JOURNAL OF MATERIALS SCIENCE 17 (1982) 469–476

A model for brittle–ductile transitions in polymers

H. R. BROWN*
Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia

A model is proposed for mixed-mode crack propagation in materials which show shear lips on the fracture surface. The model is shown to predict the existance of a "brittle–ductile" transition as the specimen thickness is decreased. The predictions of the model are compared with published experimental data on a number of polymers including polycarbonate, and good agreement is found.

1. Introduction

It is possible to change the failure mode of a number of polymers from ductile to brittle by changing either "external" conditions, such as temperature, loading rate, notch tip radius or specimen thickness, or "internal" conditions such as molecular weight, crystallinity or density. A large proportion of the studies on the brittle–ductile transition have been performed on polycarbonate, probably because the transition can be observed in standard impact tests around room temperature using samples in the thickness range 3 to 6 mm. Similar transitions have been observed in nylon [1], polypropylene [1, 2], polythylene [3], polysulphones [4] and PVC [5]. It is worth considering the fracture properties of polycarbonate in some detail as there is a considerable amount of published information on this material. Polycarbonate shows three modes of failure in impact tests: the failure can be entirely brittle, brittle with shear lips, or ductile [6, 7]. The transition from ductile to brittle failure can be caused by an increase in specimen thickness [8, 9], a decrease in notch tip radius [10], a decrease in temperature [11], a decrease in molecular weight [7, 12] or by annealing the specimen [7, 8, 13].

Fracture mechanics tests show considerable thickness effects within the "brittle with shear lips" mode of failure and a transition to ductile failure [14–17]. The transition from a slow-speed, "brittle with shear lips" failure mode to a high-speed failure has been studied in some detail.

2. Background

The effect of shear lips on brittle fracture of polymers has been analysed by assuming a type of bimodal fracture analysis. The resistance to crack growth, described by either K_c or G_c, is assumed to be a weighted mean of K_{c1} or G_{c1} coming from the centre, plain strain, section of the sample and K_{c2} or G_{c2} coming from the shear lips. The weighting factors are proportional to the areas of fracture surface which show the two modes and hence are related to the width of the shear lips. Williams and co-workers [1, 2, 14, 15] have used this model extensively using Ks and shear lip widths calculated from Equation 1 (see below). Ward and co-workers [6, 7, 16, 17] used a similar model with a weighted mean of Gs, the shear lip widths in the weighting factor being measured from the fracture surface. As $K^2 = EG$ these two approaches are in principle different (a weighted mean of K^2 being different from a weighted mean of K) but it is not clear that the experimental data are sufficiently accurate to distinguish between them. It could be argued that the use of a weighted mean of K is appropriate when studying an instability fracture toughness whereas G should be used when studying steady crack growth.

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*Present address: Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA.

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3. A model for crack propagation in polymers

A planar crack is assumed to exist in a polymeric material of which the thickness B is small relative to the other two dimensions. The front of the crack runs through the thickness B. Under applied load the state of the stress ahead of the crack tip will vary from plain strain in the interior, to plain stress at the surfaces. Due to the lack of plastic constraint in these regions the material will yield and form shear lips if the crack is forced to move.

Several assumptions are made with regard to the shear lips. Firstly it is assumed that the boundary between the shear lips and the non-sheared material is at 45° to the fracture surface and the specimen surface. Secondly it is assumed that the size (width) of the shear lips can be determined by fracture mechanics considerations, as it has been used, for example, in metals [19] Since the size of the shear lip, d, is calculated from the elastic stress singularity some distance from the crack tip, it seems therefore plausible that the applied value of the stress concentration factor, K_T, should be used. We take the well known Irwin relation, also used by Williams and co-workers, to obtain the relationship:

$$d = \frac{1}{2\pi}\left(\frac{K_T}{\sigma_y}\right)^2 \qquad (1)$$

In Equation 1, σ_y is the yield stress of the material. It can be mentioned here that Williams and co-workers used in Equation 1 for K either the value for shear lips (i.e. K_{c2}) or the mean applied K [2].

A similar relationship for the size of the shear lips in a crazing material has been proposed by the author under the condition that the shear lips only occur when the craze stress is greater than the yield stress [20]. It was shown that if $d \ll B$, the shear lips cause only a small disturbance of the stress within the material, and then

$$d = 0.4\alpha\,(K/\sigma_0)^2 \qquad (2)$$

where σ_0 is the craze stress and α is a function of (σ_0/σ_y). It was also demonstrated that when $\sigma_0 > 1.5\sigma_y$, $\alpha \simeq 0.4\,(\sigma_0/\sigma_y)^2$ so this expression is very little different from Equation 1.

