Sources of Toughness in Polymers

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ABSTRACT

Many thermoplastic glassy polymers which undergo crazing can be quite brittle because of premature fracture of the fibrils in craze matter. Such polymers can be effectively toughened in several ways by actually promoting crazing to take place at lower stress levels where the crazes survive fracture from both intrinsic processes and extrinsic defects, and where the profusion of crazes can result in extensive dilatational plasticity. The most effective strategy to achieve these conditions combines the introduction of a large density of potent craze initiation sites with the lowering of stresses for craze growth by controlled local plasticization of the polymer. Densely entangled or cross-linked brittle polymers that do not craze can also be toughened quite effectively by techniques of transformation toughening through the introduction of cavitating rubbery particles or decohering glass spheres.

KEYWORDS

Toughening, brittle polymers, craze plasticity, compliant particle toughening.

INTRODUCTION

Polymeric materials are made up of long chain molecules which govern their unique behavior in solution, in the melt, and in the solid state. Apart from some new modes of mechanical response such as crazing, which acts both as a special form of transformation plasticity and as a source of fracture, the basic fracture behavior of polymers is related to microstructural detail in a way very similar to other prominent engineering solids. It is these common features in the fracture behavior of polymers with other engineering solids that we will develop here. It should become clear then that once the basic differences of polymers and their effects on the intermediate scale microstructure between molecules and macrocracks are understood, the many tools of micromechanics which have recently been developed in the fracture of heterogeneous metals, composites, and ceramics find ready application.

THE SPECIAL MICROSTRUCTURAL FORMS OF POLYMERS

Intrinsic Properties of Homopolymers

The basic aspect differentiating polymers from more conventional and familiar atomic (metals and ceramics) or space network (oxide glasses) solids is the tetra-valent carbon atom that permits formation of long chain molecules. The long chain nature of the molecule by itself, coupled with the irregularities in its longitudinal architecture, such as placement of side groups and chain branching result in impediments to full crystallization. As a result, polymers can exist in either completely amorphous or semi-crystalline forms incorporating amorphous and chain folded crystalline phases.

Both the amorphous and the semi-crystalline forms can undergo considerable plastic flow before fracture, or can be quite brittle. Since the plastic resistance and ideal fracture strength of most solid polymers are much closer together than is the case in metals, relatively small alterations in morphology, state of aging, and presence of mild environmental effects can turn a polymer from brittle to ductile and vice versa. This bifurcation of behavior is ultimately intrinsic in origin and is thought to relate to the flexibility or inflexibility of molecular chains of the polymer which governs the way these chains pack in space. Many slight process modifications, such as small changes in pre-orientation, and modification, by blending in either the homogeneous phase or by forming heterogeneities, can produce dramatic effects in alleviating brittleness. In all these cases, the ingredients of tough behavior incorporate well-known stages of promoting plastic flow at levels of stress, which either retard the formation of flaws or their growth to fracture. Here, we will discuss primarily some prominent and unique processes that govern the fracture of glassy polymers. While this selection appears restrictive, it must be stated that glassy polymers represent a large and technologically important class of materials. Furthermore, the fracture behavior of semi-crystalline polymers also exhibits many of the features which we will discuss for glassy polymers, making this omission less consequential. The reader interested in a more specific discussion of the fracture of semi-crystalline polymers is referred to other reviews on this subject (see, e.g., Friedrich, 1983).

Of all the descriptors of the glassy state, the most informative is the segmental level internal stresses that exist between molecular segments in a glassy polymer. Recent atomistic simulations of the structure of simple atomic glasses (Egami et al., 1980), and flexible chain polymeric glasses (Theodorou and Suter, 1986) alike, have indicated that disorder on the atomic scale results in the placement of atoms or molecular segments at positions of local mechanical equilibrium far from what would be the case in a reference crystal structure of the material. This results in the presence of large, albeit balanced, forces on atoms and molecular segments. These forces can be used to define local pressures and complementary deviatoric stresses on each atomic site resulting from its interaction with its immediate surrounding. The simulation of the structure of the flexible chain, glassy polypropylene by Theodorou and Suter (1986) has shown that the root mean square pressures (or negative pressures) on each atomic site is typically 48% of the bulk modulus, while the corresponding root mean square deviatoric stress is much higher and typically 200% of the shear modulus. These atomic level internal stresses are of the same general magnitude found in atomic glasses, but proportionally to their average elastic constants at much higher levels. Clearly, as a result, in a polymeric glass, many molecular segments exist in states of local decohesion albeit over very short wave length. While similar simulations for polymers with long inflexible chain segments have not yet been performed, it is anticipated from earlier indirect measurements (Argon and Bessonov, 1977; and Russell et al., 1987), which have indicated the presence of liquid crystal-type short range order, that the atomic level internal stress in them should be substantially lower.

A further characteristic of the molecular microstructure of a glassy polymer, of importance to its mechanical behavior, is the volume density of entanglements of the long chain molecules. At such points of entanglement, molecules act as if they were tied together. Increasing entanglement density results in a direct increase in the shear modulus and an associated decrease in the network extension ratio of the polymer in the rubbery state above its glass transition temperature.

Crazing in Glassy Polymers

An important feature of the mechanical response of many glassy polymers is their ability to undergo crazing that is a direct consequence of the long chain nature of the polymer molecule. Crazes in glassy polymers incorporate uni-directionally highly aligned submicroscopic polymer fibrils with the limiting network extension ratio that are stretched across the narrow faces, as the micrograph of Fig. 1 indicates. They can be viewed for mechanical purposes as lenticular dilatational transformations arranged normal to the maximum principal tensile stress. Kinematically, they have the same properties for providing substantial inelastic strain as other well-known shear or dilatational transformations, such as mechanical twins, or martensite lamellae (Brown, 1975; Argon et al., 1983). Not all glassy polymers, however, undergo crazing. It is reasonable to expect that the flexible chain polymers referred to above, which already contain substantial fractions of decohered matter on the segmental level in their disordered state, should be craze prone, while inflexible chain polymers such as polycarbonate and all polyimides that have

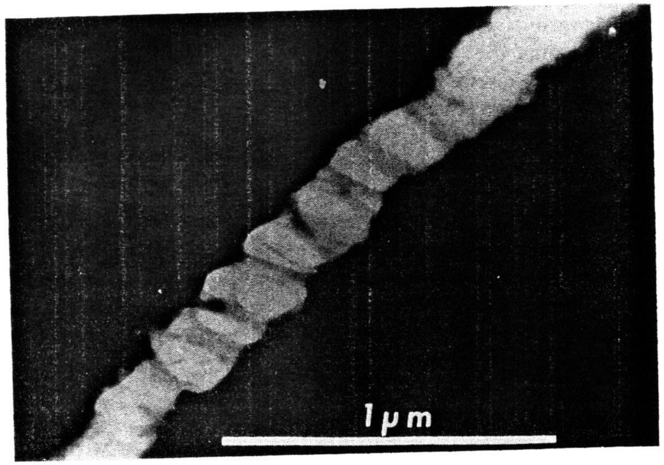

Fig. 1 Electron micrograph showing the fibril microstructure of a craze in PS (from Argon and Salama (1977); courtesy of Taylor and Francis).

