

Influence of molecular weight on the fracture of poly(methyl methacrylate) (PMMA)

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A model is proposed to explain the dependence of fracture parameters on the molecular weight of glassy polymers. The model assumes that the fracture event occurs in two stages; the first involves the orientation of polymer chain segments between entanglement points and the second, the fracture itself. A value has been calculated, ($\sim 0.6 \text{ J m}^{-2}$), for the fracture surface energy corresponding to the lower critical molecular weight between entanglements, $M = M_e$. Allowing for the simplifying assumptions made in its derivation, this value is in good agreement with that found experimentally. It is proposed that, after the chain segments between entanglements crossing a plane have been fully extended, two possible mechanisms are involved; chain 'pull-out' up to a maximum governed by the time scale of the local fracture event, or chain scission. Using the concept of a reptating chain it is proposed that above $M \sim 2M_e$ there is a relationship between the fracture energy (γ) and the molecular weight of the form $\gamma \propto M^2$ up to a critical value of M , above which γ is constant. It has been shown that there is some agreement with experimental relationships determined independently.

Keywords Reptation; fracture energy; influence of molecular weight; entanglements; crazing in glassy polymers

INTRODUCTION

The physical process of crack propagation involves the creation of new surfaces and one problem has always been the rationalization of this macroscopic phenomenon using arguments based on the molecular structure of plastic materials. It is observed experimentally that parameters related to fracture resistance of particular plastic materials are influenced by the molecular weight¹⁻⁷.

The crux of the problem lies in the fact that the measured strength of these materials is very much higher than values calculated from the molecular structure in terms of rupture of all chains crossing an area of a plane perpendicular to the applied stress⁸.

For a chemical bond to fail by homolytic scission, due to an externally applied stress, that bond must first be subjected to a critical stress. In the case of brittle, inorganic glasses the bonds quickly attain this critical stress, since these materials exist primarily as single macromolecules and little evidence of plastic deformation is found as a result of their fracture. Consequently, in these glasses it is found that the experimental and calculated values for the fracture energy are in good agreement⁸.

The molecular structure of thermoplastic materials, however, is completely different. They are composed of separate, chain-like molecular entities which at temperatures in excess of their glass transition temperature (T_g) or at high tensile stresses, are mobile, either due to chain slippage or rotation about their main chain bonds. In their lowest energy state within an amorphous phase the molecules have been shown to exist in the form of random coils⁹ and the initial effect of the application of an external tensile stress is to elongate these coils. It is not until regions of the chains reach their ultimate elongation that the bonds are subjected to

sufficient stress for failure to occur. Failure may take the form of chain scission in which only one bond per chain needs to fail to relieve the stress on the remaining chain segments or alternatively the chains may 'pull-out' from the new surface as it is formed, rather than undergo scission.

In the case of non-crystalline polymeric materials, using the three processes outlined above, it is possible to explain the observed discrepancy between experimental and calculated values of fracture energy in terms of the recoverable work done in orienting portions of the chains to the point at which failure may occur and the plastic work done in removing chains from the fracture surface.

Effect of entanglements

One current model¹⁰ describing bulk polymers proposes that the polymer chains form physical crosslinks at regular intervals along their length and that the strength of amorphous polymers is related to the long range interconnectiveness of these entanglement points¹¹. A process described by Rehage and Borchard¹², which accounts for the formation of these crosslink points, assumes that certain configurations of the polymer chain are frozen-in during cooling, the freezing-in being ascribed to the interaction of substituents on neighbouring molecules to produce potential barriers to chain mobility. Not all substituents are involved in the formation of entanglement points since the configurations of the polymer chains will not permit suitable alignment. Below T_g the crosslink density is so large that any regrouping of substituents is effectively prevented. In PMMA it is the high electron density associated with the ester groups which generate the potential barriers.

