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The effects of thermal pre-treatment and molecular weight on the impact behaviour of polycarbonate

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Notched impact fracture experiments have been conducted on specimens of polycarbonate in three different conditions, (a) as received, (b) annealed at 125° C, and (c) electron beam irradiated to reduce the molecular weight. By consideration of the behaviour of a wide range of notch geometries four different failure modes were identified which were present in different proportions for each material. (1) Razor notched specimens failed in a completely brittle manner, well described by linear elastic fracture mechanics. (2) Small notch tip radii specimens failed in an apparently brittle manner through the formation of a single craze. (3) Some intermediate notch tip radii specimens failed in a predominantly brittle manner with small shear lips indicative of plane stress yielding. A fracture mechanics approach was used here, the measured toughness correlating with the extent of plane stress yielding. (4) Fully ductile failure was observed for large notch tip radii for all materials. It has been established that the embrittlement of polycarbonate caused by annealing is due to an increase in the yield stress, whereas that caused by reducing the molecular weight is due to a reduction of the crazing stress. In both cases, more specimens of intermediate notch tip radius are caused to fail in the low energy brittle mode designated (2) above. By varying the yield stress and crazing stress independently we have thus been able to distinguish clearly how both influence the brittle–ductile transition.

1. Introduction

The fracture of glassy polymers has usually been interpreted on the basis of linear elastic fracture mechanics, often expressing the results in terms of the Irwin stress intensity factor [1, 2], and predominantly slow crack growth has been studied with considerable success. Brown [3] and Williams *et al.* [4] extended this approach to sharply-notched impact test fracture specimens where work on various polymers has shown that linear elastic fracture mechanics is also applicable [3–7].

However, many material applications are concerned with the failure of blunt notched specimens. Brown and Ward [8] showed that in impact tests on vinyl urethane polymers, the failure of blunt notched specimens correlated with the craze stress calculated on the basis of the Dugdale plastic zone model [9]. Subsequently, Fraser and Ward [6] examined the impact behaviour of PMMA, and concluded that blunt notched specimens failed at a constant critical stress at the root of the notch, supporting Gotham's previous observations [10] for notched tensile specimens.

Studies of the fracture of notched impact specimens of polycarbonate [7] revealed a far more complex situation. It was found that while linear elastic fracture mechanics could be applied to the sharply-notched and perhaps the very blunt notch situation, there was a region between these two where any one of three types of fracture could occur. This transition is associated with the change from plane strain (very sharp notches and thick specimens) to plane stress (blunt notches and thin specimens). It can also be affected by a number of physical factors, in particular temperature and sheet thickness.

The present paper describes the effect of molecular weight and thermal pre-treatment on the impact behaviour of polycarbonate, and forms a natural extension to the previous work [7]. The effect of molecular weight has not been systematically studied before although the previous work [7] did indicate its importance. In the present investigation we have used irradiation as a convenient method for changing molecular weight. Golden and Hazell have deduced that for polycarbonate random chain scission takes place with zero cross-linking up to a radiation dose of 1000 Mrads [11]. They found that the yield strength, extension to break, and brittle strength decrease on irradiation [12].

Annealing polycarbonate below its glass transition temperature is known to decrease the notched impact strength dramatically [13–16]. Allen *et al.* [15] attributed this to an increase in yield stress due to annealing, while Adam *et al.* [16] suggested that it related to the increase in strain softening after annealing.

2. Experimental details

Impact bend tests were performed on specimens of various notch geometries. The materials investigated were Lexan polycarbonate, irradiated Lexan, annealed Makrolon 2803 and irradiated Makrolon 2803. Subcritical tests were performed on Lexan polycarbonate to investigate the ductile fracture mode. In addition, tensile tests were performed in order to determine the tensile crazing stress, the engineering yield stress and the extensibility-to-break.

2.1. Specimens

The materials used were available in the form of large extruded sheets. Impact specimens were cut from the sheets and milled to the dimensions of 50 mm × 10 mm × 3 mm for the experiments using Makrolon 2803, and both 50 mm × 10 mm × 3 mm and 50 mm × 10 mm × 6 mm for Lexan. Specimens were then notched halfway along their lengths to various depths. The very sharp notches were achieved by pushing a razor blade slowly into the specimen to the depth required. The blunter notches were obtained by drilling holes through the specimen and cutting through to the hole (from the side) with a fine saw.

In addition to the impact test specimens, some tensile specimens were cut from the 3 mm-thick sheets. These specimens had a gauge length of 30 mm and a width of 6 mm. For the tensile crazing tests it was necessary to ensure that the surfaces were uniform with no stress concentrations due to surface imperfections. To achieve this, specimens were polished after the desired annealing or irradiation treatment. In the engineering yield stress and "extensibility-to-break" experiments the fracture initiated from macroscopic flaws on the side of the specimen. These were therefore polished to improve consistency between specimens.

2.2. Thermal pre-treatment (annealing)

The specimens were laid on a Teflon coated sheet, and this was placed in an oven at 125° C ± 1° C for 18 h. The specimens were then taken from the oven and allowed to cool in air before notching.

2.3. Irradiation

Irradiation was carried out at Cookridge High Energy Radiation Research Centre*, using a continuous beam of 3 MeV electrons supplying 1 Mrad $\min^{-1}$. The specimens were held in a water cooled container with no special sealing. Irradiation was therefore in air. The impact specimens had previously been notched since specimens are most easily machined at the higher molecular weight.

Radiation doses chosen were 120 Mrads and 45 Mrads for Makrolon 2803, and 35 Mrads for Lexan specimens. Table I shows the changes produced in the number average and weight average molecular weight as measured by gel permeation chromatography.

Note that irradiation causes the ratio $\bar{M}_w/\bar{M}_n$ to increase, indicating a wider distribution of chain lengths.

TABLE I Effect of radiation dose on molecular weight

Polymer	Dose (Mrads)	Weight average $\bar{M}_w$	Number average $\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
Makrolon 2803	0	20 000	9500	2.10
	45	13 450	5560	2.42
	120	8750	3500	2.50
Lexan	0	17 700	8500	2.08
	35	12 500	4800	2.60

*Cookridge High Energy Radiation Research Centre, Cookridge, Leeds.

