JOURNAL OF MATERIALS SCIENCE **34** (1999) 4831–4844

The fracture of poly(hydroxybutyrate)

Part III *Fracture morphology in thin films and bulk systems*

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This paper is the final part of a three paper series describing the fracture and ageing behaviour of poly(hydroxybutyrate). In the first two parts conventional fracture mechanics methods were used to monitor changes both during the detrimental room temperature ageing process that occurs and after a subsequent annealing process that had been reported to reverse the ageing process. This paper reports on our studies of the morphology of fracture surfaces and how fracture proceeds in different ways in the original, ductile, "fresh", material, the more brittle, aged material and the ductile, annealed material. We have used optical and electron microscopic techniques to examine fracture surfaces of samples which had already been well characterised by mechanical testing. The effect of ageing and high temperature annealing on the resultant fracture morphology is detailed for both thin films and bulk samples. We have found that PHB undergoes crazing before failure regardless of annealing history. We have studied the craze morphology using optical microscopy and scanning electron microscopy. Both aged and un-aged samples are found to deform in approximately the same manner, the primary difference on ageing being the volume of material that is plastically deformed. After high temperature annealing a different craze morphology has been observed. In thin films this is characterised by the formation of a dense zone of micro-crazes over a relatively large area. In bulk samples there is a distinct change in the resultant fracture surface. In both thin films and bulk systems there is an increased occurrence of fracture initiation in the spherulite cores after high temperature annealing which helps to extend the craze zone.

1. Introduction

Poly(hydroxybutyrate) is well known as being the main member of a class of thermoplastic bioploymers [1]. The physical properties of poly(hydroxybutyrate) and poly(hydroxybutyrate-co-hydroxyvalerate) have been studied a great deal over the past decade since they have become commercially available under the trade name BIOPOL$^{\text{TM}}$ [2]. The interest in these polymers stems largely from their biodegradability, which makes them ideally placed for many environmentally sensitive applications. However, a drawback to the widespread use of poly(hydroxybutyrate) as a consumer plastic is that it undergoes a detrimental ageing process after moulding. When freshly moulded, poly(hydroxybutyrate) has a typical extension to break of around 50%; however, after ageing at room temperature for several weeks the material appears to become brittle and the extension to break falls to about 5%.

Several authors have addressed this ageing problem, providing some suggestions for the underlying causes in terms of morphological changes and secondary crystallization. Further, it has been found that after suitable annealing treatments the material can be restored to a high extension to break which is not then subject to further ageing [3].

In the previous two papers in this series [4, 5] we have studied the fracture behaviour of bulk samples of poly(hydroxybutyrate) (PHB) using linear elastic fracture mechanics techniques. We have found that the material is never "brittle" in the strict fracture mechanics sense, and we have found that the fracture behaviour of the annealed material is quite different from that of the original "fresh" material. However, although we now have a better understanding of what has previously been simply referred to as "embrittlement", few insights into what is happening on a structural level during ageing have been gained. Nor have we been able to throw any further light on the annealing process that causes permanent, advantageous changes to the fracture behaviour. In the present paper we will concentrate on the way in which the polymers' spherulitic morphology affects the fracture process to provide a full background of information on the ageing and high temperature annealing of PHB.

Early work on the relation between morphology and failure in PHB concentrated on specially prepared thin films, and subsequent optical examination of these films after various treatments [6]. In that work [6] it was observed that cracks formed in spherulites on cooling from the crystallization temperature to room temperature and it was suggested that these were due to differences in the radial and circumferential coefficient of thermal expansion [7]. More recently [8] we have shown that the cracks and other optical features identified as cracks are caused by constraints placed on the film by the substrate (e.g. glass slide) and would not be present in bulk samples. Hence, we concluded [8] that those features, seen in the earlier work [6], could not, in fact, be responsible for the embrittlement of PHB. Although the spherulitic morphology has been extensively investigated [9–11], no other studies on the effect of morphology on fracture in PHB have been published.

We have examined the fractured samples obtained in the previous studies [4, 5] using optical microscopy and scanning electron microscopy. We are able to follow changes in the fracture morphology both on ageing and on subsequent annealing. We have also used some thin films microtomed from bulk samples to allow a closer examination of the craze formation process and the manner in which it is influenced by the underlying spherulite morphology.

This paper is intended to provide a background of morphological information to allow a better understanding to be gained of the fracture process in PHB on a microscopic scale, and the way in which ageing and annealing impact upon it.

2. Experimental details

2.1. Bulk samples

The polymer used in most of this work was poly-(hydroxybutyrate) homopolymer from batch G044. We used two distinct samples types: "nucleated" and un-nucleated samples. The nucleated samples were comparable to commercial polymers and had 1% boron nitride added to the powder before moulding—these samples had a small spherulite size (ca. 5 μm). The un-nucleated samples had no nucleating agents added and consequently had much larger spherulite sizes (typically 80 μm). Samples were prepared from the powders by first melting and extruding as a ribbon into a water bath at 60 °C to form pellets for injection moulding. These pellets were fed into an Engel ES600/125 injection moulding machine. Square plaques 150 × 150 × 3 mm were moulded. Full details of the preparation of DCB samples are given in [4]. The samples were then aged for appropriate times before mechanical testing, as reported elsewhere [4, 5]. Some aged samples were annealed prior to testing according to the method described by de Koning [3] to achieve permanently improved fracture behaviour. The annealing process we used was to hold samples for 20 min at 130 °C [5].

The bulk double cantilever beam (DCB) samples described in [4] and [5] were used for morphological examination.

To examine the crack tip in more detail, the growing crack in a DCB sample was arrested by stopping the Instron cross-head, the sample removed, and the area containing the crack tip cut out using a hack-saw. These small samples were then microtomed into thin films ~20 μm thick using a sharp steel microtome blade and examined between glass slides under the optical microscope. A number of different microtoming directions were used relative to the existing crack in the sample. We found no noticeable difference on subsequent examination, indicating that the microtoming process was not causing any substantial levels of damage which could be mistaken as being due to the original fracture experiment.

The fractured surfaces of the DCB samples were mounted on SEM stubs and coated with aluminium to protect against beam damage. The resulting surface was then examined using a JEOL 6400 SEM at an acceleration voltage of 5–10 kV. Unless otherwise stated the un-nucleated polymer was used for these studies.

2.2. Thin films

To obtain thin films for examination during strain with the optical microscope, bulk samples, prepared in the same manner as for mechanical testing [4], were aged for various lengths of time and then microtomed using a sharp steel microtome blade into thin films ~20 μm × 3 mm × 15 mm. These films were cut into an approximate dog-bone shape in order to constrain the deformation to an area that could be viewed under the optical microscope, and mounted in a simple stretching rig. The samples were then stretched slowly and observed under strain both between crossed polarisers and in bright field illumination. The microtoming process did not cause significant damage to any of the samples except for the nucleated, un-aged material, which was not used in the subsequent experiments. It should be noted that in the case of the un-nucleated polymer, the film thickness was substantially smaller than the average spherulite size (~80 μm). The spherulite sections contained within the films do not always contain the spherulite core and the orientation within them is complex. These bulk samples have been crystallized under pressure in the injection moulder and will therefore have a very low void content. This is in contrast to thin films used in previous work [6] which had been crystallized as thin films and therefore contain only diametral sections through the spherulites and may contain some voids due to contraction during crystallization [8]. Clearly the orientation within these different types of film will influence their mechanical behaviour. The primary aim of the thin film work presented in this paper was to gain an insight into the fracture behaviour of bulk samples, so films microtomed from bulk samples were used unless otherwise stated.

Two different annealing routes were used. In one case, bulk samples were first annealed at a temperature of 130 °C and then microtomed into thin films as described above (these are described as "annealed then microtomed" below). In the other case, thin films were first microtomed from the bulk samples, and then annealed at 130 °C before testing (these are described as "microtomed then annealed" below). The un-nucleated polymer was used in the initial study. The nucleated polymer was used to show the effect of sample size on the annealing process.

Copolymer films provided by Zeneca Bioproducts Business were also examined. These were an 8%HV poly(hydroxybutyrate-co-valerate) copolymer from batch D400G containing 1% boron nitride, with a film thickness of $\sim$50 μm. For examination under the SEM, the film was first stretched in the stretching rig and then fixed to an SEM stub using double sided sticky tape. After cutting the film out of the stretching rig it was found that most of the strain was maintained in the sample. The sample was then coated with aluminium and viewed in the SEM as described above.

