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The fracture of poly(hydroxybutyrate)

Part I *Fracture mechanics study during ageing*

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Linear elastic fracture mechanics techniques have been used to study the fracture behaviour of the biodegradable thermoplastic poly(hydroxybutyrate). Both the compact tension and double cantilever beam test geometries have been used and give toughness values in good agreement. The variation in fracture toughness with age after moulding has been monitored. It has been found that the strain energy release rate is reduced during ageing, but the stress intensity factor is increased. The primary change during ageing is found to be in the polymers' stiffness rather than its resistance to fracture. © *1998 Chapman & Hall*

1. Introduction

Poly(hydroxybutyrate) (PHB) and its copolymers with hydroxyvalerate are bacterial polyesters which are produced under the trade name BIOPOL^{TM} by Monsanto [1]. These polymers are thermoplastics and therefore have the potential to replace other polymers produced from synthetic routes. The advantages of using naturally occurring polymers instead of synthetic materials lie mainly in their environmental degradability. However, the PHB homopolymer, in particular, and the copolymers to a lesser extent, exhibit an ageing effect independent of environmental degradation, which embrittles the material [2–4].

The mechanical ageing of PHB has been studied using a number of testing techniques. The tensile modulus has been shown to increase linearly with log(age) from ~1.5 GPa in the as-moulded material, to 3.5 GPa after ageing for 100 days [2]. Over the same time period, the impact strength decreases [2], and there is a reduction in the magnitude of the tanδ loss peak [2, 3].

Based on the changes in the magnitude of the tanδ loss peak, it has been suggested [3] that PHB undergoes a process of physical ageing, analogous to that seen in glassy polymers. Although the glass transition temperature of amorphous PHB is ~0 °C [5], it has been suggested that, in semicrystalline polymers, the crystalline regions act as physical cross-links, constraining the adjacent amorphous material and increasing its effective glass transition temperature [6, 7]. The increase in T_g allows the amorphous regions to undergo physical ageing at temperatures above the glass transition temperature measured on the bulk, amorphous material. A linear relationship between log(tanδ) at 25 °C and log(ageing time) has been shown for PHB [3] and this was taken as strong evidence of physical ageing in the amorphous fraction of the polymer. However, it has been shown [2] that annealing at 60 °C, a temperature well above T_g, does not reverse the effect of ageing, as would be expected for physical ageing. Although amorphous PHB stored below T_g does undergo a process of physical ageing [4], it appears unlikely that this is the primary cause of the marked change in mechanical properties of the polymer when stored under ambient conditions.

An alternative explanation for the ageing behaviour has been suggested based on secondary crystallization [2]. It has been shown that, after moulding, there is a slow increase in crystallinity on storage at room temperature. The density of the polymer has been shown to increase significantly over the first 50 h, with a small further increase with prolonged storage times. No significant changes were observed by wide- or small-angle X-ray scattering (WAXS or SAXS) during ageing, so a process of lamellar perfection, in which the amorphous phase between crystals becomes constrained, has been suggested. It is particularly marked in the case of PHB compared to other polymers, as the lamellae are exceptionally thin (the long period is only ~7 nm). This constraint on the amorphous phase is suggested to be responsible for the change in mechanical properties.

Strong support for the explanation based on secondary crystallization has been found from work on the effect of high-temperature annealing on the mechanical properties of PHB. It has been found that, by annealing at temperatures above ~110 °C, the extension to break of the fresh, unaged polymer, is restored and is, to a large extent, maintained on subsequent ageing. During annealing, a lamellar thickening process occurs in which the long period increases from 6.9 nm to 11 nm. By fitting a model to SAXS data [2] it has been deduced that the widths of both the amorphous and crystalline fractions increase. It has been suggested that the increase in width of the amorphous fraction substantially reduces the impact of the secondary crystallization process at the crystal surfaces, and thus results in a final, aged, product that maintains the relatively good mechanical properties of the freshly annealed sample.