Polycarbonate irradiated as above became dark brown, but this coloration soon faded to a lighter brown and no difficulty arose in observing crazes in the tensile crazing experiments.

2.4. Impact testing

Prior to testing, the diameter of the notch tip and the length of the notch were measured with a travelling microscope.

Impact tests were performed using a Hounsfield Plastics Impact Tester, which is a Charpy type machine, supplied with a set of striking tups with a striking velocity of $2.54 \mathrm{m\,sec^{-1}}$. The energy to fracture was measured using the calibration charts provided.

Subcritical tests, in which a crack was initiated but not fully propagated were also undertaken, using a suitable crack length that required almost the full drop of the tups. By decreasing the height of fall of the tup slightly it was possible to determine the energy for crack initiation, while employing a very similar striking velocity.

2.5. Uniaxial tensile tests

Uniaxial tensile tests were performed on an Instron testing machine at constant cross-head speed, giving an initial strain rate of 8.3×10^{-6} $\mathrm{sec^{-1}}$ for the crazing stress measurements, and 5.5×10^{-3} $\mathrm{sec^{-1}}$ for the yield stress and "extensibility-to-break" experiments. Crazes were observed through a microscope, using a spot-light arranged to reflect light from the crazes as they formed.

3. Theory

Previous papers [6, 7] have been concerned with two approaches to the fracture of notched impact specimens. The first was based on linear elastic fracture mechanics and the second was a calculation of the maximum stress at the root of the notch. In both of these it is assumed that the deformation is essentially elastic up to a maximum value which corresponds to an instability. This enables a simple interpretation of the fracture energy in terms of the stored elastic energy at crack initiation. In both cases it is assumed that the stored energy is sufficient to propagate the crack completely across the specimen. In the present paper we will confirm the validity of these analyses for some situations, but in addition, a different approach will be discussed for the ductile fracture specimens.

3.1. Linear elastic fracture mechanics approach

Using the analysis first presented by Brown [3] and Williams *et al.* [4] for a linear elastic material the strain energy release rate is given by

$$G_c = \frac{U_0}{B}\frac{1}{C}\frac{dC}{da} \tag{1}$$

where U_0 is the stored energy immediately prior to failure.

B is the specimen thickness, and C is the compliance of the specimen which is a function of specimen geometry (see [3] for details). Thus G_c can be calculated from a knowledge of specimen geometry and energy absorbed. A small kinetic energy correction must be subtracted from the measured absorbed energy in order to obtain U_0.

3.2. Maximum stress at the root of the notch

The calculation of maximum stress at the root of the notch follows the approach of Fraser and Ward [6]. Briefly, the maximum stress is given by the product of the nominal stress and the geometrical stress concentration factor taken from the calculations of Neuber [17]. The maximum nominal stress of a specimen such as this, subject to pure bending is

$$\sigma_n = \frac{6\,M_0}{B(W-a)^2} \tag{2}$$

where M_0 is the maximum bending moment at failure. This is calculated from the measured fracture energy U_0 assuming a linear loading curve up to failure.

For brittle failure from blunt notches it will be shown experimentally that a critical stress criterion is preferable to the fracture mechanics approach. Although apparent fracture toughness values can be calculated for such specimens the fracture toughness obtained is not a material parameter. This can be shown simply by the following argument.

For a long crack ($a \gg \rho$) the Neuber stress analysis reduces to a critical stress $\sigma_c = 2\sigma_n\sqrt{(a/\rho)}$ where ρ is the notch tip radius. If we attempt to interpret the results in terms of linear elastic fracture mechanics, the apparent strain energy release rate G_c' can be calculated from the measured fracture stress as

$$G'_c = \frac{\pi\sigma_n^2 a}{BE}$$

In terms of the critical stress σ_c we then have

$$G'_c = \frac{\pi\rho\sigma_c^2}{4EB}$$

If σ_c is the material parameter, G'_c will depend on specimen geometry through the notch tip radius ρ and therefore cannot be understood directly in terms of the structure of the polymer.

3.3. Analysis of ductile fracture

The analysis of Section 3.1 is valid for materials that show only a small degree of plasticity during failure. (By this we mean that the size of the plastic region in front of the crack is small compared with the specimen thickness). If a higher degree of plasticity occurs then the stress field around the notch may not be approximated to the elastic solution, and hence the critical stress intensity factor of linear elastic fracture mechanics is not a valid fracture criterion.

The subcritical impact tests to be described below are valuable in two ways. Examination of the specimens which had not completely ruptured revealed the existence of a plastic zone of considerable dimensions – in some cases up to 7 or 8 mm in length. The tests also showed that the measured fracture energies for these specimens were not simply a measure of crack initiation. Further energy was necessary to propagate the ductile crack across the specimen.

The simplest alternative approach is therefore to assume that for specimens with very blunt notches, the total energy absorbed is used to propagate the crack across the remaining cross-section, and to calculate an apparent strain energy release rate G'_c as the total energy absorbed divided by the remaining cross-sectional area†,

$$G'_c = \frac{U_0}{B(W-a)} \tag{3}$$

Brown [3] has shown that this analysis satisfactorily describes the impact behaviour of notched samples of ABS, a material of similar high toughness.

It has also been proposed that the J-integral technique, introduced by Rice [18] may be used to obtain a fracture criterion [19–21]. The physical significance of J for an elastic–plastic material is that it is a measure of the crack tip field. It is postulated that fracture occurs when J reaches a critical value J_c and for linear elastic behaviour J_c is identical to G_c, the strain energy release rate.

It has been proposed by Plati and Williams [5] that ductile failure of polymers in a Charpy impact test should be described by J_c which is calculated as $2U_0/B(W-a)$. This is clearly similar algebraically to our Equation 3 apart from the numerical factor of 2. It does, however, differ conceptually from our analysis. Whereas we propose that the impact energy in the blunt notched specimens is expended in propagation of the crack across the whole specimen, Plati and Williams consider that the impact test measures the critical value of J_c required for crack initiation.