a short range packing order should be relatively craze resistant. Experimental evidence is in support of this. Furthermore, the known beneficial effects of slight pre-orientation in craze suppression in flexible chain polymers such as polystyrene (PS) and polymethylmetachrylate (PMMA) (Whitney, 1964) and the similar effects achievable by blending of these polymers with a component having inflexible chain segments (Wellinghoff and Baer, 1978) are in support of this hypothesis. In a complementary view, however, it has been proposed that the flexible chain polymers are crazable because their intermolecular interactions are relatively lower than their intramolecular ones (Kardomateas and Yannas, 1985). On the other hand, as the chain entanglement density of molecules in a polymer, or the density of actual chemical cross links between molecular chains increases, the characteristic network extension ratios in the craze fibrils must decrease and eventually fibril development must cease altogether (Kramer, 1983). Thus, thermoplastic polymers with high chain entanglement density and thermosetting polymers (e.g., epoxies) with high chemical crosslink density do not craze.

The rate of initiation of crazes in crazable polymers has been studied in considerable detail (Argon and Hannoosh, 1977; Kawagoe and Kitagawa, 1981) and mechanism inspired stress criteria combining the effects of both negative pressure and deviatoric stress have been proposed, in representative volume elements having dimensions comparable to the correlation wave length of the segmental level internal stresses of disorder referred to above. Apart from noting that such craze initiation criteria are now well established and are operationally quite reliable, their detailed form (see e.g., Argon et al., 1987) is not of interest to us here. Of greater interest to us, however are the mechanism of craze advance and eventual craze matter fracture, which have more direct relevance to the overall fracture of glassy polymers. It has been proposed (Argon and Salama, 1977) and amply verified (Donald and Kramer, 1981) that craze fibrils are produced at the craze tip and their length increased at the craze borders by a variant of a classical meniscus instability. The resulting rate of advance v of crazes has been given as:

$$v = v_o exp\left(-\frac{B}{kT}g(\sigma_\infty/\hat{Y})\right) \quad , \qquad (1)$$

where v_o is a pre-exponential factor directly proportional to the ratio of surface free energy χ to craze flow stress σ_∞, B is an effective activation free energy for plastic flow, and $\hat{Y}$ is the athermal equivalent tensile plastic resistance of the polymer. The function $g(\sigma_\infty/\hat{Y})$ gives the decrease of the activation free energy, with increasing stress, its specific form will be given specifically later when needed. From Eqn. (1), it is clear that since the craze spreading velocity increases with stress σ_∞ for a given plastic resistance, the converse is also true that similar craze growth kinetics can result at constant stress σ_∞ when the plastic resistance $\hat{Y}$ is decreased by plasticization.

MECHANISMS OF FRACTURE IN HOMOPOLYMERS

Fracture in Crazable Polymers

In crazable polymers, fracture occurs almost exclusively by the breakdown under stress of craze matter. Under ideal conditions, when no extrinsic imperfections are present, craze fibrils fracture under stress from molecular level stress concentrations inside fibrils when load bearing molecules between effective entanglements inside a fiber fracture, setting off a cascade of sequential events of molecule scissions quite similar to the inception of unstable fracture in bundles of fibers in aligned composites (Argon; 1972, 1974). While the mechanistic understanding of this phenomenon is quite inadequate (Kramer, 1983), the rate R of rupture of individual taut molecules in craze fibrils, and consequently fibrils themselves (when there are only a finite number of molecules per fibril) must be given by a rate expression of the type

$$R = \nu_D \; exp\left(-\frac{U - \sigma_\infty q\lambda\Omega}{kT}\right) \quad . \qquad (2)$$

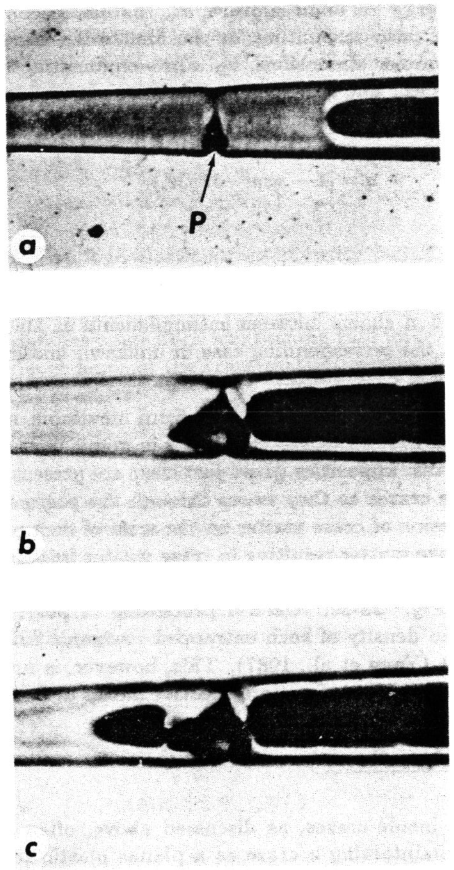

Fig. 2 A sequence of fracture of a craze (a) an advance cavitation event from a dust particle ahead of the main crack in a craze at point P, (b,c) the fracture spreading from the advance cavitation site joins the main crack (from Doyle, et al. (1982); courtesy of the Royal Society of London).

In Eqn. (2), U is the energy for bond rupture, σ_∞ the macroscopic craze flow stress, λ the craze fibril extension ratio accounting for the first order stress concentration, Ω an activation volume of monomer dimensions, ν_D a pre-exponential frequency factor of the order of atomic frequencies, and q a further stress concentration factor related to the fraction of taut bundle of molecules in the fibril, given by:

$$q = [1 - exp(-M/M_e)]^{-1} \quad . \tag{3}$$

In Eqn. (3), M is the number average molecular weight of the polymer and M_e the average molecular weight of chains between entanglements in the fibril, which could be considerably larger than the corresponding case in undrawn material – due to geometrically necessary decreases in entanglement density in fibril drawing (Kuo et al., 1985).