In this series of papers, the effect of ageing and annealing of PHB has been studied using fracture mechanics techniques and morphological examination. Linear elastic fracture mechanics has been used in order to define more rigorously what is meant by embrittlement and to understand what impact annealing has on this process. The experiments described in this series of papers have been performed in an attempt to give a broad basis of information on the mechanical behaviour of PHB. It is not intended to give an explanation for the mechanical ageing of PHB, although the results will be discussed in the context of the existing suggestions for ageing mechanisms.

In this paper, the fracture mechanics techniques used are detailed and the results of a study of the ageing process given. Unfortunately, PHB homopolymer undergoes a process of thermal degradation when held in the melt [8], making it difficult to injection mould large items with a molecular weight similar to that found in commercial products. This means that the ASTM standard for sample thickness for plane strain fracture toughness (see, for example, [9]) cannot be obtained. The thickest section material of sufficient size to machine into test pieces, but small enough not to have undergone severe molecular weight degradation, was 3 mm. As this is substantially smaller than the minimum standard thickness (~ 1 cm), two different fracture mechanics testing techniques have been used to ensure that the data obtained were meaningful. The double cantilever beam (DCB) [10–12], which gives data during stable crack growth, has been used due to its transparent analysis, and because it provides well-defined fracture surfaces and crack tips for subsequent analysis. The ASTM standard compact tension test [13] has been used in order to confirm the trends found using the DCB.

In Part II [14], the same techniques are used to study the effect of high-temperature annealing on the ageing process in PHB. In the final paper, Part III [15], the effect of the semicrystalline structure on both the failure of the thick sections used in the fracture mechanics analysis and of thin films will be examined.

2. Experimental procedure

Poly(hydroxybutyrate) homopolymer from batch G044 was used. Boron nitride (1%) was added to the powder as a nucleant for the samples described as "nucleated", and the resulting powder was then melted, extruded as a ribbon into a water bath at 60 °C, and pelletized. The pellets were fed into an Engel ES600/125 injection moulder. Square plaques 150 mm × 150 mm × 3 mm were moulded. These mould dimensions were chosen as they provided a sample of sufficient lateral dimensions to machine easily into the desired test shapes and with the maximum thickness of the available moulds before serious degradation would occur during the moulding cycle [8]. A mould temperature of 60 °C was chosen, because PHB has its minimum crystallization half-time at this temperature, and so gives the quickest production rate of plaques. This is particularly important for PHB as it allows the residence time in the melt to be kept to a minimum, hence reducing thermal degradation. The plaques were stored in a freezer as this has been shown to arrest the ageing process. Subsequent machining was estimated to take half an hour. In all cases it was estimated that samples had aged for 2 h before final removal from the freezer, and were then allowed to "defrost" for another hour before testing. Thus all "fresh" samples were nominally aged for 3 h, and the age of any sample has been taken as (length of time since removal from freezer + 2 h).

Injection-moulded plaques, as described above, were machined into DCB test pieces as shown in Fig. 1. A slot was machined down the centre of the sample as otherwise the advancing crack will tend to wander and break off one of the "arms" [10, 12]. The slot was machined on each side, using a slotting saw with a width of 0.0254 mm, to a depth of 0.5 mm, giving a 2 mm sample thickness, B', to fracture. This thickness was independently measured for each sample as the measured value of toughness is very dependent on the value of B'.

A photocopy of a steel rule with 0.5 mm gradations was glued to one arm of the test piece, allowing crack length to be measured to the nearest 0.5 mm. A crack was initiated at the start of the slot using a razor blade. Steel pins, 4 mm in diameter, were placed in each of the holes in the test piece arms. Each pin was then placed into the opposing jaws in a 50 kg load cell on an Instron mechanical testing apparatus.

The crosshead on the Instron was driven into tension at a speed of 5 mm min^{-1}. Crack length, a, load, P, and deflection, u, (i.e. crosshead displacement) were simultaneously measured.