4. Results and discussion

Our results show a dramatic change in the impact behaviour as the notch tip radius was increased beyond a critical notch tip radius which was different for each of the materials tested. This is broadly similar to the results described previously for Makrolon polycarbonate [7], to which reference will be made whenever appropriate.

All razor notched specimens of each material showed completely brittle fracture, whereas at much higher notch tip radii it was possible to

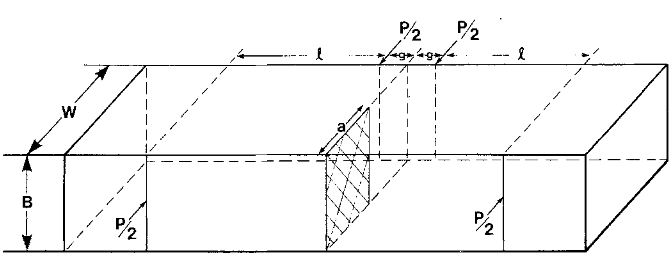

Figure 1 Impact specimen geometry.

†The symbol G_c is used here only in situations where the parameter has been shown to be geometry independent; otherwise reference is made to an "apparent" strain energy release rate using the symbols G'_c or G''_c.

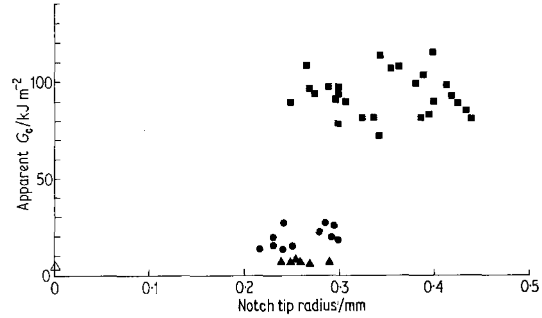

Figure 2 Impact test results on untreated Lexan; ■ Fully ductile failure, ● brittle, with shear lips, ▲ brittle, △ razor notched.

obtain completely ductile fracture in all materials except the 120 Mrad Makrolon. Between these two extremes there was a transition from brittle to ductile fracture. Figs. 2 to 4 show this transition in each material. For untreated polycarbonate (Fig. 2) ductile failure did not occur for notch tip radii below 0.25 mm. At this notch tip radius it was possible to get any one of three different fracture modes, i.e. completely brittle, brittle with small yielded zones, and ductile. This is identical to the observations reported previously [7]. For irradiated polycarbonate (Fig. 3) ductile fracture did not occur below a notch tip radius 0.37 mm, while for thermally pre-treated polycarbonate (Fig. 4) ductile fracture did not occur below 0.4 mm.

In Figs. 2 to 4, for the cases where there was brittle failure or brittle failure with surface yielded zones, the results have been analysed in terms of Equation 1. Where ductile failure occurred a value of G_c' has been obtained, using Equation 3. It will be shown in Section 4.1.1.2 that the ductile failures are only approximately described in this way, but that the analysis is of value in comparing the different materials.

For simplicity, initial discussion of the impact test results for each material will be kept separate.

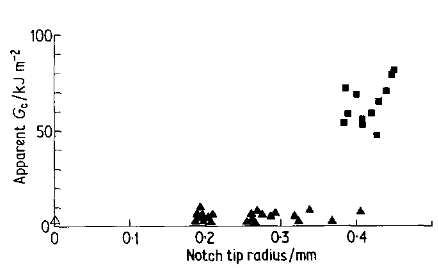

Figure 3 Impact test results on irradiated Lexan; symbols as in Fig. 2.

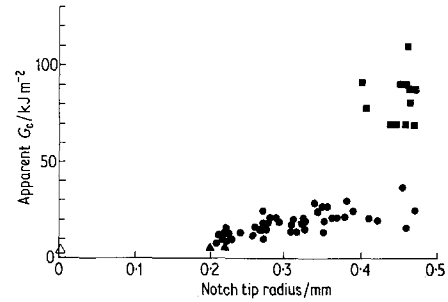

Figure 4 Impact test results on annealed Makrolon; symbols as in Fig. 2.

4.1. Analysis of types of fracture in impact tests

4.1.1. Lexan polycarbonate, untreated

4.1.1.1. Razor notched. Fig. 5 shows that the values of the strain energy release rate, G_c, calculated using Equation 1 do not depend on the reduced crack length, (a/W). This suggests that a linear elastic fracture mechanics treatment is valid for razor notched specimens. The value of G_c of 4.8 kJ m^{-2} is somewhat higher than that quoted in [7], but is in good agreement with that calculated by Plati and Williams [22].

The fracture surface of this type of specimen showed completely brittle fracture with the same features as those described by previous workers on brittle fracture. In particular there was a "mirror" zone at the base of the razor notch. Hull and Owen [23] have described the fracture surface of polycarbonate, inferring that crack growth is preceded by craze formation. The extent of this crazing is approximately the extent of the mirror zone. A measure of this zone on the specimens tested here shows it to be between 200 and 250 μm long, which is in agreement with the observations of Hull and Owen.

4.1.1.2. Very blunt notches. The present data are in good agreement with those previously published by Fraser and Ward [7] in that impact specimens

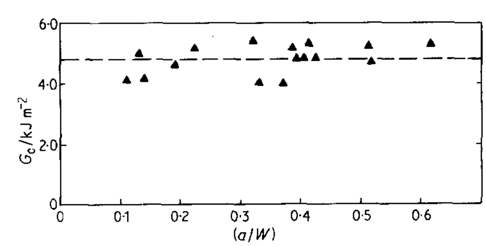

Figure 5 Critical strain energy release rate versus reduced crack length for razor notched specimens of untreated Lexan (specimens marked △ in Fig. 2).

of untreated polycarbonate with notch tip radii greater than 0.3 mm failed in a completely ductile manner, with a fracture energy much larger than for brittle specimens. Fraser and Ward analysed these ductile specimens according to Equation 1, presenting their results in terms of K_c which was shown to be essentially independent of crack length. As discussed in Section 3.3 the subcritical impact tests on blunt notch specimens performed here suggest that a fresh interpretation of these high impact energies is required. In these impact tests a crack and plastic zone were initiated, but insufficient energy was supplied to propagate them across the entire specimen. This proves that, for these specimens, fracture cannot be interpreted as an instability and so it is not correct to relate the impact energy to peak load as in [1], nor can it be interpreted in terms of a J_c criterion for initiation as proposed by Plati and Williams.

