2752 *Macromolecules* 1991, *24*, 2752-2756

A Molecular Interpretation of the Toughness of Glassy Polymers

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Received February 2, 1990; Revised Manuscript Received October 2, 1990

ABSTRACT: A model is proposed that describes the failure of glassy polymers in the crazing regime. This model is based on the realization that the cross-tie fibrils, which are known to exist between primary fibrils in all crazes, can have a profound effect on the failure mechanics of a craze as they can transfer stress between the broken and unbroken fibrils. A very simple model of crack tip stress amplification caused by the cross-ties is shown to work well in the prediction of the fracture toughness of a bulk, high molecular weight, glassy polymer. The toughness is shown to vary as the square of the breaking force of chain molecules and the square of the density of entangled strands at the interface.

Introduction

A large amount has been learned in the last 20 years about the processes of crack propagation in glassy polymers. It is now clear that the energy required to propagate the crack (essentially the toughness) goes mainly into the growth of a craze at the crack tip.[1,2] An understanding of fracture, therefore, requires an understanding of both craze growth and craze breakdown. The processes of craze growth are reasonably well understood in terms of the meniscus instability model.[3] Craze microstructure and, hence, the craze stress are controlled by the entanglement network in the polymer, and the molecular parameters that control entanglement are also fairly well understood.[4] The other area required for an understanding of crack propagation and toughness, namely, craze breakdown at the crack tip, has been shrouded in mystery. The aim of this paper is to provide a model for craze fibril breakdown at the crack tip in terms of the force required to break a polymer chain and, hence, complete the broad picture of the relations between molecular structure and toughness.

Both cohesive and adhesive failure of glassy polymers normally occur by a crazing mechanism. The only notable exceptions are very strong interfaces in ductile polymers where gross plastic deformation suppresses the crazing and very weak interfaces where crazes never form or are unstable. When crazing is the main mode of failure, crack initiation normally occurs at the craze/bulk interface,[5] but crack propagation, the subject of concern here, runs through the center of a craze that exists at the crack tip and propagates at a constant size with the crack. These crack tip crazes have been well studied in a number of materials and are best characterized in poly(methyl methacrylate) (PMMA).[1] Their shape has been shown to approximate closely to that of a Dugdale zone,[2] and so the stress along them is relatively constant. It is clear that most of the work of fracture (fracture toughness, G_c) goes into growing the crack tip craze. In some polymers, particularly polystyrene (PS), multiple crazes often exist at the crack tip and propagate with the crack, thereby increasing G_c. Schirrer and Goett[6] have shown that polymers show a characteristic temperature below which multiple crazes are more common. However, even in the multiple-crazing regime it is possible to form and propagate a single crack tip craze, thereby finding the minimum G_c for the material.[7,8] In this paper we shall consider only the single crack tip craze situation.

The fracture toughness, G_c, of PMMA has been studied over a range of over 8 decades in crack speed[1,9] and found to vary over this immense speed range by only about a factor of 2. Williams[9] was able to fit these data by assuming a constant stress across the crack tip craze, a time-dependent elastic modulus for the uncrazed material, and a failure criterion of a fixed maximum craze width v. The validity of this model was confirmed by Döll and coworkers[1] in their extensive optical studies on crack tip crazes. They showed that the maximum craze width indeed does vary very little with crack speed. Crazes are known to grow by drawing more bulk material into the craze, not by extending the preexisting fibrils.[4,10] Under slow steady crack propagation crazes fail at the center along the midrib[4] of slightly less dense material. It is hence tempting to assume a failure criterion based on a time under load concept as the material in the center of the craze has been stressed for the longest time. However, such a criterion is not capable of explaining the remarkable independence of maximum craze opening on crack velocity and hence craze lifetime.

Crazes are normally considered to consist of parallel, highly oriented, load-bearing fibrils. However, this is not the complete picture as these primary fibrils are joined by cross-tie fibrils. The cross-ties are believed to occur when the growing craze interface meets or pushes together a clump of strands between entanglements each of which span adjacent fibrils. It is then favorable for the interface to propagate around the clump rather than break the strands.[11-14] The cross-tie fibrils are capable of bearing load, though, in an unbroken craze, they are probably relaxed. However, it would seem likely that their existence should have a profound effect on the local fibril stresses near the center of craze at a crack tip. When a primary fibril close to the crack tip breaks at its center, it is prevented from complete contraction by the cross-tie fibrils that couple it to unbroken fibrils. This process inevitably increases the stress near the center of the unbroken fibrils. In this paper I demonstrate that this fibril stress enhancement by cross-tie fibrils can cause stresses that are high enough to break the active polymer chains in the craze fibrils and hence cause cohesive and adhesive failure in polymers.