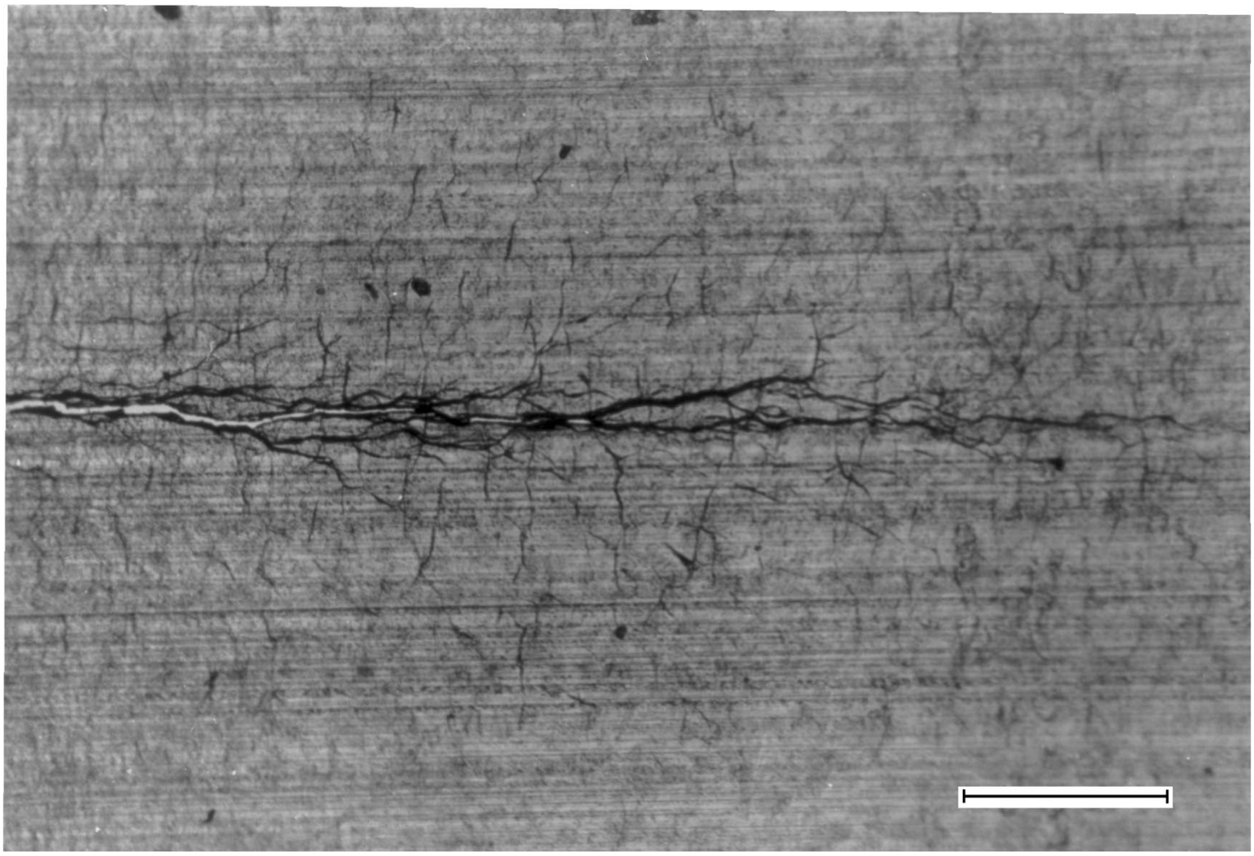
3. Results and discussion

3.1. Bulk samples

Fig. 1 shows a series of bright field optical micrographs of microtomed thin films taken at the crack tip of a fresh sample (aged for 3 h), a fully aged sample (aged for 32 days) and an annealed sample. In all three cases the main crack is clearly visible down the centre of the micrograph. Both the fresh and aged samples show relatively little crazing in the material around the main crack. The crack appears to propagate along a single path although it does wander significantly around a central plane. A greater tendency for crack wandering can be seen in the fresh than in the aged material.

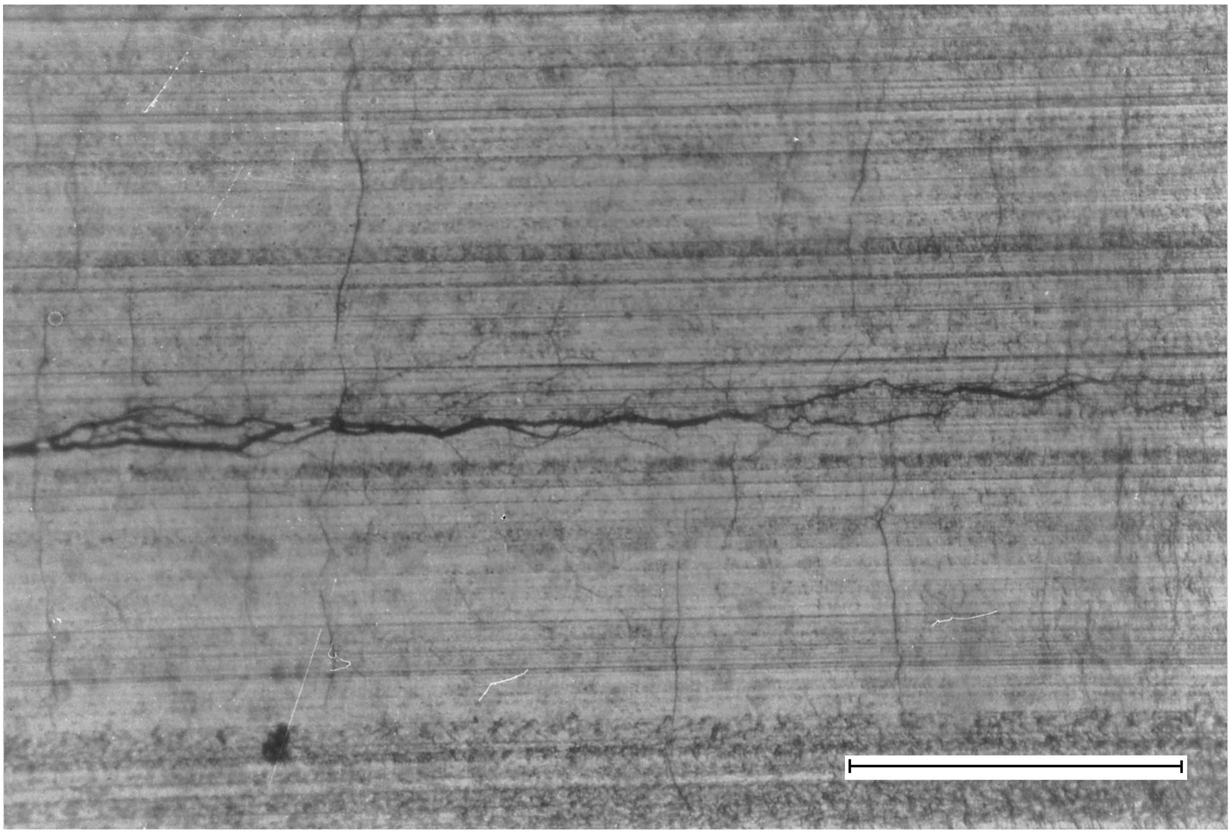
The appearance of the fracture in the annealed sample (Fig. 1c) is somewhat different. The level of crack wandering is increased significantly. Indeed, the damage zone around the crack is quite extensive, although the individual spherulites are not plastically deformed. We may conclude that the large degree of crazing and crack wandering occurring out of the plane of the main crack will act to significantly increase the energy dissipated during the fracture process. This crazing and crack wandering may be an indication of the different toughening mechanism which occurs after annealing, compared with that which occurs in the un-aged, un-annealed, polymer. We can see from sections such as that shown in Fig. 1c that, in these annealed samples, there appears to be a tendency for the cracks to pass through the central plane of the individual spherulites. In some instances it appears that small cracks which are not attached to the main fracture may have originated in the spherulite cores, as this is the most open area in the crack. We may therefore infer that the spherulite cores are local weak points in the annealed sample, which may act to dissipate the stress over a wider area than occurs in the un-annealed sample. However, care must be taken as it has been shown [12, 13] that the spherical symmetry of the spherulite will tend to act so as to concentrate stress in the spherulite core, causing early failure at these points.

Fig. 2 shows a series of SEM micrographs of fracture surfaces taken from un-nucleated DCB test pieces, again from fresh, aged and annealed samples. In Fig. 2a, for the fresh sample, a high level of damage, as expected for the relatively ductile, un-aged polymer, is apparent. Areas which could be associated with individual spherulites are sometimes visible, whereas



(a)

Figure 1 A series of optical micrographs (no polarisers) of microtomed thin films taken from double cantilever beam samples at the crack tip: (a) aged for three hours, (b) aged for 32 days, and (c) annealed at 130 °C. Scale bar 500 μm. (*Continued*)



