

A molecular theory of the fracture toughness of low molecular weight polymers

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Recent experiments by Robertson show that the fracture toughness G_{IC} of glassy polystyrene PS does not decrease to the ideal brittle value 2γ (where γ is the surface energy for PS) at molecular weights M_w below M_c the entanglement molecular weight. Instead G_{IC} is more than an order of magnitude above 2γ at M_c and decreases slowly below M_c . It is postulated that a small craze exists at the crack tip in such low molecular weight glassy polymers. However, since entanglements do not occur single molecules must span this craze; if they do not the craze becomes unstable and the crack advances. Under these conditions a critical craze surface displacement exists and G_{IC} can be computed to be

$$G_{IC} = S_c (\lambda - 1) \langle R^2 \rangle^{1/2},$$

where λ and S_c are the craze fibril extension ratio and craze surface drawing stress observed in high molecular weight crazes (both quantities should be only weak functions of M_w) and $\langle R^2 \rangle^{1/2}$ is the root mean square end-to-end distance of the PS molecule in the glass from neutron scattering measurements. The fracture toughness is predicted to decrease as $M_w^{1/2}$; this prediction and the absolute magnitude of G_{IC} are in excellent agreement with experiment.

1. Introduction

Linear elastic fracture mechanics (LEFM) plays an increasingly important role in the design of engineering structures made from polymers, ceramics or metals [1]. In LEFM it is assumed that the critical conditions for the onset of unstable crack propagation can be characterized by a single material parameter, G_{IC} , the fracture toughness, if the elastic constants of the material are known. This assumption can be rigorously justified [2] for materials which exhibit no plasticity at the crack tip where $G_{IC} = 2\gamma$ and where γ is the surface energy of the perfect cleavage surface. The analysis then leads to the fracture criterion proposed by Griffith [3] almost 60 years ago. However, in the engineering materials to which LEFM is usually applied, G_{IC} greatly exceeds 2γ due to irreversible work done in the

plastic zone at the crack tip. To compute G_{IC} under these conditions it is necessary to supply a microscopic failure criterion for the material at the crack tip in the plastic zone. Until this fundamental microscopic failure criterion can be specified, the assumption that G_{IC} is a constant of the material is dubious.

The problem can be restated somewhat differently as follows. There are methods and models for computing G_{IC} given that a crack propagates with a steady state plastic zone that can be characterized by certain displacement and stress fields. The catch is that one must find a physical mechanism or mechanisms which limits the magnitude of the allowed displacements so that the crack will advance into the plastic zone. If such a mechanism does not exist the plastic zone will simply grow in size as the stress increases until the entire uncracked

cross-section of the specimen has yielded. The usual *ad hoc* solution to this problem is to assume that a critical crack tip opening displacement, or COD, exists; if the COD is exceeded, the crack is supposed to advance. Note, however, that there is usually no justification on a microscopic basis for a fundamental upper limit on the crack tip opening displacement. In the absence of such justification, we are simply substituting a microscopic assumption for the macroscopic assumption, G_{IC} = material constant.

The important question therefore is: what makes the critical COD critical? Various attempts have been made to answer this question in metals. The COD has been linked to macroscopic tensile properties [4], to the spacing between brittle or weak-interface inclusions in steels and aluminium alloys [1, 5], or to the existence of a maximum plastic strain gradient at the crack tip [6] imposed by the assumption of a maximum density of dislocations. Although qualitatively useful, these attempts have not been successful quantitatively (for example, the inclusion model predicts an increase in G_{IC} with an increase in the yield stress of the matrix if the inclusion spacing is fixed whereas a decrease in G_{IC} is observed experimentally [1]). In part these difficulties may be attributed to the complex geometry of the plastic zone at the crack tip in most engineering alloys.

The geometry of the plastic zone in glassy polymers is relatively simple. It is now well known that this zone usually consists of a craze (or a bundle of crazes). These crazes are zones of cavitation, the surfaces of which are spanned by drawn polymer ligaments or fibrils. The craze has surfaces which are very close together, planar and almost parallel. The fibrils inside the craze are accurately perpendicular to the craze surfaces whereas the polymer outside the craze can be treated as being linear elastic. Because of this simplicity, computing G_{IC} from models of the micromechanics of the craze is straightforward. There are many measurements of G_{IC} in the literature (and for that matter many measurements of the slow crack growth curve $G_C(\dot{a})$ where \dot{a} is the crack speed) and notable attempts to relate these to craze micromechanics [7–14]. With the exception of early papers by Cessna and Sternstein [7, 8] all these attempts rely explicitly or implicitly on the assumption of the existence of a critical COD. There has been no attempt to justify this assumption. In this paper it is demonstrated that for low