Calculation of the Fracture Energy

As the aim of this work is to relate the fracture energy or toughness of the polymer to the failure of polymer chains within the crack tip craze, it is necessary to consider the stresses and crack propagation on two length scales, the macroscopic scale and the scale within the craze. The

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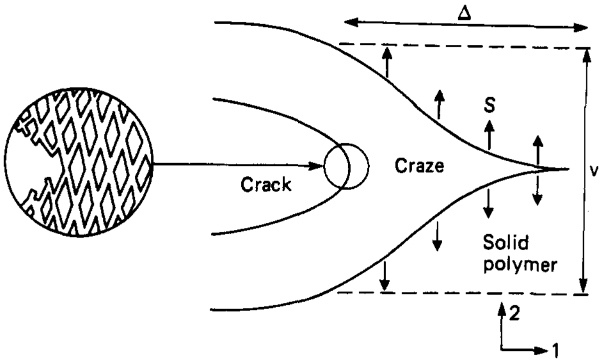

Figure 1. Diagram of the geometry of a crack tip craze. The scale in the 2 direction is expanded by at least a factor of 10 over that in the 1 direction, so in reality $\Delta \gg v$. The region around the crack tip is shown on an expanded scale to show the probable arrangement of fibrils within the craze.

toughness of the polymer, G_c, is controlled by the craze stress and the maximum craze width, v, so, as the craze stress is assumed to be understood, the problem reduces to understanding what controls v. A basic assumption of this work, as mentioned above, is that there is a stress concentration in the craze so that the stress on the fibrils close to the crack tip (in the craze) is higher than the average stress in the craze. This stress concentration factor is calculated by considering a local fracture mechanics within the craze. It must be emphasized that this local fracture mechanics, described by the lower case g and k_1, does not refer to bulk crack propagation and is used here just to obtain a relation between the average stress at the craze–bulk interface and the stress on a craze fibril just at the crack tip.

The craze is assumed to have a much lower elastic modulus than the surrounding uncrazed material so, in terms of the local fracture mechanics, the craze strip can be considered as similar to an elastomeric strip in the form of one of the classic fracture toughness specimens, the "pure shear specimen". For this specimen geometry the crack tip driving force is a function of the width of the sample. Thus we obtain a relationship between v and a local crack tip driving force, g, that applies within the craze. This local driving force, g, can then be related to the local stress intensity, k, within the craze, and hence we find the stress pattern around the crack tip. From this stress pattern we obtain the maximum stress in the fibril closest to the crack tip and therefore the force per entangled chain in this fibril. Hence, a criterion of breakage force per polymer chain can be related to v and the material toughness.

Figure 1 shows the geometry of a crack tip craze. We shall assume that this craze is much smaller than the sample dimensions, the "small-scale yielding approximation". The craze has a length Δ and a maximum width v. The movement of the interfaces v_0, which corresponds to the crack opening displacement, is given by

$$v_0 = v(1 - 1/\lambda) \tag{1}$$

where λ is the extension ratio of the craze matter. The stress at the craze–bulk interface, S, is assumed to be constant and so

$$G_c = S v_0 \tag{2}$$

The craze fibrils break at their center at the crack tip, and the cross-tie fibrils stop the broken fibrils adjacent to the crack tip from contracting back and becoming completely unloaded. If there were no cross-tie fibrils, the crack tip would be quite blunt; in fact, the crack would have a flat end, as suggested by the schematic figures in refs 1 and 2. In reality, optical observations by Doyle[8] show that the crack tip is more nearly parabolic in shape. A parabolic crack tip is to be expected if the cross-tie fibrils partially stop the broken primary fibrils close to the crack tip from contracting. It is clear that, in stopping the broken fibrils from contracting, the cross-tie fibrils will cause extra stress close to the center of the unbroken fibrils that are at the crack tip. This extra stress will depend on the number of broken fibrils that still carry load and hence must be a function of v and the effective shear modulus of the crazed matter.

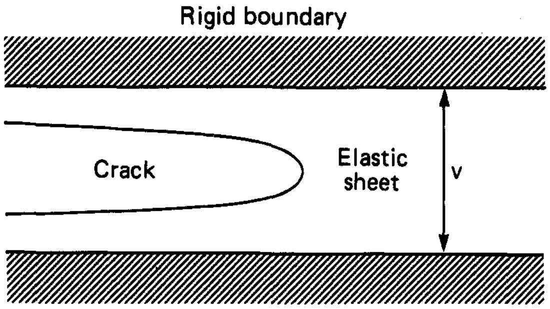

Figure 2. Geometry of the pure shear fracture mechanics specimen. The elastic sheet is held between rigid boundaries and stretched to a strain energy density W.

