Crazing by disentanglement: non-diffusive reptation

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A molecular model of disentanglement below the glass transition temperature is applied to the crazing behaviour of polymers, such as polyethersulphone and polycarbonate, in which the molecules exhibit non-diffusive reptation. For the case when chain scission is not important, molecular weight dependences of the crazing stress, flow stress and surface energy are calculated and compared with experimental results. The model provides an explanation of the observed absence of any effect of ageing on crazing, in contrast to its effect on shear deformation.

(Keywords: craze; entanglements; reptation; surface energy; disentanglement)

INTRODUCTION

The dynamics of polymer molecules in concentrated solutions or melts are constrained by their topological interactions, or entanglements. This has long been regarded as the molecular basis of viscoelasticity[1]. A quantitative model which regards each chain as constrained by an effective 'tube' along its own contour was developed into a theory for monodisperse linear melts by Doi and Edwards[2]. The one-dimensional dynamics of polymers along their tubes is termed 'reptation'. Subsequent work has sought to extend our understanding of the liquid polymeric state, and applications to phenomenona below the glass transition temperature have been made by Prentice[3] and Evans[4]. Recently Berger and Kramer[5] suggested that reptation may be important in crazing.

Crazing describes a particular mode of failure of a polymeric glass under tension. Experiments are commonly performed on thin films of polymer, which are deformed macroscopically so that microscopic regions of large deformation nucleate. These microscopic regions may themselves be deformed uniformly or contain detailed structure. Local regions of uniform deformation are commonly termed 'shear deformation zones', but under certain circumstances highly non-uniform deformation is observed in the form of crazes. The microscopic structure of a craze may be described as a crack whose faces are connected by many surface-drawn filaments. Many polymers exhibit this behaviour over some range of temperatures and strain rates: polystyrene (PS), polymethylmethacrylate (PMMA) and polycarbonate (PC) are common examples. The microscopic behaviour of crazes and their contrasts with deformation zones has been reviewed thoroughly by Kramer[6].

Recent experiments have highlighted the importance of molecular structure and entanglements in these deformation processes. First it was noted that there is a critical molecular weight, specific to each polymer, below which stable crazes do not form. Similar critical behaviour appears in the viscoelasticity of the melts, where we find a critical molecular weight above which the dynamic response is characteristic of polymers which are entangled with each other and below which they appear topologically unconstrained[2]. These two critical molecular weights are always of the same order[7].

Second, to generate the void–fibril structure of a craze, Kramer[6] has pointed out that there is a geometrically necessary entanglement loss which is not necessary for the production of shear deformation zones. This loss can be accomplished either by chain scission or disentanglement. One or other of the two processes may dominate under different conditions of shear rate and temperature. Thus, samples under identical strains may preferentially exhibit shear deformation in one range of temperatures and crazing in another. The corresponding transition temperature depends on molecular weight[8–10].

Third, the final local extension of craze fibrils of PS formed at high temperatures depends strongly on molecular weight[5]. Higher molecular weight samples have much smaller final extension ratios, suggesting that less disentanglement has occurred than is possible with shorter chains.

Fourth, at lower temperatures PS crazes lose the molecular weight dependence of their properties[10]. If this is because disentanglment is suppressed by virtue of much reduced molecular mobility then the fibrillation must occur by chain scission instead, a process clearly independent of molecular weight. In this case local stresses are indeed consistent with the need to break main-chain covalent bonds. The transition from 'scission-dominated crazing' to 'disentanglement-dominated crazing' is a smooth one[6].

Fifth, in the scission-dominated regime the final deformation of craze fibrils is constrained by the entanglement density of the polymer glass[11]. Local deformations cannot stretch chain segments between entanglements beyond their maximum extent. Experiments on different chemistries and using low molecular weight fractions to dilute the entanglement network confirm this effect.

Sixth, in experiments measuring the propagation velocity of the craze/bulk interface, v_i, in polystyrene, a

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molecular weight dependence well described by a power law is found:

$$v_i \approx M^{-2.5} \tag{1}$$

where M is the molecular weight[5]. These experiments are carried out at a fixed final fibril extension.

Berger and Kramer have suggested that local stresses in the vicinity of the craze may mobilize molecules within the glass to undergo reptation as in the melt, and interpreted equation (1) in this light. However, the magnitudes of the mobilities required are enormous if the diffusive dynamics of reptation are responsible for crazing by disentanglement[5]. They correspond to effective temperatures many tens of degrees above the glass transition temperature. This approach also requires the approaching craze front to 'mobilize' an entire molecule simultaneously to allow it to diffuse. Experiments using a gold deposition technique to measure the extent of the 'process zone' behind the craze (the region of plastic flow), however, find that it is typically much less than a radius of gyration[12]. This seems to rule out a simple picture of mobilized diffusive reptation. We examine here the consequences of a slightly different model, in which molecular reptation is forced or non-diffusive, concentrating on the case of disentanglement-dominated crazing.

