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Plane stress deformation zones at crack tips in polycarbonate

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The plastic deformation produced at crack tips in polycarbonate (PC) films stretched in tension, has been characterized by optical and transmission electron microscopy. An extensive and diffuse region of deformation is formed in unannealed specimens. Within this zone the ratio (v_f) of local film thickness to the (undeformed) thickness far away from the crack varies gradually both along and across the zone. The minimum ratio of ~ 0.5 occurs at the crack tip. In contrast to this behaviour, films annealed for a short time just below the glass transition temperature T_g showed a highly localized response, the plastic strain being confined to a well-defined flame shaped deformation zone (DZ) ahead of the crack. Within most of this DZ, v_f is constant at ~ 0.7, rising to 1 over a distance of 10 μm at the zone tip, and falling to ~ 0.5 over a distance of ~ 4 μm around the crack tip. Bi-refringence measurements show that a high degree of molecular orientation occurs within the zone. These experiments support the idea that an increase in the localization of the plastic strain response upon annealing below T_g is responsible for the embrittlement of PC by such heat treatment.

1. Introduction

Polycarbonate (PC) is generally classed as a ductile, glassy polymer and in many cases its high toughness is of great importance. However, following annealing at temperatures just below the glass transition temperature, T_g, significant changes in many of its material properties have been observed [1–8]. Most important is that in practice a drop in impact strength occurs and the polymer is "embrittled". Various workers have attempted to relate this embrittlement to changes in structure [1, 4], yield strength [2] and the amount of strain softening [5]. However, these experiments have in general been carried out on bulk specimens in which it is hard to identify and characterize the plastic deformation that precedes fracture (the magnitude and extent of which is essentially being monitored in impact toughness tests) and hence identify how its nature changes upon annealing.

In this study the deformation behaviour at a crack tip in thin solvent-case films of polycarbonate under uniaxial tension has been investigated for both annealed and unannealed films. Optical and electron microscopy have been used to quantitatively characterize the plastic deformation zones formed. These measurements enabled a comparison to be made of the zone shape during growth and at equilibrium with theoretical models. These results are presented in the following paper.

2. Experimental procedure

The polymer resin used was GE Lexan grade 130 (intrinsic viscosity, $[\eta] = 0.665$ dl g^{-1}), kindly supplied by Dr Roger Kambour. After dissolving this resin in methylene chloride, thin films (with thicknesses in the range 0.8 to 1 μm) were produced on glass slides by drawing these slowly from the solution. Using a method analogous to that developed by Lauterwasser and Kramer [9] for producing uniform thin films of polystyrene (PS), these PC films were floated off onto the surface of a water bath and picked up on annealed copper grids, the grid bars of which had been precoated with a thin film of PC. Bonding of the PC film to the coated grids was achieved by a short exposure of the

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specimen to methylene chloride vapour, and the specimen was then placed in vacuum overnight to remove excess solvent from the film. Annealing of the films was carried out on the grids for times of 0 to 88 h at a temperature of 132° C.

A new method for introducing a crack of controlled geometry into these films has been developed in the course of this investigation. Cracks in thin polymer films have been produced previously by indenting the film while still on the glass slide using a Tukon microhardness indentor [10]. However, as has been noted by Chan *et al.* [10] in their work on crazing in PS, this method has the disadvantage of causing a wall of polymer which has been pushed aside by the indentor to build up around the crack. The formation of this region of different mechanical response located at the crack tip occurs for all but the thinnest films (~ 100 nm thick for the case of PS).

To make a crack without ridges of plastic deformation at its tip, the electron beam from a JEOL 733 superprobe has been used to produce a thin slot of "burnt" material in the centre of each grid square. The absolute dimensions of this slot can be altered by changing the magnification. Within this region a very high degree of chain scission has occurred, whilst the polymer covering the remaining portions of the grid square remains unirradiated. The positioning of the probe line scan can be performed solely with the use of an optical microscope (attached to the column of the microprobe), so that the electron beam is only switched on momentarily. For PC suitable operating conditions to give a final crack of the desired dimensions (approximately 70 × 10 μm) were found to be an accelerating voltage of 25 kV and a specimen current of 25 to 30 nA acting for ~ 1 sec at a magnification of × 2000.

The appearance of the "burn" so produced in the unstressed film is shown in Fig. 1. Two features are immediately obvious. Firstly, the two ends of the burn differ in appearance because the electron beam "dwells" longer at one end of the scan than the other. This difference could be removed by the addition of a suitable beam blanking device to the column of the microprobe, but in practice the asymmetry was found not to affect the nature of the final deformation. Secondly, before any strain is applied to the specimen, the irradiated area remains intact. However, as soon as a low level of strain is applied to the specimen, the burn cracks open and the desired crack with controlled geometry is obtained.