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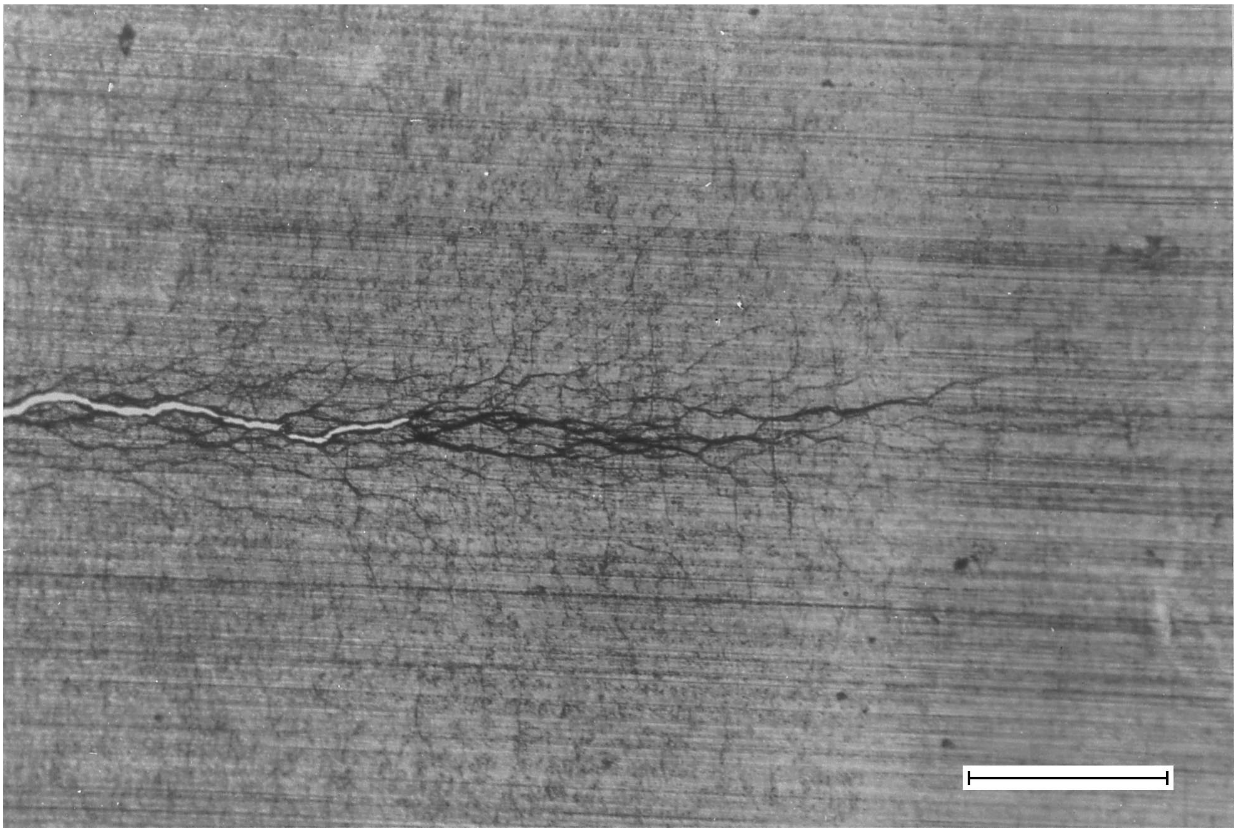
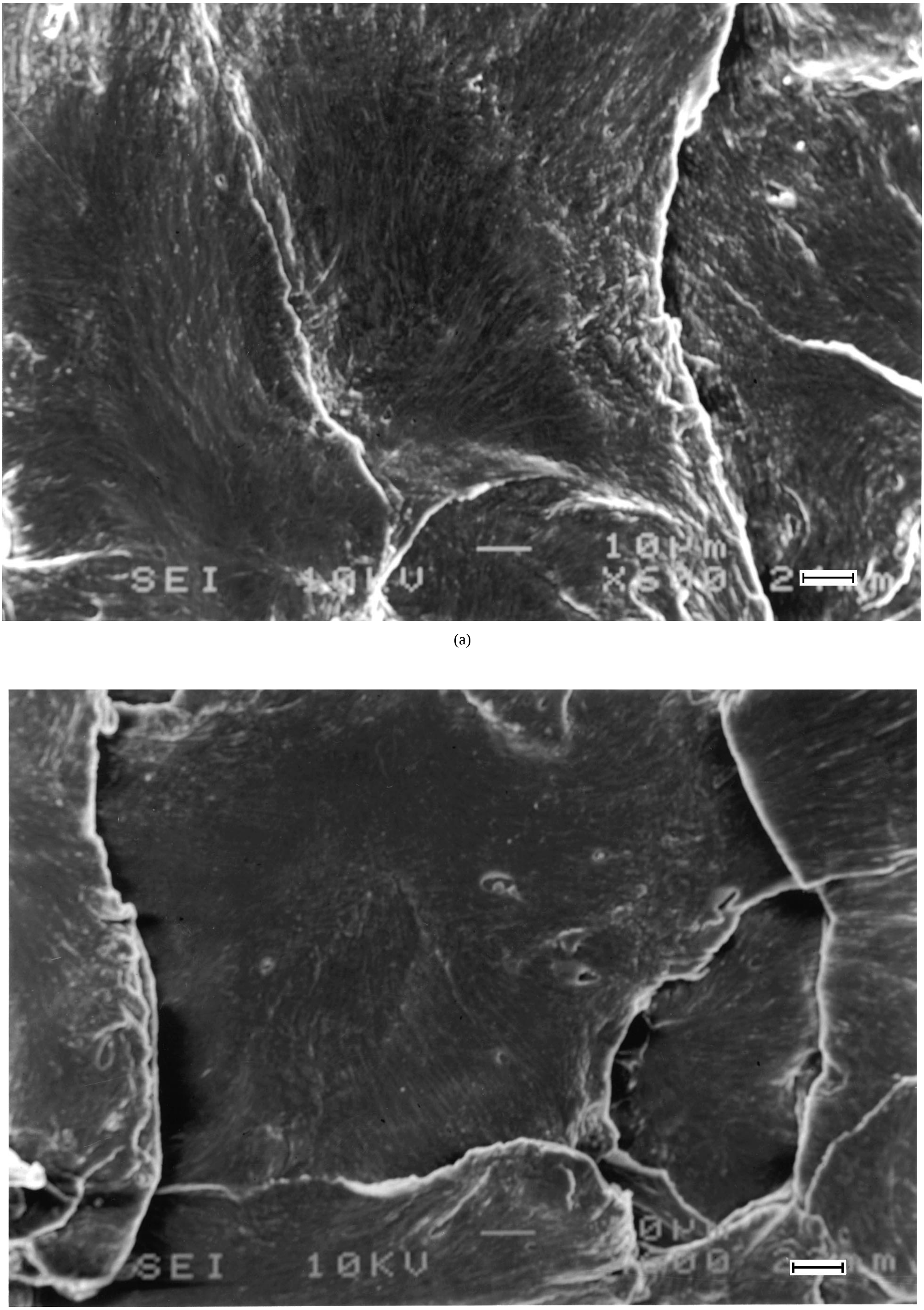


(c)

Figure 1 (*Continued*).

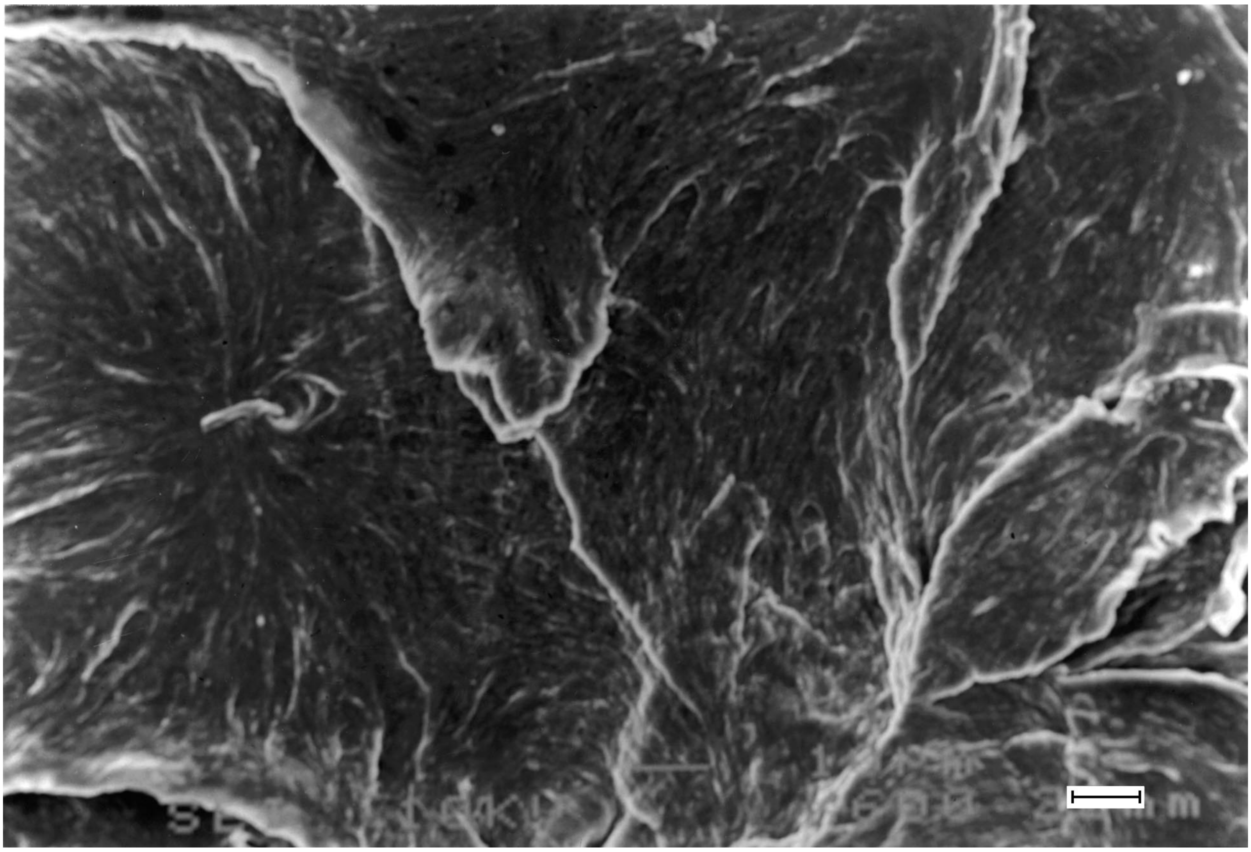
in other areas the surface is heavily deformed and fibrillated. Fig. 2b shows a sample that was aged for 32 days before fracture. Individual spherulites are now clearly visible, and have been fractured with a relatively low level of damage, as expected after embrittlement. It appears that some particular plane across the spherulites may be failing preferentially, as the boundary between individual spherulites is often visible. Alternatively, the