Although it has been suggested¹⁰ that the entanglement point exists in a knot-like form with the molecular chain

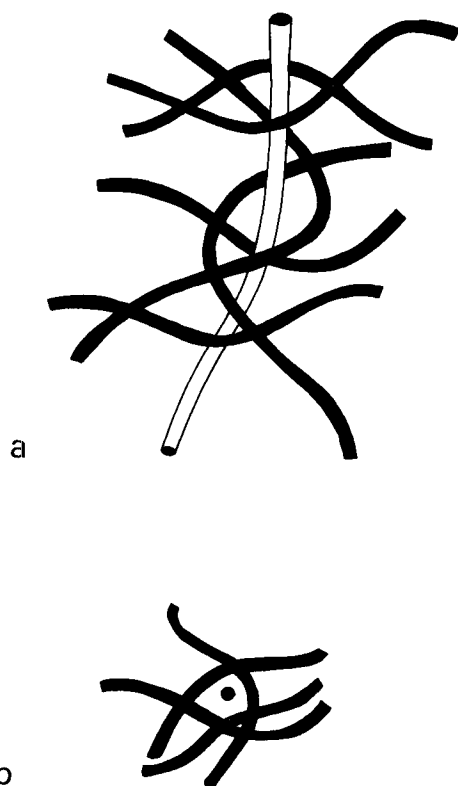


Figure 1 Idealized representation of a chain in a three dimensional network. (a) Side view showing the network, (b) plan view showing the 'tube'

folding back on itself binding one molecule to another, excessive coiling of the chain tends to bring about interference between one of the side groups and its second neighbouring substituents on either side¹³. This interference severely limits the variety of chain configurations for molecules such as PMMA having two bulky side groups per repeat unit. (In polyisobutylene for example the preferred orientation, locally, approximates to a spiral¹³). Additionally, a value quoted for the critical molecular weight for entanglement of PMMA, $M_c = 2M_e = 27\,500$,¹⁴ where M_e is the molecular weight of a chain segment between entanglement points. Since the molecular weight of each monomer unit is 100 and the length of the monomer unit is 2.11 \AA ¹⁵ this leads to a contour chain length between entanglement points of 290 \AA . From Vincent's data¹⁵ for the molecular cross sectional area of PMMA a value for the molecular diameter of 9.2 \AA is obtained, giving a value for the aspect ratio of the chain between entanglement points of about 30:1. It must therefore be assumed that in the case of PMMA, at least, the minimum radius of curvature of the polymer chain in the vicinity of the entanglement is greater than that which would permit the formation of a knot. The fact that chains are held, at least temporarily, in a three dimensional network is not in doubt since it has been shown that, for low strains, deformation of the chain segments between entanglement points is elastic and fully recoverable to the stage where the entanglement experiences an applied stress at which point it dissolves¹⁴.

Based on the above discussion, a model of a chain in a three dimensional network may be constructed as in Figure 1 where the neighbouring chains create a tube around the molecule preventing any lateral movement,

and the interactions of substituents along the chain inhibit its longitudinal mobility.

Thermodynamics of chain segment extension

If, in a high molecular weight material, i.e. $M > 2M_e$, a stress concentration leads to the propagation of a crack in a plane of the specimen, the initial effect is to extend the chain segments crossing the plane, since this is the transition requiring the least energy.

Using the simplifying assumption of Gaussian chain statistics, it may be shown from thermodynamic arguments¹⁶ that the work done on a system in a reversible, isothermal change is equal to the Helmholtz free energy:

$$dW = dA \quad (1)$$

where

$$dA = dU - TdS \quad (2)$$

U is the internal energy of the system, T is the absolute temperature and S the entropy.

The work done in reversibly moving the ends of a segment from a distance r to $(r + dr)$ is dW , therefore the force on the chain segment ends:

$$f = \frac{dW}{dr} = \frac{dA}{dr} = \frac{dU}{dr} - \frac{TdS}{dr}$$

It has been shown that the volume change of a segment during elongation is negligible and that at constant volume the internal energy contribution to the force approximates to zero^{13,16} so that:

$$f = - \frac{TdS}{dr} \quad (3)$$

Using a statistical mechanical approach it may be shown¹⁶ that the entropy of a polymeric system:

$$S = \text{constant} - k b^2 r^2 \quad (4)$$

where k is Boltzmann's constant

r is the end to end distance of the polymer segment

$$b^2 = \frac{3}{2n_e l^2}$$

n_e and l being the number and length, respectively, of the constituent bonds of the segment.

