Fracture toughness of poly(butylene terephthalate)

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The overall fracture toughness of poly(butylene terephthalate) as well as plane stress and plane strain contributions have been measured as a function of rate from 5×10^{-2} to 5×10^{3} in/min. A pronounced sample thickness dependence in K_c is observed over this range. Poly(butylene terephthalate) appears to exhibit excellent resistance to low speed crack propagation with internal voiding providing an effective crack blunting mechanism.

INTRODUCTION

As thermoplastics find wider use in engineering applications it is becoming increasingly important to secure more quantitative information on their intrinsic toughness. Such information can be extremely valuable both in predicting the performance of these materials and in modifying them for specific applications such as impact resistance. Data of this type have been collected for a number of glassy polymers such as polystyrene, poly(methyl methacrylate) and polycarbonate[1-5] and, more recently, for crystalline polymers such as polypropylene and nylon[6]. Investigations of foamed materials have also been reported[7].

The most severe test of a material is its resistance to fracture under triaxial tension. Since this type of failure can be catastrophic and occur with little warning, a measure of toughness under such conditions is often used as a lower bound for design considerations. In classical fracture mechanics analyses the *plane strain fracture toughness* is given as:

$$K_{1c} = \left(\frac{EG}{1-\nu^2}\right)^{1/2} \tag{1}$$

where E is Young's Modulus, ν is Poisson's ratio and G is the crack extension force or strain energy release rate, equal to 2γ in the Griffith analysis[8]. K_{1c} values are typically obtained on precracked specimens in which the geometry is designed to ensure that the required stress state is preserved during the fracture. A number of such 'standard' specimens has been described[9].

In thermoplastic materials exhibiting moderate or high levels of ductility, however, viscoelastic deformation in the surface skin can contribute significantly to the measured fracture energy even when relatively sharp notches are present. As a result, the measured fracture toughness occasionally shows a pronounced thickness dependence. It is often inconvenient to mould thermoplastic samples of sufficient thickness to avoid this problem. Williams has proposed that in such cases it may be useful to consider the overall fracture toughness of the specimen to be partitioned between that occurring in plane strain (K_{1c}) and that occurring in plane stress[2] (K_{2c}). Plane stress failure is assumed to be localized near the exterior surface of the specimen, where elastic or anelastic deformation of the specimen prevents development of a triaxial stress field, and to extend inwards for a distance comparable to the ductile zone size, r_{y2}. The ductile zone size can be expressed as:

$$r_{y2} = \frac{1}{2\pi}\left(\frac{K_{c2}}{\sigma_y}\right)^2 \tag{2}$$

where σ_y is the yield stress of the material at the strain rate of the experiment. Although this assignment is an arbitrary one which fails to consider the nonlinear stress field which is actually present in the test piece, it is useful in describing the extreme failure modes of the material and we have adapted it for our analysis.

Following Williams' development, the thickness dependence of the fracture toughness can be expressed as:

$$HK_c = (H - 2r_{y2})K_{1c} + 2r_{y2}K_{2c} \tag{3}$$

where H is the overall sample thickness. Combining equations (2) and (3), it can be shown that:

$$K_{1c} = \frac{H_1K_c' - H_2K_c''}{H_1 - H_2} \tag{4}$$

and:

$$K_{2c}^3 - K_{2c}^2K_{1c} - \pi\sigma_y^2H_1(K_c' - K_{1c}) = 0$$

where K_c' and K_c'' are determined on samples of thickness H_1 and H_2. Surface notched (SN) specimens, although more difficult to prepare, are used to advantage in such a study since the apparent sample thickness is considerably greater than the actual thickness[10].

In contrast to earlier studies, our experiments were carried out over a range of velocities rather than temperatures. Although the two types of tests can be correlated, the exact time–temperature relationships are not sufficiently well known in most cases to permit the direct extension of low