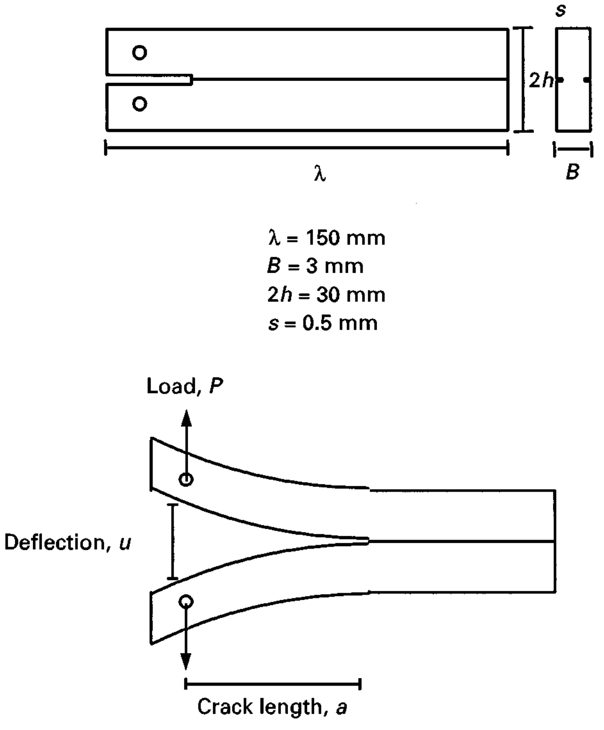

Figure 1 A sketch of a double cantilever beam test piece.

2.1. Analysis of the double cantilever beam

Values of the critical strain energy release rate were obtained using

$$G_c = \frac{P^2}{2B}\frac{dC}{da} \tag{1}$$

where the compliance $C = u/P$ [9].

Fig. 2 shows a typical load–deflection curve plotted from the collected data. Although it is common to fit a function to the compliance, based on an analysis of the geometry (for example a simple beam analysis would give $C = (8a^3)/(EBD^3)$, where D is the height of one beam and E is Young's modulus), another possibility, and the one adopted, is to obtain a compliance calibration curve for each individual sample. This method was decided upon as it is known that the modulus of PHB varies with age. Fig. 3 shows a typical compliance versus crack length curve with the fitted cubic equation, which was then used as the compliance callibration curve. R^2 values of ~ 0.99 were generally obtained for the curve fitting. Similar curves were obtained for each test, the equation differentiated and the result substituted back into Equation 1. By using the relevant values of P, B and a, a value of G_c was obtained for each data point and the average for each test taken to give a toughness value for the sample.

In order to obtain critical stress intensity factor, K_c, data the formula by Fichter [16] was used. This analysis gives

$$K_c = \frac{P}{Bh^{0.5}}(12)^{0.5}\left(\frac{a}{h} + 0.6728 + 0.0377\frac{h^2}{a^2}\right) \tag{2}$$

Fig. 4 shows the K_c and G_c data from a typical single test piece plotted against crack length. Although there is some scatter, there is no trend which may provide cause for concern over the validity of the test procedure. In all cases the K_c and G_c values stated in the text are the average of the values obtained for all the crack lengths measured.

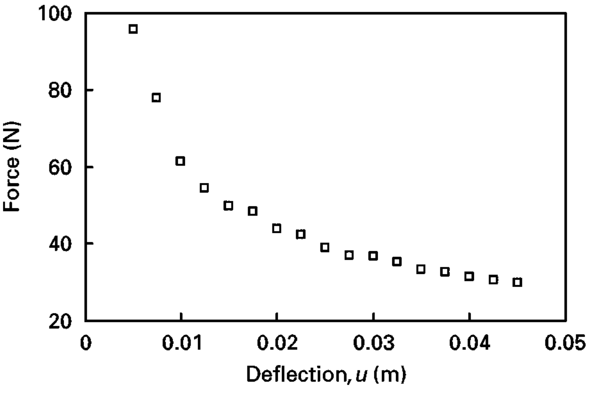

Figure 2 A graph showing the variation of load with crosshead deflection for a typical double cantilever beam test.

