Failure of Elastomeric Polymers Due to Rate Dependent Bond Rupture

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A new cohesive zone model is developed in order to study the mechanisms of adhesive and cohesive failures of soft rubbery materials. The fracture energy is estimated here using a strategy similar to that of Lake and Thomas (LT) by considering the dissipation of stored elastic energy followed by the extension and relaxation of polymer chains. The current model, however, departs from that of LT in that the force needed to break an interfacial bond does not have a fixed value; instead, it depends on the thermal state of the system and the rate at which the force is transmitted to the bond. While the force required to rupture a chain is set by the rules of thermomechanically activated bond dissociation kinetics, extension of a polymer chain is modeled within both the linear and nonlinear models of chain elasticity. Closed form asymptotic solutions are obtained for the dependence of crack propagation speed on the energy release rate, which are valid in two regimes: (I) slow crack velocity or short relaxation time for bond dissociation; (II) fast crack velocity or long relaxation time for bond dissociation. The rate independent and the zero temperature limit of this theory correctly reduces to the fracture model of LT. Detailed comparisons are made with a previous work by Chaudhury et al. which carried out an approximate analysis of the same problem.

1. Introduction

The fact that the resistance to crack propagation in many material systems increases with speed[1−6] suggests that some kind of frictional drag operates at or near the crack tip region. While energy is needed to open a crack against the intermolecular attractive forces, steady state fracture is possible only when the rate of energy supply to a crack is exactly same as the rate of energy dissipation.[7] These ideas, embodying the roles of intermolecular interaction and viscous dissipation in crack growth, were formalized in the celebrated theories of Gent and Schultz[2] as well as those of Andrews and Kinloch.[1] According to these authors, while the primary resistance to crack growth is provided by the intermolecular forces, its role is amplified by the viscoelastic processes occurring at and near the crack tip regions. Prompted by these considerations, Gent et al.[9,10] carried out adhesion and tear experiments with viscoelastic polymers and noted that their fracture energies (defined as the rate of change of strain energy per unit extension of crack area) follow the Williams−Landel−Ferry (WLF) time−temperature superposition principle as do their other rheological properties. One might anticipate that these experiments, if performed at very low velocities, would bypass viscoelastic response in the polymer thereby allowing estimation of the thermodynamic work of adhesion by extrapolation to zero velocity. However, the fracture energies obtained at velocities as low as ∼1 nm/s still show a weak but finite dependence on crack growth rate with its values being orders of magnitude larger than the thermodynamic work of adhesion. While the issue of the fracture energy being larger than the thermodynamic work of adhesion was understood by Gent et al.[9,10] in the light of a theory proposed by Lake and Thomas,[11] its rate dependence at very low velocities (∼1 nm/s) had been ignored.

According to Lake and Thomas, the fracture energies of rubbery solids are always higher than their reversible thermodynamic counterparts as all the bonds in the crack bridging polymer chains need to be excited even though only one bond per chain is broken for a crack to advance. As most of the energy stored in the chain up to the point to bond dissociation is dissipated, the interfacial fracture energy is amplified by the number of bonds per chain. This issue of the amplification of fracture energy by the number of bonds per chain is also relevant to the adhesive situations when a rubbery polymer separates from another solid substrate. There are however additional details that need to be considered in the context of how fast a polymer chain desorbs from a substrate in comparison to the rate of crack propagation.[8] If the polymer chain relaxes very fast, as is the case with van der Waals interactions, no amplification of fracture energy results as the polymer chains suffer negligible extension before disengaging from the surface. Conversely, significant amplification of fracture energy would result when the polymer chain disengages very slowly from the surface. These consid-

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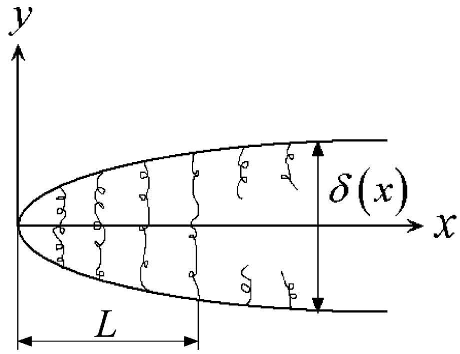

Figure 1. Crack with cohesive zone. The springs bridging the crack faces have a constant stiffness k_s. The stretch of the springs is denoted by $\delta(x)$, where x is the distance from the crack tip. L is the cohesive zone length.

erations were taken into account in a theory proposed by Chaudhury et al.,[7,8] which was inspired by some previous works of Schallamach,[12] Kausch,[13] and Evans and Richie.[14] Since this theory is central to this work, a summary is given below.