In the above relationship we have therefore a mechanism for the formation of shear lips and the dependence of their size on the applied load. However, in order to advance the crack and to maintain its growth, a certain amount of energy will have to be used. Some energy will be required for the brittle, plain-strain crack propagation (i.e. G_{c1}), and some for the shear lips (i.e. G_{c2}). Since energy is a scalar quantity, it can be reasonably assumed that the applied strain-energy release rate, G_T, is equal to the weighted mean of G_{c1} and G_{c2}. Such a relationship has been used before [17, 19, 21]. Thus,

$$G_T = G_{c1}\frac{(B-2d)}{B} + \frac{2\phi d^2}{B} \qquad (3)$$

In this equation ϕ is the energy per unit volume necessary to strain the shear lips to failure. It is therefore assumed that the G value for the shear lips varies as their volume.

The main assumption of this model is given now, and its consequences are described in the following section. It is proposed that both Equations 1 and 3 must be satisfied simultaneously for the steadily propagating crack. The state of stress and the applied stress intensity factor in operation ahead of the crack will influence the crazing, yielding and shearing of the material whilst the energy relationship will determine whether the crack can grow or not. A steady crack growth will be achieved for a given critical strain-energy release rate when the size of the shear lips is equal to the value calculated from Equation 1.

3.1. The response of the model to varying d and B

Equations 1 and 3 are represented graphically in Fig. 1. Let us consider initially a crack without any shear lips ($d = 0$). Then for the crack to start moving it will be necessary to apply $G_T = G_{c1}$. However, ahead of the crack the stress in the material causes yield in regions close to the surfaces, and with an increment of the crack length these regions will shear and give rise to shear lips. As the crack grows the width of the shear lip increases until the value of $d = d_1$ is reached. This is now a stable condition for which both Equations 1 and 3 are satisfied simultaneously. It will also be found that if the initial condition is $d_1 < d < d_2$, then d will decrease to d_1. This is explained as follows: choose any value of d between d_1 and d_2. A corresponding value of G_T lies on the parabola in accordance with Equation 3. The same value of G_T when used in Equation 1 (with $K_T^2 = G_T E$) gives a smaller value of d, as shown by the corresponding segment of the straight line. Therefore an increment in crack

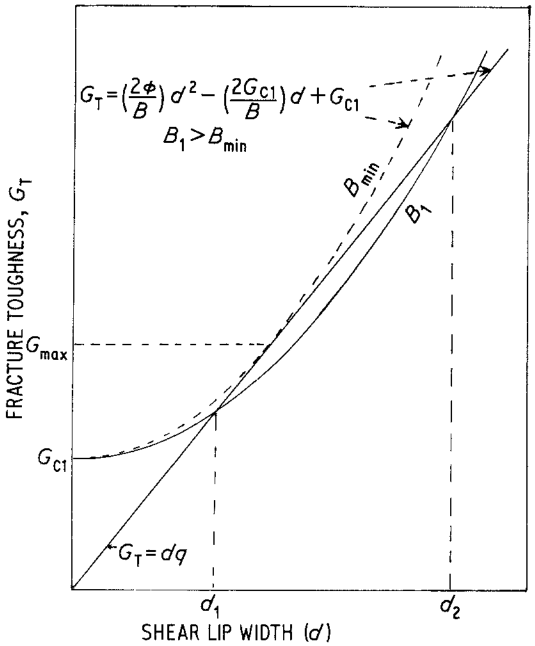

Figure 1 Variation of fracture toughness with shear-lip width from Equations 3 and 4. Two different values of specimen thickness, B, are shown.

length will be accompainied with a decreased size of the shear lips. This process will continue with every increment in crack length until the stable value of d_1 is reached. Obviously within this region of values of d we have a mixed mode of crack propagation, i.e. brittle with shear lips.