Differentiation of equation (4) with respect to r and substitution in equation (3) gives:

$$f = \frac{3kT}{n_e l^2} \cdot r \quad (5)$$

The work done in elastically extending the chain segment between entanglements prior to their dissolution:

$$W = \int_{r_1}^{r_2} f dr$$

so that:

$$W = \int_{r_1}^{r_2} \frac{3kT}{n_e l^2} \cdot r dr \quad (6)$$

where $r_1 = (2n_e)^{1/2} l$ = the root mean squared end to end distance of a chain segment containing n_e bonds, and

$r_2 = n_e l \sin \frac{\phi}{2}$ = the fully extended length of the same chain segment, ϕ being the bond angle.

Integration of equation (6) yields:

$$W = \frac{3kT}{n_e l^2} \left[\frac{\left(n_e l \sin \frac{\phi}{2} \right)^2}{2} - \frac{((2n_e)^2 l)^2}{2} \right]$$

so that

$$W = 3kT \left[\frac{n_e \sin^2 \frac{\phi}{2}}{2} - 1 \right] \quad (7)$$

for large values of n_e ,

$$W = 3kT \cdot \frac{n_e \sin^2 \frac{\phi}{2}}{2} \quad (7a)$$

Craze formation

Once the applied stress has caused the full extension of all the chain segments between entanglements lying in the plane, an additional mechanism must be proposed to describe the manner in which the material must now fail. Two mechanisms are feasible, namely chain scission or 'pull-out' of the chains from the new surface as it is formed. The dominant process is governed by either the molecular weight of the chain in question or the time scale of the local fracture event, since it has been demonstrated¹⁴ from viscoelastic data of well characterized polymers, that properties which depend principally on the longest relaxation times of the system vary systematically with molecular weight and molecular weight distribution and that these relaxation times are comparable with the experimental times of the deformation process.

Initially it may be expected that polymer chains in the region of a crack tip will deform plastically and it is now well established that in PMMA, along with other glassy polymers, a crack is preceded by a craze¹⁷ and that the craze opens without weakening by a mechanism in which fresh material is drawn into it from the new surface; the stress across the extended craze being just sufficient to permit this drawing process to occur¹⁸. These same authors suggest that the mechanism of craze fracture is complex and time dependent, involving large amounts of viscous energy. It has also been reported⁵ that a narrow craze may form at the crack tip even in very low molecular weight polystyrene, $M \sim M_e$.

The material drawn into the craze forms fibrils which have been examined experimentally using transmission electron microscopy^{17,19}. These fibrils span the thickness of the craze giving it its load bearing properties. However, when a strain of about 3% was applied stepwise to a high molecular weight polystyrene sample it was found that many of the crazes fractured²⁰ presumably because surface drawing could not occur sufficiently rapidly to permit relaxation of the stresses within the craze.

It may be envisaged, therefore, that at a given deformation rate, shorter molecules, having fewer entanglement points along their length, will be drawn into the craze more easily than longer ones. It would also be reasonable to suggest that, at a given extension rate there

will be a critical chain length, above which the time required for the chain to completely disentangle itself and be removed entirely into the craze will be greater than the time available in the fracture event.

In the present discussion a solid polymer is being considered at temperatures below its T_g , i.e. at temperatures that would normally preclude chain mobility. However, it has been suggested^{21,22} that, by increasing the free volume associated with the polymer chain, the effect of an applied tensile stress, or its associated strain, is to reduce the glass transition temperature and increase the mobility of the molecular segments until at yield the T_g is reduced to the test temperature.

It is certainly true that an increase in hydrostatic pressure decreases the chain mobility²³. Alternatively, during crack propagation, local heating occurs at the crack tip²⁴ which would be sufficient to raise the temperature in this region above T_g , enabling disentanglement to occur. Whatever the cause, there is ample evidence available to suggest that plastic deformation at the crack tip is always present in the fracture of polymers. It follows, therefore, that in this region the problem is analogous to a polymer melt or at least to a rubber-like network of physical crosslinks and as such, the concept of a reptating molecule²⁵ may be applied.