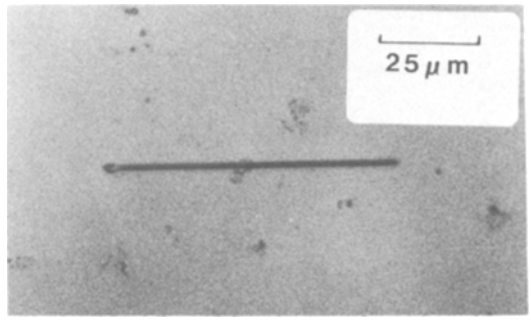


Figure 1 The appearance of an unstressed "burn" produced by irradiation in the JEOL 733 microprobe.

The geometry of the crack is chosen so that its long axis is normal to the direction in which the strain is subsequently applied. During straining, time lapse micrographs of the film were taken using an optical microscope to observe the growth of the regions of deformation. Subsequently further optical microscopy at higher magnification was carried out. Suitable grid squares could be cut from the copper grid (the plastically deformed copper grid maintains the strain in the film) for examination by transmission electron microscopy using a Siemens 102 instrument operating at 125 kV.

3. Results

3.1. Characteristics of the deformation zone

Typical areas of deformation in an unannealed specimen and a film annealed for 1 h at 132° C are shown in Fig. 2a and b. The annealed film shows a localized "flame"-shaped deformation zone extending away from the crack tip. The zone has well defined edges and as a successively higher strain is applied it grows both in length and width. Simultaneously the crack opens up and propagates slowly into the deformation zone, as shown in Fig. 3. This extending crack has a characteristic diamond shape, analogous to the diamond cracks observed in various polymers by Haward and co-workers [11–14]. The diamond crack separates "lobes" of drawn material.

In contrast to this well defined zone the unannealed PC shows a much more diffuse region of deformation extending away from the crack. The total volume of material deformed is much higher in this case than for an annealed specimen subject

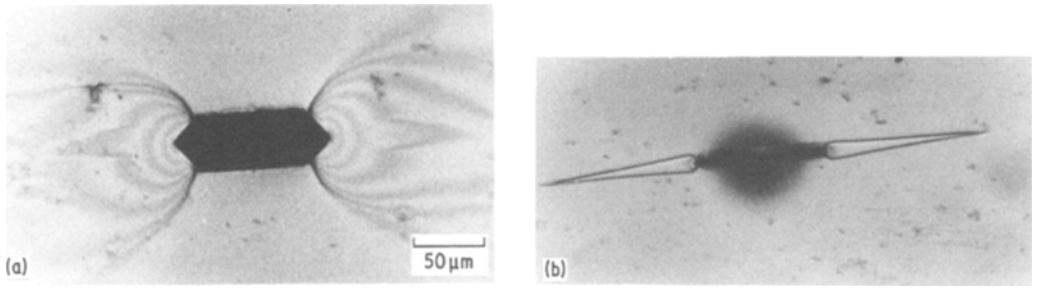


Figure 2 (a) Optical micrograph of the deformation produced at a crack tip in unannealed polycarbonate, (b) optical micrograph of the deformation produced at a crack tip in polycarbonate which had been annealed for 1 h at 132° C.

to a comparable level of strain. Once again the crack tip propagation into the film is characterized by a "diamond" structure (see Fig. 2a) as for the annealed films. Deformation initiates at significantly higher strains (3 to 4%) for unannealed specimens than for those which had been heat treated (1 to 2%).

Since it is not possible using optical microscopy alone to distinguish between matter that has voided on a very fine scale (i.e. crazes) and a zone of reduced thickness/refractive index which is unfibrillated, the nature of these zones was examined in the transmission electron microscope. For both the annealed and unannealed films, the zones are observed to be regions of local thinning which contain no voids. Crazes are rarely observed in these specimens even after the extensive annealing which Beahan *et al.* [15] have found sufficient to produce crazing in thin films of PC. Other observations of crazing in PC have either been associated with specimens of macroscopic dimensions (e.g. [16–20]) where a plane-strain stress field will exist, in contrast to the plane stress situation of these experiments, or the presence of an active ("craze producing") environment (e.g. [21–23]). It is felt that when crazes were observed in these specimens, their occurrence may be due to contamination of the film by finger grease or some other environmental crazing agent.

