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The fracture of poly(hydroxybutyrate)

Part II *Fracture mechanics study after annealing*

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The fracture behaviour of poly(hydroxybutyrate) (PHB) after high-temperature annealing has been studied using linear elastic fracture mechanics techniques. The effect of the annealing temperature on the polymers' fracture toughness both initially and after re-ageing is examined. Annealing at temperatures of 120 °C or above is found to result in an improvement in both the critical stress intensity factor and the strain energy release rate measurements of fracture toughness which is largely maintained on re-ageing. A more detailed study of the re-ageing behaviour after annealing at 130 °C finds G_c to remain approximately constant but K_c to increase slightly with age.

1. Introduction

In the previous paper in this series [1], linear elastic fracture mechanics techniques were used to study the mechanical ageing process of poly(hydroxybutyrate) (PHB) held under ambient conditions. It was found that, during ageing, the critical strain energy release rate decreased while the critical stress intensity factor increased, resulting in a product less suitable than the fresh polymer for packaging applications. However, it has been observed that the application of a simple high-temperature annealing process [2] considerably improves the polymers' mechanical properties and returns the extension to break to a value approaching that seen in a fresh unaged sample. On subsequent re-ageing these improved properties are to a large extent maintained. This annealing effect has been used as supporting evidence [2] for the suggestion that the ageing process is caused by a process of secondary crystallization and perfection at the lamellar surfaces, as described in more detail in [1].

In this paper the same fracture mechanics techniques described in [1] have been used in a study of the annealing process. A brief examination of the effect of annealing temperature has been made to confirm that the fracture toughness follows a similar trend with annealing temperature as seen in the other mechanical properties [2]. A full study of the effect of annealing on subsequent re-ageing has been made on samples annealed at 130 °C as this was the annealing temperature commonly used by Zeneca Bioproducts Business.

The annealing process is found to result in a product with substantially improved fracture properties. Not only is the strain energy release rate returned to a similar value to that seen in the unaged polymer, but also the stress intensity factor maintains and improves upon the high values seen after ageing, resulting in a product of greatly improved toughness for all potential applications.

2. Experimental procedure

PHB homopolymer from batch G044 was used. 1% boron nitride 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.

Injection-moulded plaques were machined into test pieces as detailed previously [1]. All samples were aged for 1 month under ambient conditions before being annealed in an oven pre-heated to the desired temperature. By pre-ageing the samples in this manner before annealing, the effect of the ageing process normally observed, and that seen after annealing, could be separated. The samples were held at the annealing temperature for 20 min, removed and allowed to cool to room temperature. Samples were held at room temperature for different times before testing. This procedure was used for the tests on annealed samples as the variation in fracture toughness obtained on samples tested on different days was small compared with the large differences which could be imposed by small variations in the temperature of the annealing oven.

The temperature at which a sample is annealed is of primary importance to its subsequent re-ageing behaviour [2]. A series of preliminary tests were performed to assess the effect of annealing temperature. Annealing temperatures of 65, 80, 95, 110 and 120 °C were used. Five double-cantilever-beam (DCB) samples were annealed at each temperature, using the process detailed above and tested in the manner described in [1]. Two samples were tested immediately after annealing, one after ageing for 1 day, and two more after ageing for another 335 days.

A full study of the effect of subsequent ageing after annealing at 130 °C for 20 min was carried out. For each age, after annealing, two DCB samples and, in some cases, four compact tension samples, were tested. Only a few compact tension tests were performed in order to confirm the K_c values obtained using the DCB.

3. Results

Fig. 1 shows the variation in G_c with annealing temperature at various lengths of time after annealing. Annealing at 65 °C has little effect on G_c, and it remains approximately stable on subsequent ageing. At 80, 95 and 110 °C there is an initial improvement in G_c, returning to almost the fresh value. However, after ageing for only 1 day, G_c has dropped substantially and after 1 year it has returned to a value comparable with that of an aged unannealed sample. However, the sample annealed at 120 °C shows a substantial improvement in G_c, which is unchanged after 1 day. After ageing for 335 days, G_c has fallen to 13 KJ m^{-2}. This value is comparable with that of a "fresh" unaged sample that has not been annealed. It is clear that the difference between annealing at 110 and 120 °C is substantial. Annealing at 110 °C does not result in a material that maintains its improved properties, while annealing at 120 °C does.

