Polymer Vol. 37 No. 15, pp. 3241-3246, 1996

0032-3861/96/$15.00+0.00

Cracking in spherulites of poly(hydroxybutyrate)

J. K. Hobbs, T. J. McMaster, M. J. Miles and P. J. Barham*
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK
(Received 9 August 1995; revised 23 November 1995)

Poly(hydroxybutyrate) (PHB) is a biodegradable thermoplastic. Melt-cast PHB sheets normally become brittle on storage. The embrittlement has been associated with cracks formed during cooling due to differences in radial and circumferential thermal expansion coefficients. We show that the cracks are in fact due to differences in thermal expansion between the PHB film and the constraining glass slides. The circumferential features, previously identified as cracks, are shown to be surface features formed due to volume reduction during crystallization constrained by the substrate. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(hydroxybutyrate); cracks; volume reduction)

INTRODUCTION

Poly(hydroxybutyrate) (PHB) and its copolymers with hydroxyvalerate are bacterial polyesters, which are produced under the tradename Biopol^{TM} by Zeneca Bioproducts Business[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, which embrittles the material[2-4].

In a previous paper[5] one of us has noted that cracks sometimes appear in samples of PHB. It was inferred that these cracks may contribute to the embrittlement of PHB. Two types of crack were identified, one running circumferentially around spherulites and the other running radially through them. In a further study of the thermal expansion of PHB spherulites[6], it was suggested that the circumferential cracks may be caused by thermal stresses that occur during the cooling of the spherulites from the high crystallization temperatures down to room temperature. It was argued that the difference in radial and circumferential expansion coefficients could lead to the formation of circumferential cracks during cooling.

The above-mentioned studies of cracking were all performed on specially prepared thin samples, grown between glass slides; there is therefore considerable doubt as to whether similar cracks should be expected under normal processing conditions such as injection moulding. Clearly if any cracks do appear they will probably lead to significant degradation of mechanical properties. We have accordingly undertaken a more detailed survey of the conditions under which cracks appear in PHB spherulites. We have systematically varied the sample thickness, the surface constraints during crystallization and the subsequent cooling of PHB spherulites. During these studies we have identified three distinct types of circumferential feature that might previously have been identified as cracks.

We report two distinct types of feature appearing during growth depending on the growth temperature and the constraints placed on the sample. Only one of the types of features subsequently opens up to form cracks right through the spherulites. We have also seen cracks appear on cooling in areas of the spherulites where no features were observed to form during growth. We used atomic force microscopy (AFM) to determine the depth and profile of surface features seen in the optical microscope. Similar features to those seen in PHB have been observed in other spherulitic systems. For example, Galeski *et al.*[7] have looked at localized volume deficiencies caused by spherulite growth in poly(ethylene oxide) and poly(methylene oxide).

The purposes of this paper are: to describe the three types of feature that were observed and the conditions under which each appear; to determine which features do indeed form cracks in the samples and which do not; to offer some explanations for the origin of the various types of feature; and to discuss the importance such 'cracks' may have for the mechanical properties of samples produced using commercial processing methods.

EXPERIMENTAL

The polymer used in this work was a PHB homopolymer with weight-average molecular weight 866000 and polydispersity 2.74. The polymer was purified to remove any cell-wall debris, etc., by dissolving in chloroform, filtering the solution through a 4 μm filter, and precipitating the PHB by adding ethanol. Spherulites were grown either on a single surface or between two surfaces in a Linkam microscope hot-stage. In all cases the polymer was melted at 185°C for 2 min

---

* To whom correspondence should be addressed

Figure 1 Optical micrograph (crossed polarizers) of a PHB spherulite grown at 95°C showing black circumferential features (arrowed). Scale bar 100 μm