The data from ductile specimens presented in Figs. 2 to 4 were therefore calculated using Equation 3. In Fig. 6 the validity of this approach is examined in more detail by plotting fracture energy against reduced crack length, a/W. This can be seen to demonstrate a linear relationship between fracture energy and crack length as required by Equation 3, suggesting that the strain energy release rate is constant over a considerable range of crack lengths. This leads us to define a new measure of fracture toughness

$$G_c'' = \frac{-dU_0}{da} \tag{4}$$

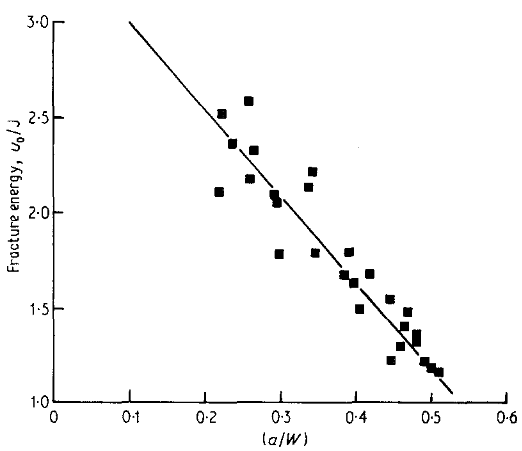

Figure 6 Fracture energy versus reduced crack length for fully ductile failures in untreated Lexan (specimens marked ■ in Fig. 2). Best fit straight line leading to $G_c'' = dU_0/da$ (see text).

which can be calculated from the gradient of plots such as in Fig. 6. Note that G_c'' calculated from Equation 4, is not identical to G_c' calculated from Equation 3 because the data do not extrapolate to the point $U_0 = 0$, $a/W = 1$. Moreover, it cannot be claimed that we have identified in G_c'', a fracture parameter which is independent of the nature of the test employed. We will, however, show that G_c'' can be used to provide comparative measures of the failure of different materials which correlates well with other properties.

4.1.1.3 Intermediate notch tip radii. Here there is a more complex situation with a mixture of modes of failure. Indeed, for a notch tip radius of about 0.27 mm there were three possible situations. Some specimens failed with negligible yielding and we have termed these brittle. Others showed yielded zones at the base of the notch in addition to shear lips extending along the surface. Finally, some completely ductile fractures were observed. This is an exactly similar situation to that reported previously.

For the specimens that showed negligible signs of yielding, we propose that fracture was governed by the achievement of a maximum stress at the root of the notch. This stress is related to the stress required to form a craze at the root of the notch as has previously been shown to be the case for blunt notched PMMA [6] as well as polycarbonate [7]. The maximum stress was calculated to be about 248 MN m^{-2} from the present data using Equation 2. This value was confirmed by testing some 6 mm-thick specimens of Lexan polycarbonate in an exactly similar manner, the onset of ductile fractures being postponed in the thicker specimens to higher notch tip radii. Fig. 7 shows that the maximum stress is independent of the tip radius. The fracture surfaces of these specimens

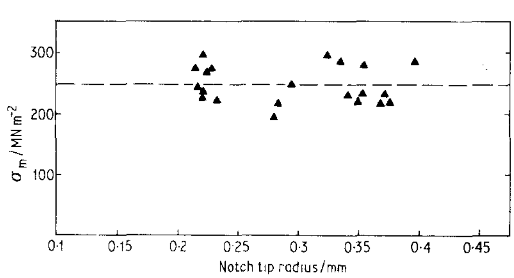

Figure 7 Maximum stress versus notch tip radius for specimens of untreated Lexan, intermediate notch tip radius showing no shear lips (specimens marked ▲ in Fig. 2).

also show a "mirror" zone at the root of the notch about 200 μm long associated with the length of the craze before breakdown.

The failure of the ductile specimens of intermediate notch tip radius was identical to that for blunter notched ones and may be analysed in the same way.

In addition there is a mode of failure which is partly brittle, but which also shows a yielded zone at the base of the notch and shear lips. This type of fracture marks the transition from brittle to ductile fracture. The fracture surface shows evidence of crazing at some distance in from the root of the notch. Following the previous work [7] it appears that loading continues until sufficient energy has been supplied to rupture the plastic region at the root of the notch. Having done this there is sufficient elastic stored energy to propagate the crack across the remainder of the specimen. The fracture energy is related, to a first approximation, to the critical strain energy release rate as the crack takes off. This involves both the fraction of the specimen which fails in a plane stress mode (the shear lips) and that fraction which fails in plane strain by craze formation and rupture. A more extensive discussion of this failure mode is given in relation to annealed polycarbonate for which more specimens fail in this manner (see Section 4.1.3).

4.1.2. Irradiated polycarbonate

The 120 Mrad Makrolon specimens were extremely brittle over all notch tip radii tested and it was not possible to obtain satisfactory impact data due to the low fracture energies involved. The 45 Mrad Makrolon and 35 Mrad Lexan are polymers of similar molecular weight, and these gave essentially the same results in the impact test. Fig. 3 shows apparent G_c against notch tip radius for 35 Mrad Lexan. Discussion will refer to 35 Mrad Lexan unless otherwise stated.

