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# The mechanism of brittle fracture in notched impact tests on polycarbonate

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The impact testing of notched polycarbonate bars that are thick enough to yield in plane strain has been investigated. Shear bands occur in the plastic zone that resemble the slip line field for yielding from a circular notch. Eventually, an internal craze nucleates at the tip of the plastic zone, where the stresses are highest, and a crack forms in the thickest part of the craze. Above − 15° C the stress for the craze to nucleate is a nearly constant multiple of the yield stress. It is shown that previous observations that annealing polycarbonate causes a ductile to brittle transition is a consequence of testing bars of thickness less than 5 mm.

## 1. Introduction

There is considerable literature on the impact strength of bisphenol "A" polycarbonate (PC). This is partly due to its position as one of the toughest glassy plastics, and partly to the interesting transitions in its behaviour that occur close to room temperature. Wolstenholme *et al.* [1] showed that the energy absorbed in a notched impact test on PC was not proportional to the notch length, and Smith [2] has given more precise data on the thickness of sheet at which the transition from ductile to brittle behaviour occurs. This transition is one between a plane stress fracture and a plane strain fracture, in the terminology of fracture mechanics [3]. The transition can also occur by changing the test temperature while keeping the specimen geometry fixed, or by changing the thermal history of the PC [4].

There has been less published on the mechanisms of the fracture process. Legrand [4] reported that in slow three-point bend tests on notched PC Izod bars, a flaw formed approximately 160 ± 10 $\mu$m below the notch tip, and that the subsequent growth of this flaw differed when the fracture was brittle from the growth when the fracture was ductile. He held that this flaw was a cohesive failure, since its surface appeared featureless at 50 000 × magnification. Garde and Weiss [5] made a careful study of similar cracks that formed below the notch in slow tensile tests of double edge notched PC sheets. They used Hill's [6] slip line field analysis, of plane strain yielding at a circular notch in a rigid-plastic material, to calculate the tensile stress necessary to nucleate the crack as being 148 ± 14 $\text{MN m}^{-2}$. Hull and Owen [7] have described the fracture surface details of PC, revealed by the scanning electron microscope. They infer that crazes grow from the notch root, and that a crack nucleates inside one of the crazes.

There appear to be two main postulated explanations of the ductile-to-brittle transition in PC brought about by annealing. The first is a simplification and adaptation of Orowan's [8] explanation of the ductile–brittle transition in metals. Allen *et al.* [9] postulated that the stress for crazing in PC is independent of temperature or thermal history (there is no experimental data), whereas the yield stress is known to increase with decreasing temperature [10], or with annealing just below the glass transition temperature $T_g$ [4]. They seemed to be unaware of any plastic constraints in yielding at a notch, for they suggested that brittle failure should occur if the crazing stress is less than the yield stress. An associated paper [11] on X-ray analysis of the microstructure, and other work [12], have shown that annealing PC below $T_g$ certainly does not cause crystallization, and has only minor effects on the glassy microstructure.

The second explanation relies on the numerous observations that the annealing of glassy polymers below $T_g$ increases the likelihood of inhomogeneous strain in subsequent plastic deformation. Camwell and Hull [13] have shown that the slow cooling of polystyrene from the melt promotes the formation of shear bands when the polystyrene is taken beyond yield in compression, and further that the intersection of these shear bands assists in the process of craze nucleation. Vincent [14] has examined a number of polymers and shown that a drop in the engineering stress after initial yield correlates with the observation of shear bands and crazes, and with a low fracture toughness. Bowden [15] has shown that strain softening after yield causes shear bands, but it is not established that strain softening causes crazing. Recently, Adam *et al.* [16] have used this approach to explain the ductile–brittle transition in PC. They observed that annealing below $T_g$ caused both the degree of strain softening after yield to increase, and the yielded volume of a broken notched impact bar to decrease, and they postulated that the former caused the latter.

The aims of this research are, therefore, to provide more experimental evidence of the mechanism of fracture in PC, and to evaluate suggested explanations of the ductile to brittle transition in notched impact tests. The relationship of the various experiments to these aims is summarized in Fig. 1.

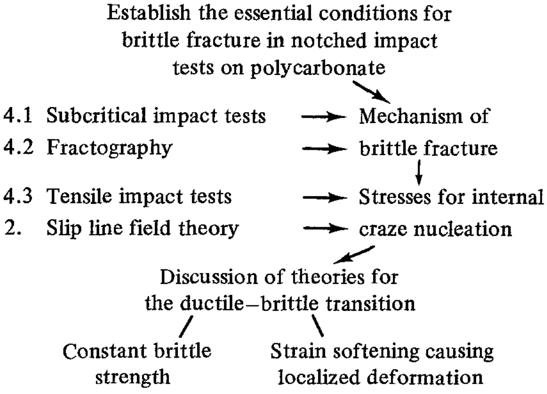


*Figure 1* Layout of paper.

## 2. Theory of the plastic stress concentration at a circular notch

Hill [6] has given a slip line field solution for the plane strain yielding of symmetrically notched bars under uniaxial tension. A rigid-plastic material is assumed, so the slip lines must extend across the bar before plastic flow is possible. The slip lines are logarithmic spirals, meeting the stress-free notch surface at 45° to the surface (Fig. 2). In polar co-ordinates $r$, $\theta$ the slip lines have the equation:

$$\theta \pm \ln(r/a) = \alpha \qquad (1)$$

where $a$ is the notch radius and $\alpha$ is a constant. The stresses in polar co-ordinates are then:

$$\begin{aligned}\sigma_{\theta\theta} &= 2k(1+\ln(r/a))\\ \sigma_{rr} &= 2k\ln(r/a)\\ \sigma_{r\theta} &= 0. \end{aligned} \qquad (2)$$

For a material obeying the von Mises yield criterion the uniaxial tensile yield stress is equal to $\sqrt{3}k$. The maximum tensile stress occurs in the $\theta$ direction at the point in the slip line field farthest from the notch.

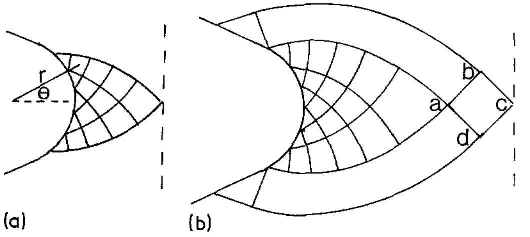


*Figure 2* Slip line field for a symmetrically notched sheet under uniaxial tension. Only half the bar is shown for (a) small (b) larger values of the ratio notch tip radius/bar width.