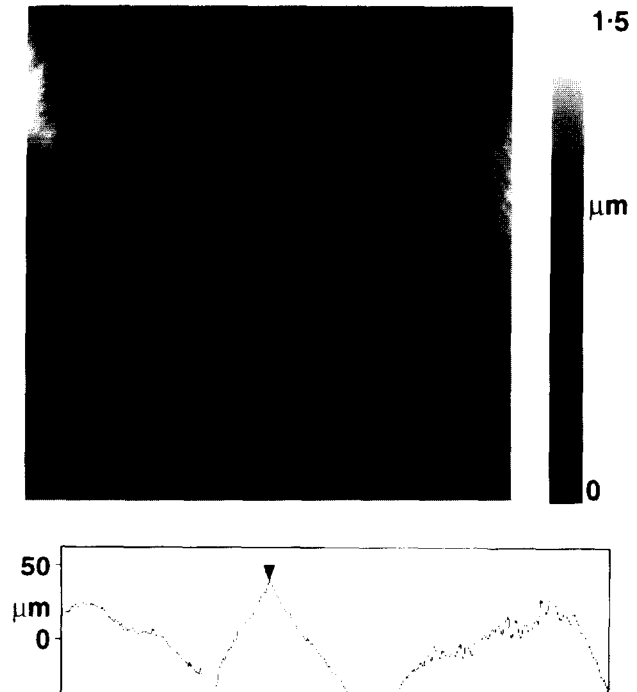

Figure 2 AFM topograph and associated line profile (top right to bottom left) of circumferential features. The vertical height difference between the markers is 1003 nm

before being cooled as quickly as possible to the desired crystallization temperature. Growth temperatures from 20 to 130°C were used. A wide variety of surface materials were investigated, including glass, mica, aluminium, mylar and NaCl. The thickness of the polymer films was measured using the focusing ring of the optical microscope. Samples with thicknesses in the range 20 to 500 μm were produced. The diameters of the spherulites grown in these films can be rather large, up to 3000 μm. Accordingly, since the diameters of the 'spherulites' often greatly exceeded the film thickness, the structures are not strictly spherulites; they are closer to planar objects. Nevertheless we shall refer to these circularly symmetric crystal aggregates as spherulites.

AFM studies were performed using a Digital Instruments (Santa Barbara, California, USA) Nanoscope III with a multimode AFM head. The instrument was operated in contact mode in air. The force–distance plot was frequently checked to ensure that the applied force was kept to as low a value as possible. Cantilevers of nominal spring constant 0.06 N m^{-1} and integral pyramidal tips were used (Digital Instruments). The J (125 μm) scan tube was used. All images were recorded at room temperature.

RESULTS AND DISCUSSION

Growth between two surfaces

During growth of spherulites between glass surfaces at temperatures up to 120°C, we found that circumferential features appeared at the growth front. A typical example is shown in *Figure 1*. These features appeared as black lines in the optical microscope, but did not appear to run right through the thickness of the spherulites. The samples were examined in the AFM to determine the depth and profile of these surface features. A typical AFM image is shown in *Figure 2*. It is clear that the features have a depth of ca. 1 μm. The semi-cone angle of the AFM tip ($\sim$35°) is such that features at the bottom of the crack could be successfully imaged. The small (ca. 1 μm) depth could be confirmed in thick samples using the focusing ring of the microscope, as it was clear that the features were confined to the surface region of the sample.

When observed during growth at all temperatures below 120°C, we found that the features described above occurred immediately behind the spherulite growth front. In spherulites grown at temperatures less than $\sim$100°C the circumferential lines were smooth. Above this temperature they were often irregular. *Figure 3* shows a series of micrographs illustrating the process. In most cases the features described above run completely around the spherulite circumference. Often the features appear at regular intervals within the spherulite. The mean spacing between the surface features is less in thicker samples. This is illustrated in *Figure 4*, which shows a graph of the mean spacing against the thickness of the film in which the spherulites grow. Although we found a clear correlation between the separation of the features and the sample thickness, we found no correlation with the growth temperature.

Since the features are seen only at the surfaces, we decided to investigate whether the surface material had any effect. In addition to glass we grew the spherulites on or between a variety of materials. In particular, we grew spherulites on combinations of mylar, kapton, mica, aluminium and NaCl as well as glass surfaces. We found that the same features always appeared at mica, aluminium and NaCl surfaces, but never at mylar or kapton surfaces. The only obvious difference between the surfaces is that the mylar and kapton are very much more compliant that the others.