The craze can be represented as an elastic sheet between rigid boundaries as shown Figure 2. This is the familiar pure-shear elastomer fracture mechanics specimen,[15] and the local crack tip driving force g is given by

$$g = vW \tag{3}$$

where W is the elastic (recoverable) energy density in the stretched craze. The main assumption used in eq 3 is that only a relatively small area of the craze around the crack tip will have a strain that is significantly different from either a stretched, uncracked craze (in front of the crack) or a completely relaxed craze (in the main body of the crack).

Crazes are grossly anisotropic structures, and it is necessary to take this fact into account when considering the relation between g and the crack tip stresses within the craze. For an orthotropic material (a material with three perpendicular planes of symmetry) the crack tip stress intensity, k_1, is obtained from the relationship[16]

$$g = k_1^{\,2}\left(\frac{a_{11}a_{22}}{2}\right)^{1/2}\left\{\left(\frac{a_{22}}{a_{11}}\right)^{1/2} + \frac{2a_{12} + a_{66}}{2a_{11}}\right\}^{1/2} \tag{4}$$

where the a's are the compliances of the craze parallel (1) and normal (2) to its plane. The suffix 6 refers to shear deformations in the 1,2 plane. It is through eq 4 that the craze microstructure enters the problem. For example, a craze with no cross-tie fibrils would have all compliances infinite except a_{22} and so zero stress intensity for a finite G. This result is consistent with the assumption that cross-tie fibrils cause the stress concentration at the crack tip. The detailed elastic properties of crazes are unknown, but crazes are undoubtedly much stiffer in the fibril direction than they are normal to the fibrils ($a_{22} \ll a_{11}$). Also the shear modulus is likely to be of the same order as the tensile modulus normal to the fibrils ($a_{66} \simeq a_{11}$). Equation 4 can hence be written approximately as

$$g = k_1^{\,2}/(E_1E_2)^{1/2} \tag{5}$$

where E_1 and E_2 are the elastic tensile moduli of the craze normal and parallel to the fibril direction. Equation 5 is clearly an approximation, but it has the advantage of having the correct limit when the two moduli are equal.

The strain energy density in the craze $W = S^2/2E_2$, so

$$k_1 = (E_1/E_2)^{1/4}(v/2)^{1/2}S \quad (6)$$

The stress on the crack plane in front of a crack in an orthotropic material is given by the same relation as that in an isotropic material

$$\sigma_{22} = k_1/(2\pi r)^{1/2} \quad (7)$$

where r is the distance from the crack tip. The stress here is the stress in the fictional continuous material that has the same average elastic properties as the craze. The stress in the 2 direction in actual craze fibrils is greater than this by a factor λ. The mean stress on the fibril closest to the crack tip can be approximated as the stress at a distance $D/2$ from the crack tip where D is the fibril diameter. The maximum fibril stress is thus given by

$$\sigma_f = \lambda k_1/(\pi D)^{1/2} \quad (8)$$

Cherepanov[17] has used a very similar relation to eq 8 (obtained using a rather more sophisticated argument) when considering the failure processes in uniaxial fiber reinforced composites.

From eqs 6 and 8 we obtain the relationship between the maximum fibril stress, σ_f, and S

$$\sigma_f = \lambda S(v/2\pi D)^{1/2}(E_1/E_2)^{1/4} \quad (9)$$

The use of the local fracture mechanics was just a device to obtain this relationship.

By combining eqs 1, 2, and 9, we obtain the relation between the fibril failure stress and the material toughness

$$G_c = (\sigma_f^{\,2}2\pi D/S\lambda^2)(E_2/E_1)^{1/2}(1 - 1/\lambda) \quad (10)$$

The process of failure in glassy polymer requires the breaking of chains, so it is reasonable to assume that the force to break a craze fibril is the product of the force to break a polymer chain, f_s, and the number of effectively entangled chains in the fibril. The areal density of entangled chains is denoted by Σ, and so $\sigma_f = \Sigma f_s \lambda$ where it has been assumed that all the effectively entangled chains in the material are drawn into the fibril. Finally the fracture toughness is given by

$$G_c = (\Sigma^2 f_s^{\,2} 2\pi D/S)(E_2/E_1)^{1/2}(1 - 1/\lambda) \quad (11)$$

Equation 11 is the basic result of this work. It relates the macroscopically measured fracture toughness of a glassy polymer (which fails by craze propagation) to the density of entangled strands that cross a plane and the force to break a strand. A knowledge of the craze microstructure is also required. This model should apply to the cohesive failure of a range of glassy polymers and also to the failure of interfaces between immiscible polymers. In principle, it should also apply to the welding or crack healing situation, but problems of chain pull-out make that more difficult.