If the width of the bar between the two notches is greater than in Fig. 2a then the slip lines can intersect the straight sides of the notch. Hill [6] shows that in region ABCD of the slip line field shown in Fig. 2b, the maximum tensile stress is:

$$\sigma_{\theta\theta} = k(2+\pi-\phi) \qquad (3)$$

where $\phi$ is the angle included between the straight sides of the notch.

Green's [17] slip line field solution for pure bending of a notched bar also has a region of logarithmic spiral slip lines from the circular part of the notch. In an elastic-plastic material a plastic zone initiates at the notch root, and grows in size as the applied load is increased.

Finite element methods have been used to compute the plastic stress concentrations in an elastic-linearly working-hardening material [18]. The position of the maximum tensile stress was found not to be at the tip of the plastic zone unless the rate of work-hardening is zero. Ewing and Griffiths [19] discuss this result, in view of the practise of etching up yielded zones in metals [3] in order to estimate the cleavage stress using Equations 2 and 3.

Note that the shape of the elastic-plastic interface can be quite different from that of the outer slip lines in Fig. 2. The former is a locus of points where the yield criterion is just satisfied, whereas the latter give the directions of the maximum shear stresses. If PC behaves as a non-work-hardening von Mises material at impact strain-rates, and if there is experimental evidence that the slip line solution is valid, then Hill's analysis of the stresses in the plastic zone can be applied.

In a real notched specimen, through thickness yielding will occur near the sheet surfaces and, as a result, the midsection of the notch will be in plane strain conditions whereas the ends of the notch are in plane stress conditions. Unless the notch tip radius is much less than the sheet thickness there will never be a plane strain yielded zone. As the plane strain yielded zone grows in length $l$, it is likely that the through thickness stress will be relieved in the region of the plastic zone to a depth of the order of $l$ from each surface. Thus eventually a transition from plane strain to plane stress yielding will occur as yielding progresses, if the width of the specimen below the notch is greater than the specimen thickness.

## 3. Experimental

### 3.1. Thermal treatment of polycarbonate

The PC used as Bayer "Makrolon" sheet, presumably made from the high molecular weight 3200 grade by extrusion through a slit die onto cooled rollers. The process unfortunately leaves some residual orientation in the polycarbonate. This was removed, together with any machining stresses, after samples had been fabricated. The PC was dried in an air circulating oven at 120° C, then heated to 160° C for 30 min while supported between glass plates. The PC was then either (a) removed and cooled rapidly to room temperature or (b) given a further 16 h heat-treatment at 135° C. The temperature of 135° C was chosen as the optimum for increasing the yield stress in a reasonable time.

The effectiveness of the thermal treatment was monitored using a Perkin Elmer Differential Scanning Calorimeter Model 2. Fig. 3 shows typical traces corrected to give specific heat versus temperature relations. The endothermic peak at 162° C only appears after annealing at 135° C. It was established by experiments carried out with the DSC that (1) The rate of cooling for the "quenched" samples is not critical. Cooling rates faster than 5° C min$^{-1}$ were sufficient to suppress the endothermic peak at 162° C. This means that even with the low thermal diffusivity of PC, which restricts the cooling rates at the centre of thick sheets, a sheet of 5 mm thickness can be prepared in a "quenched" state. (2) The PC stays in the "quenched" state at room temperature, (unlike polyvinylchloride). The endothermic peak at 162° C does not reappear in PC examined 6 months after quenching. However, water uptake occurs slowly to give a water content of about 0.2% by weight. For this reason the impact bars were tested within 1 day of preparation.

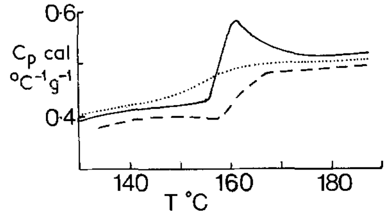


*Figure 3* Specific heat versus temperarure from differential scanning calorimeter runs at a heating rate of 40° C min$^{-1}$; ------ annealed, —— quenched, ....... re-run in DSC after cooling at 40° C min$^{-1}$.

### 3.2. Falling weight tensile impact tests

One prerequisite for the analysis of the Charpy impact behaviour of PC was a knowledge of the stress–strain behaviour at strain-rates corresponding to those in the impact test, especially the strain-hardening behaviour. Unfortunately, the literature is sparse on this point, and it is not advisable to assume for a viscoelastic material that the form of the stress–strain curve is the same as that at conventional strain-rates. Bauwens-Crowet *et al.* [20] have shown that the initial engineering yield stress of PC increases linearly with the logarithm of strain-rate up to strain-rates of 100 sec$^{-1}$, but they give no details of the shape of the stress–strain curve. The Charpy impact test used has a impact velocity of 2.2 m sec$^{-1}$, and the specimen dimensions used were such that yielding occurred at the notch tip when the deflection was ~ 3 mm in a slow bend test. Therefore, yielding occurs on a time scale of ~ 1 msec in the impact test. A falling weight tensile impact machine was constructed that was somewhat similar to one described by Donnelly and Ralston [21]. A 2 kg mass falls to 10 cm, then contacts a cone attached to the end of a waisted tensile specimen. The specimens were fabricated from 1 mm sheet, and had a minimum width of 2 mm and a radius of curvature of 12 mm to the waisted portion. The impact velocity of 1.4 m $\sec^{-1}$ causes yielding to occur in 2 msec at a strain-rate of approximately 25 $\sec^{-1}$. The specimen was supported by an Endevco Model 2103-100 quartz crystal dynamic force gauge. This has a resonant frequency of 100 kHz with the added 100 g mass of the upper grip. The output of the force gauge was amplified by a Kistler Instruments Ltd Type 5001 charge amplifier and displayed on an oscilloscope. In order to prevent shock waves from the impact producing a spurious response, the impact was cushioned by mounting the force gauge on a 3 mm thick sheet of low density polyethylene, and placing strips of plasticene approximately 2 mm in diameter on the weight catching cone.