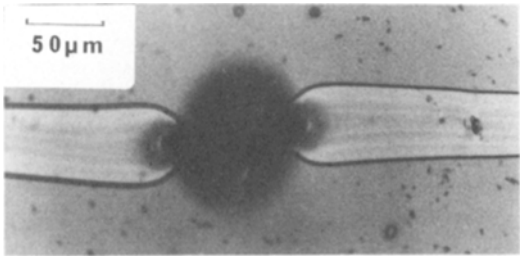


Figure 3 A highly strained annealed polycarbonate film showing the development of a diamon-shaped crack.

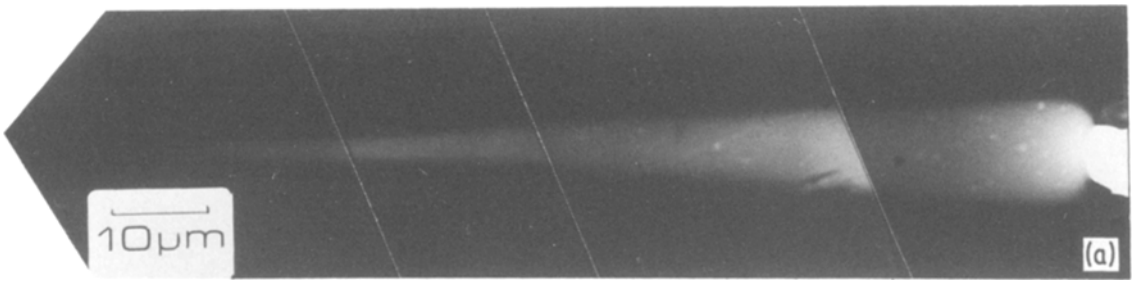
However, although both types of specimens showed an absence of crazing, the difference in the nature of the deformation due to the annealing treatment is clearly apparent. Lauterwasser and Kramer [9] and Brown [24] have independently developed a method for measuring the volume fraction (v_f) of matter in a craze using microdensitometry of the electron image plate to obtain the optical densities of the craze (ϕ_c), the film (ϕ_f) and a hole in the film (ϕ_h). The relationship,

$$v_f = 1 - \frac{\ln(\phi_c/\phi_f)}{\ln(\phi_h/\phi_f)} \quad (1)$$

then gives v_f. This method may equally well be applied to the unfibrillated matter within these deformation zones (DZs) and hence to determine the local thinning at various points of the zone, i.e. v_f is the ratio of the final to the initial film thickness.

Because of the radiation sensitivity of PC, some caution must be exercised in making these measurements. To obtain meaningful v_f values, it is necessary to expose the specimen to the electron beam for as short a time as possible to avoid a significant mass loss. (In practice, if the rate of loss of material is assumed to be the same for both the matrix and the zone, the ratio of the optical densities is unlikely to be affected by the mass loss and this limitation is not so severe as might be anticipated.) Furthermore, unless low beam exposures are used the radiation damage around the crack tip may be sufficiently severe to permit some crack propagation into the DZ, or even cause the whole zone to tear apart. With care, however, these problems can be overcome.

A composite series of electron micrographs of



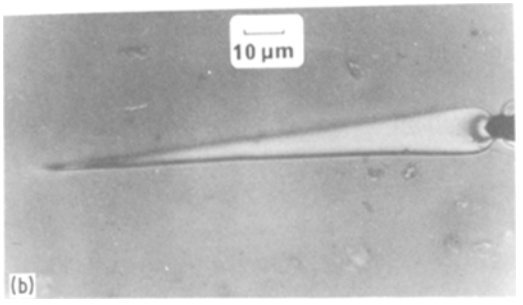


Figure 4 (a) Composite series of transmission electron micrographs of the DZ shown in Fig. 2b, (b) optical micrograph of the DZ shown in Fig. 2b, taken with monochromatic light ($\lambda = 550$ nm).