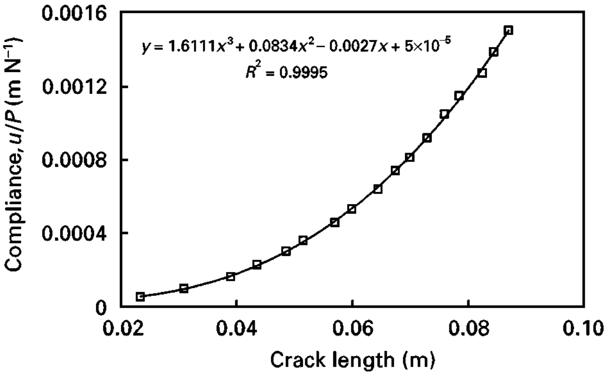

Figure 3 A graph showing the variation in compliance (u/P) with crack length with a fitted cubic equation.

2.2. The compact tension test

Compact tension test pieces [13] were cut from the injection-moulded plaques to the dimensions shown in Fig. 5. A blunt central slot was machined using a band saw, and then a sharp pre-crack, at least 5 mm long, was made by gently tapping a razor blade into the end of the slot. Values of K_c were obtained as described elsewhere [13].

2.3. Ageing

Temperature is known to have an effect on fracture toughness in viscoelastic materials such as PHB and, as water and atmospheric humidity have been shown to affect the crystallization of PHB [17], it is possible that variations in humidity may affect the polymers' mechanical properties. In order to ensure that the conditions on the day of testing were not influencing

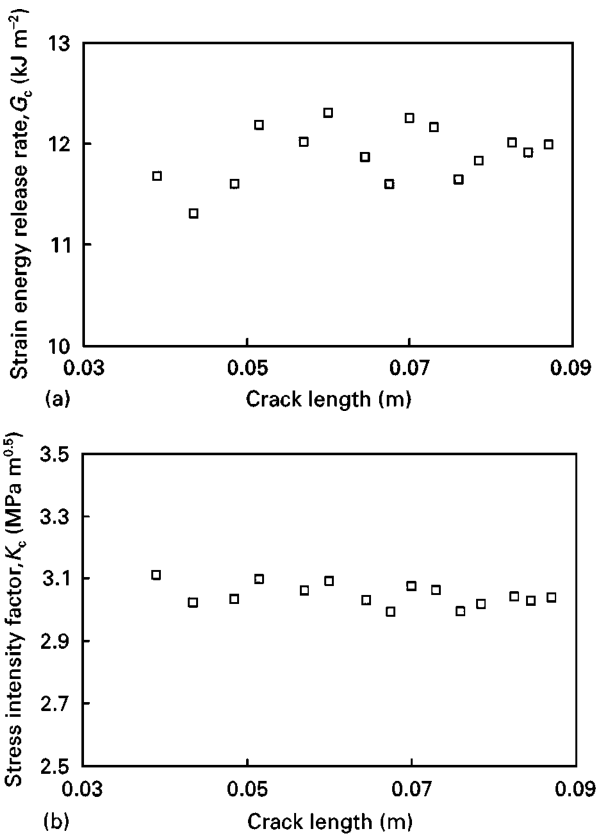

Figure 4 A series of graphs showing (a) G_c and (b) K_c data plotted against crack length for a single double cantilever beam test. There is no significant trend in the data with crack length.