4.1.2.1. Razor notched specimen. Fig. 8 suggests that a fracture toughness analysis is again applicable for razor notched specimens, giving a value of G_c of 1.43 kJ m^{-2}. These specimens are therefore appreciably less tough than the razor notched specimens of unirradiated Lexan. A very similar fracture toughness was obtained for the 45 Mrad Makrolon specimens, and this value is significantly lower than that obtained for either Makrolon 2803 or Makrolon 2400 [7], the latter

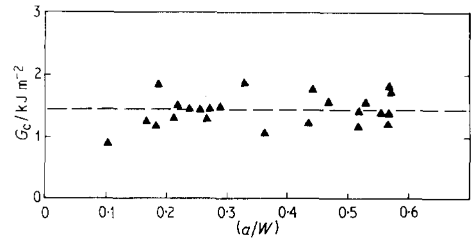

Figure 8 Critical strain energy release rate, G_c versus reduced crack length for razor notched specimens of irradiated Lexan. (specimens marked △ in Fig. 3).

being a polymer of molecular weight $\bar{M}_w = 15\,000, \bar{M}_n = 7900$.

The fracture surfaces showed similar features to those of the unirradiated polymer, the mirror zone again being present immediately below the root of the notch. It is however significant that the length of this zone was only 50 to 60 μm, indicating that the craze does not grow so large before breakdown as in the unirradiated polymer.

It has been shown that the Dugdale plastic zone model [9] provides a good representation for the craze at the crack tip in slow crack growth in polymers [24, 25]. It is likely that this will also be true for impact fracture behaviour provided that the mode of failure is similar. Following Rice's development [26] of the Dugdale zone analysis we can identify the flow stress with the craze stress σ_c. The strain energy release rate G_c is then given by

$$G_c = \sigma_c \delta \qquad (5)$$

where δ is the crack opening displacement. These results therefore suggest that on irradiation there has been a reduction in craze stress and/or a decrease in the crack opening displacement of the craze.

4.1.2.2. Blunt notch, ductile specimens. This mode of fracture occurred at a much higher notch tip radius than for the unirradiated polymer, suggesting that either the yield stress has increased or the crazing stress has decreased. Measurements of the yield and crazing stress, to be presented, show that the change is due to a reduction of crazing stress.

The plot of energy to fracture against (a/W) (Fig. 9) is a very good straight line with gradient $G_c'' = 110$ kJ m^{-2} which is a significantly lower value than that of the unirradiated polymer of 151 kJ m^{-2}.

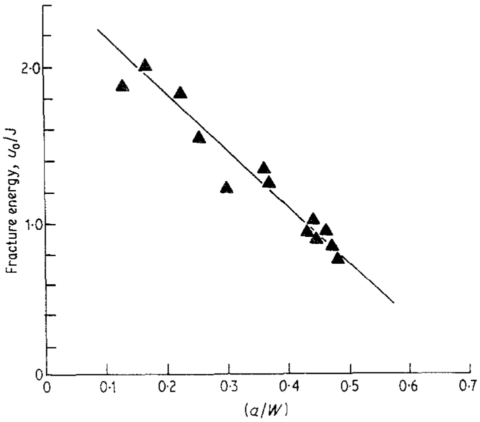

Figure 9 Fracture energy versus reduced crack length for fully ductile specimens of irradiated Lexan (marked ■ in Fig. 3).

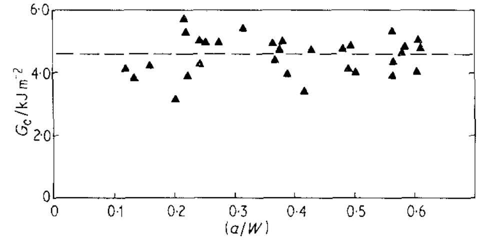

Figure 10 Critical strain energy release rate, G_c versus reduced crack length for razor notched annealed Makrolon (marked △ in Fig. 4).

4.1.2.3. Intermediate notch tip radius. These results give little direct evidence as to what governs the fracture since the data show too great a scatter. However, some indirect evidence may be noted.

(i) Most of the specimens of intermediate notch tip radius did not fail by just one single crack propagating across the specimen from the base of the notch. Many specimens broke into three or more pieces with several smaller cracks visible around the root of the notch. These in general followed the lines of principal stress radiating from the root of the notch. This result is consistent with a critical stress criterion and can be attributed to the fact that more elastically stored energy is present in the specimen than is required to propagate a single crack, once crack extension has begun.

(ii) There were no yielded zones, either at the base of the notch or in the form of shear lips, apparent on the fracture surface. All specimens failed in a brittle manner even just prior to the onset of the ductile regime. The absence of yield is largely due to the reduction in crazing stress, but this cannot be the complete explanation or else these zones would still be apparent near the ductile regime. This may be due to the reduced strain hardening in this material.

On the assumption that fracture relates to the achievement of a critical value of the maximum stress at the root of the notch, then this stress is about $170\,\mathrm{MN\,m^{-2}}$ using Equation 2. This is a significant reduction from the value for the unirradiated polymer, and is consistent with the reduction in craze stress (see Section 4.3.1).

4.1.3. Thermally pre-treated polycarbonate

The material tested was annealed Makrolon 2803 and the results should be compared with the data from untreated polymer published previously [7].

Fig. 4 shows the overall results in terms of apparent G_c. It may be seen that the ductile regime occurs at notch tip radii of greater than 0.35 mm. This is much higher than for the untreated polymer [7]. For this anlaysis each mode of fracture will be taken in turn.

4.1.3.1. Razor notched. It may be seen from Fig. 10 that fracture toughness is once again the appropriate parameter for failure. The value of G_c is 4.6 $\mathrm{kJ\,m^{-2}}$, which is somewhat higher than that presented previously [7], but agrees well with the results of Plati and Williams [22] for the same polymer without thermal treatment. The fracture surfaces appeared to be indistinguishable from those of the untreated polymer. We therefore

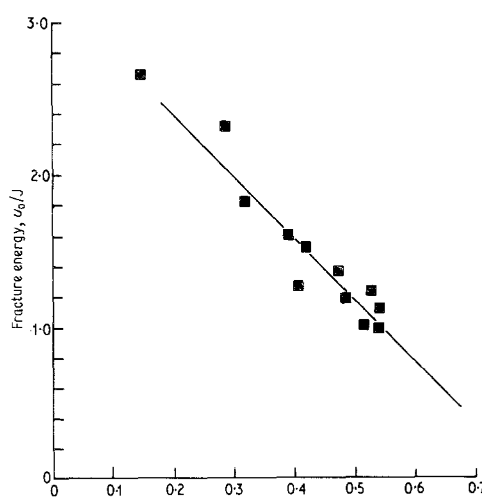

Figure 11 Fracture energy versus reduced crack length for fully ductile specimens of annealed Makrolon (marked ■ in Fig. 4).

conclude that annealing does not significantly affect this mode of fracture.