Consider now the other situation when $d > d_2$. Clearly d will increase without limit which means that the two shear lips will coalesce, and a ductile failure will result. Note that the slope of the straight line in Fig. 1 is related to the square of the yield stress and inversely to the modulus of elasticity of the material. For materials with very high yield stress, the slope of the line will be high, and consequently d_1 will tend to have a very small value. In the reverse situation when yield stress is low, the straight line and curve may not intersect and hence the shear lips will grow without limit, always resulting in a ductile fracture. Mathematically this can be expressed as follows. Equation 1 and 2 can be written in a simplified form as:

$$d = \frac{G_T}{q} \tag{4}$$

and substitution of Equation 3 gives the solution to the quadratic equation as

$$d_{1,2} = \left\{ \left[q + \frac{2G_{c1}}{B} \right] \pm \left[\left(q + \frac{2G_{c1}}{B} \right)^2 - \frac{8\phi G_{c1}}{B} \right]^{1/2} \right\} \frac{B}{4\phi}. \tag{5}$$

Let us consider now the effect of varying B. The simplest situation is for large B when the shear lip contribution to G_T is small ($G_T \gg 2\phi d^2/B$, and the shear lips are small ($B \gg d$). In this case d from the smaller solution to Equation 5 is given by

$$d \approx \frac{G_{c1}}{q} \tag{6}$$

as expected. As B is decreased, d and G_T increase until the two solution coalesce at a value of B given by

$$(qB_{min} + 2G_{c1})^2 = 8\phi G_{c1} B_{min}. \tag{7}$$

For $B < B_{min}$ there is no stable shear-lip width; as the crack grows the shear lips grow until they meet, forming a fully ductile failure. The model therefore predicts a brittle–ductile transition as B is reduced below B_{min}. In the condition where B is only slightly larger than B_{min} the two points in Fig. 1 are not far apart and so the "restoring force" for $d \neq d_1$ is not great and one would expect considerable fluctuation in experimentally measured values of d.

It is worth considering the value of B_{min} found from Equation 7 and the implications for the maximum value of G_T obtainable. Equation 7 can be written as

$$B_{min} + 4B_{min} \left(\frac{G_{c1}}{q} - \frac{2\phi G_{c1}}{q^2} \right) + \frac{4G_{c1}}{q^2} = 0. \tag{8}$$

or

$$B_{min} = \frac{2G_{c1}}{q^2} \left[(2\phi - q) + ((2\phi - q)^2 - q^2)^{1/2} \right]. \tag{9}$$

If $\phi \gg q$

$$B_{min} \approx \frac{4G_{c1}(2\phi - q)}{q^2} \tag{10}$$

and if $\phi = q$,

$$B_{min} = \frac{2G_{c1}}{\phi}. \tag{11}$$

G_T at $B = B_{min}$ can be found to be

$$G_T = \frac{G_{c1}q}{2\phi} + \frac{B_{min}q^2}{4\phi}. \tag{12}$$

Therefore, if $\phi \gg q$

$$G_T = G_{c1}\left[2 - \frac{q}{2\phi}\right] \tag{13}$$

and if $\phi = q$

$$G_T = G_{c1}. \tag{14}$$

For $B > B_{min}$ the maximum obtainable value of G_T is $2G_{c1}$ and this is only found when the shear lip energy, ϕ, is large or the shear lip size for a given G_T is large (q small).

3.2. Comparison with experiment

A quantitative comparison of the model with experimental results can be made for polycarbonate at −30° C, at which temperature all the required material constants have been measured by Pitman and Ward [17]. For high molecular weight materials they obtained the following results: $G_{c1} = 1 \times 10^3$ J m^{-2}, $\phi = 1.1 \times 10^8$ J m^{-2}, $\phi_y = 84 \times 10^6$ N m^{-2}, $E = 2.8 \times 10^9$ N m^{-2} and $\sigma_0 = 120 \times 10^6$ N m^{-2}. Furthermore, from Equations 1 or 2 (they approximately agree in this case) $q \simeq 15 \times 10^6$ N m^{-2} and hence calculations can be made using the model.

Firstly, using Equation 9, we obtain $B_{min} = 3.6$ mm. Pitman and Ward did not obtain an experimental value for B_{min} but consider that it was probably not much below the size of their thinnest specimen, 3 mm [4]. Clearly the calculated result is of the right order of magnitude, which considering the assumptions within the model can be considered reasonable agreement. In this context it should be noted that Equations 1 and 2 could be incorrect by a factor of two [20] and also that $B_{min} \propto \sigma_y^{-4}$ and so is extremely sensitive to the accuracy of determining the yield stress.