The shape of tensile specimen used was a compromise between having a short gauge length to have a high strain-rate, and avoiding elastic stress concentrations from a rapidly changing cross-section. Observation of the yielded specimens showed that uniaxial tensile yielding had occurred. The initial localized neck forms at roughly 55° to the tensile axis, as expected for a material with a von Mises yield criterion and a low rate of work-hardening. Ideally, a plane-strain yield stress should be measured, but there was no simple way of doing this at high strain-rates.

### 3.3. Charpy impact tests

Impact tests were performed using a Monsanto H20 charpy impact tester. This is a four-point bend test, with the two rounded load points on the pendulum only 6.2 mm apart. For most of the tests 6.2 x 50 mm specimens were milled from 3 or 5 mm thick PC sheet, and notched with a 45° angle and 0.25 mm tip radius to a depth of 2 mm. Tests were performed at various temperatures; in a temperature-controlled room at 23° C; by placing the impact tester inside a thermostatically controlled heated air oven, or a chamber cooled by $CO_2$ gas; and by cooling a sealed container with liquid nitrogen then removing and testing the specimens rapidly. By trial and error a pendulum and drop height were found that would just produce a visible disc ahead of the notch.

Adam *et al.* [16] kindly provided a couple of impact specimens (untreated, and annealed) that had been given sub-critical impact blows.

## 4. Results

### 4.1. Examination of impact bars given sub-critical blows

The first objective was to find the conditions that are necessary for "brittle" fracture of notched PC bars, and then to examine the fracture mechanism. A fracture was assessed as "brittle" if the crack propagation had been plane strain, with small or negligible shear lips at the sides of the fracture surface (see Fig. 7) and as "ductile" if through thickness yielding had occurred before crack propagation, so that the fracture surface is less wide than the original bar width (Fig. 6b). Brittle fractures were found to invariably occur if the bar thickness exceeds a certain value. For annealed PC, a 3 mm thickness was adequate (lesser thicknesses were not tested) whereas for quenched PC, a 5 mm thickness was required. Thus the bar thickness was of primary importance in causing brittle fracture, whereas the thermal history is only relevant if the bar thickness is around 3 mm. If the bar thickness was above the limits mentioned, then the test temperature, which was varied from −196 to 115° C, had no effect, in that the fractures were always brittle.

The fracture mechanism, under conditions that give brittle fractures, was examined by giving notched impact bars a pendulum blow having approximately 90% of the kinetic energy to cause fracture. When the unbroken bars were examined by obliquely transmitted light, in most cases a dark disc was visible ahead of the notch (Fig. 4a). The discs were highly elongated, of typical dimensions 2 mm x 0.2 mm, extending to close the sheet surfaces. This disc is definitely a craze, and not a crack as assumed by Garde and Weiss [5]. First, it is possible for collimated light to pass through this region when the angle of incidence to the specimen surface is only 60° C. Using the arguments of Kambour [22] this shows that the disc cannot be a crack, for a crack would totally internally reflect light even if it were incident on the specimen surface at a glancing angle. Secondly, the disc region can be examined by normally incident light if a thin section parallel to its plane is cut from the specimen. Kambour [23] has published normal incidence photographs of crazes at crack tips in

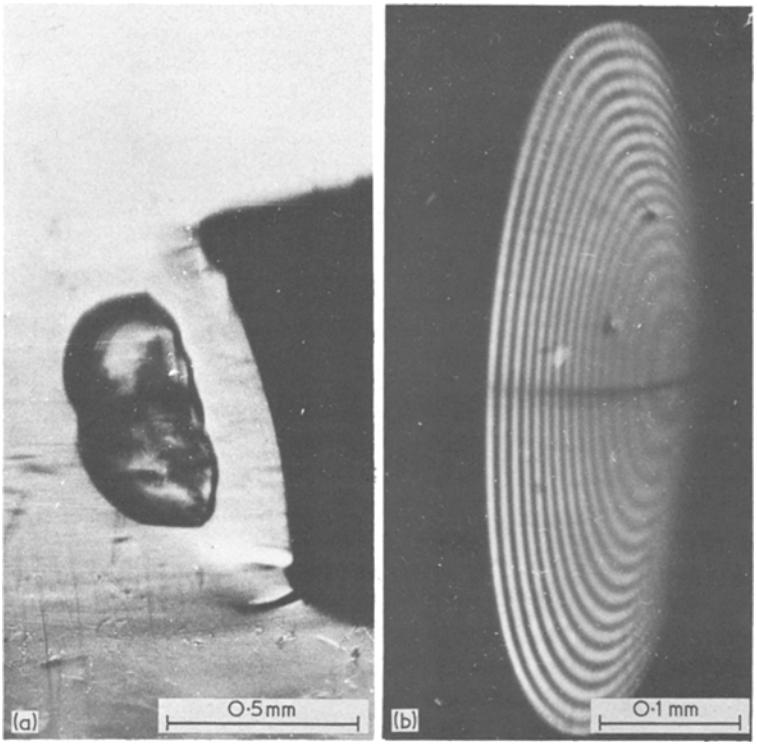


*Figure 4* Crazes that form ahead of the notch in sub-critical impact tests. (a) in annealed PC viewed by transmitted light with an angle of incidence if 60°. (b) in non-heat-treated PC, monochromatic green light normally incident on the craze.

polystyrene. Two sets of parallel interference fringes are present, one giving information on the crack thickness profile and the other on the craze thickness profile. We have examined crazes at the tip of fatigued cracks in PC, where craze fringes are found to be straighter than the crack fringes, but of lower reflectivity. Fig. 4b shows a disc in an untreated 3 mm PC bar tested at room temperature, and only the typical craze fringes are seen. The thickness fringes show that the craze is wedge shaped with a blunt end next to the notch. Finally, the craze remnants from such disc shaped regions are visible on fracture surfaces, as explained in Section 4.2.