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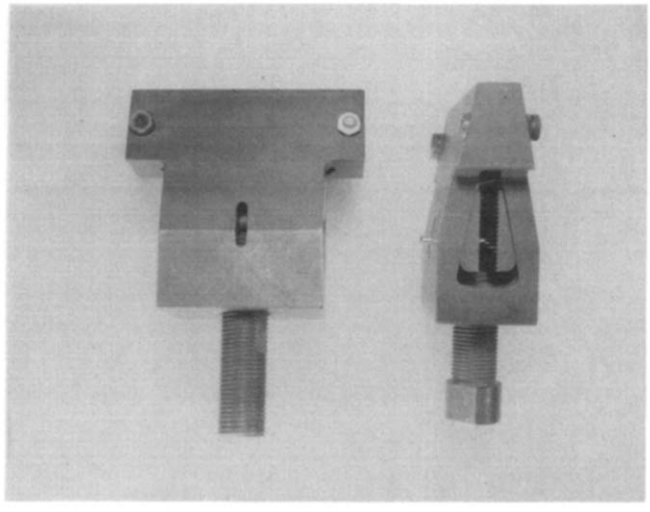

Figure 1 Wedge grips use for high speed fracture toughness testing

temperature data to high test speeds. A primary goal of this research was to evaluate the toughness of poly(butylene terephthalate) at impact speeds. The results amplify those of a somewhat less detailed study recently published by Casiraghi[11].

EXPERIMENTAL

The samples used in this study were cut from 6 in x 18 in x 1/4 in injection moulded plaques of Valox® 310 resin, an unfilled poly(butylene terephthalate) homopolymer obtained from the General Electric Plastics Division. The barrel (melt) temperature was 250°C and the mould temperature was 95°C. Those test pieces which were annealed were held at 100°C for 18 h in a circulating air oven. The SEN specimens measured 6 in x 1 in x 1/4 in and were notched by carefully pressing a new razor blade into a kerf cut with a jeweller's saw. The SN specimens were 2 in wide and notched by machining with razor sharp fly cutters 1 in and 2 in in radius.

All samples were broken in tension on an MTS closed loop hydraulic testing machine (20–5000 in/min) or an Instron testing machine (<20 in/min). A specially designed set of wedge grips (shown in *Figure 1*) was fabricated to hold the specimens without slipping at loads in excess of 2000 lb. Scanning electron microscopy was performed on an ISI Super II SEM. All samples were coated by sputtering with an Au/Pd alloy before observation.

RESULTS AND DISCUSSION

Fracture toughness measurements

Fracture toughness values were calculated from the relationships given by Srawley and Brown[9]. For the SEN specimens:

$$K_c^2 = \frac{1}{(1-\nu^2)}\left(\frac{P}{B}\right)^2 \frac{1}{W}\left[7.59\left(\frac{a}{W}\right) - 32\left(\frac{a}{W}\right)^2 + 117\left(\frac{a}{W}\right)^3\right] \quad (6)$$

where P is the load, B is the sample thickness, W is the sample width and a is the crack length. For the SN specimens:

$$K_c^2 = \frac{1.2\,\pi P^2 a}{W^2 B^2}\left[\frac{1}{\phi^2 - \left(\frac{0.2\,P^2}{W^2 B^2 \sigma_y^2}\right)}\right] \quad (7)$$

where:

$$\phi = \int_0^{\pi/2}\left[1 - \left(\frac{b^2 - a^2}{a^2}\right)\sin^2\theta\right]^{1/2} d\theta \quad (8)$$

and b is the semimajor axis of the elliptical cut and σ_y is the yield stress. The variation in yield stress with test speed was measured over the range of crosshead rates used for the fracture toughness measurements using standard ASTM (D638) Type 1 tensile specimens. These data are plotted in *Figure 2*. The K_c values calculated for both annealed and unannealed 0.25 in thick SEN specimens are plotted as a function of rate in *Figure 3*. The data points represent average values obtained for several specimens. Except at the highest test