Fig. 2 shows the variation in K_c with annealing temperature at various lengths of time after annealing. In all cases there is an increase in the K_c values with increasing age. In fact, the change in K_c on subsequent ageing is most substantial in the sample annealed at 65 °C. All but the sample annealed at 120 °C reach approximately the same value of K_c on subsequent ageing. Again, annealing at 120 °C appears to give a marked improvement compared with the other temperatures examined.

These results show a similar trend with annealing temperature in fracture toughness as previously found

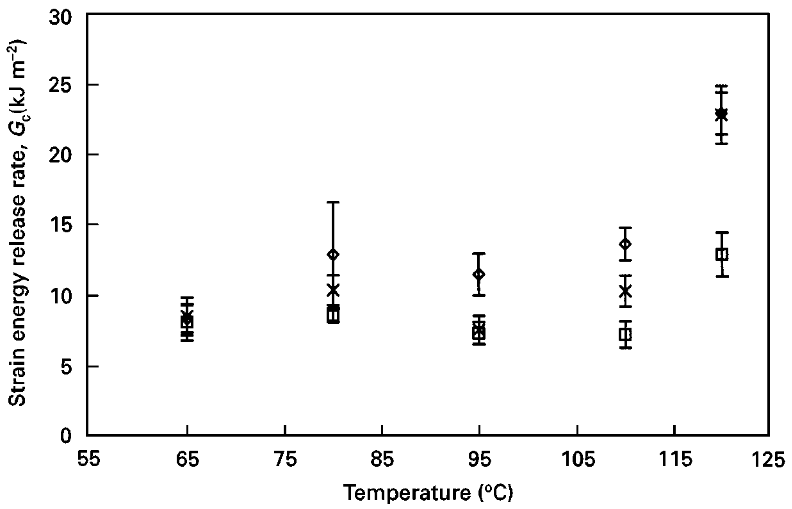

Figure 1 A graph showing the variation in G_c with annealing temperature after various ageing times. (◇), immediately after annealing; (×), 1 day after annealing; (□), 335 days after annealing.

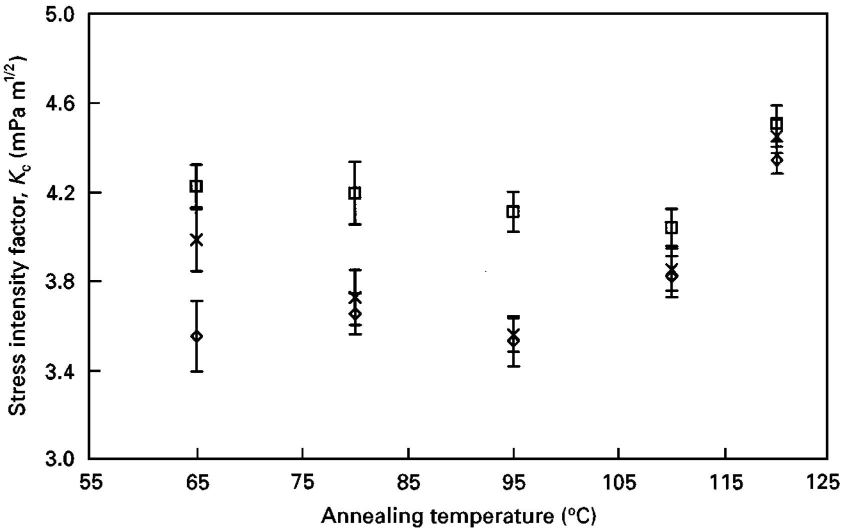

Figure 2 A graph showing the variation in K_c with annealing temperature after various ageing times. (◇), immediately after annealing; (×), 1 day after annealing; (□), 335 days after annealing.

for the polymers' extension to break [2]. The rest of the results presented here are for samples annealed at 130 °C, as described above.

Fig. 3 shows the variation in strain energy release rate with age after annealing at 130 °C for unnucleated homopolymer. Fig. 4 shows similar data for the nucleated homopolymer. It can be seen that the annealing process returns G_c to its "fresh" value, and on subsequent re-ageing there is little reduction. The annealing appears to have been slightly less effective for the nucleated polymer. This is probably because, as this experiment was performed at the beginning of the study, the importance of ensuring the even heating of the samples for the full 20 min was not realized; so some of the samples may not have reached the claimed annealing temperature.