The intrinsic behavior described above resulting from inevitable statistical variations in entanglement density and taut molecules in fibrils is in many cases rendered unimportant when micron level inorganic impurities (dust particles) are present in the polymer which become entrapped inside crazes as they sweep through the polymer. In many instances, the disruption by decohesion of craze matter on the scale of such particles can constitute a supercritical flaw in craze matter resulting in craze matter fracture, and most probably, also overall fracture – if the applied stress, σ_∞, is high enough. A typical fracture event of this type is seen in Fig. 2a-2c. Careful processing of polymers under very clean conditions can reduce the density of such entrapped inorganic flaws and raise the craze fracture stress somewhat (Yang et al., 1987). This, however, is not a practical solution. In Section IV below, we will discuss far more effective means of increasing toughness even in the presence of these troublesome inorganic particles.

Propagation of Cracks Along Crazes

When fracture develops inside crazes, as discussed above, often the crack that forms, continues to run while maintaining a craze as a planar plastic zone in front of it. Alternatively, when a sharp macrocrack in a glassy polymer is stressed in tension, a craze forms in front of it as a planar plastic zone. Such crazes ahead of cracks have often been treated by the well-known Dugdale model (see e.g. Döll, 1983). While this has been useful in modeling the extent of the plastic zone, it has not been generally useful in providing a tool for the understanding of the conditions of crack advance, as the Dugdale model represents a fully accommodated crack tip, in which the effective crack tip stress intensity has been reduced to zero. As Kramer and Hart, (1984) have pointed out, there are many instances where the experimentally determined craze face tractions along propagating cracks are not constant, but rise rather sharply as the crack tip is approached along the craze plane (Kramer, 1983). This suggests that crack advance is accomplished in a state of only partial shielding by the craze, and that a finite stress intensity often remains at the crack tip governing its advance. Kramer and Hart (1984) have treated this problem in some detail, and have demonstrated that a crack advancing with a velocity v in a self-similar configuration having a craze of constant length ahead of it, will produce a crack tip shielding plastic stress intensity factor K_p, given by:

$$\frac{K_p}{K_y} = -\frac{1}{\pi}\left(\frac{E/\sigma_y}{1-\nu^2}\right)\left(\frac{n}{n-1}\right)\frac{\dot{w}_y}{v}\left(\frac{K}{K_y}\right)^n \quad , \tag{4}$$

with

$$K = K_a + K_p \quad ; \qquad K_y = \sigma_y\sqrt{2\pi d} \quad , \tag{5a, b}$$

$$\dot{w} = \dot{w}_y\,(\sigma/\sigma_y)^n \quad , \tag{5c}$$

where K_a and K are the applied elastic stress intensity factor and net crack tip stress intensity factor respectively, $\sigma(x)$ is the local nominal craze traction, σ_y is a peak tensile stress, at the first craze fibril of diameter d at the tip of the crack, necessary for crack advance, and $\dot{w}_y$ is a reference craze fibril lengthening rate under a local craze traction of σ_y. If in addition the dependence of the craze matter fracture time t_f on the local fibril stress $\hat{\sigma}$ $(= \lambda\sigma(x))$ can be given as:

$$t_f = \frac{1}{\dot{\epsilon}_c}\left(\frac{\hat{\sigma}_c}{\hat{\sigma}}\right)^m \quad , \tag{6}$$

where $1/\dot{\epsilon}_c$ is a limiting time to fracture under a local accentuated fibril stress $\hat{\sigma}_c$, and λ is the craze fibril extension ratio, the dependence of the crack velocity on the net stress intensity K at the crack tip can then be prescribed as:

$$v = \frac{2\dot{\epsilon}_c d}{(m-2)}\left(\frac{K\lambda}{\hat{\sigma}_c\sqrt{2\pi d}}\right)^m \quad . \tag{7}$$

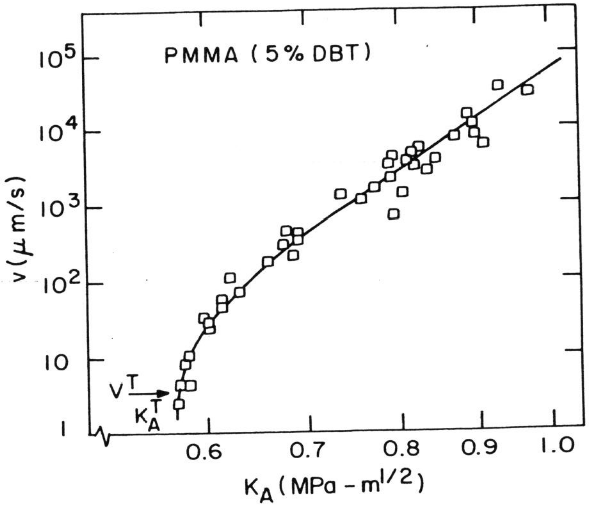

Fig. 3 Crack growth data for PMMA plasticized with 5% dibutylphthalate (from Kramer and Hart (1984); courtesy of Butterworths).

In Eqns. (5c) and (6), the exponents n and m are to be empirically determined from experimental information. Introduction of K_p from Eqn. (4) into Eqn. (5a), and the simultaneous solution of what results from this with Eqn. (7) gives a relation for crack velocity as a function of the applied stress intensity factor K_a, for the various material constants appearing in these equations. A solution for a specific case for crack growth in PMMA plasticized with 5% dibutylphthalate is given in Fig. 3 (Kramer and Hart, 1984; Aleshin et al., 1979) (for the material exponents $m = 12$ and $n = 9$). Figure 3 shows that the crack velocity has a very definite threshold at K_a^T. Kramer and Hart show that this is a result of the multi-valued nature of the dependence of v on K_a (or K on K_a), with a stable and unstable branch, bifurcating at a minimum applied $K_a = K_a^T$. This has also permitted these authors to give a quantitative development for the often reported unstable crack extension in many polymers, including epoxies at low crack opening displacement rates when the latter are applied by means of a stiff testing machine (see Kinloch, 1985; LeMay and Kelley, 1986).

Fracture in Non-Crazable Polymers

In polymers with very high entanglement or cross-link densities such as thermosetting epoxies, crazing is absent and fracture at temperatures below the glass transition temperature is of a relatively brittle nature, with a local critical stress approaching the ideal cohesive strength of the material, i.e., 0.1 - 0.12 times the Young's modulus (Kinloch, 1985). This results in a typical brittle response obeying a critical stress intensity criterion, but often with relatively high levels of fracture toughness. While this fracture toughness can be increased somewhat further still by altering the activator to epoxy ratio from the ideal stoichiometric level of unity, this has other undesirable consequences in imperfect curing, loss of stiffness, and generally increased rate dependence (LeMay and Kelley, 1986). As we will discuss below in Section 4.3, there are other much more promising ways of improving the fracture toughness of such polymers.