Using this concept a value of 3 has been obtained for the exponent of molecular weight²⁶, in good agreement with that found experimentally¹⁴ for the relationship between melt viscosity, relaxation time and molecular weight of the form:

$$\eta \sim \lambda \sim N^{3.3-3.4}$$

where N is the number of repeat units per chain, or the degree of polymerization, and is used as an alternative expression to molecular weight since it is a general term and is independent of the type of repeat unit.

Reptation of a single chain

The term reptation refers to a chain travelling in a snake-like fashion through a 'tube' created by the presence of neighbouring chains in a three dimensional network²⁶, and is concerned with the migration of complete chains through the bulk of the sample.

In the present case, because of the nature of the fracture process, we are concerned with portions of chains embedded in the surface created either side of the developing craze. The stress field acts to split the tube (see *Figure 2*). For the crack to propagate, the chain ends embedded either side of the advancing craze must be removed from one or other portion of the broken tube within the time available in the fracture event (*Figure 3*). The chain must pull out from one surface only; the one containing the shortest length.

The velocity, v , of a polymer chain moving within its tube of length, l , is related to its mobility, μ^{-1} , which is dependent on l ,

$$v = f(l) \mu^{-1}(l) \quad (8)$$

where $f(l)$ is the force acting on the chain in the direction of the tube and is also a function of the tube length. The inverse of the mobility is the molecular friction coefficient, μ .

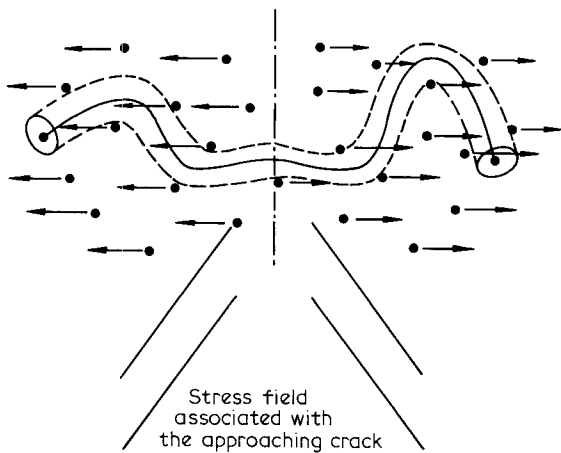


Figure 2 Schematic representation of chain 'pull-out' from its tube

The frictional coefficient is directly proportional to the tube length so that:

$$\mu(l) = \mu_0 l \quad (9)$$

where μ_0 may be regarded as either the frictional coefficient per length of repeat unit or per length of segment between entanglement points since it is this quantity which reflects the influence of entanglements¹⁰. μ_0 has the dimensions of viscosity.

Combining equations (8) and (9) we have:

$$f(l) = \mu_0 v l \quad (10)$$

i.e. at constant crack opening velocity, the force on the chain is proportional to the length of the tube remaining occupied.

The work done in totally removing one chain from the surface:

$$\gamma_0 = \int_{l=0}^{l=L} f(l) dl \quad (11)$$

where L is the total length of the tube vacated, so that at constant v :

$$\gamma_0 = \int_{l=0}^{l=L} \mu_0 v l dl$$

i.e.

$$\gamma_0 = \frac{\mu_0 v}{2} L^2 \quad (12)$$

The number of chains crossing unit area of plane, n , is a function of the molecular cross sectional area only¹⁵ and is independent of the chain length, hence the fracture energy per unit area of crack:

$$\gamma = \gamma_0 n$$

therefore

$$\gamma = \frac{\mu_0 v n}{2} L^2 \quad (13)$$

Since the length of a polymer chain and its associated tube is directly proportional to its degree of polymerization it follows that:

$$\gamma \propto N^2 \quad (14)$$

DISCUSSION

For molecular weights greater than $2M_e$, the fracture energy should be a function of (molecular weight)² up to a maximum value of M , above which it will be constant, since at this point there is insufficient time available in the local fracture process for the chain to completely vacate its tube and chain scission becomes the sole mechanism for failure.