The implication that the stiffness of the surface affects whether or not the features appear suggests that it is the constraint applied to the melt that is most important. As the polymer crystallizes there is a significant volume reduction (ca. 12% at 120°C)[5]. When stiff surfaces are used, the melt just in front of a growing spherulite may be severely constrained by the presence of the spherulite so that a considerable negative pressure may build up. It is possible that the resulting stress on the spherulite may be relieved by it detaching itself from the surface at which growth is occurring, thus partially accommodating the volume change on crystallization. The fact that there is considerable stress in the samples caused by the volume reduction on crystallization can often be seen by the growth of 'bubbles' near the growth front, which are associated with the appearance of the surface features. *Figure 5a* shows spherulite growth fronts just before a feature begins to appear. At the first appearance of the feature, a large number of bubbles appear. As the growth front continues forward, the smaller bubbles disappear

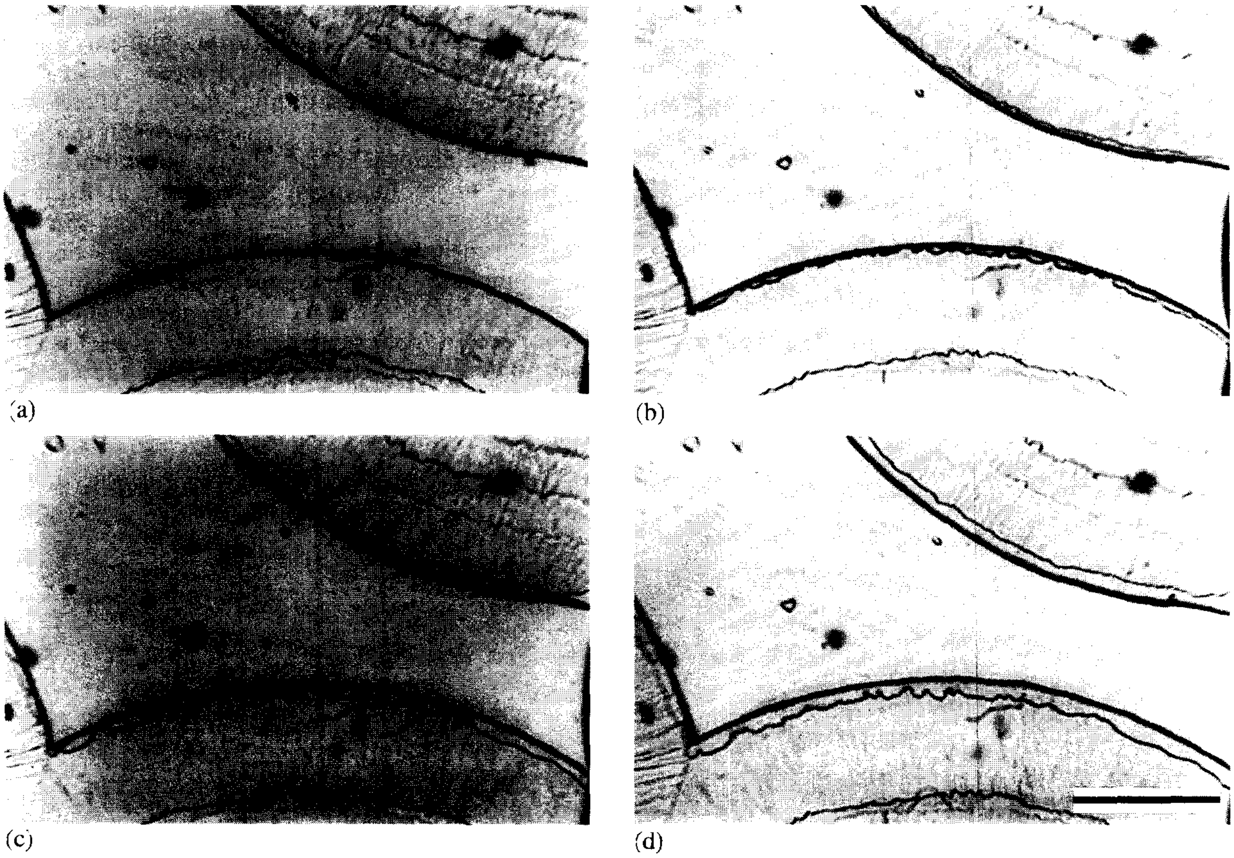

Figure 3 A series of optical micrographs (uncrossed polarizer) showing the formation of circumferential features, with pictures taken at 0.5 s intervals (T_c = 110°C): (a) spherulite growth fronts; (b) black loops appearing at the growth front; (c) loops joining together as the growth front moves forward; (d) circumferential feature left behind growth front. Scale bar 100 μm