Figs 5 and 6 show the variation in K_c with age for unnucleated and nucleated polymers, respectively. The values of K_c after annealing are approximately the same as those seen in the fully aged polymer [1], and after subsequent ageing there is a further increase in the K_c values obtained, indicating a further improvement in toughness after ageing.

Fig. 7 shows the variation in K_c with age for annealed nucleated homopolymer, tested using the compact tension test. A limited number of data points were obtained in order to check the DCB results. The values of K_c measured using the compact tension test are in approximate agreement with those measured using the DCB.

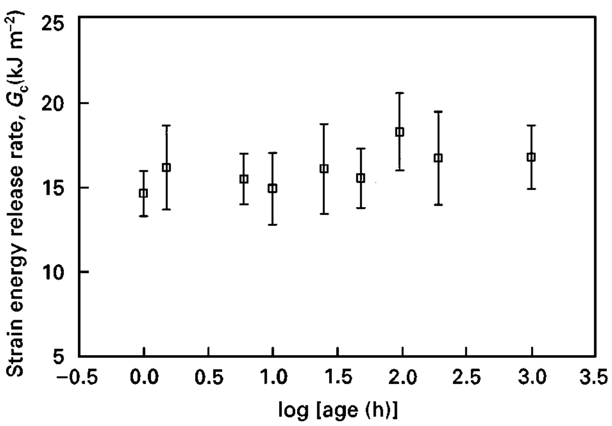

Figure 3 A graph showing for unnucleated PHB, the variation in G_c with ageing time, measured using the DCB test, after annealing for 20 min at 130 °C.

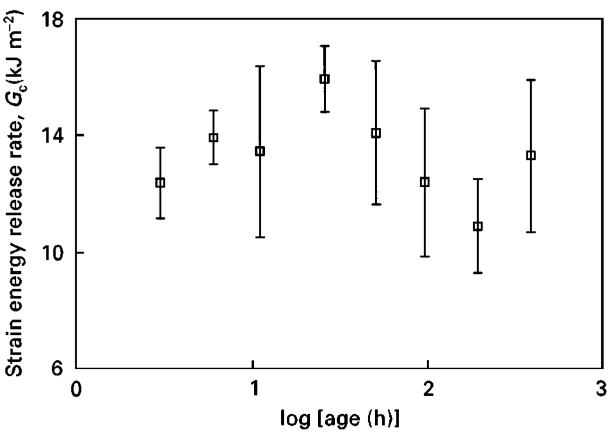

Figure 4 A graph showing for nucleated PHB, the variation in G_c with ageing time, measured using the DCB test, after annealing for 20 min at 130 °C.

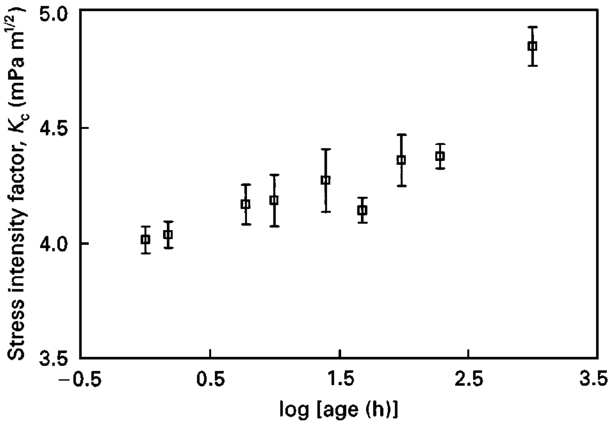

Figure 5 A graph showing for unnucleated PHB, the variation in K_c with ageing time, measured using the DCB test, after annealing for 20 min at 130 °C.

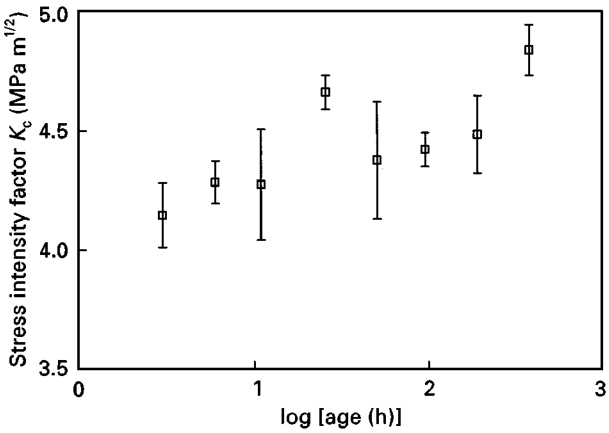

Figure 6 A graph showing for nucleated PHB, the variation in K_c with ageing time, measured using the DCB test, after annealing for 20 min at 130 °C.