Adam *et al.* [16] have published photographs taken in a circular polariscope of the unbroken specimens viewed parallel to the notch tip. These are difficult to interpret since they are a result of a small plane strain yielded zone near the mid-section, and much larger plane stress yielded zones near the surface of the specimen. It is difficult to tell from the isochromatic pattern alone, which is the plastic zone, and which is the surrounding residual elastic stress field. If, however, a section is taken from the midthickness of the bar, these difficulties are overcome, and higher magnifications can be used. Fig. 5a and b show such slices viewed by transmitted polarized white light, while immersed in oil between glass slides. The shear bands are visible in unpolarized light, but their contrast is enhanced with polarized light. Since white light is used and the fringe order is high the isochromatic fringe pattern is indistinct. Fig. 5a shows a typical central slice from an annealed 3 mm thick bar of PC tested at 19° C. Rather broad shear bands are visible at the periphery and inside the plastic zone, and the craze extends from the tip of the plastic zone. At 83 or 115° C shear bands are finer and more numerous in the larger plastic zones (Fig. 5b), and several crazes have nucleated from the intersection of shear bands. The shear bands intersect at about 70° rather than at 80° as observed previously [5]. At sub-ambient temperatures the plastic zones are similar to those in Fig. 5a but smaller. There is no evidence that annealing increases the sharpness of shear bands if the bars are sufficiently thick.

The fracture mechanism under conditions that gave ductile failures was also investigated to see what differences existed from the brittle fracture mechanism. The most important difference was that craze discs were never observed ahead of the notch. As a result the plastic zone expands in size as the impact proceeds until eventually a plastic hinge forms in the bar. Fig. 5c shows a central slice from a 3 mm thick quenched PC bar at an early

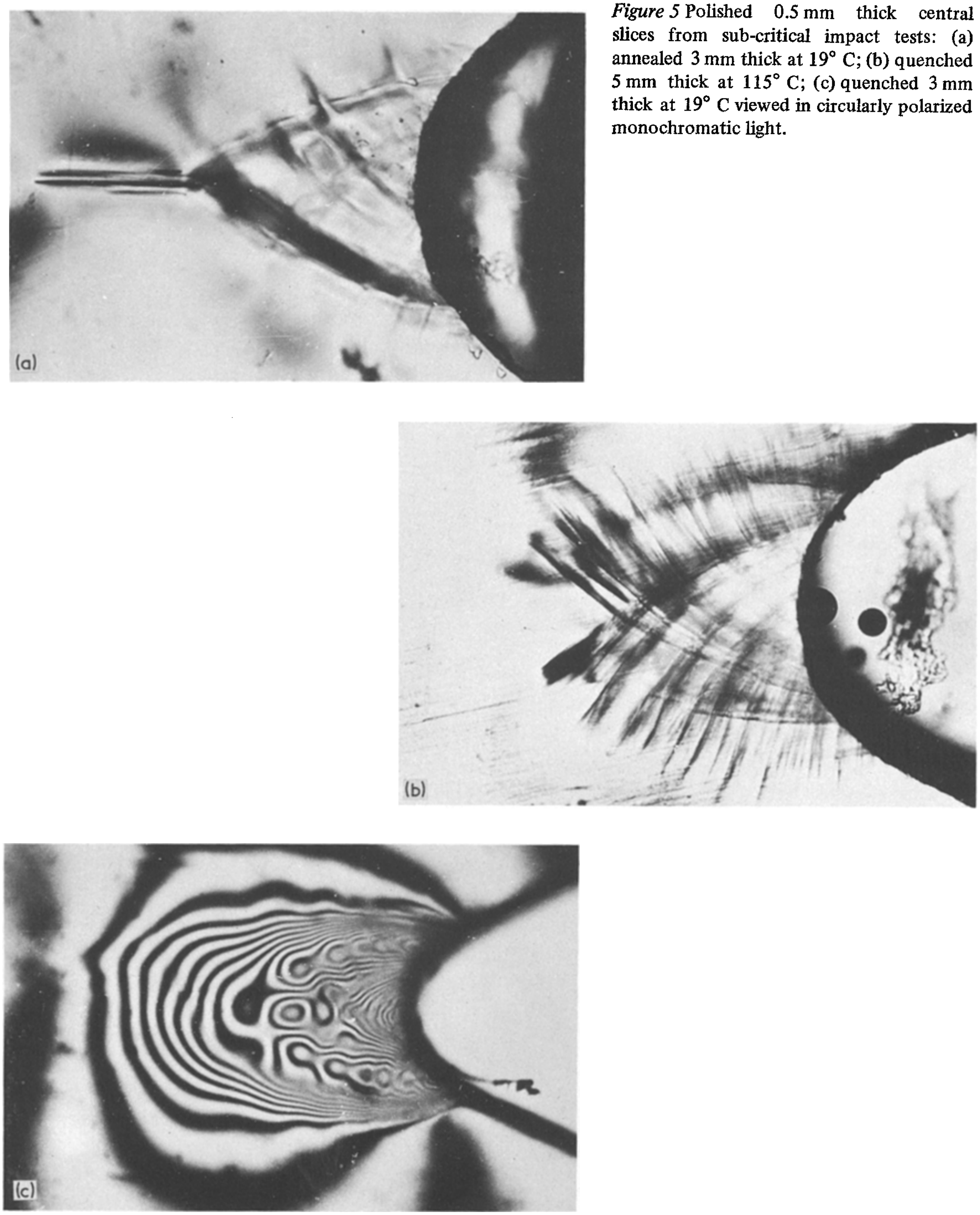
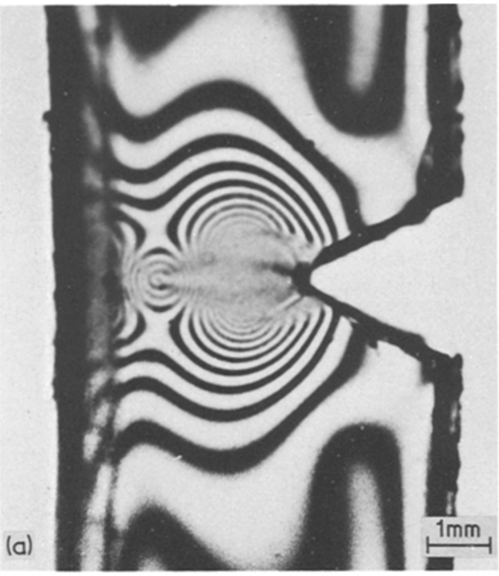


*Figure 5* Polished 0.5 mm thick central slices from sub-critical impact tests: (a) annealed 3 mm thick at 19° C; (b) quenched 5 mm thick at 115° C; (c) quenched 3 mm thick at 19° C viewed in circularly polarized monochromatic light.