the DZ shown in Fig. 2b is shown in Fig. 4a. It is found that v_f is essentially constant along the zone up to within $\sim 4\,\mu$m of the crack tip and to within $\sim 10\,\mu$m of the zone tip (i.e. along approximately 80% of the length of this particular DZ). Using Equation 1 an average value of v_f of 0.71 is obtained. At the DZ tip v_f rises up toward 1 where it clearly becomes indistinguishable from the matrix background. This behaviour is in contrast to a craze tip which also tapers approximately uniformly in width towards the tip, but which has a much smaller tip radius ~ 5 to 10 nm and a v_f which *decreases* significantly (i.e. it has an extension ratio λ which increases) within $10\,\mu$m of the tip [9, 10]. At the crack tip a crescent-shaped region of decreasing zone thickness occurs, with v_f falling away from the average zone value of 0.71 to 0.48 at the crack tip, this decrease occurring within $4\,\mu$m of the crack tip. This decrease is revealed by microdensitometry, but it is hard to detect by eye in the electron micrograph of Fig. 4a; it can be seen more easily in Fig. 4b which is an optical micrograph taken with monochromatic light. In such a micrograph a change in the order of the interference fringe indicates a change in specimen thickness, permitting ready identification of local changes in v_f. Thus, since the majority of the zone appears of uniform contrast, a constant thickness and v_f is implied. A shift of half a fringe order occurs at the crack tip, as demarcated by the crescent-shaped fringe, in agreement with the microdensitometry results.

Similarly, the increase in v_f towards 1 at the zone tip is revealed (in Fig. 4b) by the change in fringe order within $\sim 10\,\mu$m of the zone tip, again confirming the results from the electron micrographs. Although there is little variation in v_f across the width of the zone (and in particular no region corresponding to the midrib of a craze is present), the edges of the zone are much less sharply defined than the craze–matrix interface. The craze interface is typically sharp over the dimensions of the fibril radius, i.e. ~ 6 nm, whereas for the DZ v_f increases to its maximum value over $\sim 1\,\mu$m at each edge with similar deformation zones $v_f \sim 0.7$ have been previously observed in thick films of slowly cooled PC by Narisawa *et al.* [25, 26].

At low levels of strain (within the range 1 to 3.5%), there seems to be little variation in the v_f measured within the DZ with the applied strain. All such measurements lie in the range 0.65 to 0.77 with the variation not correlating with decreasing applied strain. This observation suggests that $1/v_f = \lambda$ may correspond to the "natural draw ratio" for PC, as has been suggested [9] for the λ measured for crazes in PS. To check this hypothesis, tensile tests were carried out on sheets of PC ~ 1.71 mm thick which had been annealed for 18 h at 132° C. The tests were carried out on an Instron testing machine at a cross-head speed of $1.27\,\text{mm}\,\text{min}^{-1}$ and the decrease in specimen cross-section following necking was used to estimate the natural draw ratio. From these experiments a value of $A/A_0 = 0.63 \equiv v_f$ was obtained corresponding to a natural draw ratio of 1.58, in reasonable agreement with the observed v_f of the DZs.

In contrast to this behaviour for annealed specimens, the v_f of DZs in unannealed specimens

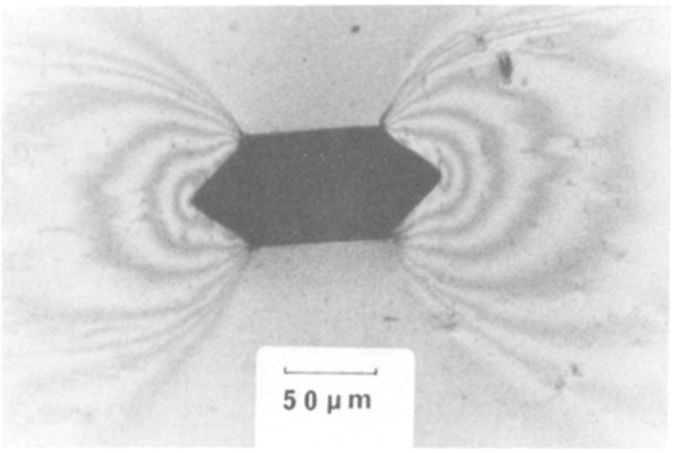


Figure 5 Optical micrograph of the diffuse deformation zone in an unannealed specimen, imaged with monochromatic light.

showed significant variation with position, varying both across the width of the zone and along its length, rising in both directions from a minimum of ~0.5 at the crack tip. Because of the large area which deforms in these specimens and because the overall level of contrast in the electron microscope is low, these samples were not easily characterized by the above method of determining v_f. However, the large size of the zone in a highly stressed unannealed sample makes it possible to use optical microscopy to map out the thickness profile if position and resolution of better than a few micrometers is not required. An optical micrograph showing the thickness fringes obtained with monochromatic light of wavelength 550 nm is displayed in Fig. 5. This shows the same variation in film thickness across and along the zone as was inferred from the electron microscopy measurements. The change in degree of strain localization can easily be seen in Fig. 6a and b, which shows contours of constant v_f for the two types of specimen.