The maximum value of G_T/G_{c1} was found in [17] to be approximately five and so is larger than the factor of 1.9 predicted by Equation 13. It is clear from Fig. 1 that larger values of G_T/G_{c1} are possible without the specimen undergoing ductile failure if $B > B_{min}$. They are not stable values however and the shear lips and hence G_T tends to decrease with crack growth. This situation could be caused by the initial notching technique or the crack moving out of plane due to material flaws or loading anisotropies. Now we can calculate the stable value of d for the width of the shear lips. Taking a value of $G_T = 2 \times 10^3$ J m^{-2} and using Equation 5 results in $d_1 = 0.13$ mm. This is to be compared with the experimentally measured value of 0.15 mm. This agreement is very good. Similarly, for $G_T = 4 \times 10^3$ J m^{-2}, $d_1 = 0.26$ mm, and the experimental value is 0.2 mm [17].

Crack propagation has been studied in polycarbonate at room temperature by Parvin and Williams [14, 15]. They found that when 5 mm thick specimens were used the failure mode could be changed from ductile to brittle by an increase in the loading rate in fracture mechanics tests. This showed that B_{min} was strain-rate dependent (probably through the rate dependence of σ_y) but was 5 mm for a polycarbonate sheet at room temperature at one strain-rate.

They measured the yield stress over the range of strain-rates used in their tests and found it to vary from 62 to 70 MPa. In addition, by use of surface notched specimens which gives a very large effective B, they found $K_{c1} = 2.95$ MN m$^{-3/2}$ and so, assuming $E = 2.2 \times 10^9$ Pa, $G_{c1} = 3.95 \times 10^3$ J m^{-2}. Kambour and co-workers [18, 22] have used single-grooved cantilever beam specimens to measure shear-lip energies directly for polycarbonate at room temperature. They found that the energy to fail varied as the shear-lip volume, as assumed in Equation 3, and that (independent of crack speed) $\phi = 32 \times 10^6$ J m^{-3}, which is much less than the value at −30° C. σ_0 has not been measured at this temperature so comparisons between this model and experiment can only be made if it is assumed that Equation 1 is correct (or $\sigma_0 > 1.5\sigma_y$). Under this assumption $q = 12.4 \times 10^6$ Pa, assuming $\sigma_y = 66$ MPa, and from Equation 9, $B_{min} = 5.6$ mm. The agreement between this figure and the experimental value of 5 mm is clearly excellent. Parvin and Williams also measured the maximum value of G_T/G_{c1} which they found to be 1.83. This is to be compared with a calculated value from Equation 13 of 1.81. In conclusion, there is good agreement between the predictions of the proposed model and the experimental results from fracture mechanics tests on polycarbonate. These are, so far, the only cases for possible quantitative comparison between the model and experimental results. Other comparisons, due to the lack of experimental data, must necessarily be more qualitative in nature.

Mixed-mode propagation and brittle–ductile transitions have been reported in polypropylene [1, 2] and nylons [1, 23]. The temperature of the brittle–ductile transition in polypropylene homopolymer was found to depend upon specimen thickness [1] and it presumably does for the copolymers also. For thick specimens of polypropylene homopolymer, where the brittle–ductile transition was found in the temperature range between 0 to 40° C, there was very little change in K_c with increasing temperature in the brittle region. For thinner homopolymer specimens and for thick copolymer specimens where the transition was in the range -60 to $-40°$ C there was a considerable increase in K_c with increasing temperature before ductile failure took over. This is qualitatively explicable from Equation 13 as it was in polycarbonate. It appears that the shear-lip energy ϕ decreases very rapidly with increasing temperature and hence from Equations 13 and 14 the increase in G_T or K_T before ductile failure is much lower at the higher temperatures. Fernando and Williams [2] did in fact calculate a plane stress K_{c2} which decreased rapidly with increasing temperature in agreement with this suggestion.

The ductile–brittle transition in nylon was described as being between semi-brittle (brittle with shear lips) and ductile failure [22]. The transition was affected by crystallinity, loading rate and water content. As all these parameters affect the yield stress the situation is not significantly different from that described for polycarbonate.

Hobbs and Bopp [25] have recently shown that the fracture of polybutene terephthalate shows sample thickness effects. They found excellent agreement with Williams' model of summing Ks and using K_{c2} in Equation 1. No sudden brittle–ductile transtion was observed however, the plastic zone size (measured on the specimen surface) and K_c just increased steadily as the loading rate was decreased until the whole specimen was "ductile". The failure in that case was only locally ductile, however, no large specimen deformation and shape change was observed unlike the situation in polycarbonate. The model described in this paper assumes considerable ductility within the shear lips and over the whole material when they coalesce so does not apply to polybutene terephthalate. In addition this material does not show the type of brittle–ductile transition predicted by the model.