stage of this process. There are no visible shear bands, and since the slice is photographed using circularly polarized sodium light the isochromatic fringe pattern is clear. The inner part of this pattern represents contours of maximum plastic shear strain in the plane of the slice, and the outer part contours of maximum elastic shear stress. In spite of the fact that the isochromatic fringe–strain relationship has been shown to differen in slope for elastic and plastic behaviour in PC [24], it is difficult to distinguish the boundary of the plastic zone. Although the plastic zone is still probably a plane strain one at this stage, it is impossible to compare the shear strain distribution in it with

Hill's theory [6] which is for rigid-plastic solids which do not shear until the slip line field extends right across the specimen. Fig. 6a shows a later stage in the yielding process, where the plastic hinge has not quite formed below the notch. The isochromatic pattern is clear in most of the bar, but is obscured below the notch by the through thickness yielding that has occurred from the surface, leaving a distorted surface. The yielded zone can be seen to extend from the notch most of the way towards the back surface of the bar. Once the plane stress yielded zone has extended across the bar, and a plastic hinge formed, a crack is initiated from the rough surface of the notch, and a tearing form of crack propagation occurs. A similar form of ductile failure has been described for tensile tests on PVC [25]. Fig. 6b shows that the width of the fracture surface at the notch has been reduced from 3 mm to 2.4 mm, and that the main fracture surface feature is lines parallel to the direction of crack propagation.



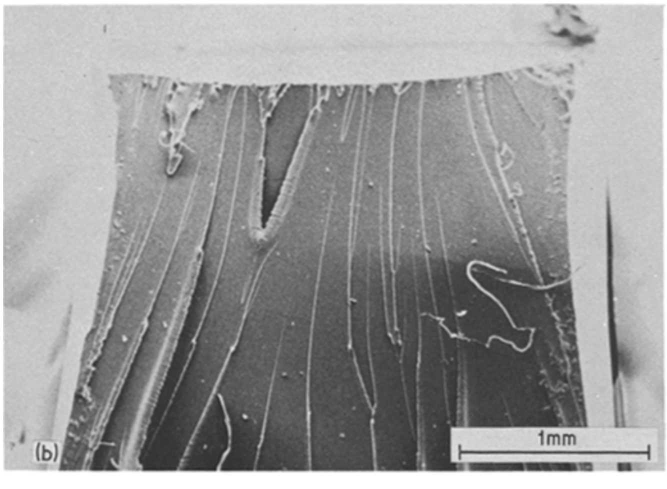


*Figure 6* Plane stress yielded zone in 3 mm quenched PC just below impact energy at which plastic hinge forms taken in circularly polarized monochromatic light. (b) Scanning electron micrograph (SEM) of fracture surface of a similar specimen.

## 4.2. Examination of fracture surfaces

The only purpose of the examination of the fracture surfaces was to search for evidence of the fracture initiation. Wherever possible reference is made to Hull and Owen [7] who describe typical PC fracture surfaces. They found that crazing occurred directly from the notch root. This was probably a result of using injection-moulded bars, which will have considerable internal orientation, since such orientation affects the ease of crazing. Fig. 7 is a scanning electron micrograph of a non-thermally treated impact specimen. This has all the features of the fracture surface of annealed samples, but some (e.g. the shear lips) are bigger and easier to see. A reflected light micrograph of such specimens was essentially similar to Fig. 4 of [7]. Note the shear lip along the notch and the specimen edges showing that ductile tearing has occurred in these regions. Hull and Owen denote as zone 1 the region inside the elliptical boundary AB. They observed that inside zone 1 there is a fracture source X in a rougher region, and a smoother region close to AB. Fig. 8a and b show in more detail the fortuitous tear in this outer region. Both fracture surfaces were examined, and one printed in reverse so that the shapes are similar. The smooth region appears to be where the craze has fractured at the craze-matrix boundary, whereas the rough region is where the craze has split on its midplane. In some places the craze has detached from both boundaries, and it can be seen how it tapers in thickness towards the boundary

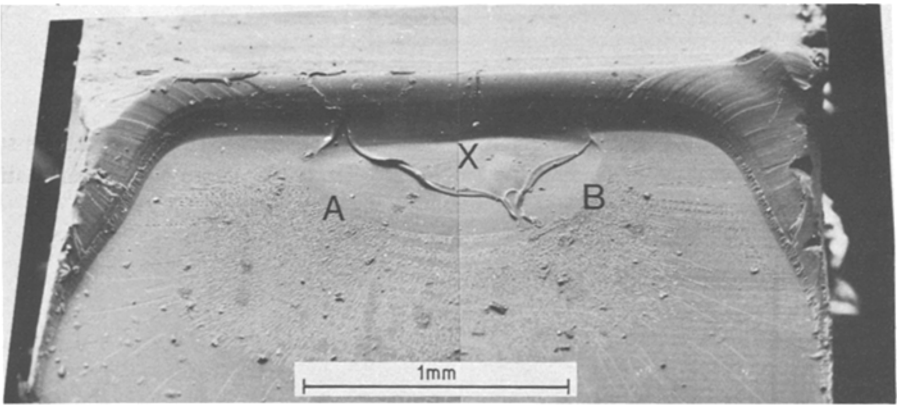


*Figure 7* SEM of fracture surface of non-heat-treated PC, AB limit of initial craze. X fracture source.

AB. At higher magnifications still (Fig. 8c) it can be seen how the rough region where the craze has split in its midplane shows slight evidence of collapsed craze remnants, whereas where the craze has split at its surface it is relatively featureless (Fig. 8d). Hull and Owen deduce that a crack initiates in the craze at X, grows initially by craze tearing, and then by rapid propagation at the craze–matrix boundary. This seems to be correct. Further features of the fast fracture region, described as zones II, III and IV in [7] were also observed, but these only reflect variations in the crack velocity once it is travelling rapidly. Examination of fracture surfaces of bars broken at −196° C showed that crazing had occurred directly from the notch.

In low strain-rate notched bend tests [4] or with centrally cracked sheet [26] the formation of a crack or craze ahead of the notch does not necessarily mean that a plain strain fracture ensues; sometimes a plane stress yielded zone forms and crack grows by tearing through this yielded zone. However, in the impact tests this possibility never occurred; if a craze formed then the fracture always became plane strain with subsequent crack growth, and the notched impact strength was of the order of 10 kJ m$^{-2}$ of cross-section area below the notch. If a plane stress fracture occurred then no evidence of crazing was seen, and the notched impact strength was about 80 kJ m$^{-2}$.