Other polymers with long stiff segments and short range ordered liquid crystalline domains, such as polyimides, or those with relatively high entanglement densities, such as polycarbonate in which craze stresses exceed the yield stress, do not craze. These polymers can undergo considerable plastic straining before the onset of strong orientation hardening, and are generally very tough in the unaged condition or in the absence of solvent crazing agents. The mechanisms of fracture of these polymers have not been widely examined. The few definitive studies have found that these mechanisms are quite similar to those well established in metallic alloys. Thus, Kinloch et al. (1986) have found that in many epoxies near their glass transition temperatures, where the fracture surface acquires a ductile appearance, cracks advance by a meniscus instability process studied by Argon and Salama (1976) in amorphous metals. In heterogeneous epoxies toughened by particle cavitation, considerable ductile cavity growth is also found (Kinloch, et al., 1983).

TOUGHENING MECHANISMS OF POLYMERS

Glassy Polymers with Potent Craze Initiators

By its very nature, crazing is strongly susceptible to stress concentrations. Thus, in homopolymers, crazing is overwhelmingly a phenomenon governed by surface imperfections. This has undesirable consequences. First, in initially crack free homopolymers, the density of surface sites with sufficient stress concentrating potency is usually quite low, making craze initiation stresses in them relatively high, and resulting in early fracture in those few crazes that do form. Second, with initiation of crazes taking place only on surfaces, overall plastic response cannot be achieved before crazes traverse across the entire part. In dynamic loading situations, this prolongs elastic behavior of the part, and results in the development of high stresses, which in turn hastens fracture. To counteract these undesirable effects, the practice has been to distribute small compliant heterogeneities with good craze initiating potency throughout the volume by a variety of synthesis and blending processes, in which a volume fraction of about 0.1 of rubber is introduced into the glassy polymer. High impact polystyrene (HIPS) and Acrylonitrile-Butadiene-Styrene (ABS) are two such prominent examples. In both of these materials, the particles are composites themselves, entrapping a large volume fraction (c.a. 0.8) of spherical glassy polymer occlusions in a topologically continuous rubber phase, and have the principal function of distributing crazes throughout the volume by acting as potent sites for initiation. Figure 4b shows a typical composite particle in HIPS. Although this practice of toughening has been quite successfully applied for decades, the exact action of the particles, and the role of their morphology has only recently been clarified (Argon et al., 1987). Figure 4 shows four different compliant particle morphologies in PS. In the first three cases roughly the same volume fraction of rubber (the black phase) is distributed in topologically different forms. In Fig. 4a, the particle is a precipitated form

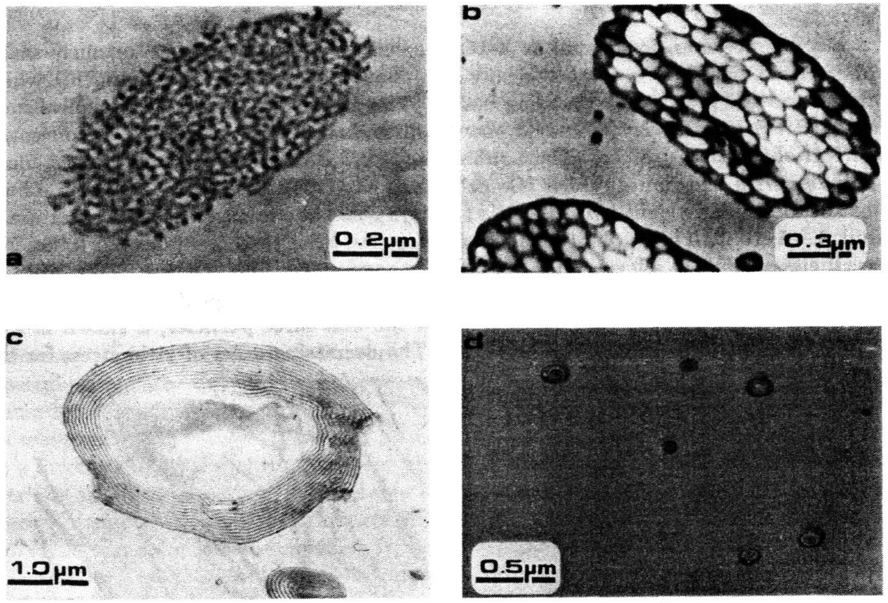

Fig. 4 Morphologies of four composite particles that have been studied in the toughening of glassy polystyrene: (a) KRO-1 resin particle, (b) HIPS particle, (c) concentric spherical shell particle, and (d) droplets of pure low molecular weight polybutadiene (from Argon, et al. (1987); courtesy of Pergamon Press).

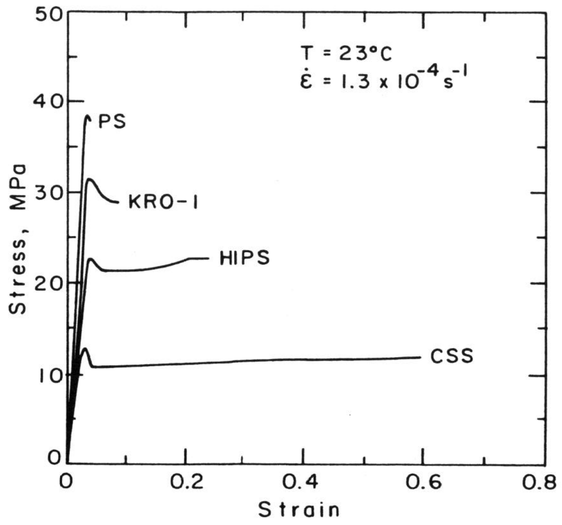

Fig. 5 Stress strain curves of craze plasticity of PS with KRO-1, HIPS, and CSS particles compared with behavior of homo PS (from Argon, et al. (1987); courtesy of Pergamon Press).

of a block copolymer designated as KRO-1, consisting of a rod-shaped tortously snaky rubber phase dispersed in a topologically continuous background phase of stiff PS, which blends smoothly into the surrounding matrix. The particle in Fig. 4b is the typical commercial HIPS morphology discussed above, while that in Fig. 4c consists of concentric spherical shells (CSS) of compliant rubber and stiff PS obtained by blending a block copolymer with additional rubber (Gebizlioglu et al., 1985). The particles in Fig. 4d are pure low molecular weight ($M_w = 2.7 Kg/$ mole) rubber at a minuscule volume fraction of about $2 - 5 \times 10^{-3}$. They do not initiate crazes as the other three are intended to do, but nevertheless, result in a level of toughness quite comparable with the best of the HIPS or CSS particles by a totally different mechanism that we will discuss in Section 4.2 below. The effect on the stress strain curve of PS of the first three particles, is shown in Fig. 5, compared with the behavior of homo PS. The decreasing order of yield stress for the

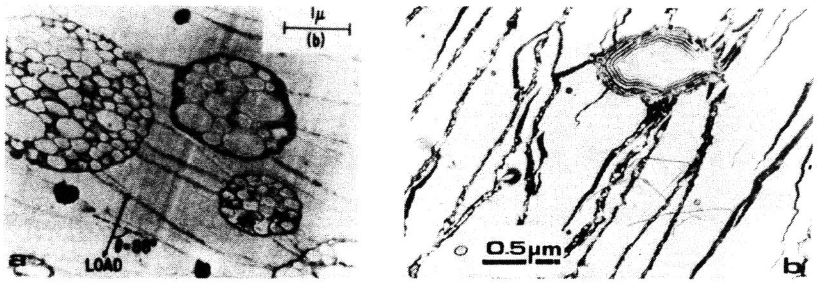

Fig. 6 Crazes in deformed samples containing particles of: (a) HIPS, and (b) CSS material (from Argon, et al. (1987); courtesy of Pergamon Press).