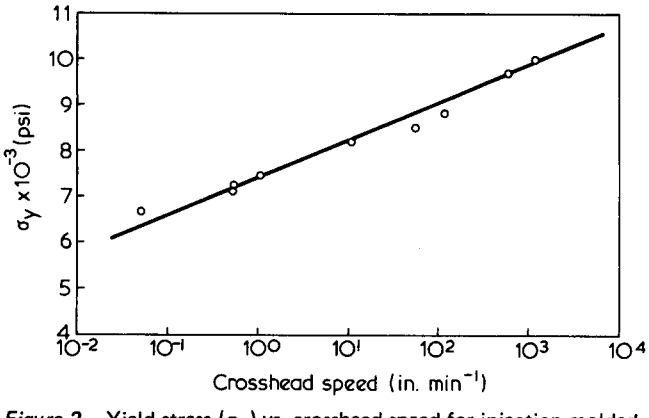

Figure 2 Yield stress (σ_y) vs. crosshead speed for injection molded PBT

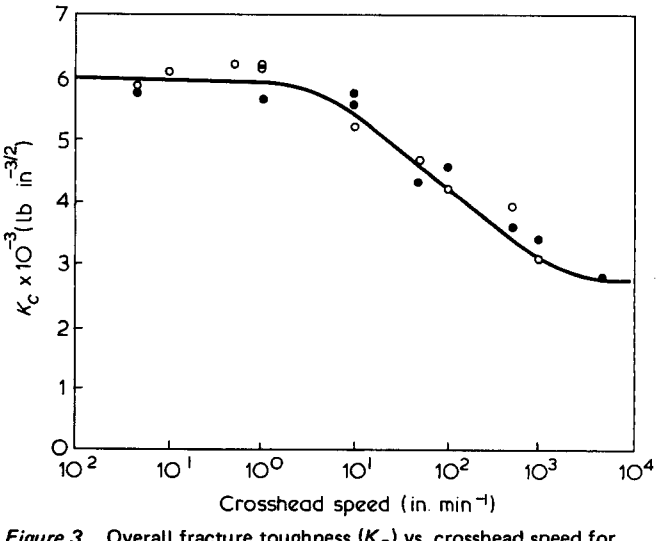

Figure 3 Overall fracture toughness (K_c) vs. crosshead speed for 1/4 in thick SEN specimens of PBT. ○, annealed 18 h at 100°C; ●, as moulded

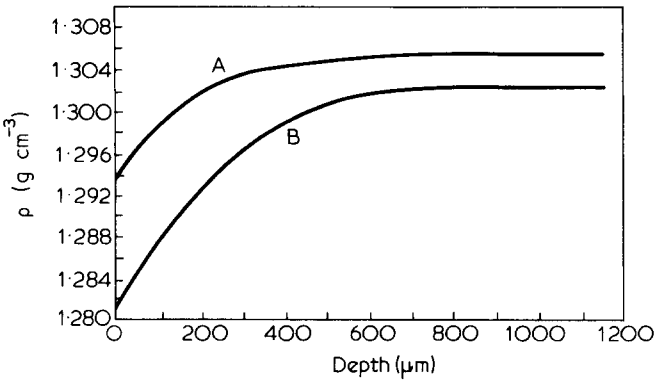

Figure 4 Variations in sample density as a function of distance from the surface for PBT specimens injection moulded using a 40°C mould and a melt temperature of 250°C. Annealing was carried out at 100°C for 16 h (Hobbs and Pratt[12]). A, 100°C ageing; B, as moulded

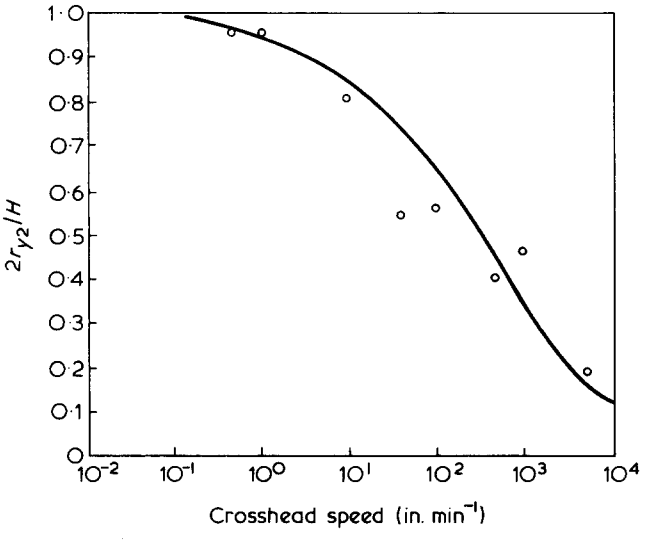

Figure 5 Variation in the ratio of ductile zone size to sample thickness with crosshead speed for 1/4 in thick SEN specimens of PBT

rates, very little difference is observed between the annealed and the unannealed specimens.

Previous investigations showed that the density increases produced by annealing injection moulded PBT specimens were confined primarily to the 300–400 μm thick surface skins (see *Figure 4*). Only small increases were observed in the core regions[12]. The current results suggest that at high speeds, plane strain failure dominates the fracture process to such an extent that changes in the density and ductility of the surface skin have little effect on K_c. Although at lower speeds failure occurs primarily in plane stress and should reflect the surface character of the sample to a greater degree, the ductile zone size becomes so large compared with the skin thickness that the measured fracture toughness is again relatively insensitive to the annealing process. The ratio of the ductile zone size to the sample thickness, plotted as a function of rate in *Figure 5*, shows approximately the same dependence on speed as the overall fracture toughness.