(a)

(b)

Figure 2 A series of SEM micrographs of fracture surfaces taken from un-nucleated double cantilever beam test pieces: (a) aged for three hours, (b) aged for 32 days, and (c) annealed at 130 °C. Scale bar 10 μm. (*Continued*)



(c)

Figure 2 (*Continued*).

material in the boundary area may be tougher than that at the core, causing more deformation in these areas and making them more distinct.

In common with the optical micrographs, the appearance of the fracture surface taken from annealed samples is quite different (see Fig. 2c). The high level of damage, characterised by elliptical features centred around what appears to be a spherulite core, is typical of all the annealed samples examined. One possibility is that crazes are initiated at the spherulite core and propagate out, interfering with other small crazes to form the elliptical features similar to those seen on a larger scale in other polymers [14]. In the example shown, Fig. 2c, the core of the spherulite has been pulled out during the fracture process. This is a common feature in the annealed samples and again possibly indicates the preferential fracture of the sample at spherulite cores. In the annealed samples, in contrast to the un-aged samples which have a similar strain energy release rate at fracture [4, 5], the damage is evenly distributed throughout the surface, with the individual spherulites often clearly visible. It appears that the fracture is occurring in a quite different manner after the annealing process has been performed.

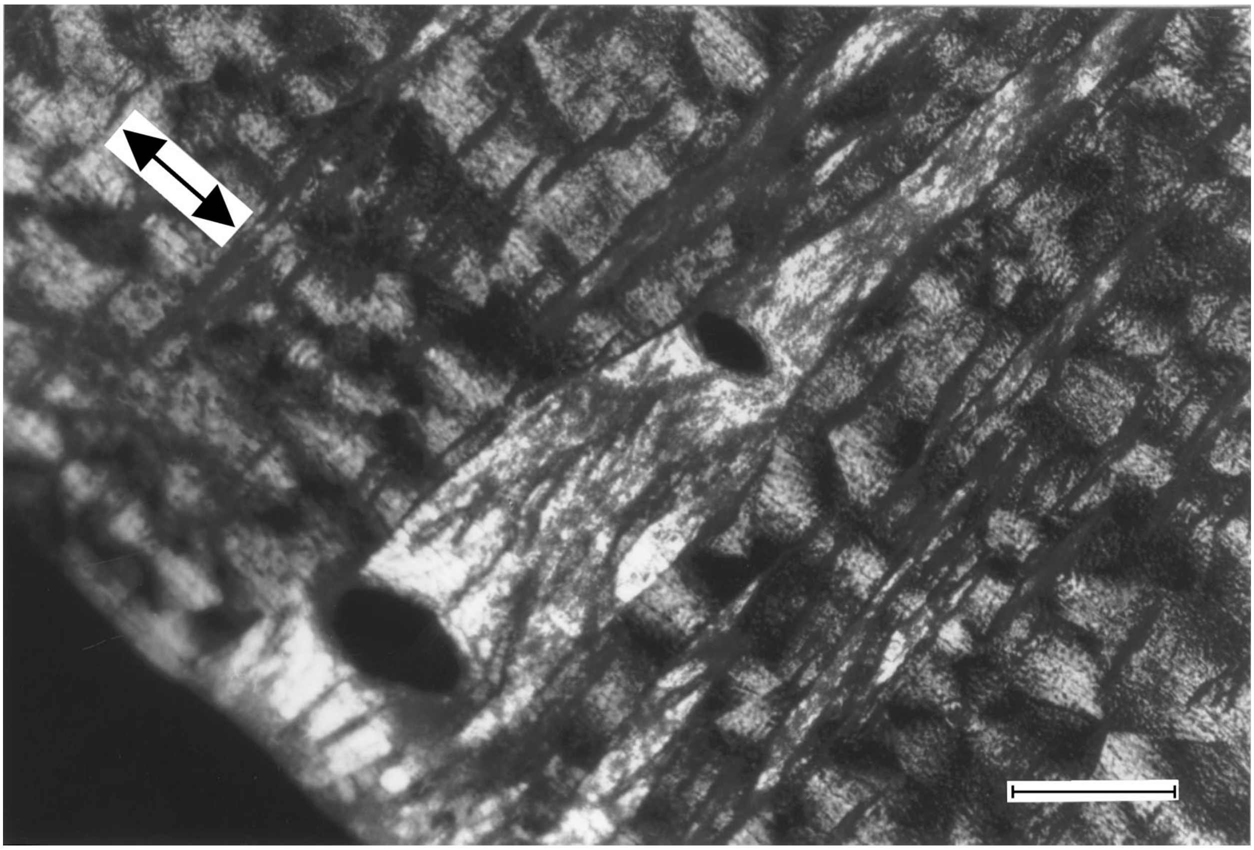
3.2. Microtomed thin films strained under the optical microscope

In this section, we begin by looking at the behaviour of un-nucleated films with large spherulite sizes so that we can associate the fracture behaviour with the spherulitic morphology. We then proceed to show some data for films from nucleated material which will bear relation to real products. We will also note that there are differences in the behaviour of the annealed films depending on whether they are annealed before, or after, being cut from the bulk sample.

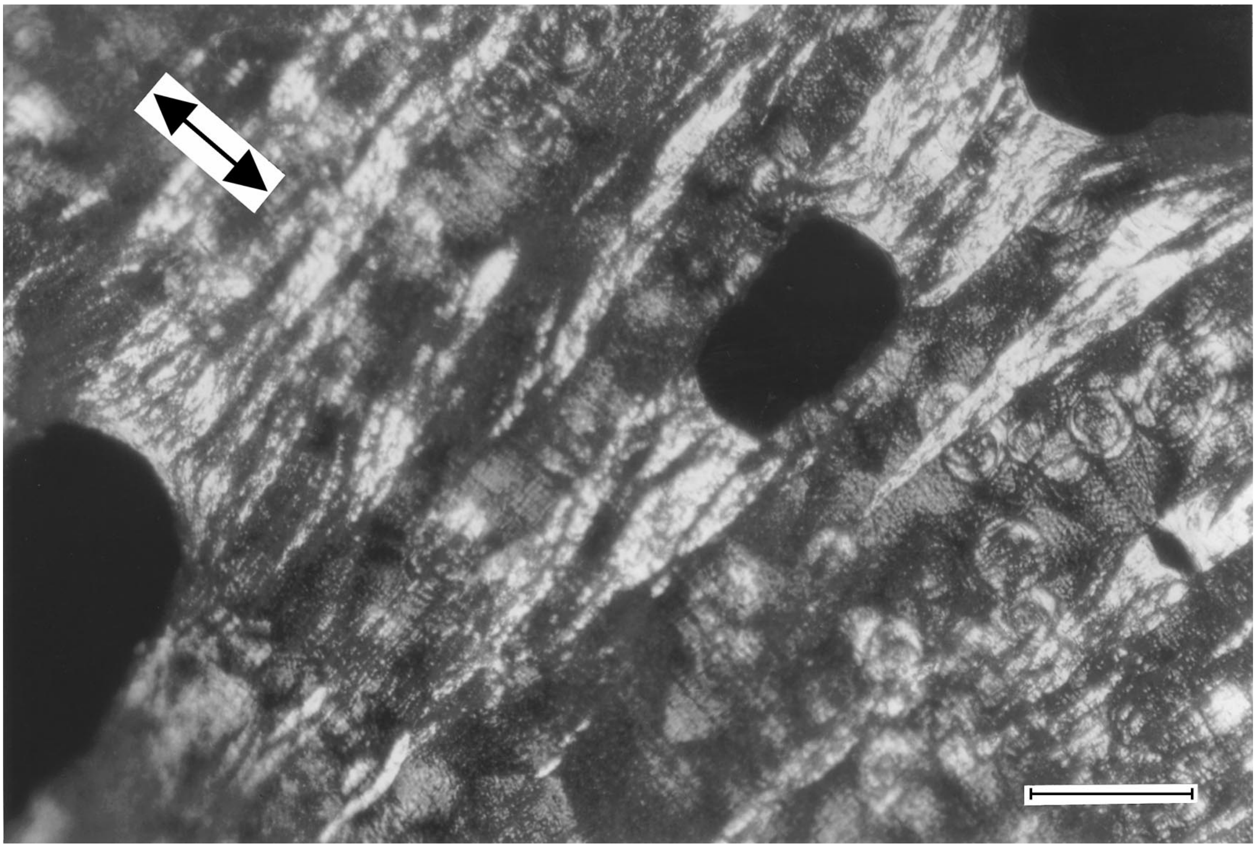
Fig. 3 shows a series of micrographs of thin films cut from bulk specimens of fresh, aged and annealed un-nucleated PHB as they are strained under the microscope. The individual spherulites within the films are clearly visible and have an average diameter of $\sim 80\ \mu$m, similar to that seen in the SEM micrographs above.