molecular weight glassy polymers the assumption of a critical COD can be rigorously justified in molecular terms. A theory for G_{IC} is derived for these materials that allows one to predict values of this quantity from $\langle R^2 \rangle^{1/2}$, the mean square end-to-end distance of a molecule in the unoriented glass, S_c , the stress to draw craze fibrils from the craze boundary and λ the extension ratio of the drawn craze fibril. Since all of these quantities can be measured, the theoretical predictions, with no adjustable parameters, can be compared with experimental results. This comparison reveals excellent agreement, both in the molecular weight dependence of G_{IC} and in its absolute magnitude.

Paradoxically, the same arguments can be extended to show that it is most unlikely that the value of the COD is the fundamental causative parameter in craze fracture in high molecular weight polymers. If the COD attains a constant value at craze fracture it is because both COD and craze fibril failure at the crack tip are functions of the same variables, e.g. time and local stress history.

2. Craze deformation and failure mechanisms

Before discussing possible craze failure mechanisms it is first necessary to define a few craze deformation parameters with the aid of Fig. 1. One important such parameter is the craze thickness T , the distance between two craze surfaces. The craze fibrils shown in Fig. 1, however, arise from the plastic deformation of a certain original layer of unoriented polymer of thickness T_0 , which also has been called the primordial craze thickness. From a mechanics standpoint, however, the most important craze deformation parameter is neither of these but rather the craze surface displacement, w . Each surface of the primordial craze

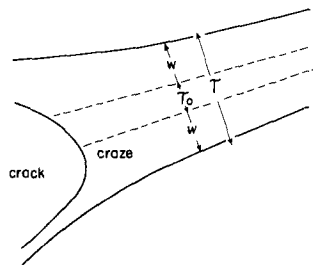


Figure 1 (a) Transmission electron micrograph of an air craze at a crack tip in a thin film of polystyrene (high molecular weight). (b) Schematic drawing of this craze showing T , the craze thickness, T_0 , the thickness of the original or primordial layer of bulk PS which fibrillates to form the craze, and w , the craze surface displacement.

layer is displaced outward by w to form the surfaces of the craze. Clearly these three craze deformation parameters are linked by the relation

$$T = T_0 + 2w. \quad (1)$$

In general, all of these parameters vary with distance x along the craze and increase as the craze grows in length and thickness. We can define the extension ratio of the fibrils as

$$\lambda = T/T_0, \quad (2)$$

and, since the plastic deformation of the fibrils occurs at approximately constant volume, the volume fraction, v_f , of fibrils in the craze is

$$v_f = \frac{1}{\lambda}. \quad (3)$$

We note in passing that if the craze/crack displacement profile $w(x)$ can be measured the craze surface stress profile $S(x)$ can be determined [15–17] (for an isolated symmetric craze) to be

$$S(x) = -\frac{2}{\pi} \int_0^\infty \bar{p}(\xi) \cos(\xi x) d\xi + \sigma_\infty \quad (4a)$$

where

$$\bar{p}(\xi) = \frac{\xi E}{2} \int_0^\infty w(x) \cos(\xi x) dx. \quad (4b)$$

Here σ_∞ is the uniform tensile stress on the plane of the crack/craze before crack/craze formation and E is Young's modulus. Finally, the true tensile stress, σ_t , in the craze fibrils is

$$\sigma_t = \lambda S. \quad (5)$$

Two competing mechanisms for craze thickening exist [17, 18]. The craze can thicken by drawing new polymer into the fibrils at the craze surface. For such a mechanism, one expects T_0 to increase as T increases and that λ of the drawing fibrils will be greatest in regions along the craze where S is greatest as dictated by the strain (orientation) hardening characteristic of the σ_t - λ curve of the fibrils. One cannot view this thickening-by-drawing mechanism as contributing to craze failure, except in the sense that regions of high λ within the craze will be preferential sites of craze fibril breakdown and crack propagation.