K_{1c} and K_{2c} values were computed from the SEN data and from data taken on SN specimens having apparent thicknesses of 0.6 in and 0.9 in using equations (4) and (5). The calculation of apparent thickness values has been described previously[10]. In low speed tests, K_{1c} was found to have an average value of 2560 lb/in$^{3/2}$ and to exhibit little dependence on test rate. Such behaviour is expected when the stress field is triaxial and viscoelastic flow is minimized. K_{1c} values determined for other polymers over relatively broad temperature ranges show similar constancy[5,6]. At the highest test rates $K_c \simeq K_{1c}$ and the approximate conditions for plane strain failure are met. The dependence of K_{2c} on test rate is shown in *Figure 6*. Some decrease which may be associated with a slight upward shift in T_g with frequency is indicated at high rates. Although the activation energy for T_g is sufficiently large that the transition is not highly frequency dependent, the glass temperature of PBT (30°–35°C) is sufficiently close to room temperature that small shifts may be expected to cause a measurable change in the energy consumed during viscoelastic deformation.

It is illustrative to compare the behaviour of PBT at low test speeds with that observed for other polymers. In *Table 1* the ductile zone sizes calculated for polypropylene, polycarbonate, nylon-6,6 and poly(butylene terephthalate) are listed for comparison. It is noteworthy that PBT shows the greatest ductility and that all three crystalline polymers exhibit a significantly greater fraction of plane stress failure than polycarbonate. It seems reasonable to believe that these results may be reversed at higher rates, although such data are not currently available for comparison. The effective crack blunting mechanisms available to PBT at low speeds suggest that the material may exhibit superior resistance to crack propagation and cyclic fatigue even when relatively sharp notches are introduced.

Morphology

In samples broken at crosshead rates below 100 in/min, striations of plastically deformed polymer were observed running perpendicular to the crack front and extending inwards for 100–200 μm. At speeds between 10 and 100 in/min this band of material, which is associated with slow

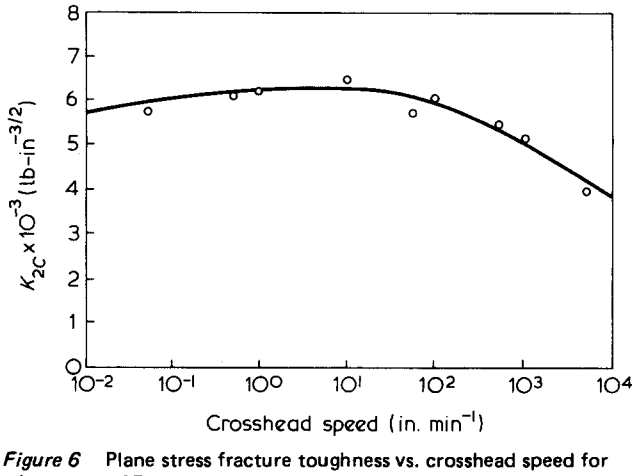

Figure 6 Plane stress fracture toughness vs. crosshead speed for 1/4 in thick SEN specimens of PBT.

Table 1 Comparative ductile zone sizes (test speed = 0.5 in/min)

Polymer	Temperature (°C)	r_{y2}(IM)
Polypropylene	–60	0.082*
Polycarbonate	20	0.045*
Nylon-6,6	20	0.070*
Poly(butylene terephthalate)	23	0.102

* Data from Williams *et al.* (references 5 and 6)