The application of this model to cohesive failure and interface failure will now be considered.

Fracture Toughness of Bulk Polymers

The fracture toughness of a bulk polymer is given directly by eq 11 in terms of f_s, the force to break a polymer chain, and the density of entangled chains that cross a plane. There is currently no direct experimental evidence that shows if craze fibrils in bulk, high molecular weight polymers fail by processes of chain slip and disentanglement or by direct breakage of the entangled strands. There is, however, plenty of evidence that chain breakage accompanies failure of polymers.[18] Disentanglement is only likely to occur at temperatures very close to T_g or when the molecular weight of the chains in the fibrils is not much above the entanglement molecular weight. Hence, the conditions for disentanglement of high molecular weight polymers are high temperature or when the fibrillation process causes considerable breakdown in the molecular weight. As craze stability in PMMA continues to increase (slowly) with molecular weight at molecular weights greater than $20M_e$,[19] it may be assumed that fibrillation does not cause massive breakdown in molecular weight so the craze fibrils must fail by scission.

The above argument is reinforced by recent experimental observations that fracture on some polymer interfaces involves chain breakage. When a number of immiscible homopolymer pairs were joined using polystyrene–PMMA diblock copolymers and the sample subsequently fractured along the interface, all the diblock molecules were shown to break near their junction points.[20,21]

It is valuable to use eq 11 to estimate what strength of a polymer chain is required to give the observed material toughness. For PMMA some reasonable estimates are $G_c = 600$ J/m², the craze stress $S = 70$ MPa, and $\lambda = 3$. The crossing density Σ is given by $v_e d/2$,[4,22] so from Berger,[14] $\Sigma = 2.8 \times 10^{17}$ m^{-2}. These numerical values give

$$f_s = 3.5 \times 10^{-9}(E_1/E_2)^{1/4}N$$

from eq 11.

The dependence of f_s on the ratio of the craze moduli is weak. This ratio can be estimated from the information on craze microstructures derived from low-angle electron diffraction (LAED) results. LAED shows that craze fibrils tend to be oriented at angles of $\pm\theta$ to the principal stress direction. This orientation occurs because the main fibrils are joined by cross-ties that occur quasi-periodically along their length, as shown in Figure 1. The model of Figure 1 is a good representation of the fibril conformations seen by small-angle electron diffraction,[11-14] but it is essentially two-dimensional. (It is worth noting in passing that the two-dimensional nature of this pattern demonstrates the relaxation of the through thickness stresses in crazes in films thin enough for TEM. This relaxation is the reason why crazes in thin films age rapidly while crazes in bulk materials do not.) For PMMA θ has been measured by Berger as 9°. The modulus ratio is likely to vary as a power of tan θ; I shall assume it varies as $\tan^2\theta$, giving a modulus ratio of 0.025. Finally one obtains a value of 1.4×10^{-9} N for f_s.

There is not a great deal of experimental information available on the force required to fracture a single polymer chain. Odell and Keller,[23] in some very elegant elongational flow experiments, were able to estimate f_s as between 2.5 and 12×10^{-9} N. Kausch[18] has also estimated the chain-breakage force at about 3×10^{-9} N. Evidently the result obtained by using the model of eq 11 and crazing and failure data for PMMA agrees well with previous estimates of the force to break a polymer chain.

The model presented here should of course apply to any glassy polymer that fails by a crazing mechanism. It would appear at first sight that a considerable variation in G might be expected amongst the different materials as G varies as Σ^2. However, this is not really the case as the materials with a higher entanglement density tend to have a higher craze stress, S. The microstructural parameters of crazes in materials other than PMMA and polystyrene are not known well enough to permit a comparison of the model presented here with experiment. This is not too important as the main aim of this model has been to show that the existence of cross-tie fibrils in crazes causes stress concentrations in the craze that can cause the craze failure.

There is no requirement in the model that the craze fibril must fail by a scission mechanism. The force per chain to cause separation could equally well be a pull-out force or some combination of chain scission and pull-out. One can make a simple estimate of the effect of polymer molecular weight on toughness by assuming that a length of the chain, probably with molecular weight M_e, at each end of the chain will be ineffective in contributing to a strand entangled across the interface. If the pull-out force for these chain-end sections is ignored, then Σ will decrease as $(1 - 2M_e/M)$ and the toughness should decrease as the square of this quantity. For narrow molecular weight distribution PMMA the toughness would hence be expected to decrease by 20% from its high molecular weight plateau value when $M \simeq 20M_e$ or about 200 000. This estimate is an reasonable agreement with the measurements of Weidmann and Döll.[1,24] A better estimate of the effect of molecular weight on toughness would require a knowledge of the force to pull out a chain as a function of its molecular weight, information that is not yet available but should be experimentally accessible using diblock copolymers at homopolymer interfaces.