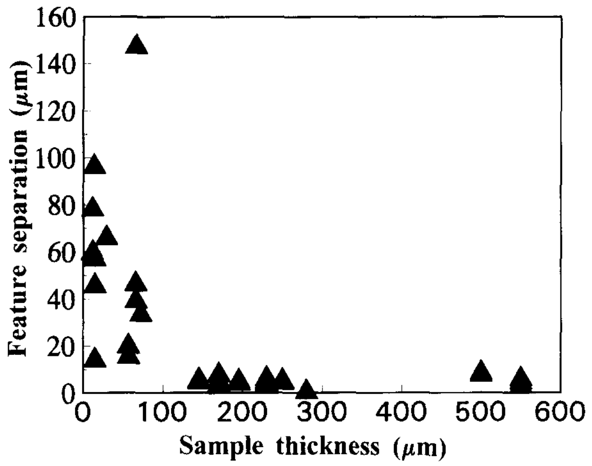

Figure 4 Graph showing mean separation of features of the type seen in *Figure 3* against sample thickness ($T_c = 95°C$)

into the feature while the large ones become larger and are eventually surrounded by newly grown crystals (*Figure 5b*), leaving holes in the spherulite structure.

On cooling fully grown spherulites, large cracks are seen to grow circumferentially around and radially across the spherulites. *Figure 6* shows a series of micrographs illustrating this process. *Figure 6a* shows the uncracked spherulite. In *Figure 6b* a crack has begun to form without any obvious optical feature as a nucleus, and in *Figure 6c* it can be seen to have propagated across the spherulite.

Growth with one free surface

A significantly different pattern of behaviour is found in spherulites grown with one surface free. In very thick samples we still occasionally see the circumferential features described above at the bottom (constrained) surface. However, in many cases, deeper features grow circumferentially around the spherulites at a distance of ca. 50 μm behind the growth front. Some of these features develop into cracks right through the sample on subsequent cooling. A typical example of these cracks is shown in *Figure 7*. Cracks typically grow at speeds in the range 2.5 to 6 mm^{-1}. On cooling fully grown spherulites, these features are seen to open up and then further cracks grow between them. The behaviour described above occurs in most samples regardless of substrate. There are, however, several cases where no cracks appear. These are: when the films are very thin (< 25 μm); and when the growth temperature is outside the range 70–120°C.

Possible mechanisms for the formation of the various features

Galeski *et al.*[7] defined the circumferential features as denoting the edge of an area where the spherulites had left contact with the coverglass, and they associated them exclusively with the occurrence of occluded growth. This cannot be the case here as these features are seen to occur in individual spherulites without contact with any other spherulites in areas of the melt only constrained by the glass coverslips. The AFM images show that they are more similar in nature to a groove or surface craze.

The fact that, when compliant surfaces are used, no features are seen at all strongly suggests that the stresses induced by the volume change on crystallization are responsible for all the effects. When the melt is constrained by two, stiff, foreign surfaces, and by the growth front of a spherulite, a significant negative pressure can be built up due to the volume change on crystallization. This negative pressure will lead to some flow of the melt towards the growth front, and will also generate stresses inside the growing spherulite. The maximum stresses are likely to occur where the constraints are most severe, i.e. at the surfaces near the growth front. As the spherulite grows, the stresses become larger. Once some critical stress is reached the features we see are formed, and the stress is released. The process then repeats itself as the spherulite continues to grow. If the stress reached is sufficient to overcome the cohesion of the melt, one or more bubbles are formed in the melt at the growth front—some impurity may be necessary to act as a nucleus for a bubble to form.