KRO-1, HIPS, and CSS particles indicates an increasing order of craze initiation potency of these particles. The micrographs in Fig. 6a and 6b indicate that the HIPS and CSS particles are indeed very effective in initiating a profusion of crazes. There is little direct evidence that the KRO-1 particles initiate crazes - in agreement with the relatively poor performance of these particles. The effective Young's moduli of these three particles calculated by either a self-consistent method (KRO-1 and HIPS) or by a direct finite element analysis (CSS) (Boyce et al., 1987) are given in Table I (Argon et al., 1987). These are to be compared with the Young's modulus of homo PS at 3.25 GPa. From here, it is clear that the effective modulus misfit between the KRO-1 particles and PS is too little to make these particles effective, while the difference between PS and the HIPS and CSS particles makes them 89.8 and 95.8% as effective as a spherical cavity (parenthetically, it should be pointed out that while spherical cavities should be the most effective in nucleating crazes, they are not effective toughening agents, since they have no means of offering eventual load support as particles do, and therefore, constitute supercritical flaws in crazes to result in immediate fracture of the crazes that emanate from them). Since no special precautions were taken in the preparation of the three blends in Figs. 4a-4c, they must have contained roughly the same density of inorganic particles to initiate fracture in craze matter. Thus, the increasing strains to fracture with decreasing flow stress level is a direct consequence of the increased probability of survival of craze matter for longer periods as the stress acting across crazes decreases. This effect is replotted in Fig. 7, as derived from tests at constant uniaxial strain rate and is typical of most extrinsic flaw governed, time dependent fractures. It must be noted, that the pattern of performance given in Fig. 7, as well as its level, is quite insensitive to morphology of glassy polymers, and holds for the craze fracture of a large family of pure block copolymers of PS and polybutadiene (PB) rubber (Argon, et al., 1984), indicating that the behavior is indeed governed by extrinsic flaws and their state of adhesion to their surroundings.

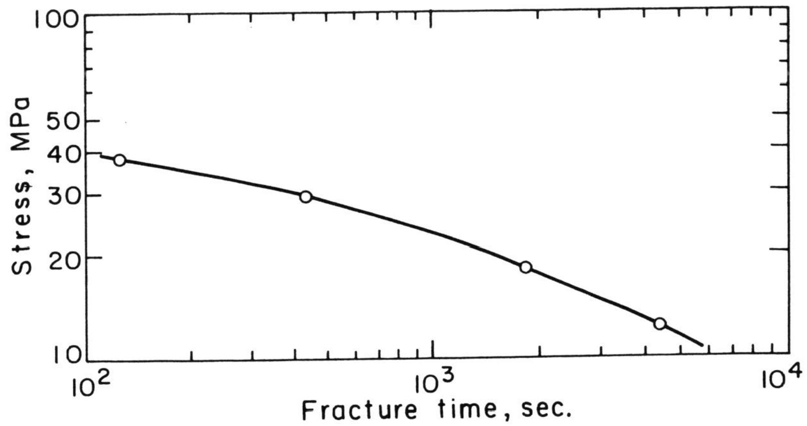

Fig. 7 Stress dependence of time to fracture of craze matter in PS (from Argon et al. (1987); courtesy of Pergamon Press).

TABLE I Effective Young's Moduli of Particles in PS, GPa

KRO-1	HIPS	CSS	PB Rubber
2.400	0.333	0.138	0.047

Toughening Glassy Polymers by Controlled Solvent Crazing

In a series of blending experiments of commercial PS with very small concentrations of very low molecular weight PB ($M_w = 2.7Kg/$ mole), Gebizlioglu et al. (1988) have discovered a new mode of toughening brittle glassy polymers through craze plasticity. They noted that while PB of this description produces only modest effects of plasticization in PS below the solubility limit of about $4x10^{-3}$ of PB, dramatic improvements in toughening were obtained once the low molecular weight PB precipitates out in the form of tiny droplets of roughly 0.1 μm diameter, as shown in Fig. 4d. The resulting decrease in craze flow stress and change in strain to fracture with increasing volume fraction of precipitated PB is shown in Figs. 8a and 8b. The maximum level of toughness of 4.5 MJ/m^3, at fracture, attained at a volume fraction of $1.2x10^{-2}$ of PB, is fully equal to that attained by a commercial HIPS shown in Fig. 5 containing roughly an order of magnitude more in PB dispersed in the composite particles. Electron microscopy indicated that while the plastic strain in these samples was all accounted for by crazes, there was little evidence of nucleation of crazes from the small particles in agreement with conventional expectations (Argon, et al., 1985). Key small angle X-ray scattering experiments from the crazed samples, examining the morphology and size scale of the craze matter in these blends have established that the low molecular weight PB is acting as a controlled solvent crazing agent in the manner sketched in Fig. 9 (Brown et al., 1988). The advancing crazes, nucleated from free surfaces or other occasional imperfections, cut into the dispersed population of droplets of PB, which at this low molecular weight acts like a liquid, and drains the contents of the droplets onto the surfaces of the craze. Although the solubility ν_o of the PB into PS under standard conditions of room temperature and atmospheric pressure is negligibly small (of the order of $4x10^{-3}$), this should increase greatly in the presence of a negative pressure, by the well-known expression of (Brown et al., 1988):