At the craze tip, immediately prior to the dissolution of entanglements, the maximum extension ratio of the chain segments between the entanglement points:

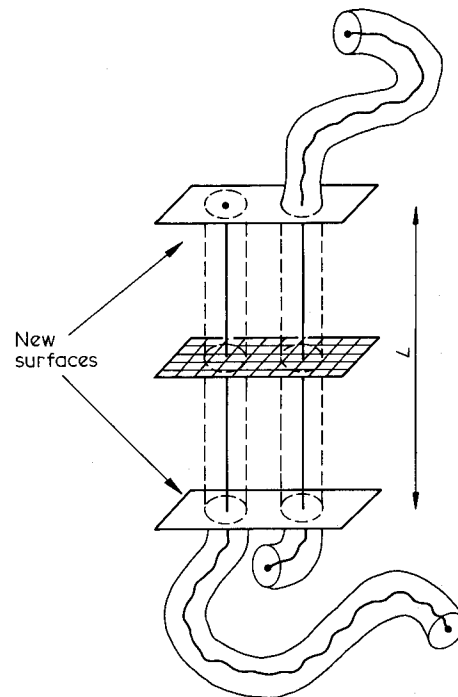


Figure 3 Schematic representation of the formation of new surfaces

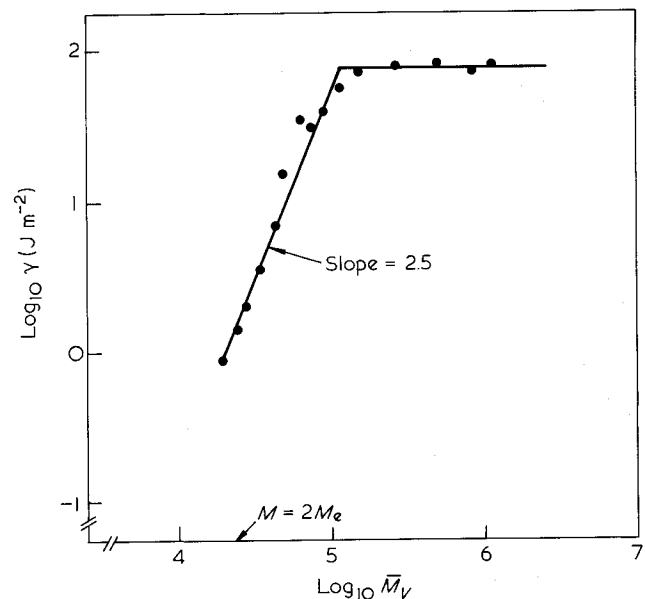


Figure 4 Log fracture surface energy versus log molecular weight of PMMA. Cleavage bar test (from ref. 4)

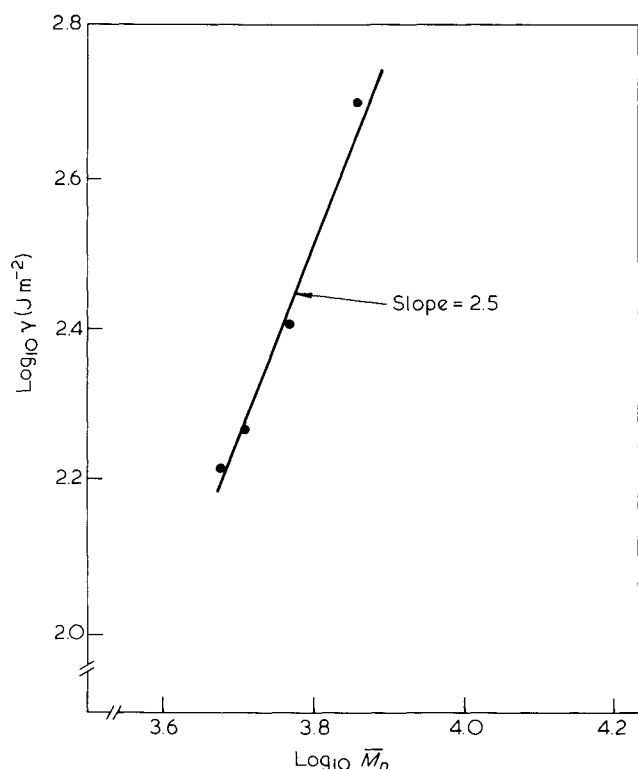


Figure 5 Log fracture surface energy, measured in plane strain, versus log molecular weight of polycarbonate (from ref. 7)

$$\epsilon_{\max} = \frac{r_2}{r_1} \quad (15)$$

i.e.,

$$\epsilon_{\max} = \left(\frac{n_e}{2}\right)^{\frac{1}{2}} \sin \frac{\phi}{2} \quad (15a)$$