THE MODEL

Mechanism and mobility

A schematic picture of the craze/polymer interface is shown in *Figure 1*. Polystyrene of molecular weight $M \sim 500\,000$ crazes with a typical fibril spacing of 10–20 nm, whereas the radius of gyration of a molecule is of the order of 50 nm. The number of different molecules within a volume spanned by a radius of gyration is large, growing as $M^{1/2}$, and these must be distributed among several fibrils as the craze front advances. If chain scission is unimportant, then the fibrils must form and grow by chains disentangling along their own contours.

The idealization of this process is that a single chain is drawn out of the bulk polymer glass by a tension applied to a random segment of its contour, which might be anchored in a growing fibril. We require an expression for the mobility of one of these trapped polymers. Of course there is no diffusion below the glass transition, so we cannot use a simple fluctiation–dissipation argument. Instead we have to assume that the cooperative barriers to centre-of-mass motion may be overcome by the highly localized stress applied along the chain contour. Inside the polymer glass, segments are located in a distribution of local environments which may be modelled as energy wells of depths $E(s)$ (s here is a monomer label or contour variable) and width b (a monomeric length parameter). In this case individual segment mobilities are proportional to $\exp\{-E(s)/kT\}$. The inverse mobilities of all the segments add so the total mobility of a single chain μ will be given by

$$\mu^{-1} \approx \mu_0^{-1} \int_0^L \exp\{E(s)/kT\}\,\mathrm{d}s/b \tag{2}$$

where the effective friction constants of monomers along the chain add. μ_0 is a high temperature monomeric mobility. The simple Arrhenius form is more appropriate than the Vogel–Fulcher relation because we are not concerned with the cooperative dynamics of bulk viscosity[13], but with highly localized response. From equation (2) the mobility is clearly inversely proportional to molecular weight, which is all that is needed for the following section. However, as will be shown in the final section, the wide distribution of monomeric mobilities that appears below T_g in contrast to the melt, will dramatically affect the ageing behaviour.

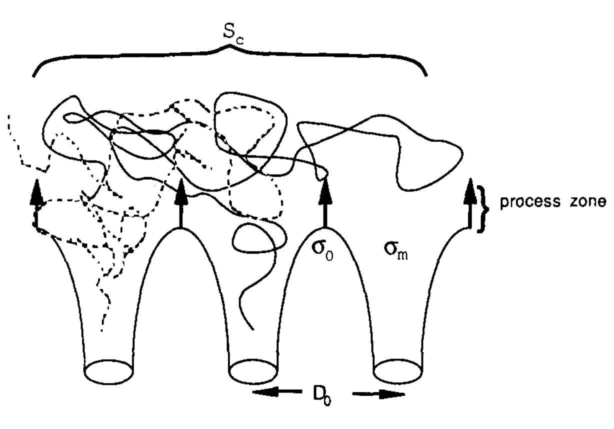

Figure 1 Idealized craze/bulk interface. The bases of three fibrils are shown and typical contours of two molecules, indicated by a solid and broken curve. Arrows indicate the propagation of the craze into the bulk. σ_0 is the stress midway between fibrils, σ_m is the stress at their bases. S_c is the bulk stress preceding the craze front. The typical extent of the process zone is shown

Constitutive behaviour under scission and disentanglement

The problem before us requires answers to two questions: first, what is the constitutive behaviour of a disentangling polymeric glass, i.e. its stress–strain history relationship? Second, what stresses are required to create the new surfaces and fibrils in the particular geometry of a craze? The ultimate goal of a molecular model such as that outlined above must be to answer both, but notable progress has been made in the case of scission-dominated crazing by concentrating on the second, while assuming a non-Newtonian flow law for the constitutive behaviour:

$$\sigma = \sigma_{yc}(T)[\dot{\varepsilon}/\dot{\varepsilon}_c]^{1/n} \tag{3}$$

Though not derived from a molecular model, this is consistent with the picture described above: to maintain a stress requires a deformation rate (below T_g any configuration is near to a local energy minimum into which the system rapidly relaxes). Also we expect a 'yielding' behaviour, which equation (3) models if $n \gg 1$. Under this interpretation $\sigma_{yc}(T)$ is the (temperature dependent) critical local stress for shear deformation and $\dot{\varepsilon}_c$ is the local strain rate at this critical stress.