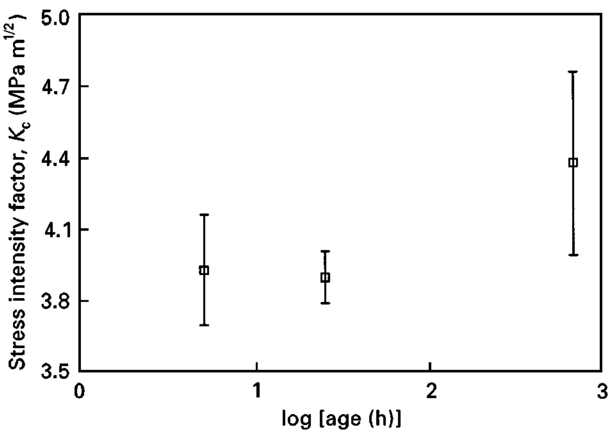

Figure 7 A graph showing for nucleated PHB, the variation in K_c with ageing time, measured using the compact tension test, after annealing for 20 min at 130 °C.

4. Discussion

Annealing at temperatures above 65 °C has some immediate impact on the PHB's fracture toughness, increasing G_c so that it approaches that of a fresh sample and slightly increasing K_c. However, on subsequent ageing, G_c decreases towards the value of an aged unannealed sample; the improved fracture toughness is not retained. Also, although the K_c value increases more rapidly in the samples annealed at temperatures up to and including 110 °C, the final value reached is no higher in samples that have been annealed than the final value in samples which have not. In contrast, annealing at 120 °C results in a final sample which maintains a substantially improved value of G_c and also obtains a higher value of K_c than seen in the samples annealed at lower temperatures. As observed previously [2], annealing at temperatures above 110 °C results in a product with improved mechanical properties which are largely maintained on subsequent ageing.

On annealing at 130 °C the essentially constant high value of G_c is in good agreement with the premise that annealing returns the polymer to its "fresh" state, with regard to mechanical properties. However, the stress intensity factor starts at approximately the same value as the aged sample and increases on subsequent ageing. It is clear that the annealing process results in a substantial improvement in the properties of PHB, returning the strain energy release rate at fracture to that of the fresh polymer while maintaining, and eventually improving upon, the high stress intensity factor of the aged polymer. From this it must be inferred that the annealing process will result in a substantial improvement in the performance of products manufactured from PHB.

It has been suggested [2] that the annealing process, and its resultant lamellar thickening, would allow a secondary crystallization process to occur at the crystal surfaces without having the same affect on the bulk of the amorphous material. This can explain the return to the "fresh" value of G_c, but not the increase in K_c on annealing. A loosening of the amorphous material might be expected to result in a reduction in K_c. However, it is possible that the K_c measurement is indirectly giving a measurement of the crystallinity of the material in the area of the crack tip. Although density measurements do not show an increase in crystallinity after the first few days [2], it is very possible that the crystallinity is still changing but resulting in a reduction in the density of the amorphous phase or, in extreme cases, opening up voids in the bulk sample. Annealing at elevated temperatures results in an increase in crystallinity over and above that attained through ageing, and this may correlate with the increased K_c values.

5. Conclusions

The effect of high-temperature annealing on the fracture behaviour of PHB has been studied using linear elastic fracture mechanics techniques. Annealing at temperatures of 120 °C or above has been found to result in an increase in both the critical strain energy release rate and the stress intensity factor at fracture, and a significant improvement over the aged unannealed material is maintained after re-ageing for 1 year. Lower annealing temperatures result in a temporary improvement in G_c which is then largely lost on subsequent re-ageing.

Annealing at 130 °C has been found to result in a material with significantly improved fracture properties which are to a large extent maintained on subsequent re-ageing. Both the stress intensity factor and the strain energy release rate at fracture are higher in the annealed samples than in the aged samples, implying that the annealed polymer will perform better in most applications. A basis of fracture mechanics data on the high-temperature annealing of PHB has been presented which should help a better understanding of the mechanism behind the improvement to be reached in the future.

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