$$\frac{\nu}{\nu_o} = exp\left(\frac{\sigma M}{\rho RT}\right) , \qquad (8)$$

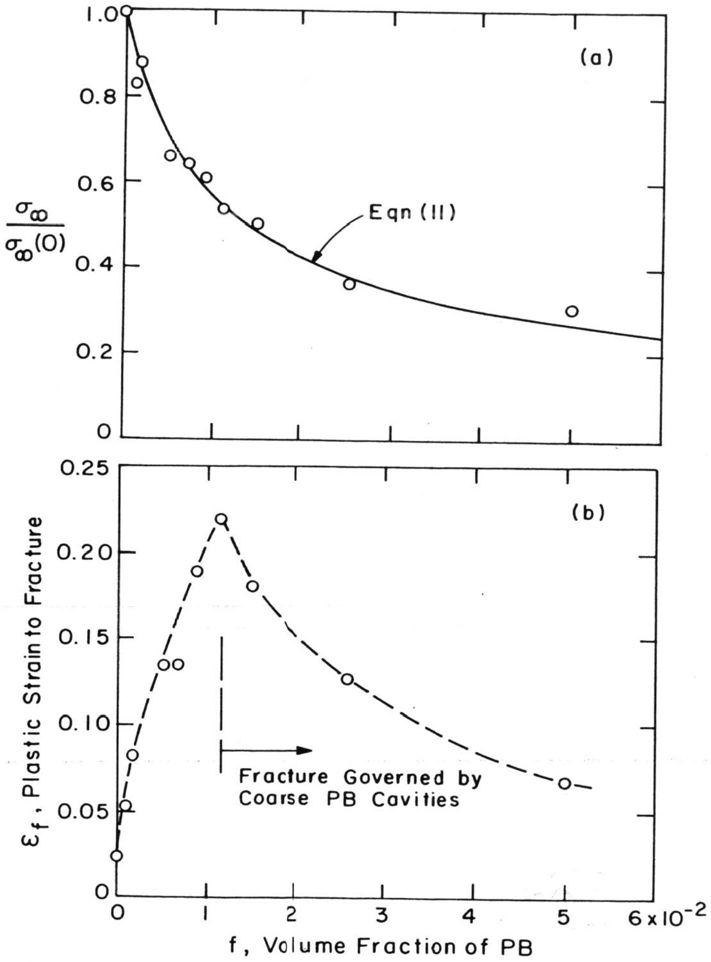

Fig. 8 Effect of small droplets of pure low molecular weight PB (Fig. 4d) on the toughness of PS: (a) dependence of craze flow stress on volume fraction of rubber, and (b) dependence of strain to fracture on volume fraction of rubber (from Gebizlioglu, et al. (1988), submitted for publication).

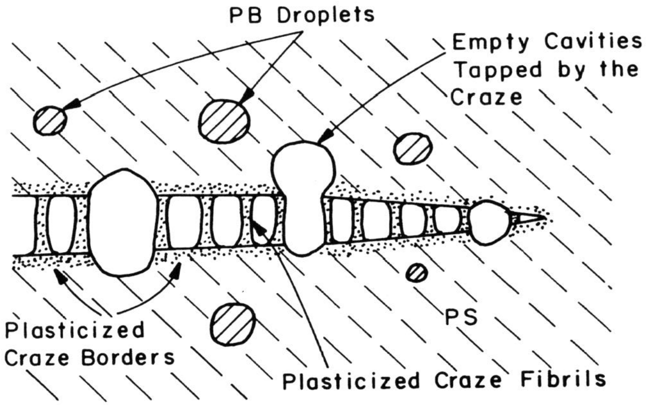

Fig. 9 Craze growing through a field of tiny low molecular weight PB droplets, which drain their contents onto the craze surfaces to rapidly diffuse the PB into the fringing layer under negative pressure.

where ν is the solubility in the presence of a negative pressure σ acting on the PS, M is the molecular weight of the PB diluent, and ρ is its density. Since at the craze tip and at the craze borders where fibrils are drawn out of the solid polymer (at the sockets of the fibrils) deformation induced negative pressures of the order of the craze flow stress σ_∞ can develop, it is easy to demonstrate that the solubility of the PB into the PS can increase these by many orders of magnitude (Argon, et al., 1988) until the process is stopped when the induced swelling relieves the negative pressure. Since the increase in concentration of the PB diluent will produce swelling and increase in free volume (Cohen and Turnbull, 1959), the shear viscosity η, the athermal plastic resistance $\hat{Y}$, and the diffusion constant D of PB in PS can all be expected to depend on the diluent concentration ν by expressions of the type:

$$\eta = \eta_o \; exp(-\beta_1 \nu); \quad \hat{Y} = \hat{Y}_o exp(-\beta_2 \nu); \quad D = D_o exp(\beta_3 \nu) \;, \qquad (9a,b,c)$$

where $\eta_o, \hat{Y}_0$, and D_o are the zero shear rate viscosity, the athermal plastic resistance, and the self-diffusion constant of homo PS at atmospheric pressure. The coefficients β_1, β_2, and β_3 (probably all of rather similar magnitude) need yet to be measured.

In the cases of interest, the plasticization of the fringing layers of the crazes in PS due to the take-up of the PB is almost instantaneous on the time scale of craze tip advance. Then the uniaxial strain rate $\dot{\epsilon}_c$, governed by crazing, should be given by the basic kinematical rate equation of (Argon et al., 1983):

$$\dot{\epsilon}_c = C_v v = C_v v_o \;\; exp\left[-\frac{B}{kT}\left(1 - \frac{\sigma_\infty \lambda'}{\hat{Y}}\right)^{5/6}\right] \qquad (10)$$

where C_v incorporates the effective dilatational transformation strain of a craze and the active craze front length per unit volume, λ' a function dependent on the craze fibril extension ratio (≈ 1.85 for PS), and where v_o, B, and $\hat{Y}$ were defined in connection with Eqn. (1). Substitution of Eqn. (9b) into (10) and solving for σ_∞ as the craze flow stress for a given machine strain rate of $\dot{\epsilon}_c$ gives (Argon et al., 1988):

$$\frac{\sigma_\infty}{\sigma_\infty(o)} = exp\left[-\left(\frac{a\beta_2}{3C}\frac{\hat{Y}_o}{\lambda'}A\right) f\left(\frac{\sigma_\infty}{\sigma_\infty(o)}\right)\right] \;, \qquad (11)$$

where $\sigma_\infty(o)$ is the initial craze flow stress of the pure PS homopolymer, a is the PB particle diameter, f is the volume fraction of precipitated PB in the blend, C is a product of the fibril diameter and the craze flow stress, known to be constant ($= 0.55 \; J/m^2$ for PS; Brown, 1988), and A is given by:

$$A = \left[1 - \frac{kT}{B}\ell n\left(\frac{C_v v_o}{\dot{\epsilon}_c}\right)\right]^{6/5} \;. \qquad (12)$$

In Eqn. (11), all quantities other than β_2 are relatively well known. The latter, which as a first approximation can be taken as the reciprocal of the volume fraction of PB in PS at the solubility limit was considered as adjustable in relating the theoretical prediction to the experimental data in Fig. 8a. The solid curve in the figure was obtained with a choice of β_2 of 118. Clearly, the development leads to the proper form of the dependence of σ_∞ on f, and the magnitude of β_2 is reasonable.