The same considerations may justify such an approximate constitutive equation in the case of disentanglement-dominated crazing. We expect a critical local stress $\sigma_{yd}(T)$, which will be temperature dependent, to initiate disentanglement. The difference is that now chains do not break, so that molecular weight will enter the constitutive equation. Because disentanglement stresses are transmitted along chains, each segment requiring an equal stress to mobilize it on average, we can take σ_{yd} to be proportional to molecular weight so that the constitutive equation becomes

$$\sigma = \sigma_{yd0}(T)(M/M_e)(\dot{\varepsilon}/\dot{\varepsilon}_c)^{1/n} \tag{4}$$

where σ_{yd0} is now the yield stress for molecules of the entanglement molecular weight, M_e, *and* $\dot{\varepsilon}_c$ the critical local deformation rate.

This result needs to be combined with an understanding of the surface energy of the forming fibrils, as first deduced by Paredes and Fischer[14] and developed by Kramer[6]. We briefly summarize here the argument, established for scission-dominated crazes, which relates the bulk (non-local) stress during craze propagation, S_c, to the craze surface energy Γ and the local yield stress for disentanglement σ_{yd}.

The flow of material into the craze fibrils is governed by the stress gradient at their bases. This is approximated to within a geometric factor by a linear interpolation between the stress at the base of the fibrils σ_m, and the stress midway between them where new surface is formed, σ_0 (see *Figure 1*).

$$|\nabla\sigma| \cong \frac{2(\sigma_0-\sigma_m)}{D_0} \tag{5}$$

D_0 is the mean separation between fibrils. Now σ_m is directly proportional to the bulk stress S_c, and σ_0 is dominated by the energy of the new surface at the fibril base:

$$\begin{aligned}\sigma_m &= \beta S_c\\ \sigma_0 &= \frac{\Gamma}{D_0}\end{aligned} \tag{6}$$

The additional assumption is that the fibril spacing corresponding to the maximum possible value of $|\nabla\sigma|$ (fastest craze growth) is observed. Differentiating equation (5) with respect to D_0 gives this observed spacing D_0^*:

$$D_0^* \approx \Gamma/S_c \tag{7}$$

where we have omitted dimensionless prefactors.

Finally, the stress gradient in equation (5) may also be related via the constitutive equation to the local deformation rate

$$|\nabla\sigma| \approx (\sigma_{yc}/h)(\dot{\varepsilon}/\dot{\varepsilon}_c)^{1/n} \tag{8}$$

where h is the width of the 'process zone' where deformtion is significant. Now the bulk crazing stress S_c can be related to the constitutive and surface energy parameters directly:

$$S_c \approx [\sigma_{yc}(T)(\dot{\varepsilon}/\dot{\varepsilon}_c)^{1/n}\Gamma_s]^{1/2} \tag{9}$$

Here Γ_s denotes the surface energy of a scission-dominated craze. If we can discover the appropriate form of the surface energy for a disentanglement-dominated craze, Γ_d, we can write down the form of the crazing stress in this regime:

$$S_c \approx [\sigma_{yd0}(T)(M/M_e)(\dot{\varepsilon}/\dot{\varepsilon}_c)^{1/n}\Gamma_d]^{1/2} \tag{10}$$

Surface energy of a disentanglement craze

The expression for Γ_s was first given by Kramer[15]:

$$\Gamma_s = \gamma + (1/4)d\nu_E U \tag{11}$$

Here γ is the Van der Waals surface energy. The second term is due to chain scission, and counts the number of segments joining entanglements across a unit area of surface. U is the covalent bond energy, ν_E the density of entanglements and d the spatial separation of linked entanglements. Recent experiments on polystyrene by Berger and Kramer[10] confirm the form of equation (11) quantitatively.

When new surfaces form by disentanglement, the second term in equation (11) must be replaced by the energy required to disentangle all chains which cross a unit area of surface. We first calculate the energy required to withdraw a single entangled chain from the glass, following Prentice[3] and Evans[4]. The force along the chain is proportional to the rate of disentanglement ($\approx\dot{\varepsilon}$) and to the fraction of chain still entangled λ. Thus the total energy for disentanglement u_d is

$$u_d \approx \dot{\varepsilon}\mu^{-1}\int_0^1 \lambda d(M\lambda) \approx \dot{\varepsilon}M^2 \tag{12}$$