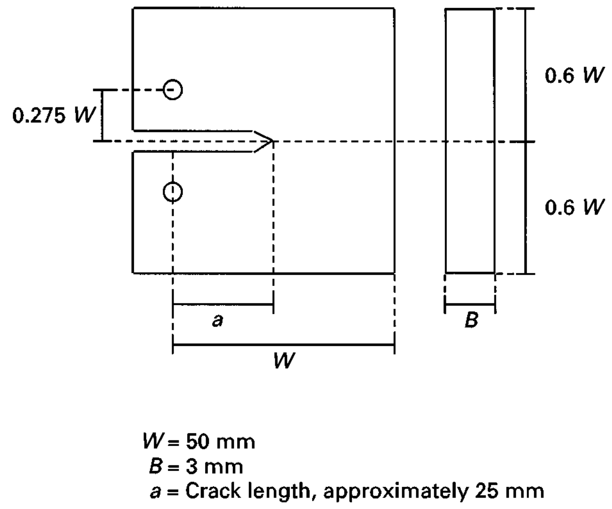

Figure 5 A sketch of a compact tension test piece.

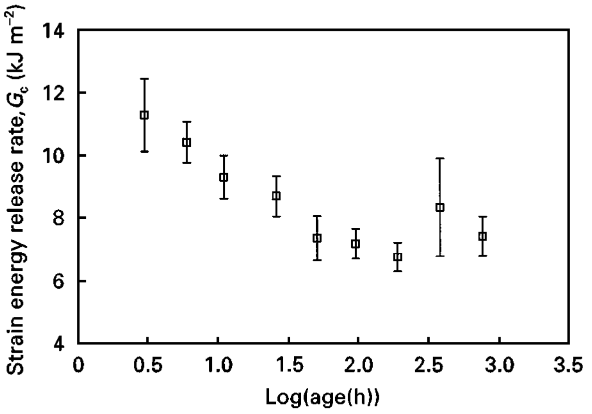

Figure 6 A graph showing the variation in strain energy release rate, G_c, with ageing time for unnucleated PHB, using the double cantilever beam test geometry.

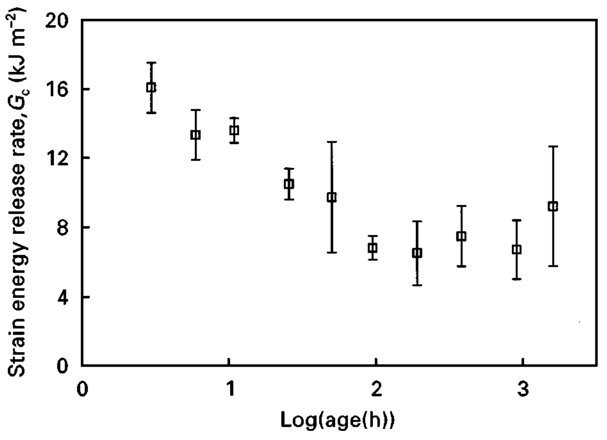

Figure 7 A graph showing the variation in strain energy release rate, G_c, with ageing time for nucleated PHB, using the double cantilever beam test geometry.

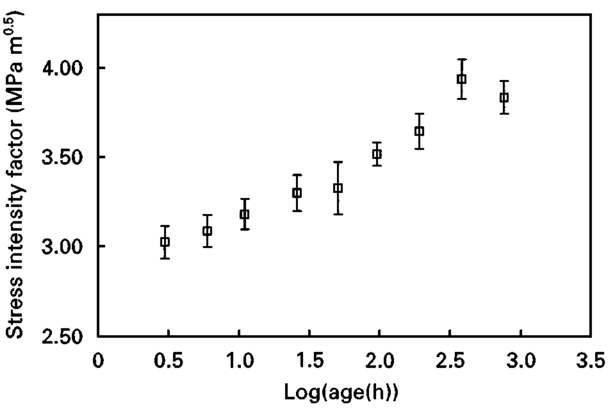

Figure 8 A graph showing the variation in stress intensity factor, K_c, with ageing time for unnucleated PHB, using the double cantilever beam test geometry.