4.1.3.2. Completely ductile specimens. These results cannot be compared with those of the untreated polymer [7] because of the different treatment of results. This mode of fracture occurred at higher notch tip radii, indicative of a rise in yield stress due to annealing. The plot of energy to fracture against (a/W) (Fig. 11) shows a good straight line with $G''_c = 151\ \mathrm{kJ\,m^{-2}}$. The same experiment was undertaken on untreated Makrolon 2803, for comparative purposes, and this gave a value of $G''_c = 175\,\mathrm{kJ\,m^{-2}}$. Thus we see that annealing Makrolon 2803 results in a decrease in G''_c.

4.1.3.3. Intermediate notch tip radii. For notch tip radii of less than 0.35 mm ductile fracture no longer occurred. At a notch tip radius of about 0.20 mm it was possible to get two modes of fracture, i.e. brittle and brittle with yielded zones. Between this and the onset of ductile fractures only the brittle with yielded zone type of failure was in evidence.

(i) *Brittle.* The fracture surfaces showed negligible yielding and again the "mirror" zone may be seen at the root of the notch. Its length is about 200 μm, showing no significant change from the length of this zone in the untreated polymer. The maximum stress criterion (Equation 2) proposed for the other materials for this mode of fracture seems a reasonable fit, giving a value of about $250\,\mathrm{MN\,m^{-2}}$. This is a lower value than that previously reported for the untreated polymer [7], so in order to compare the effect of annealing on this stress some specimens of 6 mm thick Lexan polycarbonate were annealed in the same way for comparison with the value for the 6 mm thick untreated Lexan specimens. The

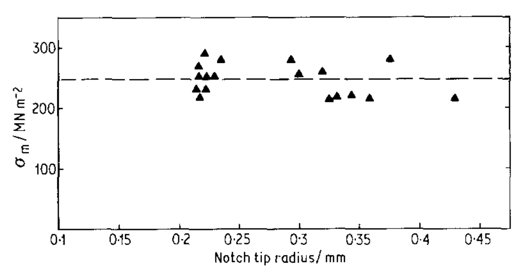

Figure 12 Maximum stress at root of notch versus notch tip radius for 6 mm-thick specimens of annealed Lexan (not shown in Fig. 4).

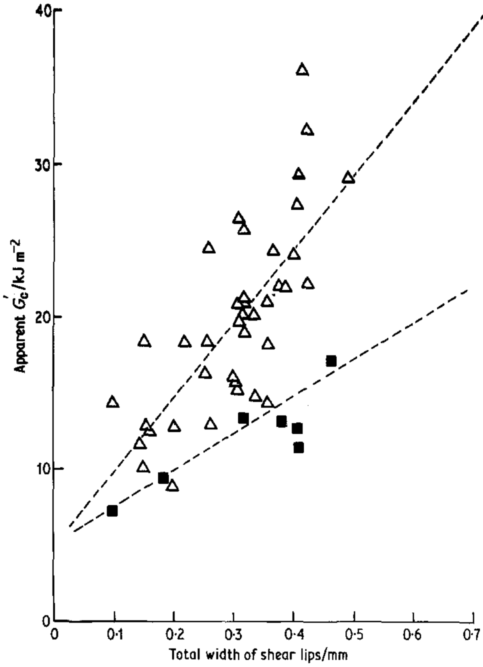

Figure 13 Apparent strain energy release rate versus shear lip width for annealed specimens. △, 3 mm-thick Makrolon specimens (those marked • in Fig. 4), 6 mm-thick Lexan specimens. The dashed lines join the plane strain values of G'_c at zero shear lip width with the plane stress value for a shear lip width equal to the specimen thickness.

results are shown in Fig. 12, giving a value of $246\,\mathrm{MN\,m^{-2}}$. It is concluded that annealing does not affect the maximum stress criterion in this mode of fracture, which is consistent with direct measurements of craze stress (see Section 4.3.1).

(ii) *Brittle with yielded zones.* This is the sole mode of fracture for samples with notch tip radii between 0.25 and 0.35 mm. The values of energy to fracture extend over a similar range to that of the untreated polymer, but for any particular notch tip radius the extent of yielding apparent on the fracture surface has been reduced by annealing giving a lower energy to fracture. This is in line with previous results on the decrease of the extent of yielding in the Charpy test [16].

Fig. 13 shows the apparent strain-energy release rate G'_c (calculated from Equation 1) as a function of the total width of the shear lips at the assumed fracture take off point i.e. at the beginning of the mirror zone associated with the craze which forms ahead of the growing crack. Consistent with the previous work [7], there is an excellent linear correlation for two different situations (annealed Makrolon 2803 (3 mm) and annealed Lexan

(6 mm)) which indicates that for these specimens there is a simple additivity of the strain-energy release rates in the plane stress and plane strain modes. As the width of the shear lip tends to zero G_c' tends towards the plane strain value of $4.6\,kJ\,m^{-2}$. It should be emphasized however that problems arise with this approach when one considers the considerable yielded region right across the root of the notch which forms and ruptures before the crack takes off casting doubt on the use of Equation 1. It must also be appreciated that the "fully plane stress" value of G_c' obtained by extrapolation of the lines in Fig. 13 to the point where the two shear lips meet in the centre of the specimen corresponds to a situation where there is still no rigorous analysis available. (There is a conflict between the values G_c' and G_c'' calculated for fully ductile failures from Equations 3 and 4 respectively, as shown in Section 4.1.1.2).