It is clearly of interest to know how the nature of the deformation changes with length of annealing time. For these films it was found that even only a 5 min anneal at 132° C was sufficient to produce the typical annealed form of the DZ with its characteristic flame shape and well defined edges. Increasing the length of time of annealing neither changed the appearance of the zone nor altered the average value of v_f significantly from 0.71. Thus it can be inferred that the molecular rearrangements that are affecting the strain localization occur very rapidly, in contrast to the changes in modulus and yield stress which continue to increase significantly over a much longer time scale of annealing [1, 4]. However, an increase in annealing time did tend to lower the strain at which the DZs first appeared, with a critical strain of ~3.5% for a specimen annealed for 50 min, compared with ~1.5% for an annealing time of 18 h at 132° C. Since the length of annealing was found to be relatively unimportant, a standard treatment of 1 h at 132° C was selected for most of the experiments performed.

3.2. Determination of the nature of orientation within the DZ

When crazes form in glassy polymers such as PS, the polymer chains tend to align preferentially along the fibril axes as revealed by X-ray [27, 28], electron diffraction [29, 30] and bi-refringence [30, 31] measurements. However, because of the structure of a craze, optical bi-refringence measurements are difficult to interpret since form bi-refringence makes a very large contribution to the overall measurement, and modelling the craze structure adequately to obtain the true orientation contribution to the bi-refringence is hard to achieve [30].

However, in the case of the deformation zones here in PC, the problem of form bi-refringence does not arise for either the annealed or unannealed specimens since fibrils are not present. A Berek compensator was used to measure the retardation within the zones. Knowing the original thickness of the thin films (measured using a Zeiss interference microscope) and the v_f within the DZs (measured using transmission electron microscopy and Equation 1), it is then possible to calculate the bi-refringence within the zone.

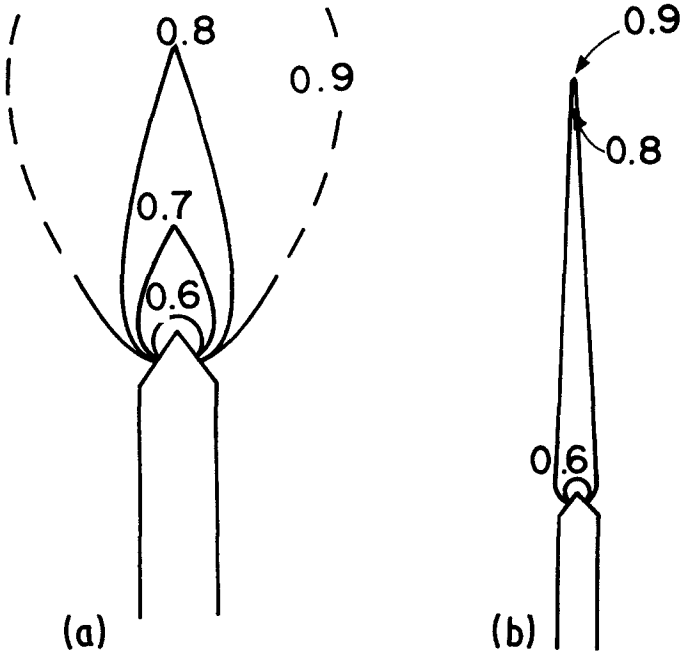


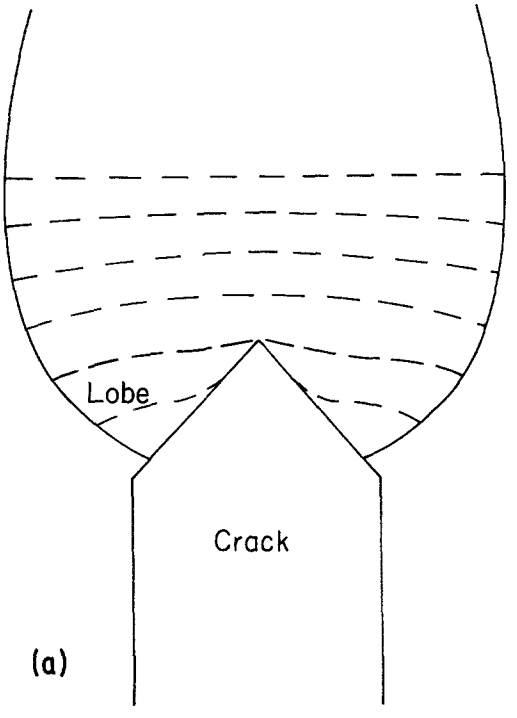
Figure 6 (a) Map showing contours of constant v_f for an unannealed specimen. As $v_f \rightarrow 1$ the outer edge becomes indistinct, (b) map showing contours of constant v_f for an annealed specimen.