On the other hand, the craze fibrils once formed can continue to deform in creep. This further creep of the craze fibrils also makes a contribution to craze thickening. Unlike the

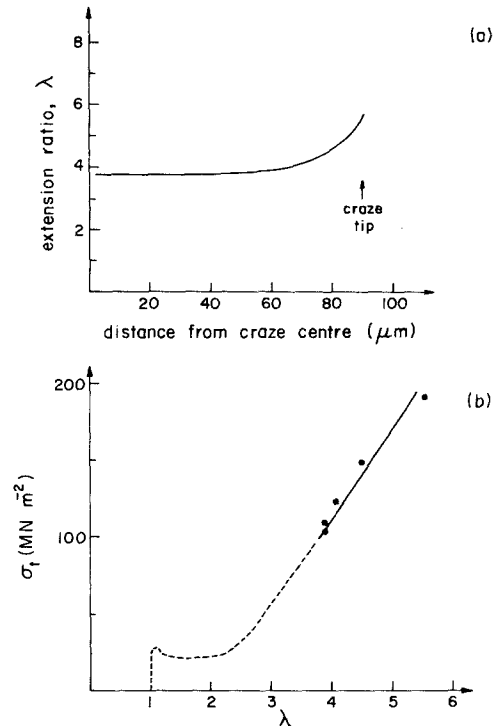


Figure 2 (a) Extension ratio of craze fibrils versus position along the craze (after [19]). (b) True fibril stress versus fibril extension ratio (after [19]).

surface drawing mechanism, however, the fibril creep mechanism produces craze damage and ultimately leads to fibril rupture.

To know which of these mechanisms is the dominant mechanism of craze thickening we must appeal to experiment. For air crazes in commercial polystyrene (PS) ($M_n = 0.98 \times 10^5$; $M_w = 3.1 \times 10^5$) the answer is clear from transmission electron microscopic measurements [19]. As shown in Fig. 2a, λ is approximately constant along the length of the craze, rising only just behind the tip where S increases moderately. A true stress-extension ratio curve for the craze fibrils is shown in Fig. 2b. These results indicate that the major mechanism of air craze thickening is by drawing new polymer into the craze fibrils at the the craze surfaces.

A plausible explanation of the rapid increase in σ_t with λ in Fig. 2b is that it results from the increasing resistance of the entanglement network to further deformation due to orientation of the network chains. In fact, assuming a molecular weight between entanglements M_c of 35 000 as inferred from melt viscosity data [20] the limiting extension ratio of the PS entanglement network would be $\lambda_{\max} \approx 6$. In this picture, further

deformation of the fibrils by creep would involve disentangling the chains. The best current model [21, 22] of this chain disentanglement is that of chain diffusion or "reptation" in a tube representing the chain surroundings. In any case, it is clear that there should be no casual relationship between the craze surface displacements, w (or craze thickness) and this chain disentanglement process which leads ultimately to fibril failure. In fact, from Equation 4 it can be demonstrated that an increased w at the crack tip always leads to a decrease in S (and σ_t as long as surface drawing is the major craze thickening mechanism) so that an increase in w by surface drawing will always retard craze fibril breakdown. However, both craze displacement and chain disentanglement are time and stress-dependent processes so that w may reach a certain value at the same time fibril failure is complete.

Now let us turn our attention to low molecular weight PS where the molecular weight is approximately equal to or less than M_c . It is well known that below M_c the polymer exhibits a very low fracture stress and low fracture toughness [23–26]. Further it has been observed by electron microscopy that long craze fibrils (and therefore crazes themselves) are not stable below M_c [27–29]. It has been suggested that since metastable entanglements cannot form, crazes cannot develop [23]. One would expect no strain-hardening in the fibril stress–strain curve and thus no fibril formation. Following this reasoning further, one would expect the fracture toughness, G_{IC} , to approach $2\gamma \approx 0.08 \text{ J m}^{-2}$ for PS once the molecular weight is reduced below M_c . Recent experiments by Robertson on PS with a very narrow molecular weight distribution, however, show that this expectation is not realized [25]. Rather G_{IC} is about one order of magnitude greater than 2γ just below M_c and only appears to extrapolate to 2γ at a molecular weight approximately corresponding to the dimer.

In retrospect this result is not surprising. While long craze fibrils cannot be stable, shorter craze fibrils could be stable below M_c if the ends of a single polymer molecule are embedded in the undeformed polymer* on either surface of the craze. Transmission electron micrographs of craze tips in higher molecular weight PS indicate that

these taper to thicknesses less than 25 Å. Thus even in low molecular weight PS, one expects that a craze of very narrow thickness will form at the crack tip. Unlike the case of higher molecular weight PS where the fibrils fail by chain disentanglement, however, these low molecular weight crazes will fail when the craze surface displacement increases to the point where single molecules cannot span the surfaces of the craze.

