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A wide-angle X-ray scattering study of the ageing of poly(hydroxybutyrate)

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The ageing of poly(hydroxybutyrate) at room temperature has been studied using wide-angle X-ray scattering. The observed unit-cell parameters and crystal density did not change on ageing. A small increase in crystallinity was observed during the first 32 h storage. No change in crystallinity was detectable after this time. These results are discussed in the light of theories relating to the embrittlement of poly(hydroxybutyrate).

1. Introduction

Poly(hydroxybutyrate), (PHB), is a biodegradable [1], biocompatible [1] polymer formed by many species of bacteria when they are deprived of certain nutrients [2]. The polymer extracted from *Alicagenes eutrophus* is the most widely used. It has an orthorhombic unit cell [3] with a melting point of 180 °C and a glass transition temperature of between 0 and 30 °C depending on the degree of crystallinity [2]. In its semicrystalline form, it has found commercial use in biodegradable packaging [4] and has undergone trials as a biomedical implant [5, 6]. However, its commercial viability is limited by an ageing or embrittlement phenomenon which occurs after the polymer has been moulded [7–11]. This embrittlement occurs over a timescale of days and weeks and causes a dramatic reduction in the extension to break and an increase in the Young modulus. This levels off after about 150 days [8]. The impact strength drops as the sample is aged. This also levels off after about 150 days [8].

Dynamic mechanical thermal analysis of the glass transition of the amorphous component of the semicrystalline material indicates an increased constraint over the first weeks of storage [12, 13]. Such an effect could result in the changes observed in the bulk properties. However, the cause of this increase in constraint remains a matter of debate. Physical ageing is unlikely to be a sole cause because the embrittlement cannot be fully reversed by heating the sample above the glass transition temperature [8, 10].

DSC studies indicate that some secondary crystallization may occur over a timescale of days [11]. Secondary crystallization may proceed via either a thickening of primary crystal lamellae or an insertion of new crystal lamellae between primary crystal lamellae [14,15]. Although the insertion mode seems to be indicated by some of the DSC data, either mechanism could lead to an increase in constraint of the amorphous phase by increasing the crystallinity. Concerns have been raised about the insertion mode of secondary crystallization occurring to any extensive degree because of the small size of the amorphous layers into which new crystal would have to be inserted [13,16].

Step-wise motion of chains through the crystal has been proposed as a mechanism for embrittlement in other polymers [17], leading to increased constraint in tie chains at the expense of loosening folds on the other side of the crystal. This mechanism is also possible in PHB.

The density of PHB samples has been observed to increase with time, levelling off after the first 50 h or so of ageing [8] – a much shorter timescale than the changes seen in mechanical properties and in the glass transition [8, 12, 13]. The timescale of the changes is clearly important and it has been suggested that more than one mechanism of embrittlement may be in operation [16]. We have reviewed the current theories of embrittlement in more detail in another paper [16].

Knowledge of any changes in the crystal structure or the crystallinity with age is clearly important in the consideration of the mechanism of ageing. This paper reports a study of the wide-angle X-ray scattering profile of a sample of PHB as it is aged. The unit-cell parameters, density of the crystal phase and crystallinity are monitored as a function of ageing time.

2. Experimental procedure

2.1. Sample preparation

Pure PHB homopolymer powder was melt pressed into plates. Care was taken to use the least extreme conditions possible to minimize chain scission [18–20]. After melting, the sample was crystallized in water at 60 °C for 10 min, then removed and allowed to cool to room temperature. At this point the ageing begins; the embrittlement is studied by examining

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samples after they have been stored for a measured period of time, or in some cases, for no time.

2.2. The scattering experiment

A Siemens D500 diffractometer controlled by a Siemens software package was used to examine samples in reflection with a θ–2θ step scan between 5° and $50°2\theta$. Each step increased 2θ by 0.05° and X-rays were collected for 15 s at each step. The sample, a square plaque 50 mm by 50 mm by 1.8 mm thick, was put into the machine directly after processing and the first scan started at once. The scan was repeated at various intervals without removing the sample from the machine or adjusting any machine settings.