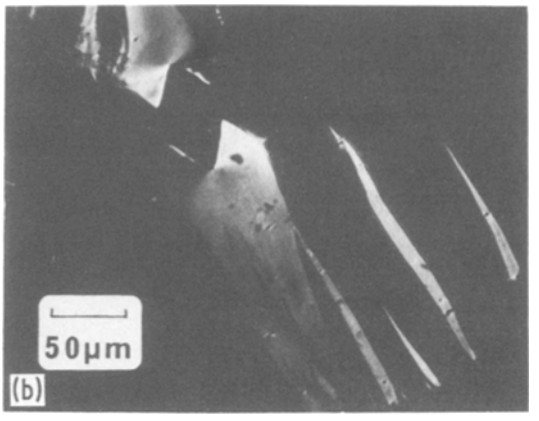
For the case of the annealed specimens, which had a uniform v_f across the zone, this procedure was straightforward. The average value of the bi-refringence Δn so obtained (averaged over 6 specimens) was 0.117 ± 0.005. As might be anticipated from the fact that the λ value within the zone was essentially independent of either total applied strain or length of annealing time, it was found that the measured Δn was also independent of these variables. This value of Δn can be compared with the maximum theoretical bi-refringence calculated assuming total alignment of the polymer backbone [32]. For PC this has been computed to be 0.236 [33, 34].

Precise correlation of retardation with local thicknesses is harder to achieve for the unannealed specimens because the deformation is more diffuse and there is a gradual variation in thickness both across and along the zone. However, estimating local values of v_f near the crack tip yields a value for Δn in the unannealed specimens comparable with that measured in the heat-treated samples.

Further information on the orientation of the polymer chains during deformation can be obtained for both types of specimens by observation of the isoclinics when the zones are viewed through crossed polars. This information is most easily obtained for highly strained specimens where the crack has penetrated some distance into the zone and well defined lobes have formed around the crack (Fig. 7a). For the annealed specimens the zero degree isoclinic extends over the majority of the zone extending away from the crack. However, the rotation of the principal axes of strain in the lobes relative to the remainder of the zone is such that they remain locally normal and tangential to the direction of the outer edge of the flame-shaped zone. Similarly, analysis with a full-wave plate shows that the "fast" direction rotates in such a way that both in the bulk of the zone away from the crack and in the lobes it remains normal to the outer edge of the zone.

Thus, the annealed specimens showed essentially three areas with different orientations of the principal axes, the two lobes and the remainder of the DZ behind the crack tip, with only a minimal area of transition between these regions. In contrast to this behaviour, the unannealed specimens showed a gradual rotation of the isoclinics. A comparison of the two types of behaviour is shown in Fig. 7b and c. In Fig. 7a the isoclinic extends over almost the entire area of one lobe, whereas in the unannealed specimen the isoclinic is more localized and spirals around as the specimen is rotated. Thus, as with the variation in v_f across the zone in the unheat-treated samples, there is a much more gradual variation in the orientation of the principal strain axes across the zone compared with unannealed specimens.





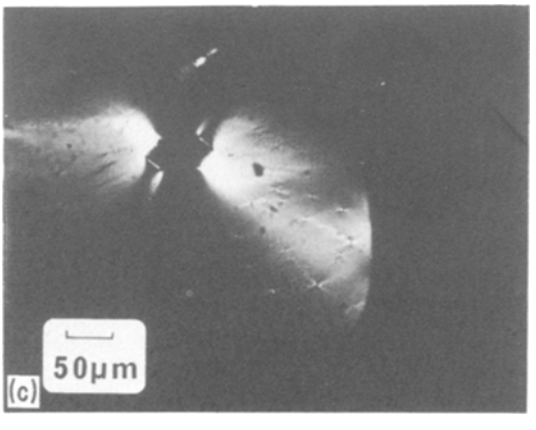


Figure 7 (a) Schematic representation of the molecular orientation within a DZ in annealed PC; dotted lines represent molecular orientation, (b) isoclinic in annealed PC, and (c) isoclinic in unannealed PC.