Fig. 3a shows a fresh, un-aged film. The Maltese crosses of the individual spherulites are slightly distorted. This distortion occurs before the sample starts to craze, and is caused by elastic deformations. The distortion is similar to that observed in many polymers during straining, for example polyethylene [15], and is evidence that some re-alignment in the strain direction is occurring. However, in PHB, this mode of re-alignment does not continue as the overall strain increases, rather a number of small crazes open up in the film. We have observed that there is an increased probability of a craze initiating at a spherulite core, although other initiation points do often occur.

As a craze opens it appears as a brightly birefringent region which is a second order yellow/green from the Michel-Lèvy chart of birefringent colours, and is positive in sign. On addition of $n = 1.49$ refractive index oil to the sample, the colour in the craze changes from yellow/green to white, but maintains its positive sign.

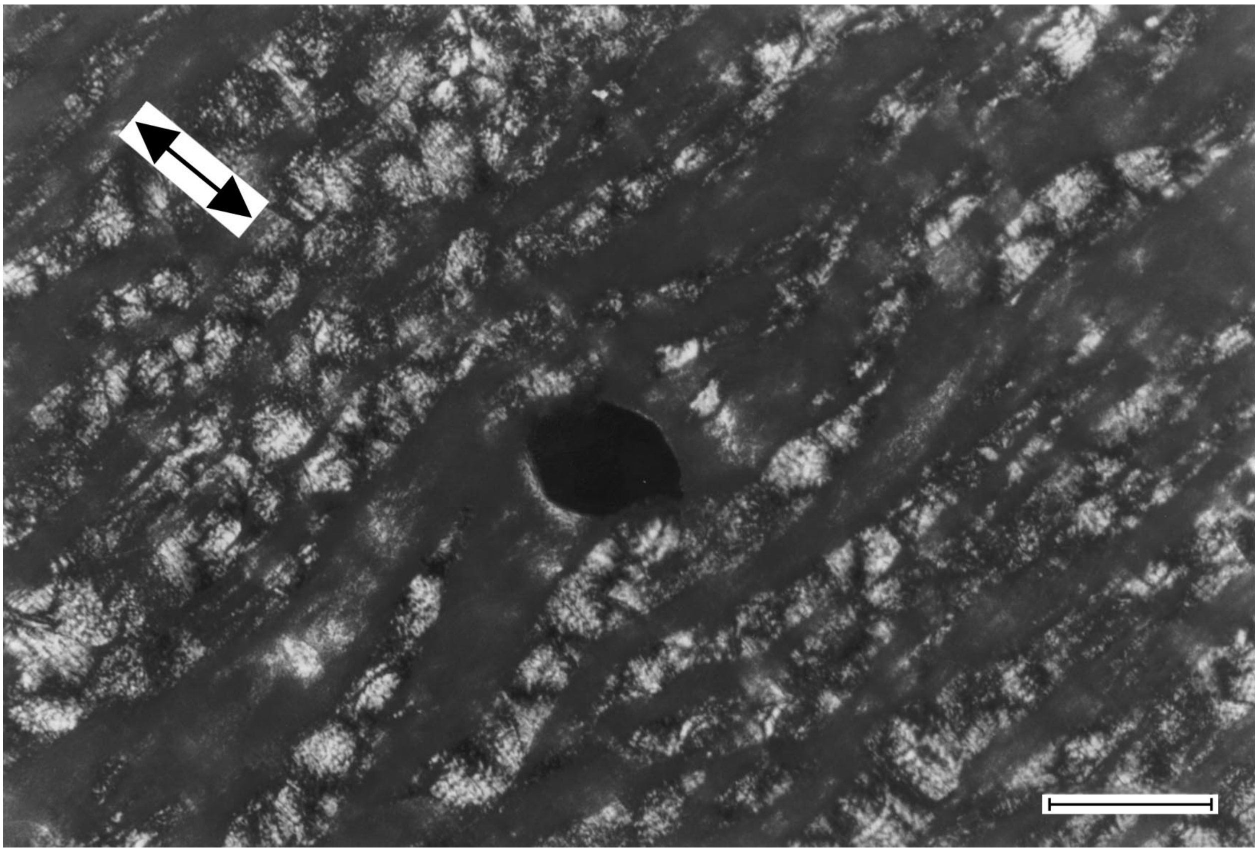


(a)



(b)

Figure 3 A series of optical micrographs taken between crossed polarisers showing microtomed thin films stretched under the microscope. Individual spherulites are clearly visible: (a) aged for three hours, (b) aged for 32 days, and (c) annealed at 130 °C. The arrow indicates the strain direction. Scale bar 100 μm. (*Continued*)



(c)

Figure 3 (*Continued*).

This change in colour on addition of the refractive index oil shows that some of the birefringence is "form" birefringence. It is known that during crazing a fibrillation process occurs [e.g. 16], with micro-voids opening up in the sample, their long axis parallel to the strain direction. It is likely that crazes formed in PHB contain voids, which have dimensions perpendicular to the strain direction that are substantially smaller than the wave length of light, reducing the effective refractive index in this direction and thus increasing the magnitude of birefringence. On addition of refractive index oil most voids will probably be filled by the oil, and returned to an approximately similar refractive index to that of the polymer, leaving primarily the birefringence due to the alignment of the polymer. The fact that the birefringence is positive in sign implies that the "*c*" axis is aligned with the strain direction [9]. The range of colours, and behaviour on addition of refractive index oil, is common to all the birefringent craze zones examined in this paper.

As the deformation of the PHB film is increased the craze is seen to grow by pulling material from the surrounding matrix. In many cases islands of undeformed material are pulled into the craze zone. This method of craze thickening has also been observed in polypropylene [17]. The level of alignment, as measured by the birefringent colour, does not change as the craze increases in width. It should be noted that the level of strain within the craze is very high indeed, at least several hundred percent, although it was not measured exactly.

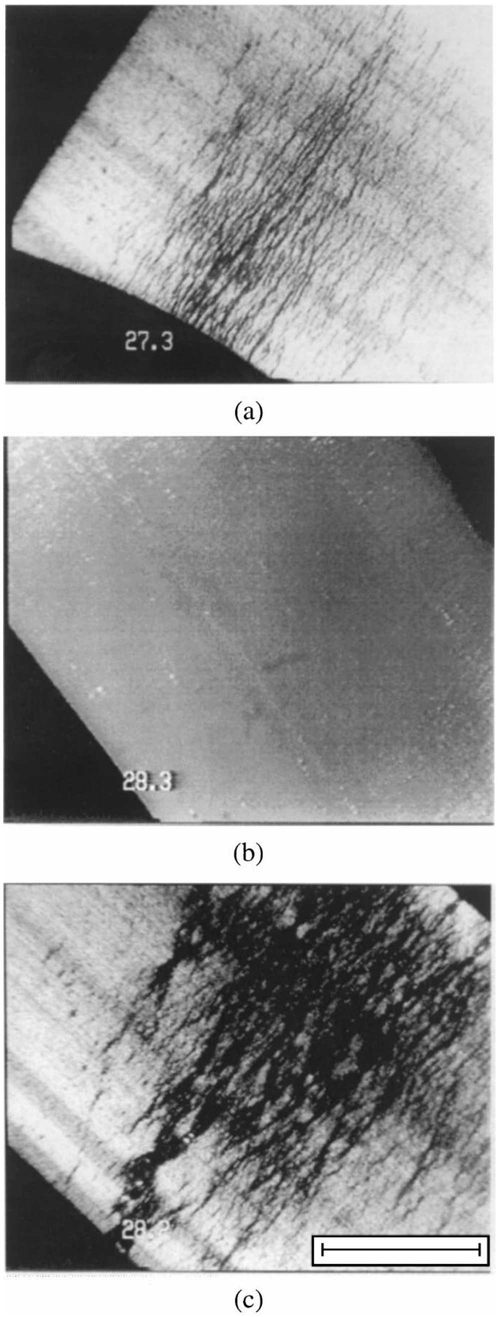
As the deformation is further increased toward failure, holes open up in the existing craze. In all the thin films studied in this paper, holes of a roughly similar profile occur in the craze zone before failure. The hole then spreads along the craze, maintaining approximately the same profile at its advancing side, until failure occurs. Close examination of the birefringence at the advancing hole "tip" shows that the polymer is aligned along the edge of the hole, and not parallel to the strain direction. This is strong evidence that the craze is failing through a process of viscous flow and chain pull out rather than chain scission.