2.3. Data correction

A constant background of about 1000 counts was estimated by averaging the intensities of the first five points of the trace and subtracted from all points. The size of this background did not change systematically with ageing time. The reflection geometry introduces a systematic error into the peak positions because the sample is not ideally thin and X-rays are scattered not only from the surface of the sample but also from below it. The correction required in the scattering angle, 2θ, caused by diffraction from points in the sample a vertical distance, x, from the centre of the diffractometer of radius, R, taking into account the absorption coefficient and thickness of the sample is [21]

$$\Delta 2\theta = -\left\{\frac{\sin 2\theta}{2\mu R} - \frac{2t\cos\theta}{R\left[\exp\left(2\mu t \operatorname{cosec}\theta\right) - 1\right]}\right\} \quad (1)$$

The thickness, t, of the samples used in this work was 1.8 mm, and the radius, R, of the diffractometer 200.5 mm. The linear absorption coefficient, μ, is calculated as follows [22]:

$$\mu = \frac{1}{abc}\sum_{\text{cell}} \mu_i \quad (2)$$

where abc is the volume of the orthorhombic cell and μ_i the linear absorption coefficients of the atoms within that cell. Because the PHB unit cell contains four PHB units, the summation over the cell can be simplified to a summation over four identical PHB units. One PHB repeat unit has the formula $C_4H_6O_2$ and values for the atomic absorption coefficients are [23] $\mu_C = 9.170\ \text{cm}^{-1}$, $\mu_H = 0.073\ \text{cm}^{-1}$, and $\mu_O = 30.500\ \text{cm}^{-1}$. Values for a, b and c are taken from PHB fibre data [3] as $a = 0.576$ nm, $b = 1.320$ nm and $c = 0.596$ nm. The correction is relatively insensitive to the exact values used. Using these parameters, a value of $\mu = 8.66\ \text{cm}^{-1}$ is obtained. The correction in Equation 2 was applied to all our measurements of peak positions.

2.4. Data analysis

The CCLRC Daresbury Laboratory program "Fit" was used to model the data*. A series of Gaussian peaks, and a cubic amorphous halo were fitted to the corrected profiles. The trace was fitted up to an angle just beyond the (0 4 0) peak. All traces were treated in the same way so that comparisons might be made between them.

3. Results

Fig. 1 shows the corrected data obtained with the indexing reported in the literature [3]. Any changes are clearly small. Fig. 2 shows the fit obtained and its constituent parts for the unaged sample.

Fig. 3 shows the values of the ratios

$$\frac{2\theta_{0\,4\,0}}{2\theta_{0\,2\,0}} \quad \text{and} \quad \frac{2\theta_{2\,2\,2}}{2\theta_{1\,1\,1}} \quad (3)$$

which should be precisely equal to 2. The quoted uncertainty in the measurement arises from the broadness of the peaks and the fact that X-ray data were only collected at intervals of 0.05°. The agreement is good providing an internal indication that the data corrections applied to the peak positions are acceptable.

The cell parameters a, b and c of the orthorhombic unit cell, calculated from the positions of the (0 2 0), (1 1 0) and (1 2 1) peaks are plotted against the age of the sample in Fig. 4. Ageing causes no change in the cell parameters. The average values of a, b and c are

$$a = 0.5675 \pm 0.0004\ \text{nm} \quad (4)$$

$$b = 1.3058 \pm 0.0011\ \text{nm} \quad (5)$$

$$c = 0.5997 \pm 0.0007\ \text{nm} \quad (6)$$

The density of the crystalline phase may be calculated from the cell parameters. The unit cell of poly(hydroxybutyrate) contains four monomer units [3], each of formula $C_4H_6O_2$, and so weighs 86 a.m.u. The crystal density is plotted against the age of the sample in Fig. 5 and does not change within the uncertainty of the experiment. The average density of the crystalline phase is.