We note that this contribution to the surface energy is dissipative, and therefore rate dependent. As an aside, it is worth pointing out that the value above is also dependent on chains experiencing a constant contour velocity with respect to their local environments as they disentangle. This is the case in the craze geometry (*Figure 1*). An alternative geometry shown in *Figure 2* would also require the creation of a free surface by disentangling the chains initially crossing it. In this case, however, since a chain typically crosses the surface many times, the contour velocity is amplified along its length via a 'block and tackle' mechanism, and u_d would vary as $\dot{\varepsilon}M^3$ in contrast to the $\dot{\varepsilon}M^2$ relevant to crazing. Such a geometry occurs in 'cleavage bar' and 'single edge notch' experiments. This means that Prentice's calculation[3], equivalent to equation (12) above, is not appropriate to the experiments to which he refers, which are of the latter types.

The total contribution of disentanglement to the surface energy is the product of u_d and the number of different chains crossing a unit area of surface, n_s. This is not independent of molecular weight, as stated by Prentice[3], because of multiple crossings. The scaling relationship may be found from the properties of random walks of radius of gyration R_g and molecular weight M:

$n_s \approx$ (area spanned by chain)$^{-1}$(number of chains at fixed density within volume of one chain)

$$\begin{aligned}&\approx R_g^{-2}(R_g^3/M)\\ &\approx M^{-1}(M^{3/2}/M)\\ &\approx M^{-1/2}\end{aligned} \tag{13}$$

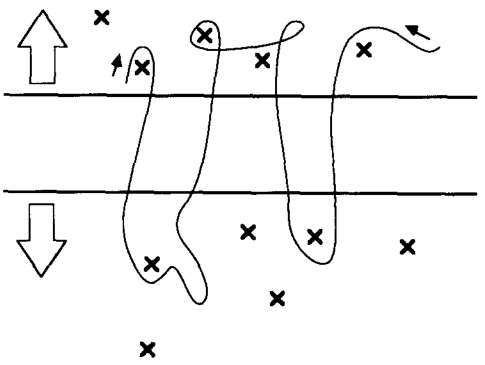

Figure 2 An alternative geometry for surface formation by disentanglement. The motion of the separating surfaces is indicated by the open arrows. The solid arrows show the local contour velocity of the disentangling chain. This increases towards the chain ends

So the total work done by disentanglement is

$$U_d = n_s u_d \approx \dot{\varepsilon} M^2 M^{-1/2} \sim \dot{\varepsilon} M^{3/2} \qquad (14)$$

This is the result of crazing; the analogous result for cleavage bar experiments is a molecular weight dependence of surface energy varying as $M^{2.5}$. This is in exact agreement with the experiments of Kuzy and Katz[16] referred to by Prentice[3].

We now have the expression for Γ_d analogous to equation (11) that we sought:

$$\Gamma_d = \gamma + w(\dot{\varepsilon}/\dot{\varepsilon}_c)(M/M_e)^{3/2} dv_E \qquad (15)$$

where w is the contribution of a single entanglement length to the disentanglement dissipation; w is certainly temperature dependent, but should be bounded above by the covalent bond energy U.

We may evaluate the molecular weight dependence of the bulk crazing stress S_c by using equation (15) in equation (10) to find:

$$S_c \approx \{\sigma_{yd0}(T)(M/M_e)(\dot{\varepsilon}/\dot{\varepsilon}_c)^{1/n} (\gamma + w(\dot{\varepsilon}/\dot{\varepsilon}_c)(M/M_e)^{3/2} dv_E)\}^{1/2} \approx M^{5/4} \qquad (16)$$

when the constant γ term is negligible. This will be the case in polymers of high entanglement density such as polyethersulphone (PES) and PC. Recent measurements of S_c in PES and PC by Plummer and Donald[9] are consistent with this scaling. For PES at a temperature of 390 K, for example, the strain to craze for a polydisperse sample of $M_w = 69\,000$ was 1.66 times that for a sample of $M_w = 47\,000$. The predicted ratio (for monodisperse material as assumed throughout the model described above) is 1.61 (for small γ). At this temperature both samples have identical temperature dependence of the crazing stress, indicating that they are crazing by the same mechanism. For other polymers, PS in particular, the γ term may be more important. In the limit where it dominates we note that we would find $S_c \approx M^{1/2}$ rather than the 5/4 scaling at the opposite limit. Experiments on the molecular weight dependence of the crazing stress in PS at constant deformation rate similar to those on PES and PC referred to above would shed light here.