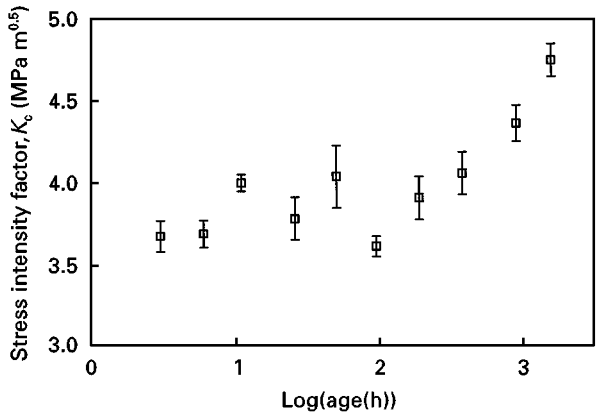

Figure 9 A graph showing the variation in stress intensity factor, K_c, with ageing time for nucleated PHB, using the double cantilever beam test geometry.

the toughness values obtained, all the tests on aged samples were carried out on a single day. In order to do this, test pieces were removed from the freezer at different lengths of time before the test day and kept at room temperature in order to "age". All samples in a given ageing batch were then tested on the same day. This procedure was adopted for all ageing tests unless otherwise stated in the text. For each "age", two DCB tests and four compact tension tests were performed.

3. Results

Figs 6–9 show fracture toughness data obtained using the double cantilever beam test geometry. Fig. 6 shows the variation in strain energy release rate, G_c, with log(age) for unnucleated PHB. It can be seen that G_c decreases approximately linearly over the first 8 days. After this, the values of G_c rise slightly and level off at a value of $\sim 8\,\mathrm{kJ\,m^{-2}}$. Fig. 7 shows the variation in G_c for the nucleated homopolymer, which decreases linearly to a value of $6\,\mathrm{kJ\,m^{-2}}$ after 4 days before levelling out.

Fig. 8 shows the variation in stress intensity factor, K_c, with log(age) for the unnucleated homopolymer. It is clear that the toughness as measured by K_c increases linearly with log(age). Fig. 9 shows the data for the nucleated polymer, which follows a similar trend.

Figs 10 and 11 show fracture toughness data obtained using the compact tension test. Fig. 10 shows the variation of K_c with age for the unnucleated homopolymer. Fig. 11 shows the corresponding graph for the nucleated polymer. In both cases, although the

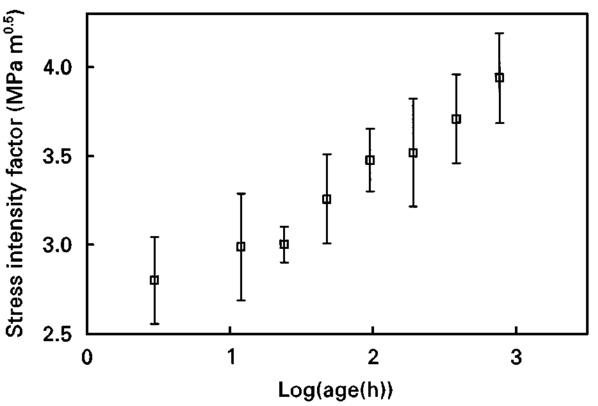

Figure 10 A graph showing the variation in stress intensity factor, K_c, with ageing time for unnucleated PHB, using the compact tension test geometry.

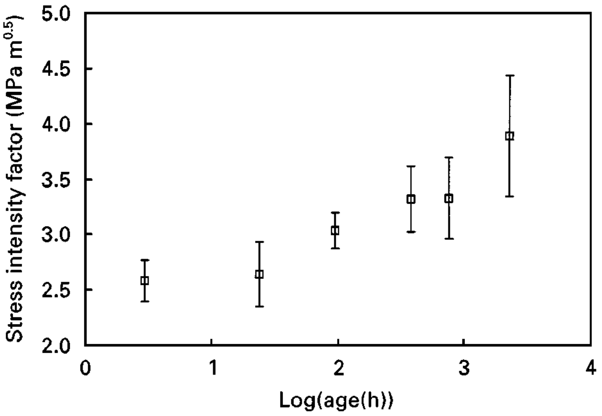

Figure 11 A graph showing the variation in stress intensity factor, K_c, with ageing time for nucleated PHB, using the compact tension test geometry.

scatter is quite large, there is clearly an upward trend in the value of K_c during ageing. The agreement with the K_c data taken from the DCB is good, and can be regarded as convincing confirmation of these values. The value for the fresh sample agrees well with the value given elsewhere [8] of 3.0 MPa m$^{0.5}$.