$$\rho_c = 1.285 \pm 0.030\ \text{g cm}^{-3} \quad (7)$$

The crystallinity, obtained by dividing the area under the crystalline peaks by the total area, is plotted against the age of the sample in Fig. 6. It increases from 53.5% to 58.7% in the first 32 h and does not increase thereafter within the uncertainty of the experiment. The sensitivity of the value calculated for crystallinity to the start parameters of the fitting program was assessed by performing each fit ten times. The same value was obtained each time to the third significant figure. Because the sample was not moved during the experiment, the changes observed must be due to changes in the sample.

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* Fit is one of many programs written by the computing staff at Daresbury for the analysis of X-ray data. This one was written by R. Denny as part of the CCP13 project.

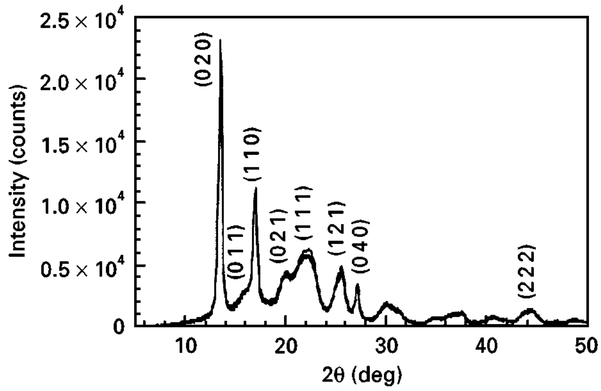

Figure 1 The wide-angle patterns from a sample of poly(hydroxybutyrate) recorded when the sample was, 0, 4.83, 9.66, 24.00, 32.30, 101.75 h old. The differences are not large; careful measurement or profile fitting is required for their examination.

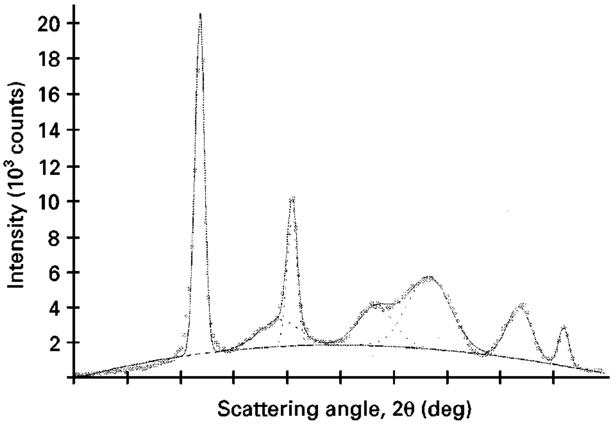

Figure 2 Output of the "Fit" program. Gaussian peaks and a cubic amorphous halo are fitted to the wide-angle trace of unaged poly(hydroxybutyrate). The program provides the positions, heights, widths and areas of all these, and the area under the amorphous halo. This last, together with the area under the trace as a whole, allows the crystallinity of the sample to be calculated.

Peak widths were also obtained from the "Fit" program. In principle, the Debye–Scherrer equation could be used to calculate crystal size. The size of the crystals normal to the $(h\,k\,0)$ planes was clearly larger than that normal to $(h\,k\,l)$, confirming the lamellar morphology. However, the values obtained of the thickness of the crystal parallel to the a, b and c axes were variable and depended upon the peaks used for their calculation. This may be because broadening of diffractometer peaks due to defects within the crystals is also significant. Because of their unreliability, the values are not discussed further here.

4. Discussion

No new peaks appear in the WAXS profile over time. This suggests that ageing does not cause the poly(hydroxybutyrate) crystals to undergo any phase transformations. The crystal structure does not change with time. This is consistent with previous reports [10].