The model described in this paper can therefore explain qualitatively some of the properties of the brittle–ductile transitions observed in polycarbonate, nylon, polypropylene and polyethylene.

4. Blunt-notched impact failure

It is worth considering the relevance of this crack propagation model to ductile–brittle transitions in blunt-notched impact failure. In this context a blunt notch is any notch whose tip radius is greater than that of a naturally propagating crack. Ward and co-workers [6] have shown that polycarbonate can show three different modes of failure in impact tests: brittle, brittle with shear lips and ductile. We shall mainly be concerned with the transition between the latter two modes of failure.

Fracture surface studies on the "brittle with shear lips" failure mode in impact have shown that, as well as the shear lips, yield zones form along the root of the notch [6, 8] and also that the shear lips decrease in size as the crack propagates. Examination of specimens which failed in a ductile mode have shown that a crack or craze can form under the notch but it does not propagate across the specimen [13]. The existence of these crazes has also been demonstrated using subcritical impact tests, that is, impact tests where the energy in the pendulum was not sufficient to break the specimen [7, 8]. Mills [8] suggested that the craze forms at the intersection of shear bands under the root of the notch [26].

We shall assume therefore that during the loading period of the impact test, shear lips form at the edge of the specimen and eventually a craze is nucleated at the specimen centre. We shall further assume that the craze propagates at a similar G_{c1} to a crack [14] and in fact will turn into a crack when it propagates far. Shear lips, being formed on the surface of the specimen, can be relatively large and we shall assume that they are large with respect to the notch root radius. In this case the size of the shear lips will be controlled only by the applied G_B, that is the G that would be calculated for a similar loading situation if the notch were sharp. Hence, from Equation 1,

$$d = \frac{1}{2\pi}\frac{EG_B}{\sigma_y^2}. \qquad (15)$$

Within this model the shear lip size at craze propagation will depend only on the applied G_B independent of notch root radius.

The yield zones at the centre of the specimen at the notch tip are small and we shall assume (following Williams [24]), that the craze propagates when the calculated elastic stress reached a critical value at a certain (small) distance below the notch. Hence, when

$$G_B \approx \frac{\rho}{2c} G_{c1} \tag{16}$$

where c is a characteristic distance in Williams' model and ρ is the notch root radius. The shear lip size at craze propagation is hence given by

$$d = \frac{\rho}{4\pi c} \frac{EG_{c1}}{\sigma_y^2} \tag{17}$$

and so increases with notch root radius. From the model of mixed-mode crack propagation described earlier, it follows that if d is greater than d_2, (see Fig. 1), thus the shear lips will continue to grow and ductile failure will result (with a small craze or crack beneath the notch). If the shear lip size is less than d_2, then it will decrease to d_1 as the crack propagates giving a semi-brittle failure. As d_2 increases with increasing B, the size of the notch radius at the ductile–brittle transition will also increase with B.

It is not possible to compare this condition directly with experiment as the necessary material properties have not been measured at impact rates. It is possible, however, to get some information by making more approximations. If it is assumed that $q \gg 2G_{c1}/B$, as is normally the case, and that $B \gg B_{min}$ then Equation 5 can be written

$$d_2 \approx \frac{qB}{2\phi}. \tag{18}$$

If σ_c is a critical stress for craze/crack initiation, then from Williams [24]

$$K_B \approx \frac{\sigma_c}{2} (\pi\rho)^{1/2} \tag{19}$$

and therefore

$$d \approx \frac{\rho}{8} \left(\frac{\sigma_c}{\sigma_y}\right)^2. \tag{20}$$

The brittle–ductile transition occurs when $d = d_2$, so from Equations 18 and 20 when

$$\rho = \frac{8\pi B}{\phi\sigma_c^2} \frac{\sigma_y^4}{E}. \tag{21}$$

This relation shows that the notch-tip radius at the brittle–ductile transition increases linearly with the specimen thickness and as the fourth power of the yield stress.