4. Discussion

Due to the tendency of PHB homopolymer to undergo thermal degradation during injection moulding, it was not possible to obtain samples sufficiently thick to satisfy ASTM standards for plane strain fracture toughness testing. The stress state across the thickness of the sample will vary and it is unlikely that any single state will dominate, although the presence of slots in the DCB specimens will increase the constraint. Both the double cantilever beam and compact tension samples give similar values for K_c despite having different thicknesses. In some previous fracture mechanics studies of polymers, it has been found that conservative estimates of fracture toughness can be obtained using samples that do not reach ASTM thickness criteria [18]. In all the fracture tests reported here there was no evidence of shear lip on examination of the fracture surfaces or of significant crack tip bowing, as might be expected if there was a marked difference in the stress state across the sample thickness. For the purposes of comparison of fracture toughness values during ageing and annealing, the data presented in this paper and in Part II are acceptable. However, the treatment of the actual values obtained as truly conservative estimates of the plane strain fracture toughness should be approached with some caution.

The DCB and CT test geometries give a consistent set of fracture mechanics data during the ageing of PHB. There is very little difference between the toughness values measured on the nucleated and unnucleated samples, and so, although commercial products generally contain nucleating agents, it is reasonable to assume that observations made on either system are applicable to both.

During ageing, the strain energy release rate at fracture decreases in the expected way, showing that there is a reduction in fracture resistance. However, the stress intensity factor actually increases on ageing. This result is surprising, as it would seem that the embrittlement process in PHB actually results in an increase in fracture toughness. However, the K_c measurement gives an index of the stress level near the crack tip which is necessary to cause fracture, and as such is equivalent in many ways to a measure of the material's strength. It is not necessarily surprising that, with an increase in the modulus and tensile strength, there is also an increase in K_c. This behaviour indicates that the ageing process in PHB is not simple embrittlement. Similar behaviour, in which K_c increases while G_c decreases, has been observed in silica particle-filled epoxy resin composites [19]. In this engineering plastic it is the K_c behaviour which is more important, as it is this that will influence its structural properties. Unfortunately, PHB's main market is as a packaging polymer and it is thus impact resistance and an ability to survive large strains that is important. G_c is the more relevant fracture criterion in this case and its reduction on ageing confirms the premise that the ageing process is detrimental.

One explanation for the ageing is based on secondary crystallization [2]. The variation in toughness on ageing is explicable in these terms. It might be expected that a tightening of the amorphous phase would result in an increase in the stress levels which the material could survive. This tightening would, however, clearly reduce the ability of the chains to flow and plastically deform, so a reduction in G_c would be expected.

5. Conclusion

It has been shown that consistent fracture toughness data can be obtained for PHB. The variation in G_c and K_c during the mechanical ageing of PHB has been reported in order to provide a basis of fracture data on which subsequent studies of the ageing phenomenon can draw.

It has been found that the ageing process does not consist of a simple embrittlement, but rather a reduction in the energy dissipating properties of the material, coupled with an increase in its ability to survive high stress levels. The primary change during ageing is in stiffness, and it is suggested that, for some applications, the aged material may actually perform better than the fresh polymer. However, as PHB's unique biodegradability suggests a packaging market, toughening procedures, such as the use of copolymers, plasticisers, or the high-temperature annealing process studied in Part II, are likely to be necessary to obtain optimum performance.

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