We also note that this model gives us a guide to the molecular weight dependence of the fibril spacing D_0. Equation (7) together with the results above allows us to eliminate S_c. In the limit of small γ we find

$$D_0 \approx M^{1/4} \qquad (17)$$

and in the (rather unphysical) limit of dominant γ,

$$D_0 \approx \mathrm{M}^{-1/2} \qquad (18)$$

Physically realizable cases must lie somewhere between these two limits, which suggests a rather weak dependence should be observed. This is indeed seen in recent experiments by Berger *et al.*[10] on PS, where v_E is rather lower than in PC or PES.

Propagation velocity of the craze/bulk interface

For both classical reptation and the present case of 'forced' reptation we can define a disengagement time τ_d, the characteristic time for a chain to escape its original entanglements. Forced reptation gives a less universal prediction for τ_d than classical reptation because it is not a Brownian process. One consequence of this is that the interface velocity required to produce a given final fibril deformation, considered as a function of molecular weight by Berger and Kramer[5] is not a universal function of molecular weight, but depends principally on any residual scission in the crazing process. This may be seen as follows.

If F is the down-chain force on an entangled polymer, then the contour velocity is proportional to F/M, and the disengagement time scales as

$$\tau_d \approx M/(F/M) \approx \mathrm{M}^2\mathrm{F} \qquad (19)$$

If the craze front is propagating through the glass at a velocity v_i, then another characteristic time arises: that of the residence time of a single chain in the process zone, τ_{res}. This is the time taken for the craze front to cross a radius of gyration, so

$$\tau_{res} \approx R_g/v_i \approx \mathrm{M}^{1/2}/\mathrm{v_i} \qquad (20)$$

Both the down-chain force F and the interface velocity v_i are proportional to the local deformation rate $\dot{\varepsilon}$. The final extension ratio $\lambda = \mathrm{f}(\tau_d/\tau_{res})$ for some function f, as noted by Berger and Kramer[5]. This means that within the present picture there is no dependence of λ on v_i. The experimental evidence[5] is that there is a weak dependence with a low-rate value of ≈ 7 dropping to ≈ 4 at high deformation rates. The latter value is the case for pure scission, suggesting that increasing amounts of chain scission are responsible for the non-constant λ. Since this is rate dependent, we can see that the presence of scission is entirely responsible for a molecular-weight dependence of interface velocity at fixed λ. Further work, however, is needed before we can make quantitative statements about this regime.

Effect of ageing

Finally we comment on the prediction of this model on the effect of ageing, or annealing, the polymer. The expression for the inverse mobility of the chain below the glass transition equation (2) may be written as an integral over the probability distribution of energies $\phi(E)$:

$$\mu^{-1} \approx \mu_0^{-1} M \int \exp\{-E(s)/kT\}\phi(E)dE \qquad (21)$$

If the well distribution has a lower cut-off, as it must, for the energies are bounded below by the ground state E_0, then it is easy to show that the mobility is governed by this cut-off and not by the average well depth due to the exponential term in equation (21). For example, we can consider a density of states at the 'band edge' which is locally a power law:

$$\phi(E) = H(E - E_0)(E - E_0)^{\alpha} \qquad (22)$$

Here $H(x)$ is the Heaviside step function. Now equation (21) becomes

$$\mu^{-1} \approx \mu_0^{-1} M(kT)^{\alpha+1} \exp\{-E_0/kT\} \int_0^{\infty} e^{-x} x^{-\alpha} dx \qquad (23)$$

Ageing a sample affects the average of the distribution, lowering energies and increasing yield stresses for processes that do not require every monomer to move, such as shear deformation. However, disentanglement can only occur by exciting every monomer out of its local well, and will be dominated by the lowest (rare) energies of local configurations, which are not affected by ageing providing that they approach the lower bound of the distribution of states. For a further discussion of mobility effects of energy distribution in glasses see Vilgis[17]. This qualitative prediction is supported by experiments[9] which show very strong dependence on ageing in the critical stress for shear deformation of PES and PC, but no observable change in the crazing behaviour of the same samples.

CONCLUSIONS

The non-diffusive reptation model of polymer crazing can account for observed molecular weight dependencies of crazing stress, fibril separation and interface velocity when chain scission is not important. When these dependencies are power laws we find that polymers may differ in the scaling exponents depending on the relative importance of Van der Waals surface energy to the disentanglement energy, taking one of two limiting forms.

The absence of any effect of ageing on disentanglement crazing may also be explained if the chain mobility in the glass is dominated by rare low energy local configurations. It would be interesting to explore the possibility of observing these spectroscopically.

Further consideration needs to be given to cases where both scission and disentanglement occur together, as much experimental data lie in a crossover regime.

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