4. Discussion

4.1. The shape of the deformation zones

It has previously been shown [35] that crazes in PS grow in such a way that the orientation of the fibrils lies parallel to the major principal stress axis and that the direction of craze growth follows the minor principal stress trajectory. These conclusions were originally derived from observations of craze growth around a circular hole in a sheet of PMMA tested in tension. Bevis and Hull [36] extended this work to consider craze growth near a stationary edge crack in PS. Using the solution to the stress fields for this geometry previously obtained experimentally by Post [37], they demonstrated that the minor principal stress axis determines the direction of craze growth for this geometry also.

The form of the principal stress trajectories, as determined by Post [37], are shown in Fig. 8. From this diagram it is clear that the edge of the characteristic flame-shaped zone observed in the annealed specimen corresponds closely to the shape of a minor principal stress trajectory. Furthermore, the analysis of the molecular orientation in these zones has shown that this follows the major principal stress axis. Thus, despite the fact that voiding and fibrillation have not occurred in these thin films of PC, it is clear that their yielding behaviour is closely analogous to the crazing of PS. However, rather than a closely-packed bundle of crazes enclosed in an envelope defined by a maximum principal stress contour, only the single zone is formed.

In contrast to this behaviour is the diffuse nature of the yielded zone in the unannealed specimens. In this case, as deformation proceeds the area ahead of the crack acquires a thickness gradient which leads to a more complex stress state. As the deformation extends, secondary zones are nucleated from inclusions in the film. Although at the centre of the zone these lie normal to the direction of the applied stress, towards the edge, pairs of zones subtending an angle of $\sim 40^\circ$ to each other nucleate from a single dust particle. These can be seen in Fig. 7c which was taken through crossed polars. This observation suggests that some shear in the plane of the film is

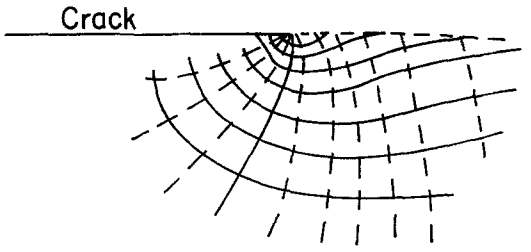


Figure 8 Principal stress trajectories at a crack, after Post [37]; dotted lines represent the major, and solid lines the minor principal stress trajectories.

occurring locally. Closer examination of the area at the crack tip in early stages of straining suggests diffuse shear bands are formed at all stages of growth. A similar observation was made by Cornes *et al.* [13] who observed the progress of fracture from surface crazes in PC using scanning electron microscopy. In this work cavities nucleated at the centre of crazes and angled shear bands propagated away from the cavities.

The occurrence of shear bands in conjunction with normal yielding in PC has also been noted by other workers [20, 38, 39]. In fatigue experiments [38, 39], shear bands emanated from crack arrest band formed during fatigue crack growth. It has been suggested [39] that the existence of the "epsilon" plastic zone formed by the two shear bands and (in their case) craze may account for the relative stability of discontinuous crack growth regions in PC.

4.2. Relationship with macroscopic measurements of impact toughness

It has long been known that annealing of PC causes embrittlement, with a consequent reduction in impact strength. Various workers have attempted to correlate this embrittlement with molecular rearrangements leading to changes in free volume, loss modulus, etc. (e.g. [1, 7]). Changes in surface morphology following annealing, as revealed by electron microscopy, have also been reported [4, 40]. However, although significant differences in such material parameters do occur, it has not yet been possible to determine precisely how the observed changes lead to embrittlement.

Other workers (e.g. [2, 5, 6]) have found it more useful to consider macroscopic properties to characterize embrittlement and it has been shown that the yield strength increases with annealing time. The heat treatment also leads to an increased "yield drop" and therefore an enhanced tendency for strain localization [41, 42]. By viewing broken Izod test-pieces in polarized light, Adam *et al.* [5] were able to show that the volume of strained material was much less for annealed specimens than for similar unheat-treated samples.

An alternative argument to explain embrittlement in thick PC sheets was put forward by Broutman and Krishnakumar [43]. They suggested annealing removed the surface compressive stresses which in quenched specimens will hinder craze and crack propagation. However, as has been pointed out by Saffell and Windle [44], an extruded sheet in practice has little residual surface compressive stress and thermal history must be affecting the toughness in some other way. By the same token while residual stresses may be important in some quenched specimens of macroscopic dimensions, they clearly cannot account for the severe localization of strain observed upon annealing these PC films.

The importance of the contribution of crazing to yielding behaviour in bulk specimens cannot be assessed from the results presented here on thin films where crazing was virtually never observed. However, it would appear from the literature that air crazing (as opposed to environmental crazing) is not a particularly important mode of failure for PC in either annealed or unannealed samples. Indeed, it is hard to produce extensive crazing, in clean tensile samples unless the surface has been contaminated (e.g. by finger grease).