For this mode of failure we can also find other correlations betwen the measured fracture toughness and specimen geometry. For example in Fig. 14 the measured values of G_c' are plotted versus the *total* yielded area of the fracture surface (i.e. the area of the plastic zone at the root of the notch plus the area of the shear lips). Again a linear plot is obtained which extrapolates to the expected value of $G_c = 4.6\,kJ\,m^{-2}$ for a specimen failing completely in plane strain, and G_c increases linearly with the extent of plane stress yielding. The area of yielding in these specimens depends primarily on notch tip radius as shown in Fig. 15,

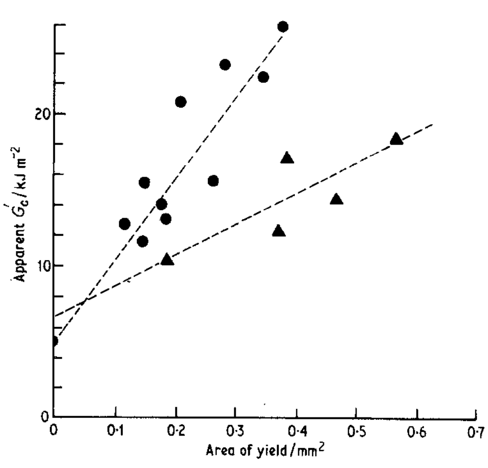

Figure 14 Apparent strain energy release rate G_c' versus total area of plane stress yielding for 3 mm specimens of annealed Makrolon (marked • in Fig. 4). ○, $a/W = 0.05 \pm 0.05$; △, $a/W < 0.15$.

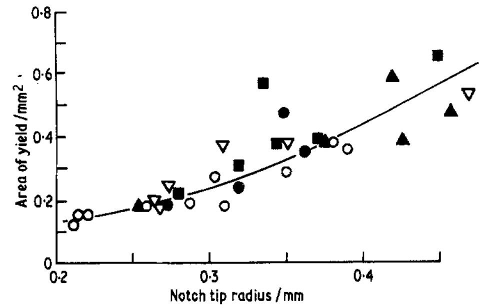

Figure 15 Area of yield versus notch tip radius for specimens of annealed Makrolon (marked • in Fig. 4). ▲, $a/W = 0.1 \pm 0.5$; ▽, $a/W = 0.2 \pm 0.05$; •, $a/W = 0.3 \pm 0.05$; ■, $a/W = 0.4 \pm 0.05$; ○, $a/W = 0.5 \pm 0.05$

and so for specimens of the same notch tip radius a long crack will give a larger proportion of yielded zone than a short crack and so G_c' rises more steeply with yielded area for long cracks than for short ones.

Closer inspection of Fig. 14 reveals that G_c' increases extremely rapidly with yielded area and would extrapolate to an improbably high value of fracture toughness for a fully plastic failure. With these factors in mind we suggest that at present the most satisfactory analysis of specimens with yielded zones is in terms of the width of shear lip at take off as shown in Fig. 13 although we must await a theoretical justification of this approach.

4.2. Tensile tests

Three experiments were performed on tensile specimens. These were (i) the uniaxial tensile crazing stress, (ii) the engineering yield stress, and (iii) the extension to break.

The uniaxial tensile crazing stress was determined at a cross-head speed corresponding to an inital strain rate of $8.3 \times 10^{-6}\,sec^{-1}$. The results are shown in Table II, from which we see that irradiating polycarbonate lowered the crazing stress in tension. This is consistent with the drop

TABLE II Effect of treatment on tensile crazing stress of Lexan polycarbonate.

Treatment	Tensile crazing stress ($MN\,m^{-2}$)	Mean critical maximum stress of brittle impact specimens ($MN\,m^{-2}$)
Untreated	60–62	248 ± 6
35 Mrads	31–41	170 ± 12
Annealed	60–65	246 ± 5

in the critical stress at the root of the notch in the impact test. At these very slow strain rates the final fracture of the irradiated specimens was by brittle fracture, while the untreated and annealed specimens were ductile. This would suggest that the craze in the irradiated polymer is a weak one and having formed requires little additional energy to cause breakdown and brittle fracture. It seems therefore that there is a fall in both crack opening displacement and crazing stress. The effect of this on the impact behaviour is a reduction in both the toughness of the razor notched specimens and the maximum stress at the root of the notch for the completely brittle intermediate notch tip radii specimens. In addition ductile fracture is postponed to a higher notch tip radius and the likelihood of any small scale yielding is reduced.

Annealing does not affect the crazing stress in the tensile tests. This is therefore consistent with the observation that the stress at the root of the notch was about the same for the brittle impact specimens with intermediate notch tip radii. It is also consistent with the similar values of G_c for the razor notched specimens for the annealed and untreated polymer, suggesting that the crack opening displacement remains the same.

The engineering yield stress and extension to break were obtained from measurements at a cross-head speed corresponding to an initial strain rate of 5.5×10^{-3} sec^{-1}. It should be noted that at these strain rates all these materials failed in a ductile manner, yielding and drawing to fracture as distinct from the crazing behaviour observed at low strain rates. Although it would seem most unusual for a material to fail in a brittle manner at very slow strain rates and in a ductile manner at moderate strain rates, similar behaviour has also recently been observed in torsion on polycarbonate [27]. In these tests crazes were observed to initiate fracture at low strain rates and the brittle–ductile transition was associated with the large difference in strain rate dependence between crazing and yielding. Typical stress–strain

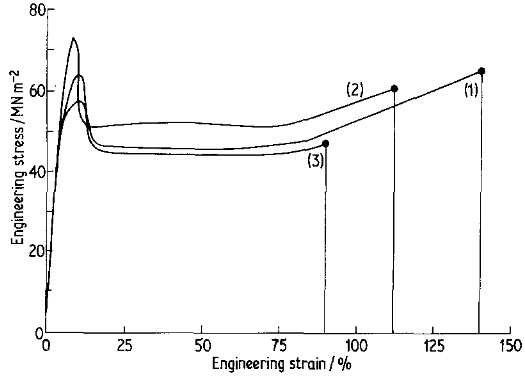

Figure 16 Engineering stress–strain curves (1) untreated Lexan, (2) annealed Lexan, (3) irradiated Lexan. Initial strain rate = 5.5×10^{-3} sec^{-1}.

curves from the present measurements are shown in Fig. 16, and the key data are summarized in Table III.