The situation is somewhat different when only one surface is constrained during growth. There is still a reduction in volume on crystallization but much of this volume change can, at least in part, be accommodated by a reduction in thickness of the melt in front of the growing spherulite. However, in thicker samples the polymer melt will need to flow considerable distances to accommodate the full volume reduction. This flow will generate viscous stresses in the melt, which will be transferred to the growing spherulite. If we assume that the polymer melt does not flow along the constrained surface, then the maximum stresses will occur at the free

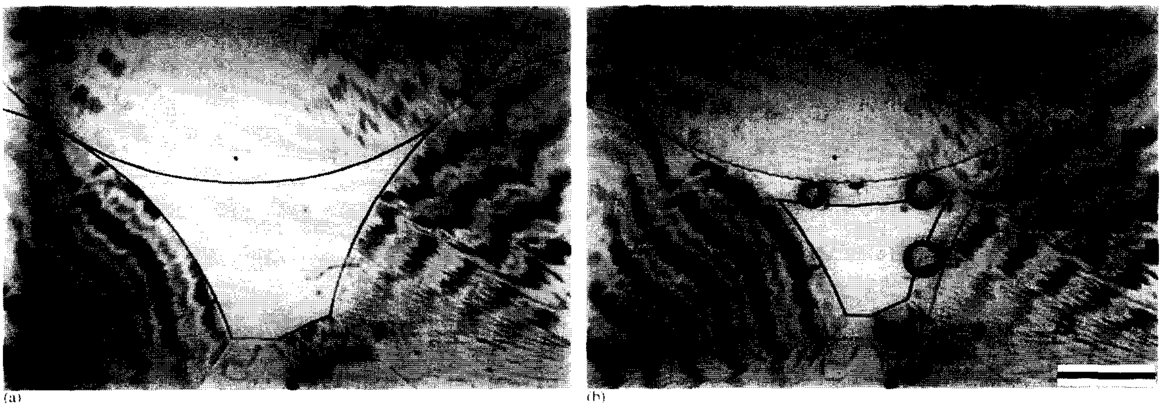

Figure 5 A series of optical micrographs (uncrossed polarizers) showing bubbles forming with a circumferential feature ($T_c = 95°C$): (a) spherulite growth fronts after 53.6 s from start of crystallization; (b) the growth front having grown beyond the bubbles—after 63.0 s. Scale bar 100 μm