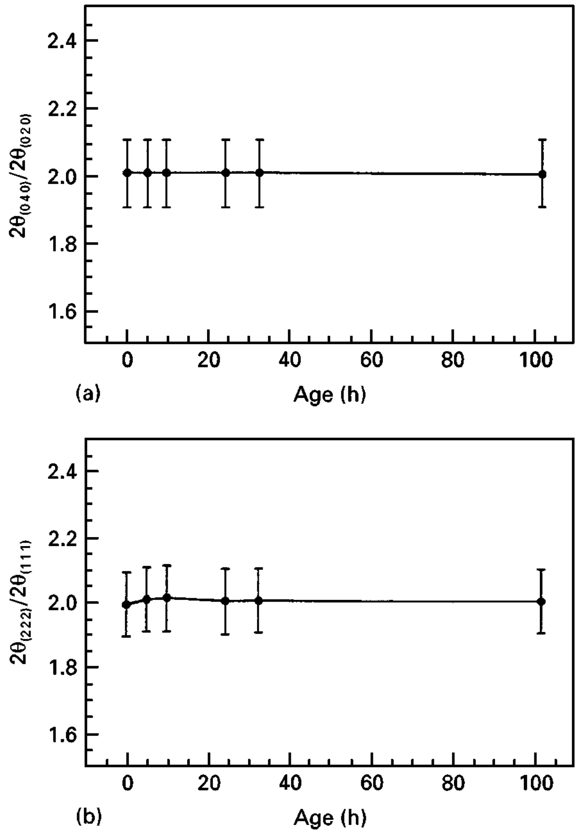

Figure 3 The ratio of the positions of the first and second orders of (a) (0 2 0) and (b) (1 1 1) reflections plotted against time. These values do not deviate from the expected value of 2.

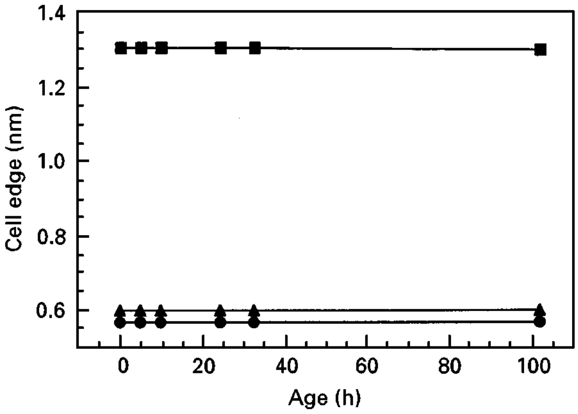

Figure 4 The unit-cell parameters of PHB plotted against time. (●) the a direction, (■) the b direction, (▲) the c direction. The edges of the orthorhombic unit cell do not change as PHB is aged. Whatever else may happen, the crystal structure of PHB is unaffected by the passage of time.

The unit-cell parameters do not change over time. The values measured ($a = 0.5675$ nm, $b = 1.3058$ nm and $c = 0.5997$ nm) differ slightly from the various values in the literature [3, 24–26], the values of a and b being slightly lower while c is slightly higher. The difference may arise from the difference in orientation or may be a systematic error introduced by sample height in the diffractometer. However, because the samples remained in the diffractometer throughout the experiment, all changes in parameters, or lack of them, may be believed.

The density of the crystals does not change over time. The mean value of the density of the crystals of

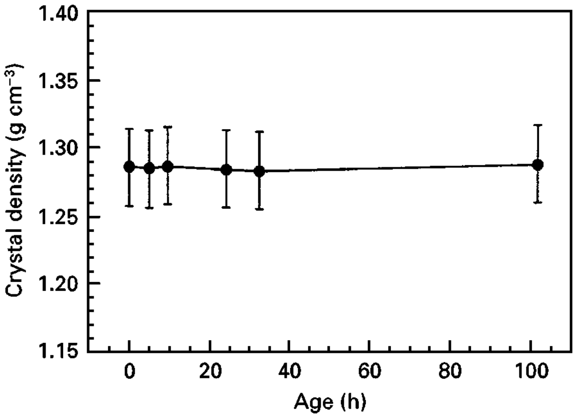

Figure 5 The density of the crystalline phase plotted against time. This does not change as poly(hydroxybutyrate) is aged.