Let us examine the requirements for this critical condition in more detail with the aid of Fig. 3. In Fig. 3a, the thickness profile of the craze is shown and a highly extended molecule is shown at a position behind the craze tip such that any further thickening of the craze in that position will cause these ends to be incorporated in the fibril and the craze will fail. For this to happen the primordial craze thickness must approach the size of the molecule in the undeformed glass as shown in Fig. 3b. We can reduce our requirement for low molecular weight craze stability to a requirement that the polymer molecule in the unoriented polymer span the primordial craze thickness. This idea has also been emphasized by Haward *et al* [30] in their recent paper on craze stability. To first order one may set the critical craze condition for fracture to be

$$T_0 \geq \langle R^2 \rangle^{1/2}, \quad (6)$$

where $\langle R^2 \rangle^{1/2}$ is the root mean square end-to-end distance of the polymer molecule in the undeformed glass. This assumption will be examined later using the full statistical treatment of the spanning problem due to Haward *et al*.

The further assumptions will be made that as long as the low molecular weight craze is stable, the deformation characteristics of the craze are similar to those of higher molecular weight PS. In particular, the craze is assumed to thicken by drawing fibrils from the craze surface at an average extension ratio λ of about 4 (Fig. 2a). Rewriting Equation 6 with the aid of Equations 1 and 2 we derive the critical craze surface displacement, w_c (the craze surface displacement at the crack tip) to be

$$w_c = \frac{1}{2} (\lambda - 1) T_{0c} = \frac{1}{2} (\lambda - 1) \langle R^2 \rangle^{1/2}. \quad (7)$$

For a polystyrene molecule in the glass $\langle R^2 \rangle^{1/2}$ has been determined by neutron diffraction studies

*In order for the low molecular weight chains to flow past each other viscously even in the absence of entanglement, the polymeric glass must be brought to a state of yield and this molecular mobilization happens over a very small distance at the craze surface.

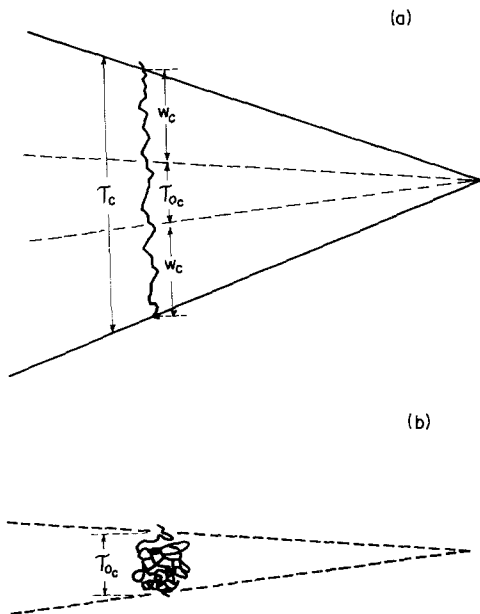


Figure 3 (a) Schematic drawing of craze thickness profile with a highly extended molecule at the critical position along the craze. (b) Schematic drawing of the craze primordial thickness profile T_0 showing the molecule just spanning T_0 in the undeformed glass at the critical position.

[31–33] to have the same value it has in dilute solution in a theta solvent, i.e.

$$\langle R^2 \rangle^{1/2} = 0.07 M_w^{1/2} \text{ nm} \quad (8)$$

so that for $\lambda = 4$, the critical craze surface displacement is

$$w_c = 0.105 M_w^{1/2} \text{ nm}. \quad (9)$$

3. Fracture toughness and craze micromechanics

The planar geometry of the craze makes for considerable simplicity in computing the fracture toughness, G_{IC} . Assume the craze at crack tip propagates together with the crack and maintains a steady state displacement profile. The work done on the craze per infinitesimal unit area of craze advance is G_{IC} and can be shown to be

$$G_{IC} = -2 \int_{a_0}^a S(x) \frac{dw}{dx} dx = 2 \int_0^{w_c} S dw, \quad (10)$$

*We will argue the craze surface stress, since it is the stress for plastic deformation (drawing fibrils from the craze surface) should be insensitive to molecular weight at least over the range considered here. This constancy is also indicated by the constancy of the stress for craze initiation observed in other experiments [26].