Fig. 3b shows an optical micrograph of an aged film strained under the microscope. In this case there is not sufficient elastic deformation of the spherulites to give any visible re-orientation. At low strains the sample starts to exhibit multiple crazes of the same type as described above for the fresh sample. However, the crazes in aged samples do not grow as large as those in the fresh samples before macroscopic holes form and begin to open up. Failure occurs by lateral growth of these holes. The main differences between the aged and unaged polymer are in the lower level of initial elastic deformation and in the smaller width of the crazes prior to failure in the aged material. We note that the level of alignment and route to craze failure is the same in both fresh and aged samples. It is clear that even after ageing the polymer is able to undergo a substantial level of plastic deformation, in which small areas of the polymer have supported a high level of strain. Considering the level of local strain implied by micrographs such as the one shown here, it is likely that individual lamellae have been highly deformed and reorganised before failure, in a similar manner to that suggested to occur during the crazing of other semicrystalline polymers [16].

Fig. 3c shows a series of optical micrographs of films that were annealed then microtomed. There is no visible elastic deformation of the spherulites, the Maltese crosses remaining unchanged on application of strain. The crazing in the annealed material is much more evenly distributed over the whole of the sample. This behaviour is in contrast to that of both the aged and un-aged samples where a few crazes nucleate in the sample and then progressively open until failure occurs. From micrographs such as the one shown here it is apparent that the vast majority of the spherulites in the film have a small craze nucleated at their core. It appears that the annealing process is somehow weakening the spherulite cores relative to the rest of the sample, allowing them to act as craze nuclei and thus reducing the stress concentration that would normally occur at the first craze to nucleate.

The crazes in the annealed polymer appear quite different from those in the un-annealed polymer. They are dark areas whether viewed between crossed polars or with unpolarised light. Within them there are hints of a high magnitude of birefringence but it appears that the majority of the light is being scattered by the craze. Addition of refractive index oil reveals the crazes as brightly birefringent areas, similar to those described above, from which it can be concluded that the scattering is happening at polymer-air interfaces caused by the craze. In the annealed polymer the visible craze consists of multiple microscopic crazes.

Now that we have been able to identify morphological features in un-nucleated samples with large spherulite sizes, we will look at nucleated samples where the spherulite size is much smaller and which are more similar to real commercial materials. Fig. 4 shows a series of strained thin films cut from nucleated bulk samples. Fig. 4a shows an aged film, just prior to failure, in which the low level of damage is visible which is quite consistent with our observations on un-nucleated films. Fig. 4b shows a film which was cut from a bulk sample which had previously been annealed. Here the entire sample is covered with dense crazing and a relatively high level of strain can be sustained, again the observations are consistent with our work with un-nucleated films. However, when we examined a film which was cut from the bulk sample and then annealed, i.e. annealed as a thin film (Fig. 4c) we found a different behaviour. The micrograph of Fig. 4c was taken just prior to failure (just as those of Fig. 4a and b) and although there is a small increase in the strain sustained and the level of crazing, there is no significant change. The annealing process does not appear to have "worked". We also observed the same process in the un-nucleated polymer but it is not so clearly seen from a single example. It appears that the thickness of the sample during annealing is influencing the impact of the annealing process on mechanical properties.



(a)

(b)

(c)

Figure 4 A series of optical micrographs taken between crossed polarisers showing nucleated microtomed films stretched under the microscope: (a) a film aged for 32 days, (b) a film microtomed from a block that had previously been annealed at 130 °C, and (c) a film microtomed from an aged block and then annealed at 130 °C. Scale bar 500 μm.

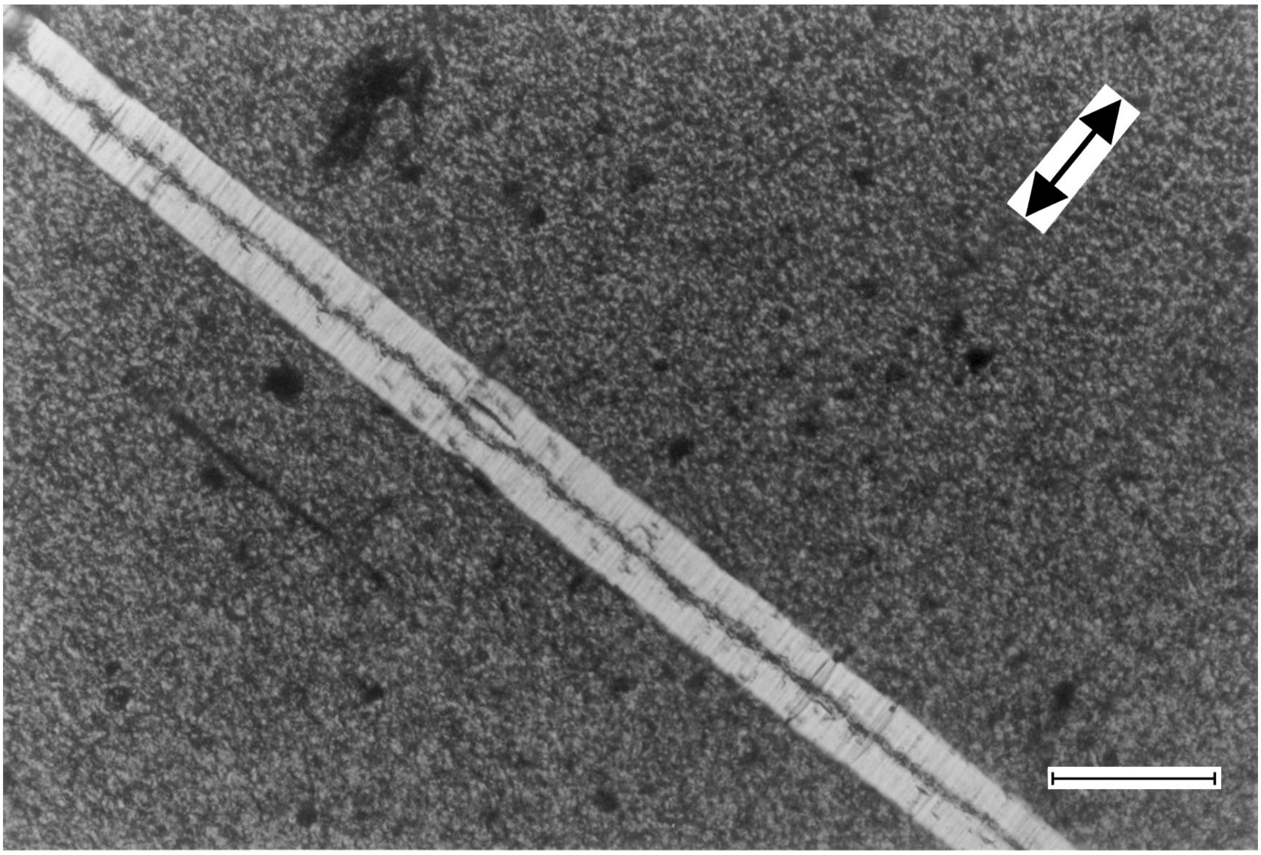
It is possible that there is a different level of damage caused by microtoming between the films annealed before and after the annealing process has been carried out. There are no visible holes in the samples when viewed optically or by SEM, so it seems unlikely that this is responsible for the difference in behaviour, although the possibility remains that microscopic holes or grooves could be locally weakening the microtomed and then annealed sample which did not exist in the annealed and then microtomed sample as this was tougher at the time of microtoming. Another possible cause is the influence of the spherulite boundaries on the fracture process, although the spherulite size in the nucleated thin films is around 5 μm, compared to a film thickness of approximately 20 μm, so it is unlikely that the change in effect of annealing is due to the relationship between sample thickness and spherulite size.

An attempt to explain the ability of the annealing process to improve mechanical properties has been made in terms of the change in lamellar thickness that occurs [3]. However, this change in thickness is likely to be dependent only on the annealing temperature and will not be influenced by the film thickness, assuming the film is substantially larger than the individual lamellae (as is the case here). As it is reasonable to assume that the lamellar scale morphology is similar in both sets of annealed samples it is unlikely that it is the change in this morphology on annealing that is responsible for the impact of the process on mechanical properties. The fact that the film that was annealed and then microtomed does exhibit improved properties removes the possibility that some change in the stress state within the sample is responsible for the lack of effectiveness of the annealing process on the microtomed and then annealed samples. The impact of film thickness during the annealing process implies that a transport phenomenon of some sort may be partly responsible for the change in properties on annealing. One possible component that is normally present in PHB bulk samples, although at low concentrations (∼0.5% by mass) is water, and it has been shown that this has an impact on the crystallization behaviour of PHB [18]. It may be that movement of water around the sample is in some way influencing its final mechanical properties. Another possibility is low molecular weight PHB. Further work on this subject is underway in this laboratory to try to understand this observation more clearly.

