallization behaviour, between material near to a surface and that in the bulk. New insights into the effect of a free surface on crystal growth will be important for both an understanding of polymer crystallization in general, and for applications such as thin films that are composed of essentially all surface and interface. The latter are becoming more commonplace, for example as barriers, as membranes, and for applications such as data storage

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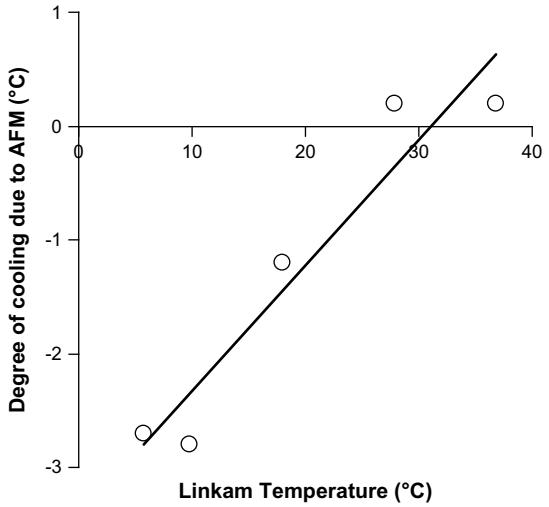

Fig. 1. Calibration plot showing the cooling effect of an AFM tip in close proximity to a heated sample between 5 °C and 40 °C. The linear line of best fit was used to correct recorded temperatures.

and medical implants. In this work an unusual dual morphology is observed during the isothermal cold crystallization of PHB.

2. Experimental method

Poly(3-hydroxybutyrate) was obtained from Fluka ($M_w = 300{,}000$, $M_w/M_n = 2.75$). The PHB was first dissolved in hot chloroform then this solution was precipitated in methanol leaving a fine PHB suspension. The powder was extracted, dried under vacuum and then dissolved in hot chloroform for sample preparation. PHB films were cast from this solution onto glass slides which were then dried under vacuum at room temperature for several hours producing films with thicknesses between 1 and 5 μm.

Optical micrographs were captured on a Nikon Eclipse ME600 attached to a computer controlled Pixelink PL-A742 CCD camera. For accurate temperature control samples were kept on an FTIR600 Linkam hot stage during image capture so that in-situ observations of isothermal crystallization could be made.

AFM images were captured on a Dimension 3100 AFM (Veeco, Santa Barbara) attached to a Nanoscope IIIa controller and a phase extender unit. Tapping Mode™ was employed using Olympus microcantilevers with nominal spring constants of 42 N m^{-1}. Again, in order to facilitate in-situ observations at various crystallization temperatures an FTIR600 Linkam hot stage was used in conjunction with the AFM as in Ref. [13]. Due to the temperature difference that exists between the AFM scan head and the sample with this experimental setup a calibration was made in order to account for the cooling effect of the scan head with sample temperatures above room temperature, and the heating effect of the scan head at temperatures below room temperature (see Fig. 1). This effect is described in detail in Ref. [14] on a slightly different experimental setup. The calibration was produced by looking at *n*-alkane melting points while undergoing AFM observation. All quoted sample temperatures in this work while under AFM observation have had this calibration applied to them.

3. Results

Fig. 2a shows a bright field optical micrograph of a PHB film undergoing crystallization at 23 °C under ambient conditions. The three spherulites in the image area display two circular and clear boundaries in contrast to the single boundary seen around typical spherulites. In the outer regions of the spherulites showing two boundaries the crystal morphology appears rough and less predictable in its ordering than that in the smoother central region.

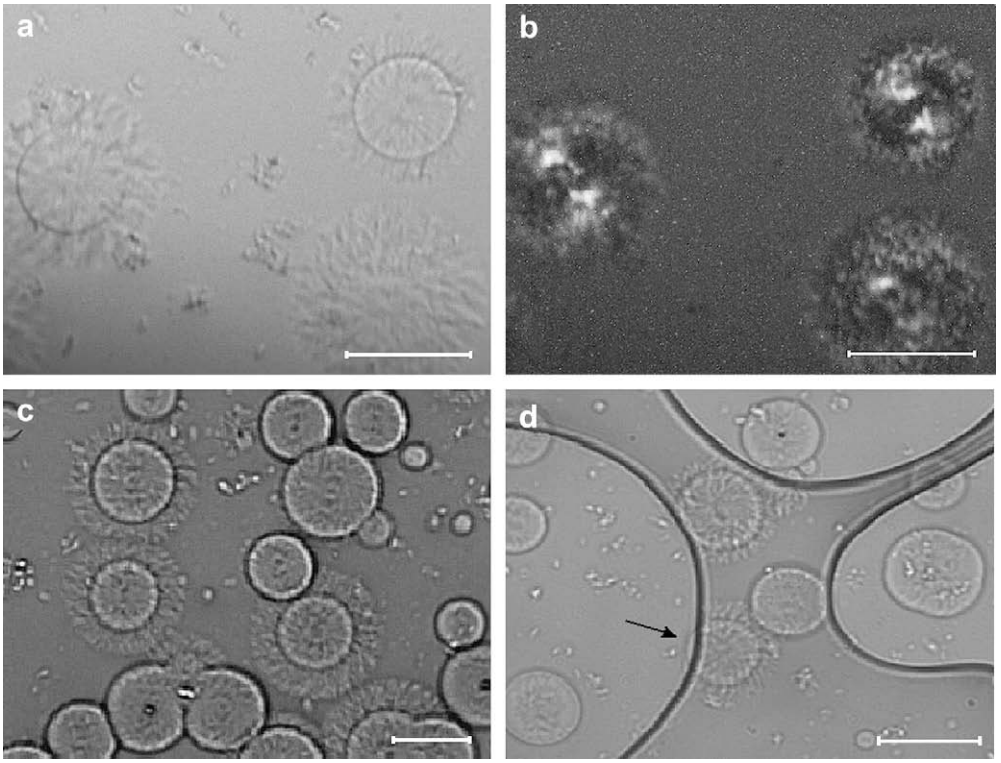

Fig. 2. Optical micrographs captured during isothermal crystallization. (a) 23 °C in air. (b) same area as (a) with crossed polarisers. (c) 24 °C under a nitrogen atmosphere and in the presence of a desiccant. (d) Partially sandwiched PHB film between two glass slides undergoing crystallization at 30 °C. All scale bars represent 20 μm.