For PMMA, where the molecular weight between entanglement points, $M_e = \frac{27500}{2}$, the molecular weight of each monomer unit = 100 and each monomer unit contributes two bonds to the chain, the number of bonds, $n_e = 275$. Taking the bond angle, ϕ , as the tetrahedral angle, 109.5° , we arrive at a value for the maximum possible extension ratio:

$$\epsilon_{\max} = 9.5$$

However, the same arguments apply for the total extension of the chains as were used for excessive folding, since the planar zig-zag configuration of the fully extended chain is unable to accommodate the side groups on alternate carbon atoms. The exact fraction of the total contour length of the chain that is possible is difficult to compute even from scale models, but an approximate value for PMMA may be obtained using the crystallographic data tabulated by Vincent¹⁵, which suggests a value of the extended length of the monomer unit of 2.11 Å, which is ~83% of the theoretical value calculated for a planar zig-zag configuration, giving a more realistic value of:

$$\epsilon_{\max} = 0.83 \times 9.5 = 7.8$$

which is of the order of the maximum extension ratio at the craze tip reported by Kramer⁴ for polystyrene.

Solving equation (7a) for PMMA, where n_e is again 275 and $\frac{\sin^2 \frac{\phi}{2}}{2} = \frac{1}{3}$, and allowing for the fact that the chain may only reach 83% of its contour length, we may calculate the work done extending each chain segment between entanglements at $T = 293$ K to be:

$$W_e = kT \times (0.83)^2 \times 275$$

i.e.

$$W_e = 0.77 \times 10^{-18} \text{ J per segment}$$

From Vincent's data¹⁵, 1.5×10^{18} segments cross a plane of area 1 m^2 , therefore the work done extending all segments in a plane:

$$W = 1.18 \text{ J m}^{-2}$$

Since the crack generate two surfaces, this corresponds to a fracture surface energy of $\frac{W}{2} = 0.59 \text{ J m}^{-2}$ which, allowing for the simplifying assumptions made, is in good agreement with the experimental value ($0.45 \pm 0.25 \text{ J m}^{-2}$) obtained for the minimum surface energy by Kuzy and Turner²⁷, (a value of 0.4 J m^{-2} was also obtained for polystyrene, $M \sim M_e$ by Robertson²⁸). These values may be interpreted as the energy required to elongate these chains and, since there are no entanglement points along the chain, they behave as a viscous liquid and fail by decohesion. Below this critical molecular weight Kuzy and Turner assume the fracture energy to be independent of molecular weight, whereas Kramer⁵ shows that for polystyrene below $M \sim M_e$ the fracture energy is proportional to $M^{\frac{1}{2}}$. The present analysis predicts that below this value M_e the fracture energy should be linearly proportional to the molecular weight. Experimental difficulties, due to the extreme brittleness of PMMA with $M < 2M_e$, have so far prevented satisfactory investigation in this region.

In the case of higher molecular weight samples, i.e. $M > 2M_e$, various workers have determined the dependence of fracture energy on molecular weight, but by far the most comprehensive study is that of Kuzy and coworkers^{3,4,27}, in which γ was determined from both cleavage bar and single edge notched experiments on PMMA samples having molecular weights ranging from 2×10^4 to 1.2×10^6 . (The lower value being approximately equal to the critical molecular weight for entanglements, $2M_e$).

Results from the Kuzy and Katz study⁴ are replotted in Figure 4 and it is found that above $2M_e$ a slope of about 2.5 is obtained for a plot of log fracture energy vs. log molecular weight; very close to that predicted. A similar relationship between the fracture surface energy and molecular weight is found in the results of Pitman and Ward⁷ for polycarbonate measured in plane strain. These results are represented in Figure 5, and again a slope of about 2.5 is obtained. The plane strain condition minimizes the contribution of gross deformation at the edges of the specimen due to plastic flow.