The large effect of annealing on the brittle–ductile transition in polycarbonate has been explained by the fact that annealing increases σ_y and decreases ϕ [6, 11]. The changes in σ_y and ϕ are not large but as Equation 21 is very sensitive to σ_y, the total effect is considerable. Pitman *et al.* [7] measured σ_c, admittedly from brittle fracture, and found that it was independent of annealing but decreased on irradiating the polycarbonate. They also measured σ_y and ϕ at low strain rates. It is reasonable to assume that σ_y and ϕ vary in the same manner with strain rate for untreated, annealed and irradiated polycarbonate. In this case the variation of ρ with treatment can be found from the variation of $\sigma_y^4/\phi\sigma_c^2$ using the measured values. The results are shown in Table I.

These figures imply that both annealing and irraditiation would be expected to double the notch-tip radius at the brittle–ductile transition. In fact ρ increases from 0.25 mm in untreated material to 0.4 mm in both annealed and irradiated material. It is not clear tha the model should be applicable in the irradiated material, however, as shear lips were not visible on the fracture surface in this case and so the transition was from brittle, rather than semi-brittle, to ductile failure. Nonetheless, it appears from these figures that the proposed model is capable of explaining the effects of annealing and maybe irradiation on the brittle–ductile transition in polycarbonate.

5. Discussion

Brittle–ductile transitions occur in a range of polymers, both crystalline and anmorphous, and in all cases the transition is affected by both the internal state of the material and the specimen dimensions. Mixed-mode crack propagation has also been reported in most of the materials which show a brittle–ductile transition. It seems likely therefore that there is some relation between the two phenomena. Also, as these brittle–ductile transitions occur in polymers with a range of micro-

TABLE I

Treatment	$\sigma_y^4/\phi\sigma_c^2$ (Pa)	ρ_{exp} mm
Untreated	1.28×10^8	0.25
Annealed	2.61×10^8	0.4
Irradiated	2.91×10^8	0.4

structures, it seems unlikely that the explanation of the transition occurs in detailed microstructural processes. Similar brittle–ductile transitions have been observed in metals where extensive work has been published. It is possible that the model described in this paper is applicable to that situation also.

The important assumptions of the model are that the G or K for the shear lips increases with shear-lip size and that the shear-lip size is some function of the applied G on the specimen. There is good evidence for the first of these assumptions, particularly in polycarbonate [17, 18], polysulphone [4] and some metals [19]. The evidence for the second assumption is not great but it seems plausible when the shear-lip size is large. It therefore seems likely that, even if the precise details of the model are incorrect, the basic mechanism, a coupling between shear-lip size and fracture energy to cause a brittle–ductile transitions, will occur in a number of materials.

As mentioned in Section 1, polycarbonate, together with a number of other polymers, can show a transition between a slow-speed, relatively high-energy, "brittle with shear lips" failure mode and a high-speed, lower-energy, brittle failure mode. This transition has been ascribed to an adiabatic–isothermal transition [14] though not all authors agree [18]. It seem likely that this low-energy failure mode can be equated with the brittle failure mode observed in impact tests [6, 7]. It is possible that the process of brittle (rather than "brittle with shear lips") failure in blunt-notch impact tests starts with the initiation of crazes rather than a yield zone, under the root of the notch. These crazes were described by Hull and Owen [27] who also observed a small amount of plastic deformation between the crazes in the centre of the section. As yield zones existed at the centre of the specimen they must also have formed at the edges where crazes were not observed. The instability condition may be when one central craze starts to break down and hence propagate faster than the others as it is on the line of maximum stress. If the surface yield zones are large enough at that point to hold all the applied G, ductile failure will result. If, on the other hand, there is sufficient plane strain G to accelerate the craze/crack beyond its adiabatic transition to its low-energy mode, the failure will be entirely brittle with the low-energy craze cutting through the incipient plastic zones right out to the surface. This condition is very close to that involved in that derivation of Equation 21, the only difference being that G_{c1}, which was already small, has been reduced further, so Equation 21 should still describe the transition. This also explains why transitions from both brittle and semi-brittle to ductile failure occur at the same notch tip radii in untreated polycarbonate.

6. Conclusions

A model has been proposed for mixed-mode crack propagation in polymers. The model predicts the existence of a brittle–ductile transition at a specimen thickness which is a function of a number of mechanical properties of the material. The predicted specimen thickness agrees well with published results in polycarbonate. The model has also been extended to the blunt notch case and compared with results on impact tests in polycarbonate.

Acknowledgement

I would like to thank Dr Z. H. Stachurski for valuable discussions and considerable help in the preparation of the manuscript.

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Received 16 December 1980
and accepted 15 July 1981