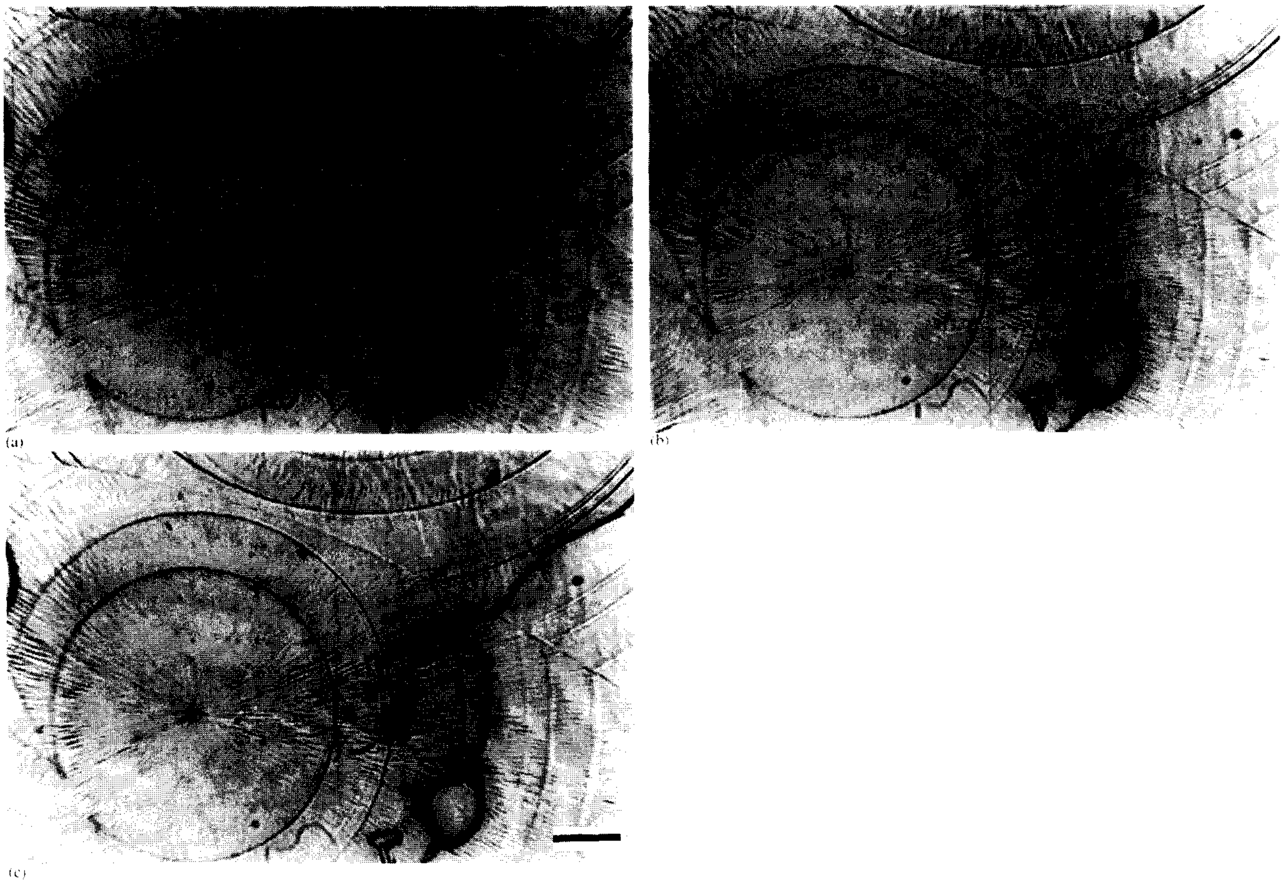

Figure 7 Optical micrograph (uncrossed polarizers) showing circumferential cracks at a free surface, formed during growth (T_c = 95°C). Scale bar 100 μm

surface where the maximum flow rate occurs. Tensile stresses will develop at the top (free) surface. The maximum stress will not occur at the growth front but should appear some distance behind as further shear stresses diffuse to the surface. Thus, once this maximum stress exceeds some critical value, we should expect to see cracks growing on the top surface around the spherulite (i.e. normal to the stress).

Once the spherulites are allowed to cool, further stresses will develop due to differential thermal expansion between the glass (or other stiff) substrate and the PHB. These stresses probably account for the cracks occurring on cooling seen in *Figure 6* and the further growth of the free surface cracks.

CONCLUSIONS

We have shown that cracks and crazes formed in spherulites of PHB, during growth and on cooling, are due to constraints imposed by the supporting substrate of the thin film and are therefore unlikely to be of importance in determining the ultimate mechanical properties of the bulk material.

ACKNOWLEDGEMENTS

We wish to thank Zeneca for the supply of materials. J. K. Hobbs wishes to thank Zeneca and the EPSRC for his Studentship Grant No. U43838.

REFERENCES

1 Hammond, T. and Liggat, J. J. 'Degradable Polymers: Principles and Applications' (Eds. G. Scott and D. Gilead), Chapman and Hall, 1995, Ch. 5, p. 88

2 Holmes, P. A. 'Developments in Crystalline Polymers' (Ed. D. C. Bassett), Vol. 2, Elsevier, London, 1988, p. 1

3 Scandola, M., Ceccorulli, G. and Pizzoli, M. *Makromol. Chem. Rapid Commun.* 1989, **10**, 47

4 de Koning, K. J. M. Ph.D. Thesis, Technische Universiteit Eindhoven, 1993

5 Barham, P. J. and Keller, A. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 69

6 Martinez-Salazar, J., Sanchez-Cuesta, M., Barham, P. J. and Keller, A. *J. Mater. Sci. Lett.* 1989, **8**, 490

7 Galeski, A. and Piorkowska, E. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 1299