Parenthetically, we note that the unique toughening effect results from the greatly increased solubility of PB and its diffusion into PS because of the deformation induced negative pressures in the fringing layers of the crazes. There is no solubilizing of PB in or diffusion into the surrounding PS of the initial PB droplets, since in their case, the PB itself is under a negative pressure, while the surrounding PS is under a compensating small pressure due to a thermal expansion misfit (see Argon, et al., 1983).

In Fig. 8b, the strain to fracture is shown first to rise sharply with increasing volume fraction of rubber. In this range, the rubber particles (or droplets) have a relatively uniform size in the 0.1 μm range, making the intercepted and drained PB cavities less severe flaws than the regularly incorporated dust particles which continue to govern the strength. The strain to fracture increases because the craze matter survives under the decreasing overall stress levels for longer periods of time. Above about 1.2% rubber, the variability in size of the PB droplets increases sharply (probably through droplet fusion during the viscous gel phase of the solvent cast sheets) (Gebizlioglu et al., 1988). Above this volume fraction of rubber, these large intercepted and drained PB cavities become the dominant flaws initiating premature craze fracture, as was observed earlier in other blends by Gebizlioglu et al. (1985). This mode of toughening of a brittle glassy polymer by controlled and contained solvent crazing has a great potential in toughening other glassy polymers, and is currently under serious further development.[1]

Toughening of Brittle Thermosetting Polymers

Brittle epoxies have been successfully toughened by the applications of principles of transformation toughening (Budiansky et al., 1983) relying on crack tip shielding by various inelastic background mechanisms. Kinloch (1985) and coworkers, who have studied the fracture behavior of a typical family of epoxy resins DGEBA (diglycidylether of bisphenol A) in both homogeneous, unmodified form, and modified with cavitating rubber particles and/or decohering glass spheres, have found them to undergo a rather brittle appearing fracture below their glass transition temperatures. Although the appearance of the fracture surfaces in the unmodified resins were smooth and relatively featureless, typical of brittle fracture, the fracture energies G_{IC} that were measured were more substantial than what can be expected from a truly brittle solid – being in the range of 0.22 KJ/m^2. Nevertheless, the fracture obeyed a simple critical stress intensity criterion that could be interpreted as the reaching of a critical tensile stress $\sigma_{\theta\theta} = \sigma_c$ at a structural distance δ ahead of the crack tip, where $\sigma_C \approx (0.12 - 0.14)E \approx 400 \;\; MPa$ and δ should be a small microstructural dimension. Moreover, these investigators found that while the fractures were stable at low temperature and high strain rates, they became unstable at higher temperatures approaching T_g and at lower strain rate – with repeated steps of acceleration and arrest of the crack under a constant rate of crack opening displacement. Some increase in fracture energy was found to accompany this behavior, without any perceptible change in the appearance of the fracture surfaces. Around T_g, the fracture energies rose sharply, as is shown in Fig. 10, with accompanying changes in the fracture surfaces

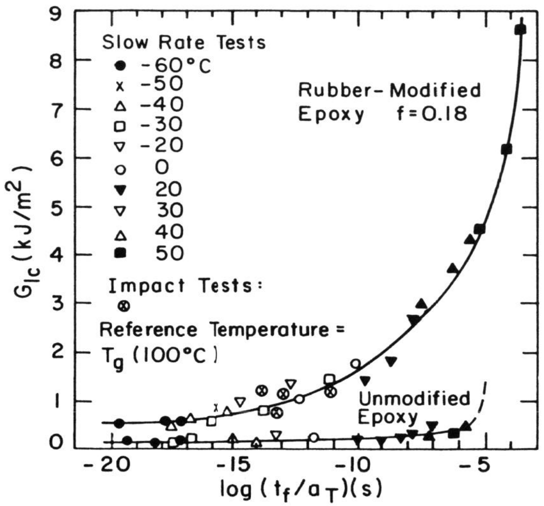

Fig. 10 Dependence of fracture energy of unmodified and modified DGEBA epoxies on temperature and strain rate; a_T is the viscoelastic shift factor based on a reference T_g of 100°C. (from Kinloch (1985); courtesy of Springer).

to a more disrupted and rough appearance (Kinloch, 1985).

When the neat epoxy was modified by the incorporation of rubber particles or glass spheres, the fracture energy could be increased by factors of 4-5 at all levels of temperature, as is shown in Fig. 10. As we will presently demonstrate, these observations represent an almost classical behavior of transformation toughening by crack tip shielding of a brittle solid (see also Evans et al., 1986).

First, we note that G_{IC} for crack propagation is far too high (by at least an order of magnitude) for a truly brittle solid, and that considerable plastic dissipation must have accompanied the *propagation* of the crack in the unmodified material without apparently blunting it. This suggests the presence of crack tip shielding by plastic deformation in an inelastic zone surrounding the crack to a depth of R_c, as depicted in Fig. 11. Thus, in the model below, we consider the epoxy resin to respond plastically and with strain hardening, following a non-linear constitutive behavior between equivalent strain ϵ_e and equivalent stress σ_e, according to a power law of:

$$\epsilon_e = \epsilon_y \left(\frac{\sigma_e}{Y}\right)^n \quad \therefore \quad \epsilon_y = \frac{Y}{E} \quad , \tag{14a, b}$$

where Y is the initial yield strength of the epoxy and n its stress exponent. Hence, we expect a crack tip characterizable by the usual HRR distributions with:

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[1] Patent applications in the U.S.A. and several other industrial countries have been filed by Gebizlioglu, Argon, and Cohen for the protection of this mechanism of toughening.

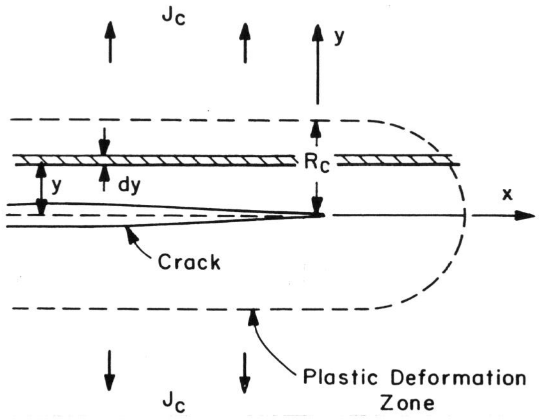

Fig. 11 Sketch of a plastic dissipation zone of thickness R_c along the propagating cracks in epoxies.