3.3. Copolymer thin films

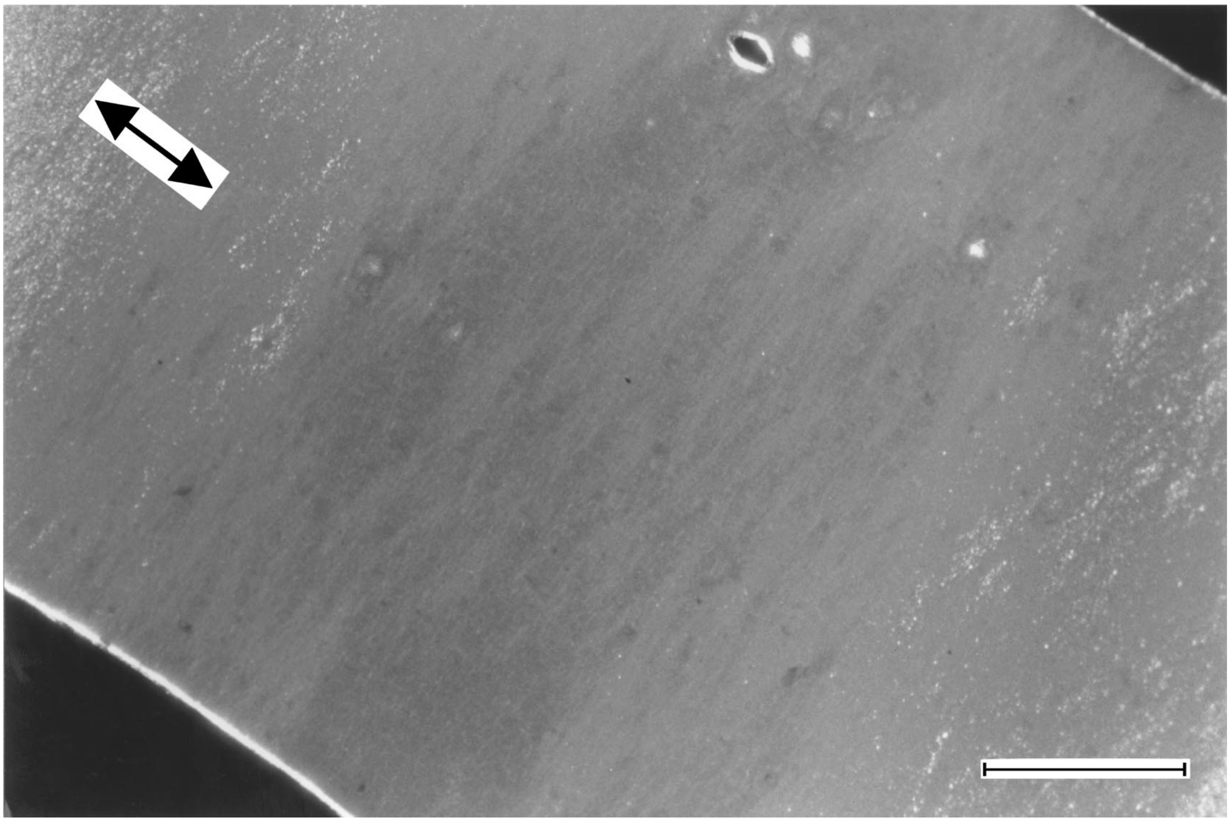
Fig. 5 shows optical micrographs of aged and annealed thin films from batch D400G strained under the optical microscope. The aged film contains a single bright birefringent craze with no visible orientation in the rest of the sample. On further application of strain this craze opens up and rapidly fails. The film which has been annealed at 130 °C is almost entirely covered with a dense population of microcrazes in a similar manner to that seen in the annealed then microtomed samples described above. In this case the annealing process appears to have "worked" for the thin film. The reason for this is unclear. It may be that the sample is sufficiently thick for the annealing process to work or the fact that it is a copolymer may be influencing its response to annealing.

Fig. 6 shows a series of SEM micrographs of crazed areas in aged and annealed thin films. In the case of the aged polymer it can be seen that the damage is entirely isolated to the craze zone. In that zone the material appears to be aligned, but there is no sign of individual fibrils. Fig. 6b is very similar to craze zones observed in medium to high molecular weight polypropylene [19]



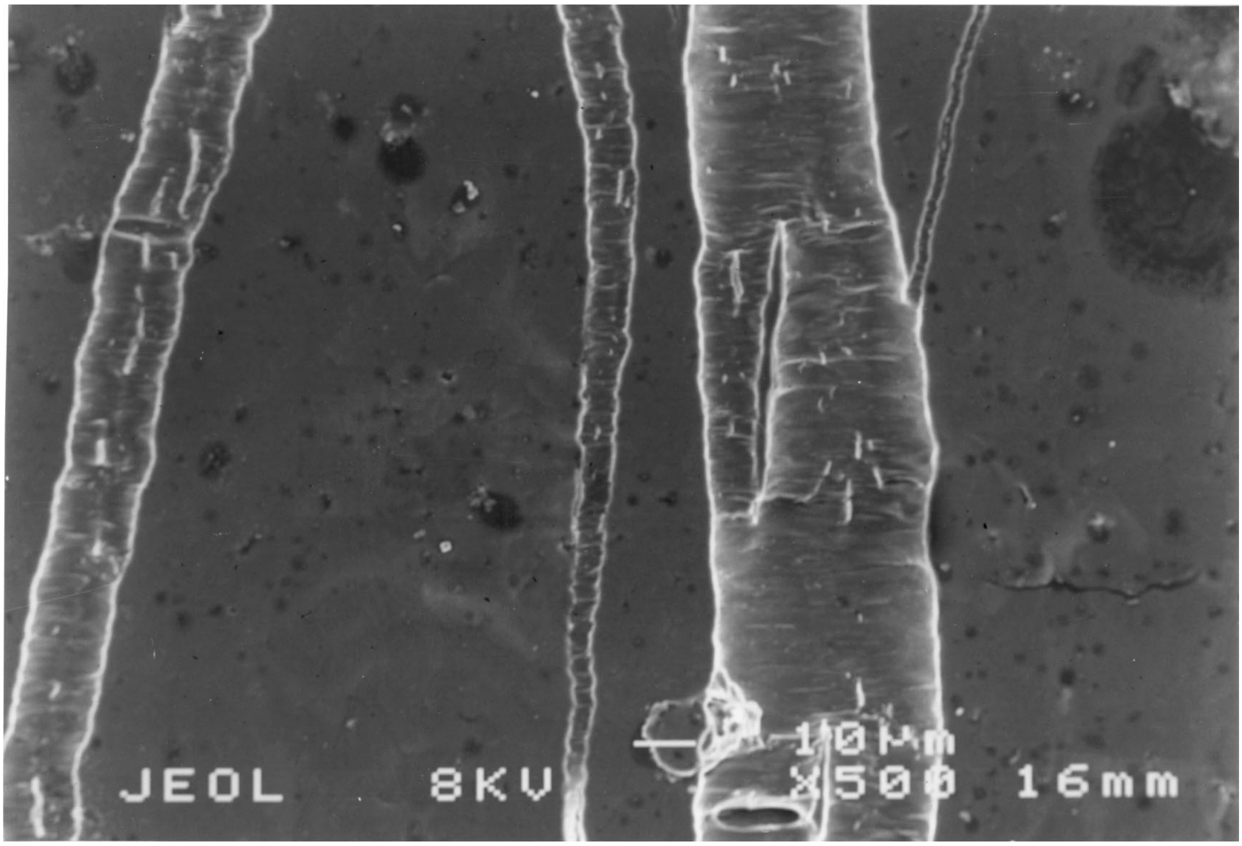
(a)

Figure 5 A series of optical micrographs taken between crossed polarisers showing copolymer thin films from batch D400G strained under the optical microscope: (a) as received, aged film, scale bar 100 μm and (b) film annealed at 130 °C, scale bar 500 μm. The arrow indicates the strain direction. (*Continued*)