Interfaces between Dissimilar Polymers

A number of pairs of immiscible polymers can be joined by using a diblock copolymer as a coupling agent at the interface. Such interfaces can be expected to fail by crazing, but here the situation is not mechanically symmetric. The craze will grow only into the material with lower crazing stress. Interfacial failure is hence to be expected at one side of the primary crack tip craze rather than along the middle of the craze. Thus for a given craze fibril breakage stress, σ_f, the craze opening v in the asymmetric case will be half that expected in the symmetric situation. Asymmetric joints may therefore be expected to show, at a maximum, half the toughness of the material with lower craze stress as long as the interface width is still small with respect to craze widths. To observe this effect, it may be necessary to drive the single craze along the interface and hence use an asymmetric fracture toughness specimen.[25]

Diblock copolymer coupled interfaces in favorable cases are ideal experimental systems to test the model presented here. The system where the homopolymers are poly(phenylene oxide) (PPO) and PMMA and the diblock copolymer is PS–PMMA is such a system. The diblock has been shown to organize at the interface so that the PS from the diblock is in the PPO and the PMMA from the diblock is in the PMMA.[20] The toughness of the joint is a function of the number of diblock molecules per unit area at the interface independent of their molecular weight (as long as it is high enough to entangle),[26] and fracture of the interface causes the diblock molecules to break in the middle. The density of entangled strands at the interface must therefore just be the interfacial density of diblock molecules. Figure 3 shows the dependence of the toughness of the interface on the diblock density Σ in the form of a log–log plot. The data show a relationship of the form

$$G \simeq \Sigma^{1.9\pm0.2}$$

in complete agreement with the model presented here.

Crack Propagation within a Preexisting Craze

The main aim of this work has been to model the crack propagation process, and so it has been assumed that the crack and craze propagate together. However, this model may also apply to a portion of the crack initiation process in crazing materials. In such materials cracks normally initiate at the craze–bulk interface in a large preexisting craze. Crack initiation is normally caused by an impurity in the material. After initiation the crack must grow within the craze, and it is reasonable to assume that the stress criteria discussed above must control its growth. Further discussion of this point is beyond the scope of this paper.

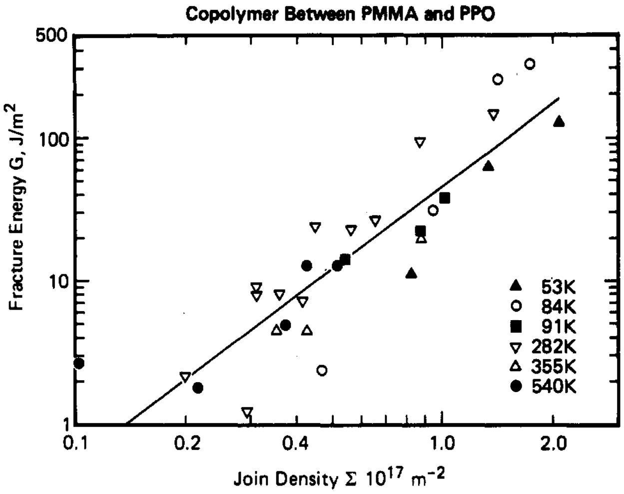

Figure 3. Variation of the toughness of a joint between PS and PPO with the areal density of PS-PMMA diblock molecules at the interface. The different symbols correspond to diblock copolymers of different molecular weights.

Conclusions

The main aim of this work has been to derive a model for the failure of glassy polymers in the crazing regime. The most significant departure from previous work has been the realization that the cross-tie fibrils, which are known to exist between primary fibrils in all crazes, can have a profound effect on the failure mechanics of a craze. A very simple model of crack tip stress amplification caused by the cross-ties works well in the prediction of the fracture toughness of a bulk, high molecular weight, glassy polymer in terms of the breaking force of a single molecule. The variation of the toughness of interfaces between incompatible polymers with amount of block copolymer present can also be derived from the model.

Acknowledgment. I acknowledge valuable discussions with Professors H. H. Kausch, E. J. Kramer, and A. S. Argon. In addition, the manuscript has been much improved by comments from Professors Kramer, Argon, and C.-Y. Hui.

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