The results presented in this paper are entirely consistent with the ideas put forward by Adam *et al.* [5] that the reduced impact toughness following annealing is associated with a greater tendency for strain localization. Using the combined techniques of optical and electron microscopy it has been possible to determine some of the underlying changes in the molecular orientation under stress but no attempt is made here to relate this to fundamental changes in the molecular packing which may occur during annealing.

The overall picture that can be seen is therefore one in which the profuse but diffuse regions of deformation in as-received samples change to a few localized regions in annealed test-pieces. As the strain is increased, the annealed samples respond by pre-existing zones growing in length and width because of the strain-softening character-

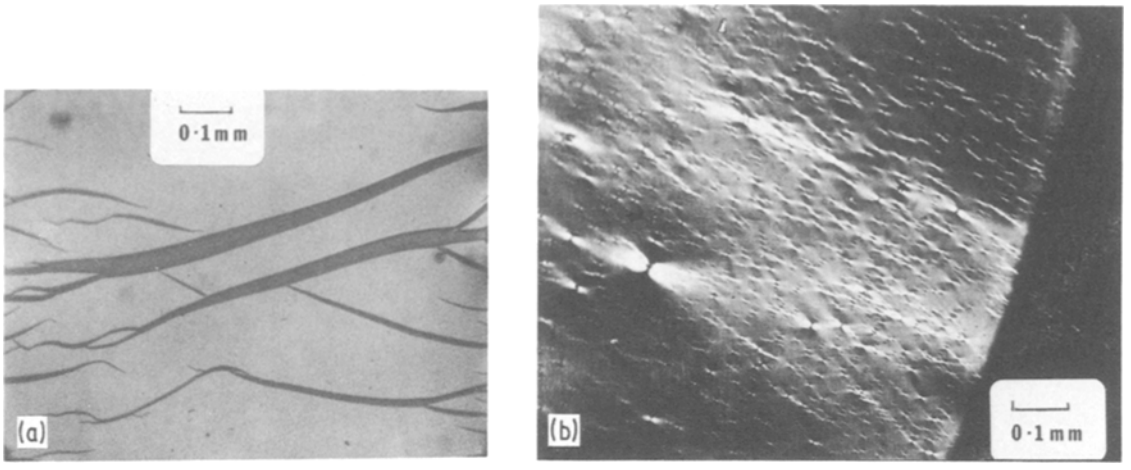


Figure 9 (a) DZs in an uncracked specimen of annealed PC. (b) Diffuse deformation in an uncracked specimen of unannealed PC (polarized light).

istics of the material. In contrast to this behaviour new zones are nucleated in unannealed samples as the strain is increased whilst pre-existing zones do not grow extensively. This conclusion can best be demonstrated by studying thin film specimens which have not been precracked, so that the only stress concentrations present are due to random imperfections in the film. Fig. 9 shows two such samples and the numerous low contrast regions in the unannealed samples can be compared with the few zones nucleated in the annealed film, where a small volume of material is highly strained.

In terms of the total plastic work accompanying the deformation, far more energy is absorbed in generating profuse regions of low strain rather than in a few zones of high strain. This conclusion can be made more quantitative by comparing the volume of deformed material within the DZ at a crack tip in annealed and unannealed specimens for equal amounts of crack-tip advance. This comparison shows that the displacement (and thus the energy absorbed since the stresses in the zones are similar) in the unannealed specimen is approximately twice that of the annealed sample at an equivalent point along the zone (the zone being of almost equal length in the samples studied). Thus the unannealed samples have correspondingly greater ability to absorb energy in impact tests than heat-treated samples and this will be reflected by the embrittlement of the material following annealing. The presence of shear bands in the unannealed samples will also serve to increase the total work of plastic deformation relative to the annealed specimens.

Although the results obtained here clearly relate to a different type of stress state from that set up in macroscopic specimens (i.e. plane stress versus plane strain conditions) it is nevertheless felt that the underlying response of the material must be the same. Clearly under different situations the precise form of any "deformation zones" generated may be altered, but the way the behaviour of such zones in these thin films changes with heat treatment will be reflected in the response of bulk specimens to annealing. Mills [45] has argued that a ductile–brittle transition is only observed in specimens sufficiently thin that plane stress conditions hold and that for thick specimens thermal history does not affect the mode of failure. However, the results presented here clearly demonstrate the profound effect annealing PC has on strain localization under plane stress conditions.

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