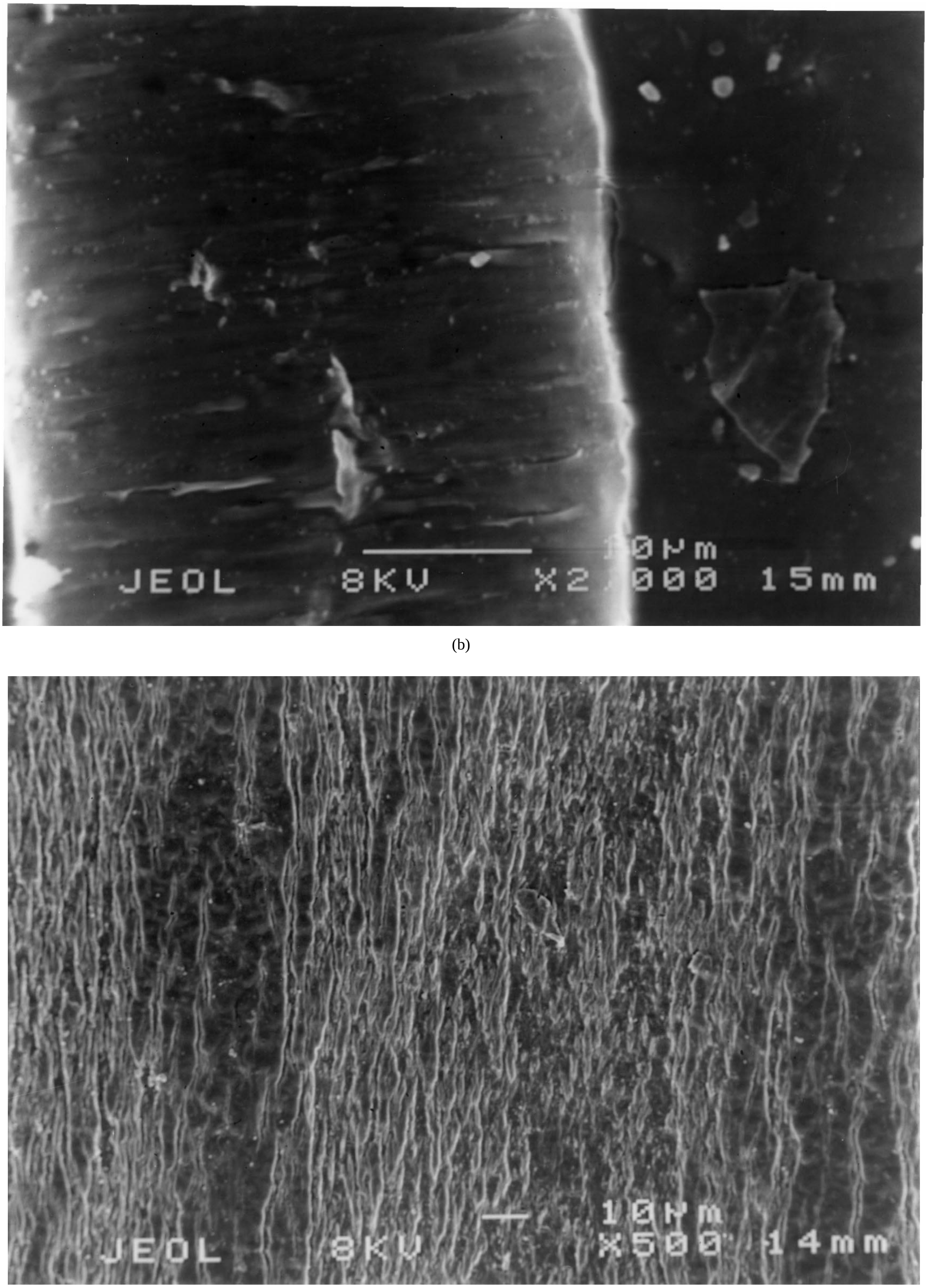
(b)

Figure 5 (*Continued*).



(a)

Figure 6 A series of SEM micrographs of crazed areas in copolymer films from batch D400G previously strained under the optical microscope: (a) a low magnification micrograph showing crazes in the aged film, (b) a higher magnification image of part of (a), (c) a low magnification image showing a highly crazed region in an annealed film, and (d) a higher magnification image showing part of a crazed region in an annealed film. (*Continued*)

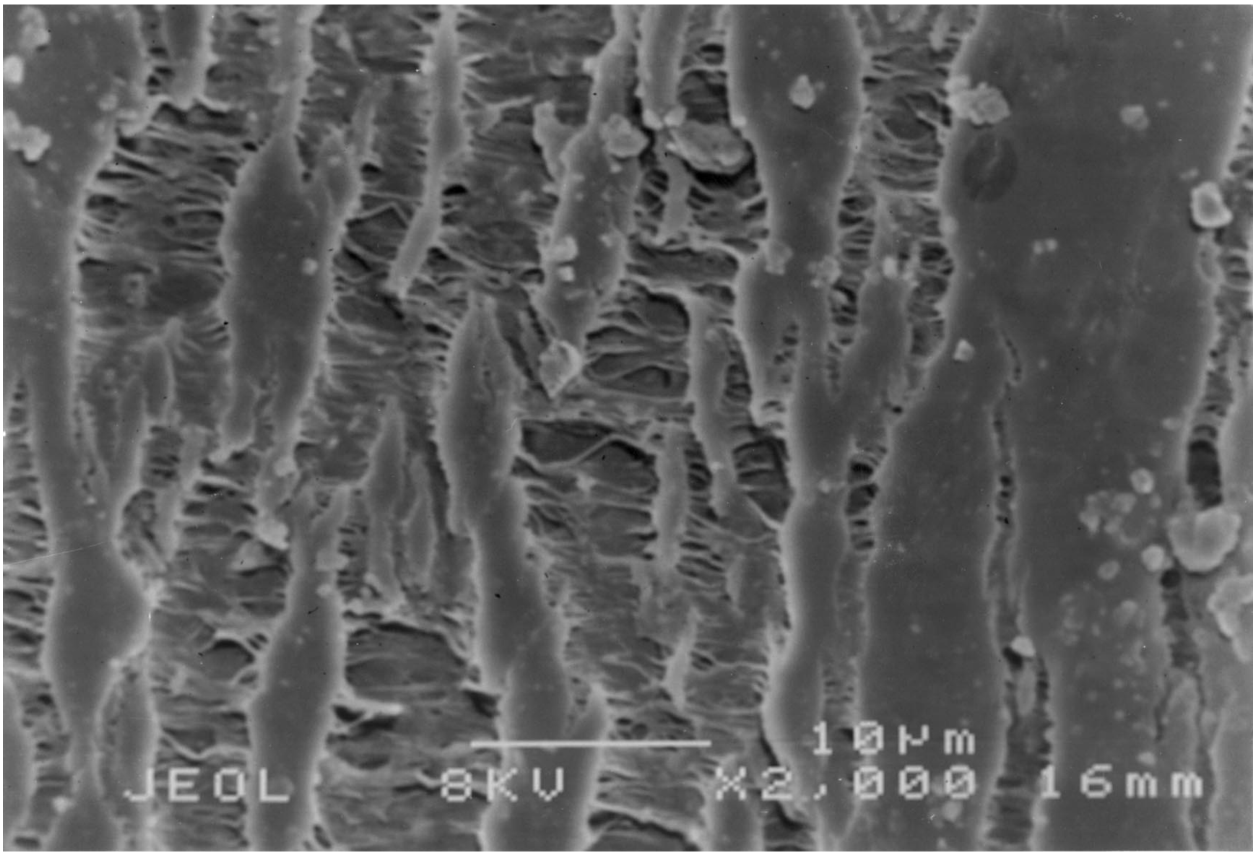


(b)

(c)

Figure 6 (*Continued*)

where the dense craze structure was taken as indication of a very even fibrillation process. Fig. 6c and d show SEM micrographs of a strained annealed film. It is apparent that the sample is covered with multiple microcrazes. These crazes are $\sim 2\ \mu$m across. There appears to be no large crazes of the type seen in the un-annealed sample, which is in good agreement with the inferences made from the optical microscopy. The



(d)

Figure 6 (*Continued*).

areas in between the crazes appear undamaged. Fig. 6d shows a close up of a lightly crazed region. In this figure individual irregularly spaced fibrils are visible, in contrast to the aged polymer where the fibril zone appears to be much denser. The fibrils have a diameter of 250–500 nm, which is very similar to that seen in crazes in other semicrystalline thermoplastics above their glass transition temperature [16].

Both the microtomed samples taken from an annealed block and the copolymer thin films appear to undergo a similar process of multiple micro-crazing when strained. It may be that after annealing the polymer strain hardens to a greater degree than previously and thus the crazes become stable before a critical level of strain is reached, enabling another area of the sample to reach a sufficiently high stress level to nucleate a craze. However, the individual microcrazes observed under SEM display a surprising level of fibrillation and void formation, which seems inconsistent with the hypothesis that the annealed sample has a more stable craze zone. It may be that this level of voiding only occurs at the surface of the sample. It is also possible that the very high level of crazing which is seen at the sample surface is not representative of the bulk of the sample. The undeformed material may be lying on the surface of a heavily drawn area, effectively an artefact caused by the surface, although how, or why, such a deformation process should occur is difficult to envisage. Similar dense craze zones have been observed at notches in polyethylene, poly(oxymethylene) and a number of other ductile polymers.

4. Conclusions

The effect of morphology on the fracture behaviour of both thin films and bulk samples of PHB has been studied in an attempt to lay a basis of information for future studies of the effect of ageing and the high temperature annealing process on the polymer. PHB has been found to undergo crazing during deformation regardless of its annealing history.

The bulk samples used in previous fracture mechanics studies [4, 5] have revealed a difference in the fracture mechanism between the fresh and annealed samples despite some similarities in their mechanical properties. The annealing process results in more uniform deformation and a distinctive fracture surface in which crazes appear to nucleate at spherulite cores. This tendency for the fracture process to nucleate at the spherulite cores in the annealed samples has been confirmed by work on thin films.

In thin films it is apparent that although the ageing process results in a reduction in the total strain to break, there is very little change in the fracture mechanism. In both aged and un-aged samples a few crazes open up and then fail after reaching very high local levels of strain. In the un-aged samples more material is pulled into the craze so a higher total strain is supported. This is in contrast to the annealed films in which the crazes consist of a large number of microcrazes which nucleate over a far larger proportion of the sample. It appears to be this ability of the polymer after annealing to dissipate energy through a large number of crazes which leads to its improved toughness.

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.

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Received 22 September 1997
and accepted 21 August 1998