$$\sigma_{ij} = Y D \left(\frac{R_c}{r}\right)^{\frac{1}{n+1}} \tilde{\sigma}_{ij}(\theta, n) \quad \therefore \quad D = \left(\frac{J_c E}{Y^2 I_n R_c}\right)^{\frac{1}{n+1}} \quad , \tag{15a, b}$$

$$R_c = \frac{J_c E}{Y^2 I_n}\left(\tilde{\sigma}_e\left(\frac{\pi}{2}\right)\right)^{n+1} \quad , \tag{15c}$$

and where $J_c(= G_{IC})$ is the well-known J integral at its critical level, I_n an integration constant dependent on n, and where purely elastic behavior is expected outside the inelastic zone of extent R_c. Assuming, as a first approximation, that for a propagating crack this same HRR distribution of stress is retained in depth, away from the fracture surface, in the inelastic zone of thickness R_c, the shielding ΔJ that develops due to diffuse plastic flow can be readily calculated, and is:

$$\Delta J = 2\int_{\delta}^{R_c} \Delta U(y)dy = 2n\frac{Y}{E}\int_{\sigma}^{R_c} dy \int_{Y}^{\sigma_e(y)} \left(\frac{\sigma_e}{Y}\right)^n d\sigma_e \quad , \tag{17}$$

giving

$$\Delta J = \frac{2n}{(n+1)}\frac{Y^2}{E}R_c A_n = J_c\frac{2nA_n}{(n+1)I_n}\left(\tilde{\sigma}_e\left(\frac{\pi}{2}\right)\right)^{n+1} \tag{18}$$

where $$\Delta U = \int_{\epsilon_y}^{\epsilon(y)} \sigma_e d\epsilon_e \quad \therefore \quad A_n = \left[(n+1)\ell n\left(\left(\frac{\sigma_c}{Y}\right)\frac{\tilde{\sigma}_e\left(\frac{\pi}{2}\right)}{\tilde{\sigma}_{\theta\theta}(o)}\right) - 1\right] \quad . \tag{19a, b}$$

Since in nearly every case for all $n, \tilde{\sigma}_e\left(\frac{\pi}{2}\right)$ is very nearly unity (Shih, 1983), the equations (15c), (18), and (19b) simplify further.

If, based on the fracture appearance, it can be concluded that the actual propagation of the crack is accomplished when $\sigma_{\theta\theta} = \sigma_c$ at $r = \delta$ ahead of the crack regardless of whether there is or is not plastic dissipation, a reference $J_o = G_{co}$ can be defined as:

$$J_o = \frac{\sigma_c^2(2\pi\delta)(1-\nu^2)}{E} \quad , \tag{20}$$

where

$$\frac{\delta}{R_c} = \left(\frac{Y}{\sigma_c}(\tilde{\sigma}_{\theta\theta}(o))\right)^{n+1} \quad . \tag{21}$$

Since

$$J_c = J_o + \Delta J \quad , \tag{22}$$

J_c can be given in units of the reference J_o, which is assumed to remain unaltered for crack propagation even in the presence of particle modification of the epoxy. This gives:

$$J_c = J_o\left[1 + \frac{nA_n}{(n+1)} \; \frac{(\sigma_c/Y)^{n-1}}{(\tilde{\sigma}_{\theta\theta}(o))^{n+1}\,\pi\,(1-\nu^2)}\right] \quad . \tag{23}$$

When the epoxy is modified with cavitating rubbery particles or decohering glass spheres with a combined volume fraction of f, additional toughening results, primarily from an effective reduction of the plastic resistance, Y. The effect of this is obtained by formally replacing J_o with $J_o(1-f)$ and Y with $Y(1-f)$ in Eqn. (23) to give:

$$J_{c(cav)} = J_o(1-f)\left[1 + \frac{nA'_n}{(n+1)} \; \frac{(\sigma_c/Y)^{n-1}}{(1-f)^{n-1}(\tilde{\sigma}_{\theta\theta}(o))^{n+1}\pi(1-\nu^2)}\right] \tag{24}$$

where

$$A'_n = (n+1)\ell n\left[\frac{(\sigma_c)}{Y}\frac{1}{(1-f)(\tilde{\sigma}_{\theta\theta}(o))}\right] - 1 \quad . \tag{25}$$

To test the model against the experiments, it is necessary to know the plastic resistance Y and stress exponent n of epoxies. Kinloch (1985) reports an average value of 115 MPa for Y for the epoxies they have tested, resulting in an average ratio of $\sigma_c/Y = 3.5$. No information is available for the exponent n for any epoxy. Consideration of the above expressions in the context of the experimental data of Kinloch suggests that $n = 8$ should be an appropriate exponent. For this, we have $\sim \sigma_{\theta\theta}(0,8) = 2.418$ and $I_n = 4.68$ (Shih,

1983), giving for $A_n = 2.33$ for the σ_c/Y ratio of 3.5. Thus, from Eqn. (18), we obtain that $\Delta J/J_c = 0.885$, or a J_c/J_o ratio of 8.7, which is reasonable for the initial unmodified epoxies. Furthermore, using the overall average figure of 220 J/m^2 for the externally measured fracture energy J_c, we calculate for the non-linear zone thickness $R_c = 10^{-5}m$, and for the dimension $\delta = 3.5\text{x}10^{-7}$m at the crack tip where $\sigma_{\theta\theta} = \sigma_c = 400 \; MPa$ is reached. These are generally very reasonable values for epoxies.

In Fig. 10, results are given for the fracture energies of epoxies modified with rubber particles and glass spheres to a combined volume fraction of $f = 0.18$. We evaluate this toughening effect where cavitation occurs at the particles by means of the ratio of Eqn. (24) to Eqn. (23) for the quantities given above to obtain:

$$\frac{J_{c(cav)}}{J_{c(hom)}} = 3.93 \quad . \tag{26}$$

The average ratio of the above quantity measured by Kinloch is 5.7, indicating additional effects of crack tip shielding attributable directly to the cavitation that we have not accounted for.

CONCLUSIONS

Glassy polymers which are an important class of engineering materials show fracture behavior characteristic of all polymers, below T_g, including many semi-crystalline polymers.

Crazing occurs in many flexible chain glassy polymers, and is often the principle flaw which initiates overall fracture through fracture of the fibrils of craze matter.

When properly managed to assure a high volume density of potent craze initiation sites and relatively ready craze growth by controlled local plasticization, craze flow stresses can be decreased markedly, resulting in a greatly improved probability of survival of crazes under stress and vastly improved strains to fracture with very substantial increases in accompanying levels of toughness.

An important ingredient of the above mechanism of toughening is the very large improvements achievable in craze growth rate through controlled and contained solvent crazing produced by free rubber of low molecular weight.

Glassy polymers with long stiff segments that result in a short range ordered liquid crystalline molecular packing and those with moderately high entanglement densities are generally very tough and need no improvement.

Thermosetting polymers with a high cross-link density can be plastically deformed, but harden rapidly to result in brittle behavior. Such polymers can be effectively toughened by principles of transformation toughening by incorporating cavitating rubbery particles or decohering glass spheres to produce effective crack tip shielding.

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