## 4.3. Falling weight impact tests

Fig. 9 shows load versus time curves from the falling weight impact tests. The engineering yield stress has been calculated from the height of the initial load maximum. Past this point a neck forms, propagates and finally fractures. Little significance is placed on the shape of the curve past the initial maximum because (a) the plastic strains in the neck are much larger than those found in the notched impact tests, (b) the deformation is not plane strain, (c) the plastic work in the neck causes it to heat adiabatically to well above room temperature. All that is concluded is that the rate of work-hardening at high strain-rates must still be very low for a localized neck to form. The results are shown in Table I.

TABLE I Uniaxial tension engineering yield stress of polycarbonate at high strain-rates

| Thermal history | Temperature (° C) | Strain-rate (sec$^{-1}$) | Engineering yield stress (MN m$^{-2}$) |
|---|---|---|---|
| Quenched | 20 | 25 | 84 ± 1* |
| Annealed | 20 | 25 | 99 ± 1 |
| As-received | 40 | 100 | 73 |
| from | | | [10] |
| manufacturer | 80 | 100 | 63 |

* Standard error of the mean.

It has been shown that the yield criterion of PC is best described by a pressure-modified Von Mises criterion [27]. In a plane strain plastic zone, if the principal stresses are written as $(p+k, p-k, p)$ where $p$ is the hydrostatic component of stress, the yield criterion can be expressed as

$$k + \sqrt{(3/2)}\,\mu p = k_0$$

$k_0$ being the value of $k$ when $p = 0$. The experimental value of the constant $\sqrt{(3/2)}\mu$ was found to be 0.06 ± 0.04. The slip line field analysis of yielding at a notch cannot easily be modified to allow for a pressure-dependent yield criterion. On the other hand, it predicts that the hydrostatic stress $p$

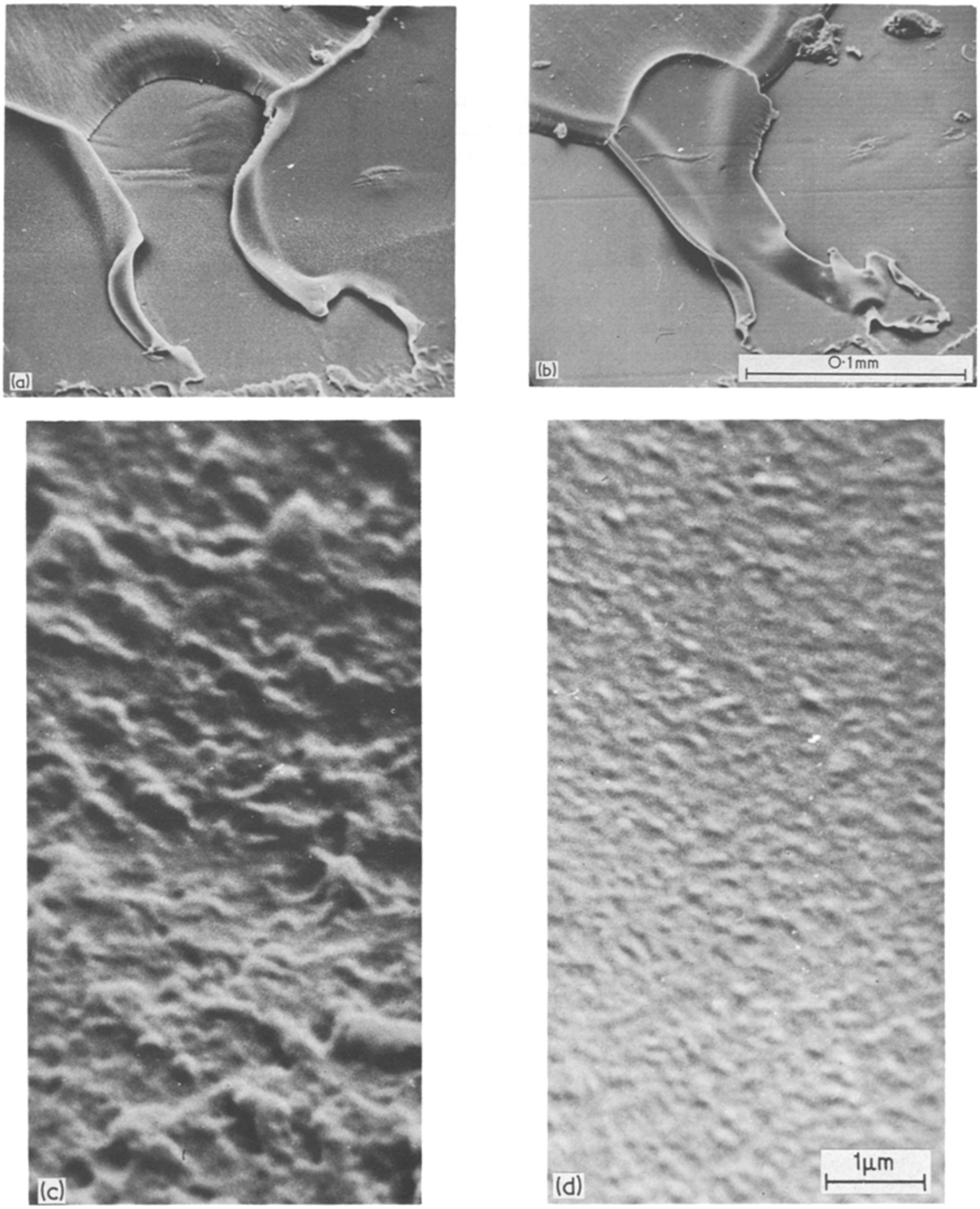


*Figure 8* (a) and (b) Opposite fracture surfaces at higher magnification of the tear in the craze in Fig. 7. (c) Higher magnification still, near the fracture source X, and (d) where the craze has torn on its surface.

only increases from $k$ at the notch root to a maximum of $3.36k$ at the tip of the yielded zone if the included angle of the notch is 45°. Therefore, if the slip line analysis is used to calculate the stresses, using a value of $2k$ equal to 1.15 times the uniaxial tension yield stresses in Table I, then these values are unlikely to overestimate the true stresses by more than 15%.