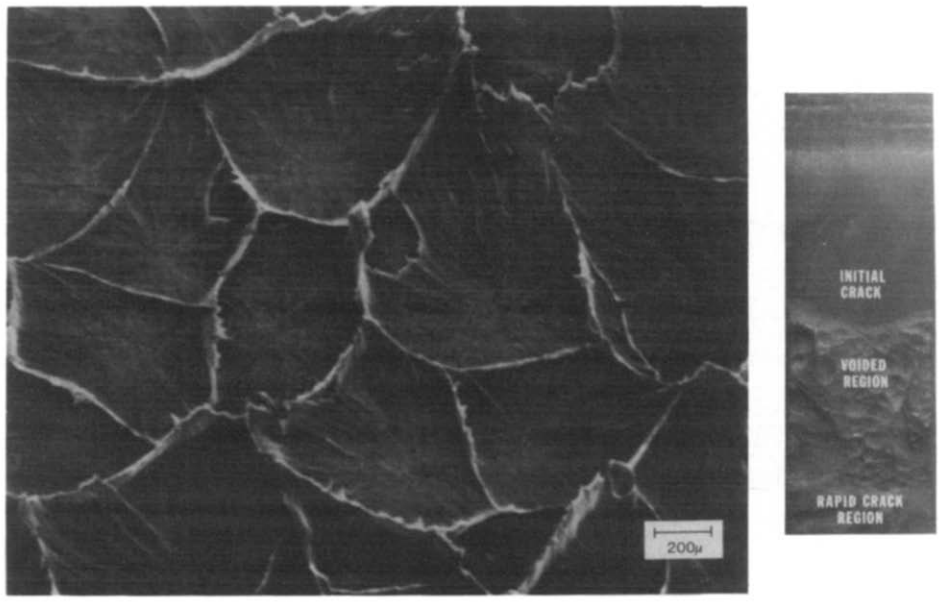

Figure 7 Photograph of PBT SEM specimen broken at 1 in/min and showing characteristic void development preceding brittle fracture. An SEM enlargement of the voided area is shown to the left

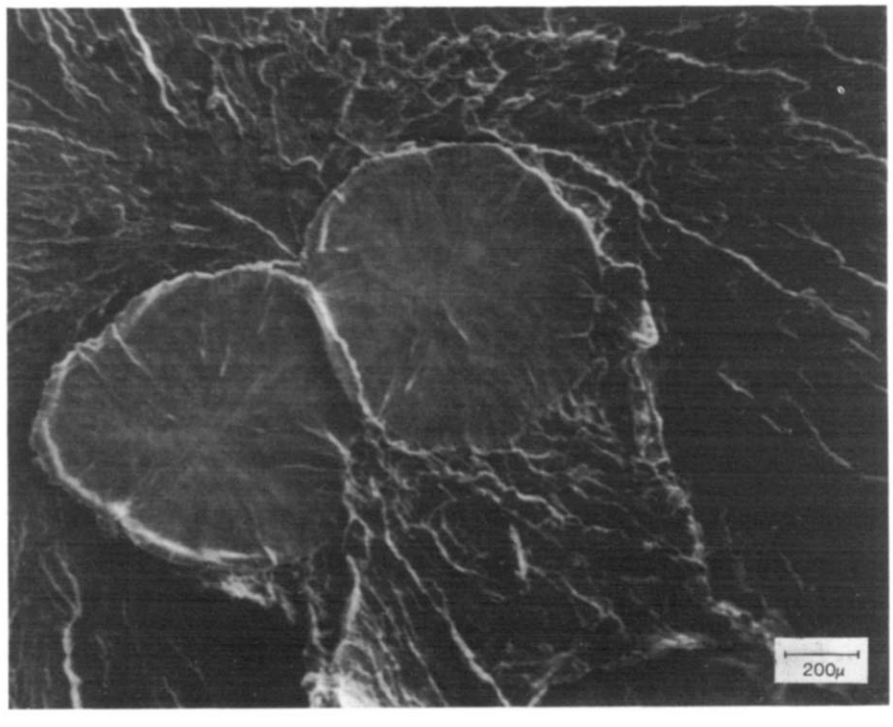

Figure 8 SEM photograph of PBT fracture surface showing isolated voids terminated by rapid crack growth

crack growth, terminated abruptly in the mesa-like fracture morphology characteristic of high speed crack propagation. At lower speeds, numerous pockmarks left behind by the formation of internal voids separated the two regions. These are shown in *Figure 7*. The polyhedral shape of these voids and the thin shreds of material at their boundaries indicate that stable growth had occurred up to the time of impingement. In some, but not all of the voids, pieces of foreign matter could be seen near the centre. The relatively straight lines of intersection between voids of different sizes showed that the growth rate was constant with time. In most of the samples examined, void growth appeared to represent a stable deformation response to dilational stresses building up near the crack tip. On occasion, however, void growth was interrupted by the passage of a rapidly moving crack and isolated voids could be observed on the fracture surface as shown in *Figure 8*. In such cases no plastic deformation was visible on the outer perimeter.