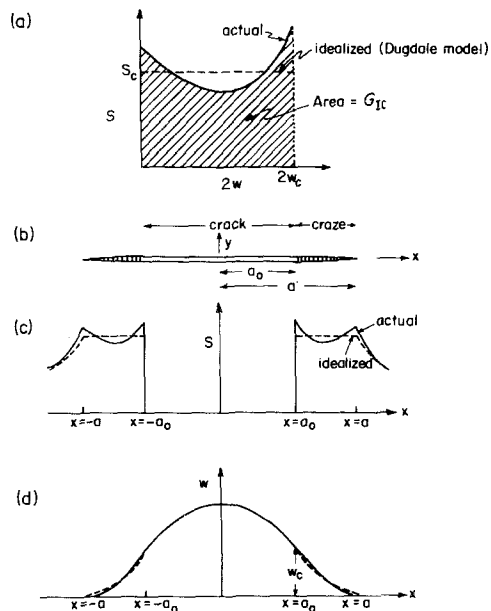


Figure 4 (a) Plot of craze surface stress versus total opening displacement. (b) Crack and craze geometry. (c) Craze/crack surface stress profile. (d) Craze/crack surface displacement profile. Solid lines show realistic craze S and w profiles; dashed lines show idealized profiles according to the Dugdale model.

where $2a_0$ and $2a$ are the crack length and crack plus craze length, respectively, and w_c is the craze surface displacement at the crack tip as shown in Fig. 4. If S is plotted against the corresponding $2w$ at various points along the craze surface, G_{IC} is simply the area under that curve (Fig. 4).

Our previous experiments [19] on polystyrene crazes indicate that the craze surface stress rises to ~ 35 MPa at the craze tip and falls to a value of ~ 25 MPa at the craze base. For purposes of estimating G_{IC} therefore, it is reasonable to assume that the craze surface stress is constant over the craze at a value $S_c = 30$ MPa*. Such a model of a crack with a plastic zone of constant traction at its tip is known as the Dugdale model [34, 35] and it leads to the very simple result:

$$G_{IC} = 2w_c S_c. \quad (11)$$

Substituting w_c from Equation 9, and $S_c = 30$ MPa, one predicts

$$G_{IC} = 0.0063 M_w^{1/2} \text{ J m}^{-2} \quad (12)$$

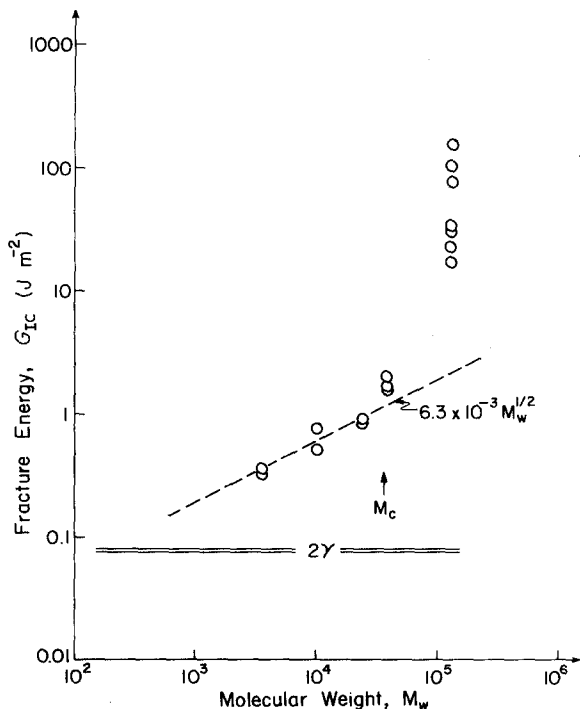


Figure 5 Fracture toughness, G_{IC} , versus molecular weight (peak of the distribution) for narrow molecular weight fractions of polystyrene (after Robertson [25]). Dashed line shows the prediction of the present theory (Equation 12). 2γ is G_{IC} for ideally brittle fracture and M_c is the chain entanglement molecular weight from viscosity measurements.

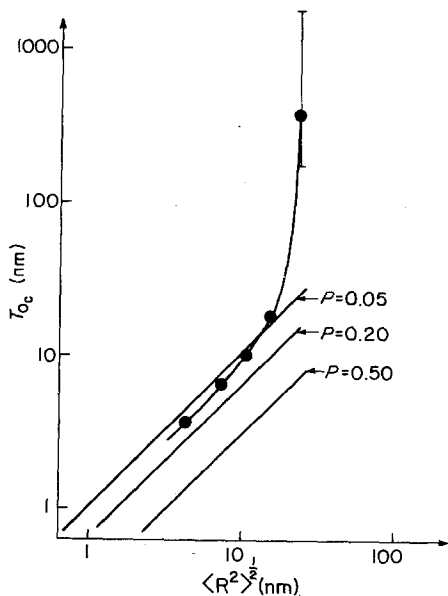


Figure 6 Critical primordial craze thickness derived from G_{IC} via Equation 13 versus $\langle R^2 \rangle^{1/2}$, the mean square end-to-end distance of polystyrene molecules in the glass. The G_{IC} data are average values taken from Robertson's Table I [25]. The lines of constant P are lines of constant probability that a PS molecule will span the primordial craze thickness from the theory of Haward *et al* [30].