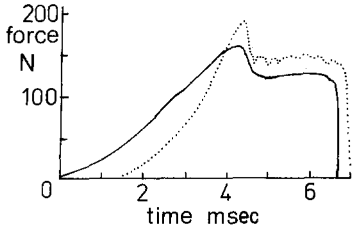


*Figure 9* Force versus time records, from an oscilloscope, of falling weight tensile impacts on ......... annealed, and ——— quenched PC.

### 4.4. Stresses for internal craze nucleation

The maximum extent of plastic zones have been measured from central slices of sub-critically impacted bars. To avoid any magnification errors in photographs of the slices, the ratio of the zone length to notch tip radius has been plotted in Fig. 10 for both annealed and quenched PC. There is no significant difference between the annealed and quenched results. There is only a slight increase in the plastic zone size with increasing temperature. It is possible to test the Orowan hypothesis, of a cleavage stress that is independent of temperature, by plotting in Fig. 10 the variation in zone size that would be expected if the value of the tensile stress $\sigma_{\theta\theta}$ at the plastic zone tip was constant. This has been done by substituting in Equation 2 a value of 230 MN m$^{-2}$ for $\sigma_{\theta\theta}$, and then calculating $2k$ from the high strain-rate tensile yield stress of 99 MN m$^{-2}$ for annealed PC. For temperatures other than 20° C, literature data for the low strain-rate tensile yield stress of non-heat-treated PC was used [5, 10]. This was corrected to a strain-rate of 100 sec$^{-1}$ using the observation [20] that the variation of yield stress of PC with strain-rate follows a relation of the form

$$\sigma_Y(\dot{\epsilon}_1) = \sigma_Y(\dot{\epsilon}_2) + AT(\ln\dot{\epsilon}_1 - \ln\dot{\epsilon}_2)$$

where $A$ is a constant and $T$ the absolute temperature. Finally, since the thermal history of PC used in [10] was not the same as the annealed PC used here, the literature yield stresses were scaled by a constant multiplier so that the value of $2k$ at 20° C became 114 MN m$^{-2}$, to match the value calculated from Table I. The solid line in Fig. 10 then represents the expected variation in $r/a$ for a constant maximum $\sigma_{\theta\theta}$ of 230 MN m$^{-2}$. It appears in Fig. 10 that below $-15°$ C the data are consistent with the Orowan hypothesis (by extrapolation the plastic zone size should reach zero at $-196°$ C, as observed). However, above $-15°$ C the data diverges strongly from the Orowan criterion. In particular on the basis of a constant cleavage stress it is predicted that above 40° C ductile fractures must occur. This is shown in Fig. 10 as the intersection of the solid line with the dashed line representing the slip line field size above which no further stress intensification occurs (given by Equation 3 for a notch angle $\phi = \pi/4$). In fact above 40° C brittle fractures occur, and the $r/a$ ratio is nearly constant at 2.2 implying that the stress $\sigma_{\theta\theta}$ to initiate a craze is nearly a constant multiple of the tensile yield stress namely $3.6k$. Note that this implies that the actual stress for annealed PC is about 15% higher than for quenched PC, since the tensile yield stresses differ by this amount. By applying the slip line field analysis to the data shown in Fig. 10, the principal stresses for craze nucleation of annealed PC at 20° C are $\sigma_{\theta\theta}$ = 204 MN m$^{-2}$, $\sigma_{rr}$ = 90 MN m$^{-2}$. If the PC obeys the Von Mises yield criterion, then since there is zero plastic strain in the thickness or $z$ direction, the stress in this direction is given by

$$\sigma_{zz} = \tfrac{1}{2}(\sigma_{rr} + \sigma_{\theta\theta}) = 147\,\mathrm{MN\,m^{-2}}.$$

This is also the value of the mean hydrostatic tension at the tip of the plastic zone.

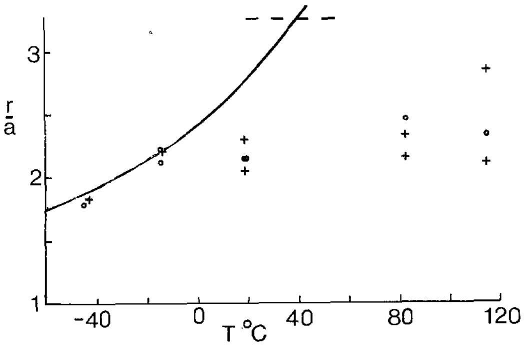


*Figure 10* Ratio of plastic zone extent to notch tip radius versus temperature of impact test for 0 annealed 3 mm and + quenched 5 mm PC. ——— theoretical curve for craze stress of 230 MN m$^{-2}$, -------- limit of brittle failure.

## 5. Discussion

Of the factors examined as requirements for brittle fracture in notched PC bars, only one, that of sufficient bar thickness, has been shown to be essential. The others, thermal history and test temperature, are irrelevant so long as the thickness of the bar is sufficient. The reason why these factors have played a large part in earlier investigations [4, 7, 9] of the fracture of PC is that relatively low thicknesses were used. If the slip line field analysis of the stresses in plane strain yielding from a notch is accepted, then the actual thicknesses found to be sufficient here are only valid for a notch tip radius of 0.25 mm. For other notch tip radii the specimen dimensions should be scaled accordingly.

The mechanism of "brittle" fracture in PC impact tests has been shown to involve the nucleation of an internal craze, followed by crack formation in the craze, and subsequent crack propagation. Furthermore, the analysis of the shear band pattern in impacted but unbroken bars allowed the maximum principal stress for craze nucleation to be calculated as 204 MN m$^{-2}$ at room temperature, and the mean hydrostatic tension as 147 MN m$^{-2}$. Such a stress level could not be reached if only plane stress yielding occurred at the notch tip. Since the yielding in this case would be plane strain tension [26] the principal stresses would be ($2k$, $k$ and 0), with $2k = 114$ MN m$^{-2}$ at 20° C. Thus the ductile to brittle transition with increasing bar thickness in PC can be rationalized as a plane stress to plane strain failure transition, with the critical stress for craze nucleation only being reached under plane strain conditions. The effect of temperature on the situation is shown in Fig. 11, in which the experimental data for the critical $\sigma_{\theta\theta}$ stress appears as a solid line together with dashed lines representing $2k$ (the plane strain tension yield stress) and $4.36k$ (the maximum principal stress in any slip line field from a 45° notch). If $\sigma_{\theta\theta}$ exceeds 4.36 then ductile failures occur, and if $\sigma_{\theta\theta}$ is less than $2k$ then brittle failures occur without prior plastic zone formation.