At testing rates in excess of 100 in/min, there was little evidence of plastic flow and relatively featureless failure mirrors appeared near the centre of the samples immediately behind the notch tips. The mirrors, which varied from semicircular to parabolic in shape, decreased steadily in size with increasing test speed. Some craze remnants were occasionally visible at the edges of these areas, but, for the most part, rapid crack growth initiated sharply at the boundary and continued across the remainder of the sample.

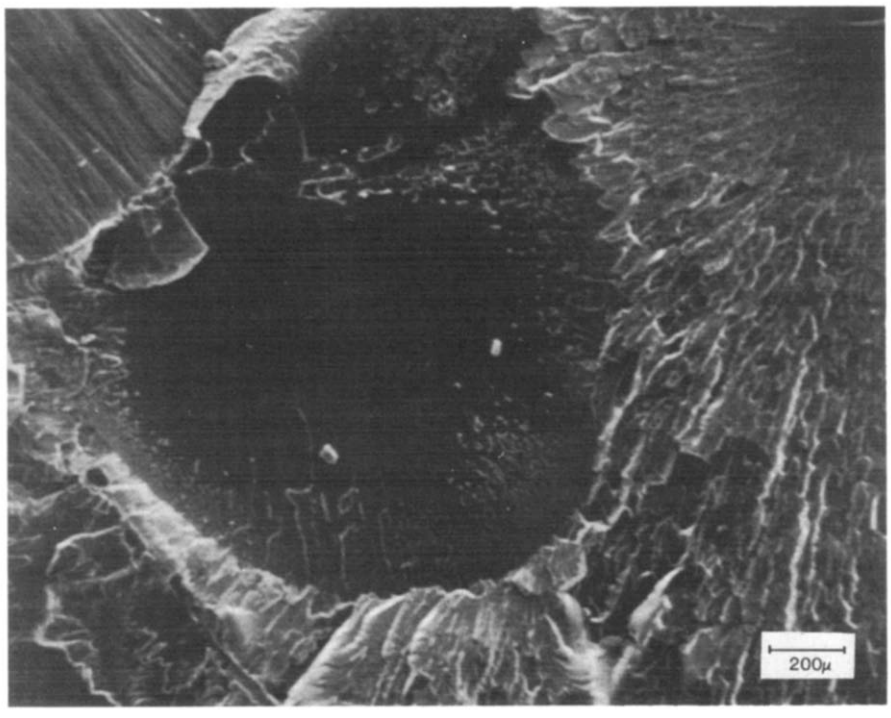

Figure 9 SEM photograph of PBT fracture surface showing typical failure mirror associated with high speed fracture

SUMMARY AND CONCLUSIONS

Values for K_c, K_{1c} and K_{2c} have been determined for PBT at test rates between 5×10^{-2} and 5×10^3 in/min. The greatest sample thickness dependence was observed over the range of 10–1000 in/min. K_{1c} appears to be a constant function of testing speed at all rates with an average value of 2560 lb/in$^{3/2}$. K_{2c} drops from 6000 lb/in$^{3/2}$ to 3900 lb/in$^{3/2}$ over the last two decades.

The rate dependence of K_c parallels that observed for the rate dependence of the ductile zone size. The drop in r_{y2} at high speeds reflects the fact that viscoelastic response in the sample exterior is not sufficiently rapid to make a significant contribution to the fracture toughness.

Annealing, which produces significant density changes only in the outer 300–400 μm of the test specimens, has no effect on the K_c measured at high or low speeds. Apparently, at high speeds, plane strain failure dominates the fracture process to such an extent that changes in the surface skin are unimportant. In contrast, at low speeds r_{y2} becomes so large compared with the skin thickness that changes in the surface are masked by the response of central regions of the sample.

PBT exhibits a superior capacity for crack tip blunting at low test speeds which imparts a greater ductility to this polymer than an acceptedly 'tough' material such as polycarbonate. We feel that this behaviour may be reflected in superior resistance to static or cyclic fatigue and are currently evaluating the resin in this respect.

In low speed tests, sharply notched SEN and SN specimens develop microscopic voids ahead of the crack tip in response to the triaxial stresses which build up in this region. Fracture ultimately starts outside this region, however, and occurs in a brittle manner. At higher rates a characteristic failure mirror develops at the centre of the crack front and precipitates the failure with little, if any, plastic deformation.

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