5. Comparison with experiments

Robertson [25] has measured the fracture toughness of narrow fractions of PS by measuring the critical stress intensity factor K_{IC} ($G_{IC} =$ 1386

K_{IC}^2/E) for propagation of a cleavage crack in a $10 \mu\text{m}$ thick layer of the PS between two sheets of high molecular weight PMMA. His data are shown in Fig. 5. Note that as the molecular weight is decreased from 10^5 to $35000 \approx M_c$, the entanglement molecular weight, that G_{IC} drops drastically but that below M_c the dependence of G_{IC} on molecular weight becomes much less pronounced and that at the lowest molecular weights tested, 3500, G_{IC} is still more than a factor of four higher than 2γ , the true surface energy of a polystyrene surface. Also plotted on Fig. 5 is the G_{IC} predicted by the theory (Equation 12). Not only is the predicted dependence of G_{IC} on $M_w^{1/2}$ closely followed below M_c but also the magnitudes of the G_{IC} s predicted are in excellent agreement with those observed.

One can demonstrate this agreement in a different way and gain some additional insight into the microscopic critical condition for craze fracture. By combining Equations 7 and 11 one can show that the critical value for the craze primordial thickness T_{0c} is given by

$$T_{0c} = \frac{G_{IC}}{(\lambda - 1) S_c} \quad (13)$$

Substituting the same values for S_c and $\lambda - 1$, one can then plot T_{0c} versus $\langle R^2 \rangle^{1/2}$ as shown in Fig. 6 to test Equation 6. Below M_c $T_{0c} \approx \langle R^2 \rangle^{1/2}$ but above M_c , T_{0c} greatly exceeds $\langle R^2 \rangle^{1/2}$, presumably

due to the fact that long fibrils can be drawn out from the craze surfaces once an entanglement network can be formed in the fibrils. Note also the large scatter in derived T_{0c} values for 110 000 molecular weight; the scatter may reflect the fact that T_{0c} in this molecular weight regime cannot be considered to be a fundamental parameter controlling failure of the craze (or as suggested by Robertson that more than one craze nucleates randomly at the crack tip).

What percentage of molecules below M_c must be embedded in the craze surfaces for the craze to still be stable? The statistical theory of Haward *et al.* offers a way to compute this percentage since they give expressions for P , the probability that a molecule (Gaussian chain) with a given $\langle R^2 \rangle^{1/2}$ will span a distance T_0 . The lines for $P = 0.05$, $P = 0.20$ and $P = 0.50$ on Fig. 6 represent their theory. By comparing these with the experimental data it appears that for the lowest molecular weight, approximately 10% of the molecules must span the craze for the craze to be stable but considering the assumptions of the theory and the scatter in the original data one cannot place too much reliance on this value.

It would be satisfying to be able to directly observe the craze at the crack tip in these low molecular weight PS. Unfortunately, such observations will not be easy. One can calculate the critical length of the craze, Δa , expected from the Dugdale model to be

$$\Delta a = \frac{\pi}{8} \left(\frac{K_I}{S_c} \right)^2 = \frac{\pi}{8} \frac{EG_{IC}}{S_c^2} \quad (14)$$

and the maximum craze thickness T_c to be

$$T_c = \lambda T_{0c} \simeq \lambda \langle R^2 \rangle^{1/2}. \quad (15)$$

The computed critical craze lengths range between 0.4 and 1.1 μm and the maximum craze thicknesses range between 17 and 40 nm. Since the crazes are so short and their thicknesses are much less than the wavelength of light, one cannot expect to be able to observe evidence of their presence optically, either directly or on the fracture surface. While there is some hope of detecting such a craze with transmission electron microscopy, our experience to date indicates the fragile films made from these low molecular weight polystyrenes are very difficult to handle. If a stable crack tip (usually at the end of a long crack) is located, it appears to have undergone significant antiplane strain (mode III) opening. There is evidence of some cavitation in

front of the crack tip but there is also a significant component of shear displacement normal to the film.

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