The two main theories for the brittle–ductile transition in PC can now be compared with experiment. The first [9] postulates that the stress for crazing is independent of temperature or thermal treatment. This may possibly be true below − 15° C, but Fig. 11 shows that it is not true above this temperature, so this theory may be discarded. The second theory [16] argues that the annealing of PC, by increasing the strain softening after yield in a low strain-rate test, causes the yielded volume at fracture to be smaller and hence the notched impact strength to be less. A related suggestion by Vincent [14] was that surface craze formation in PC is a consequence of the plastic instability in a tensile test. In neither of these papers are the deformation mechanisms discussed, so for further discussion the details of the fracture mechanism found here are incorporated into the following outline theory.

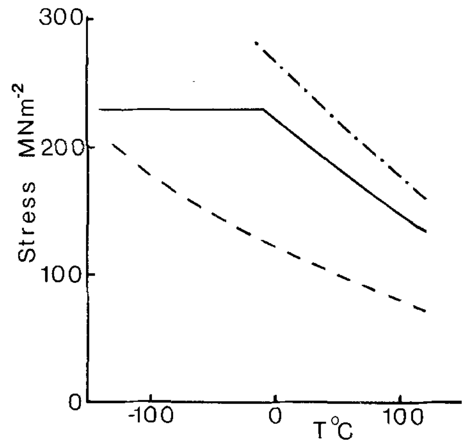


*Figure 11* Stress for craze nucleation versus temperature ———, compared with the temperature variation of $2k$ --------, and of $4.36k$ —·—·—.

(1) Strain softening in plane strain deformation causes strain inhomogeneities (shear bands).

(2) Intersecting shear bands cause a stress concentration.

(3) The stress concentration nucleates an internal craze.

(4) Crack nucleation occurs in the craze, and crack propagation occurs without further plastic defomation of the bar.

There is theoretical backing for step 1 [15]. Note that plane strain deformation experiments must be made to establish that strain softening occurs in a particular polymer. The falling weight tensile tests carried out here only provided evidence that plane stress localized necks should form. However, there is sufficient experimental confirmation of the theory to take the observation of shear bands in the impact bars as evidence for strain softening occurring in both quenched and annealed PC. The second and third steps draw on observations on silicon–iron single crystals [28] where cleavage cracks are nucleated at low temperature by the intersection of deformation twins. There is a stress concentration ahead of the propagating tip of a shear band, similar to that at the head of a pile-up of edge dislocations. However, there is no direct way of estimating the stress concentration when a propagating shear band intersects at right angles an existing shear band. Indirectly, the maximum stress concentration can be estimated as follows: the largest principal stress in any yielded zone in a non-work-hardening solid is given by slip line field theory as $2k(1 + \pi/2)$ or $5.14k$. The calculated $\sigma_{\theta\theta}$ values from the observed notch slip line fields were $\sim 3.6k$ above − 15° C. Therefore, the greatest possible stress concentration due to intersecting shear bands is a factor of 1.43. Experimentally it was found that the thermal history of the PC had no effect on the narrowness of the shear bands (for plane strain conditions), and consequently the stresses for craze nucleation were the same multiple of the yield stress at a given temperature. Thus the theory of Adam *et al.* [16] does not apply to plane strain fracture, and is only a description of the plane stress to plane strain fracture transition. However, there may still be something in the four-stage mechanism outlined above. The stress concentration of intersecting shear bands must contribute slightly to craze nucleation process since the crazes appear at such intersections at the extremity of the shear band pattern. However, crazes do not occur at other intersections of shear bands closer to the notch, where the principal stresses are lower. For this reason, and for the earlier reason, the stress concentration effect at the intersections must be small.

Some tentative suggestions can be made to explain the variation with temperature of the stresses required for internal crazing in PC. At temperatures above −15° C the tensile stress to nucleate a craze is approximately 1.8 times the plane strain tension yield stress $2k$, and the other principal stresses are tensile. The question can then be raised as to whether these stresses are sufficient to cause an initially submicroscopic hole in the PC to expand by plastic flow. If the hole is an isolated sphere this is unlikely. Drabble *et al.* [29] have shown that the required hydrostatic tension at infinity would have to be $4.6k$ for a spherical hole to expand adiabatically to infinite size into a block of polystyrene. PC has a ratio of yield stress to Young's modulus similar to polystyrene so a similar stress would be required. Haward and Owen [30] have made a finite element analysis of a collection of parallel cylindrical holes in an elastic-plastic material under tension perpendicular to the cylindrical axes. They show that for a 9% by volume hole content a biaxial tension of $2.6k$ would cause general yielding. Since the final structure of a craze is a series of connected holes, it seems likely that a model of this kind can explain internal craze nucleation in PC under principal stresses of approximately $3.6k$, $2.6k$, $1.6k$, so long as some evidence can be produced for the initial presence of submicroscopic holes.

An alternative possibility for craze formation at low temperatures is that the theoretical tensile strength of PC is exceeded. There are unfortunately no computed values of this quantity. The best comparison is with the value computed for solid argon at 0 K from the Lennard Jones potential of the Van der Waals bonding [31]. PC has similar bonding between the polymer chains, which explains why its room temperature Young's modulus is of the same order as that of argon at 0 K. It is not expected that PC molecules would separate entirely since melt rheology studies suggest that the molecules are entangled on average once every 24 monomer units [32]. The calculated triaxial tension of 254 MN m$^{-2}$ for the theoretical strength of argon should, therefore, be an order of magnitude estimate for the "cleavage" of the sections randomly oriented PC between entanglement points.

Finally, it is hoped that further investigations of the fracture mechanics of notched impact tests on PC will be able to explain the ductile to brittle transition with thickness. Experiments are in progress to measure photoelastically the stress intensity factor $K$ as which crazes are nucleated in slow four-point bend tests. If this can be done for various thermal histories or temperatures, then the requirement for a valid plane strain fracture toughness test [3] that the specimen thickness $> 2.5\ (K/\sigma_Y)^2$ can be checked.

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