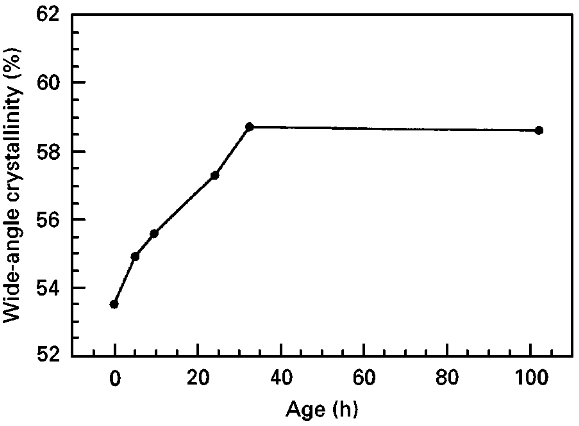

Figure 6 The crystallinity of poly(hydroxybutyrate) as measured by wide-angle X-ray scattering plotted against time. This parameter rises during the first 32 h storage. It then stops to within the accuracy of this experiment.

1.285 g cm^{-3} is a little higher than values from the unit-cell parameters in the literature, though they fall within the quoted uncertainty.

The constancy of the unit-cell parameters indicates that any new crystal which may be formed during ageing is identical in packing to that of the original crystal.

The crystallinity rises slightly with age from 53.5% to 58.7%, and although there is uncertainty in these values arising from the division of intensity into that deriving from crystalline and amorphous regions, the trend is clear as demonstrated by the reported fitting error estimated above.

If the increase in crystallinity is assumed to arise from a thickening of the crystal lamellae during secondary crystallization, a rough estimate of the extent of the thickening can be made. Small-angle analysis reveals that the thickness of a crystal lamella in the *c*-direction in a fresh sample of semi-crystalline poly(hydroxybutyrate) crystallized at 60 °C is 3.6 nm [16]. Molecular modelling [13] suggests that the width of the fold surface between the crystalline and amorphous phases is about 0.35 nm. Subtracting the width of a transition layer from both sides of a crystal and assuming that all the increase in the crystallinity can be accounted for by extension of the crystals parallel to the stems, the total increase in thickness would be very roughly 0.3 nm. This is equivalent to the addition of about half of a *c*-repeat or four bonds to each crystal lamella. The increase in crystal dimensions which would be caused by these changes in crystallinity would therefore be very small.

An alternative cause of increased crystallinity could be secondary crystallization via the insertion mode. This is what seems to be implied by the DSC results of Biddlestone *et al.* [11]. However, the changes they report appear to occur over rather longer timescales than those seen here and the inserted crystals would have to be very thin to fit between the primary crystal lamellae.

The timescale of the changes in crystallinity approximately matches that of the increase in sample density reported by de Koning and Lemstra [8]. The increase in crystallinity here could explain the increase in overall density observed by those authors. However, this timescale is much shorter than the timescale of change seen for the embrittlement process [8]. This perhaps lends support to the idea that there is more than one mechanism leading to embrittlement and that different timescales apply for different mechanisms. Given the short times over which the changes in crystallinity occur, it seems unlikely that they can account fully for the deterioration in mechanical properties observed in PHB.

5. Conclusion

No changes were seen in the unit-cell parameters and hence the crystal density during ageing. Small changes in crystallinity were present, but these occur within the first 32 h storage. The mechanical properties deteriorated over a longer timescale.

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