The upper critical molecular weight for PMMA is found to be approximately 1×10^5 and microscopic analysis of the fracture surfaces has indicated that a change in fracture mechanism may be occurring at about this value²⁹. Above this molecular weight the size of the mirror region on the fracture surface of a specimen broken

in three point bending is found to be constant and to be surrounded by characteristic parabolas which increase in size and decrease in number as the molecular weight is increased. Below $M = 1 \times 10^5$ the mirror region is found to decrease in size with decreasing molecular weight with no evidence of parabolas. Similar results have been reported by Kuzy and Turner³⁰, with a critical molecular weight again occurring at 1×10^5 for PMMA. The decrease in size of the mirror region below the upper critical molecular weight could imply that the value of the critical crack opening displacement (COD) is also decreasing with molecular weight. However, the fully extended length of a PMMA chain of molecular weight 1×10^5 is about a factor of 3–4 smaller than the experimentally measured value of the COD^{27,30}. It seems reasonable to assume that the substituents on neighbouring chains also interact with each other during the pull-out process causing the formation of cohesive bundles of chains which span the craze and ultimately fail along its centre line. This proposal is borne out to some extent by experiment¹⁷ since the fibrils spanning the craze are found to have a diameter of ~ 60 Å which, assuming a close packing arrangement in a plane perpendicular to the fibril length, corresponds to about 25 chains and there is a region of lower density running along the middle of the craze, the mid-rib, where the fibrils have failed by decohesion.

CONCLUSION

By assuming that the fracture of a polymeric material occurs by a combination of three possible mechanisms, i.e., chain segment elongation up to the point where the entanglements experience a stress and begin to dissolve, followed by chain pull-out within the time-scale of the local fracture event. Then if the chain may not be completely removed from one or other of the new surfaces in this time, chain scission becomes the sole remaining mechanism by which the chain will fail and permit the passage of the crack. The value of $\sim 0.6 \text{ J m}^{-2}$ calculated for the fracture surface energy, γ , of PMMA at the critical molecular weight for entanglements, $M = M_e$, is in good agreement with that found experimentally by other workers. Above this lower critical value there is a relationship between γ and the molecular weight of the form $\gamma \propto M^2$ up to a second critical molecular weight, above which γ is constant. This is presumably because, after the maximum amount of pull-out has occurred in the time available, rupture of main chain bonds is the only remaining mode of failure and each bond of the chain has an identical dissociation energy.

The value of 2 for the exponent of the molecular weight was derived on the assumption of a monodispersed sample, i.e., one having a very narrow molecular weight distribution. However, gel permeation chromatography (g.p.c.) analysis shows that this is not the case and that in all instances the molecular weight distribution is somewhat broad. It has been suggested⁷ that the longer chains in the distribution have a greater influence on the material toughness than the shorter ones, assuming this to be the case it would account for the higher value, 2.5, for the exponent determined experimentally.

The analysis described in the present work suggests that the viscous energy necessary to overcome the frictional drag of the entanglements during the formation of a craze is the major contributing factor to the overall toughness of

glassy polymers. The molecular friction coefficient, μ_0 , in equation (10) must in some way be related to the free volume associated with the polymer chain, so that any influence on this parameter, such as environmental effects, will also affect the force required to remove the chain from its tube. Kramer *et al.*^{31,32} have described the plasticizing effects that aggressive environments have on the stress necessary for craze growth. It is stated that the effect of the environment cannot be due to a change in the chain entanglement molecular weight, but must result rather from an easier slippage of molecular entanglements in the drawing glassy fibrils³¹. It was also demonstrated, in the case of polystyrene, that a decrease in the glass transition temperature in an atmosphere of carbon dioxide was accompanied by an increase in specimen volume. These results suggest that the effect of the aggressive environment is to lower the frictional coefficient so as to permit a less inhibited pull-out of chains from the craze surface and to lessen the interaction of chains within the craze, resulting in a decrease in the craze stress.

The model for craze formation and crack propagation described here is analogous to that proposed by Wool and O'Connor^{33,34} for crack healing in polymers. They use the concept of a self diffusing chain which migrates across the interface of damaged surfaces to penetrate the bulk material either side of the damaged region.

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Influence of MW on fracture of PMMA: P. Prentice

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