The reduction in yield stress due to irradiation was much less than the reduction in crazing stress. In contrast, the crazing stress for Lexan was unaffected by annealing while the yield stress substantially increased. This manifested itself in the impact test in the fact that ductile fractures were not obtained until notch tip radii exceeded 0.35 mm, and that the area of yield was found to decrease on annealing for any particular notch tip radius.

The ductile failure may be considered to arise from the successive yielding and drawing to failure of elements in front of the crack [28]. It is the amount by which these elements can be drawn that largely determines how much energy is used in the fracture. Therefore we would expect a correlation between the energy to break and the apparent strain energy release rate G''_c for blunt notched specimens.

Table IV shows this correlation. Both the irradiation and the thermal pre-treatment result in a decrease in the extensibility of the material and

TABLE III Effect of treatment on yield stress and extension to break of Lexan polycarbonate.

Treatment	Yield stress (MN m^{-2})	Extension to break (%)
Untreated	64.5 ± 0.3	138 ± 5
35 Mrads	57.3 ± 0.3	91 ± 5
Annealed	72.3 ± 0.3	110 ± 5

TABLE IV Ductile failure

Treatment	Tensile specimens		Impact specimens
	Extension to break (%)	Energy to break (MJ m^{-2})	G''_c (kJ m^{-2})
Untreated	138 ± 5	2.20 ± 0.10	151 ± 12
35 Mrads	91 ± 5	1.28 ± 0.06	110 ± 10
Untreated	138 ± 5	2.20 ± 0.10	*175 ± 12
Annealed	110 ± 5	1.73 ± 0.09	*151 ± 11

*Makrolon 2803 tested.

therefore a reduction in the energy to break a tensile specimen. In the impact test this results in a reduction in the value of G_c'' obtained. The correlation between G_c'' and the energy to break a tensile specimen is considered reasonably good considering the difference between the two tests.

By changing the notch tip radius we are changing the state of stress within the specimen. We may view the brittle-to-ductile transition as a competition between the different fracture mechanisms. At one extreme the notch is very sharp and a condition of plane strain exists for virtually the whole width of the notch. Under these conditions the yield stress of the material is sufficiently high for crazing to be preferred. Finite element analysis has shown that a state of plane strain is not realised in the centre of a notched specimen until the thickness of the plate is greater than four times the radius of the notch [29]. It has also been shown that the maximum value of principal stress may occur at some distance below the root of the notch [29]. It is conceivable therefore that the criterion for crazing may be met at some distance below the root of the notch, after yielding has started at the root of the notch. At even higher notch tip radii the state of stress approaches the other extreme, i.e. plane stress. In this case the principal stress to produce yielding at the root of the notch is lower and so completely ductile fracture occurs. By changing the yield stress or the crazing stress, the notch rip radii for which these modes of fracture can occur is altered.

The criterion for fracture in razor notched specimens is the energy required to load the specimen up to the point where incremental crack growth occurs. Once this energy has been supplied the elastic energy stored in the impact specimen is sufficient for catastrophic crack growth to occur. For the brittle intermediate notch tip radii specimens, a stress condition must be met at the root of the notch to form a craze, and once formed the energy stored is then sufficient to extend the craze and cause catastrophic crack propagation. For brittle-with-yield-zone specimens, energy must be supplied until the ductile zone ruptures, and at this point, again there is sufficient energy stored to propagate the crack across the remainder of the specimen.

Finally, for ductile failure the situation is complicated since the energy needed to break the specimen is that required to form and propagate a plastic zone and crack through the specimen in a stable manner. The elastic energy stored in this case is insufficient for further crack propagation and external work is necessary even after crack extension has begun.

4.3. Comparison with standard Charpy test

The standard Charpy impact specimen has a 90° V-notch with a tip radius of 0.25 mm. Comparison of the present data with those reported in the literature on standard Charpy specimens is difficult due to the possibility of the transition from ductile to brittle failure at this notch tip radius for small differences in molecular weight, specimen thickness and test temperature. However, it can be seen that most untreated Lexan specimens in the present investigation fall into the brittle with yielded zone mode, with only a few brittle fractures. This results in a value of G_c' of between 12 and 17 $kJ\,m^{-2}$, which falls to between 7 and 13 $kJ\,m^{-2}$ for annealed specimens. This is consistent with values reported by previous workers [16]. Irradiation results in an even greater reduction of the fracture toughness for standard Charpy specimens, our data showing a value for G_c' of about 2.5 $kJ\,m^{-2}$.

It is evident from the present studies that any attempt to explain the effect of variation in polymer structure on the impact behaviour in a standard Charpy test must consider the possibility of several completely different modes of failure. We have shown that it is not possible to interpret the effects of annealing and molecular weight without taking this into account.

5. Conclusions

It has been confirmed that several distinct modes of failure can occur in notched impact tests on polycarbonate. The failure should be analysed in four different ways.

(1) Conventional linear elastic fracture mechanics is applicable for brittle failure of sharply notched specimens.

(2) A critical stress criterion applies for some intermediate situations. This is identified with the crazing stress.

(3) For some other intermediate situations there is a mixed mode failure where the energy to fracture is largely determined by the extent of yielding.

(4) There is a ductile failure mode for very blunt notches which can be approximately analysed in terms of an apparent G_c.

The effects of molecular weight and annealing treatment can be satisfactorily understood in terms of changes occurring in the crazing stress, the yield stress and the extension to break. Molecular weight primarily affects the crazing stress and the extension to break, whereas annealing primarily affects the yield stress.

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