Let us consider a crack, the apposing surfaces of which are bridged by polymer chains, that propagates with a steady-state velocity V. As each of the polymer chains is stretched with a force F, the activation energy of dissociation is reduced by $F\lambda$ for any of the bonds in the chain, λ being a characteristic activation length. The stretched polymer chains ahead of the tip of the steadily growing crack fail according to the rate law[8]

$$\frac{D\Sigma_b}{Dt} = -\frac{n\Sigma_b}{\tau_-}\exp\left(\frac{F\lambda}{kT}\right) \tag{1}$$

where Σ_b is the number of load bearing polymer chains per unit area, k is the Boltzmann constant, and T is the absolute temperature. n is the number of monomer units of a polymer chain between cross-links for cohesive failure as any of the bonds can fail. For interfacial fracture, n is equal to unity as the failure is restricted to only one bond at the interface. The relaxation time of bond dissociation τ_- is

$$\tau_- = \frac{h}{kT}\exp\left(\frac{E_a}{kT}\right) \tag{2}$$

where E_a is the activation energy of bond dissociation and h is Planck's constant. According to (1), the number of load-bearing chains per unit area decreases extremely rapidly as the force increases. The region where the chains are stretched and subsequently broken is defined as the cohesive zone. Inside the cohesive zone, the crack separates by an amount δ, which is equal to the stretched length of a polymer chain bridging the crack faces (Figure 1).

The force acting on a chain is assumed to be directly proportional to the opening displacement of the crack, δ, which is a function of the horizontal distance x from the moving crack tip

$$F = k_s\delta \tag{3}$$

By considering that the spring constant k_s to be independent of δ, the net normal traction σ resisting the crack opening is given by the following expression

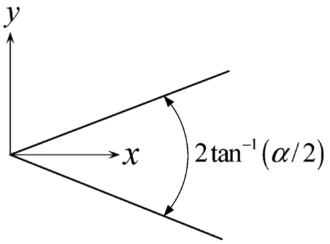

Figure 2. The crack opens up to a wedge with an internal angle 2 $\tan^{-1}(\alpha/2)$.

$$\sigma = \Sigma_b F = \Sigma_b k_s \delta \tag{4}$$

Equation 4 provides an approximate model for the cohesive zone. Since Σ_b decays rapidly away from the tip of the crack, the crack can be modeled as semi-infinite, which is loaded by a remote stress field of the form

$$\sigma(x \rightarrow -\infty) = K_A/(-2\pi x)^{1/2} \tag{5}$$

K_A is the applied stress intensity factor that is related to the applied energy release rate G_A by

$$G_A = K_A^{\,2}/E^* \tag{6}$$

Here, $E^* = E/(1 - \nu^2)$; E and ν being Young's modulus and Poisson's ratio of the elastomer, respectively. For nearly impressible elastomers, $\nu \approx 1/2$ so that $E^* \approx 4E/3$. The above formalism is also applicable to a crack growing at the interface of an elastomer and a rigid substrate, provided that the elastomer is incompressible. In that case, E^* in (6) should be replaced by $2E^*$ since the substrate has no strain energy.

In this theory, the interface has no unique strength other than that provided kinetically by the bridging chains. As the failure of the interface is defined by $\Sigma_b \rightarrow 0$, the cohesive zone is formally infinitely long (although its effective length is actually very small) and occupies the entire crack face.

Several implicit assumptions in the above model are as follows:

1. The spring constant k_s is constant, i.e., independent of the extension of the polymer chain.
2. The crack tip is well-defined, that is, the polymer chains ahead of the moving crack tip can never break.
3. The crack faces open into an infinite planar wedge with an internal angle of 2 $\tan^{-1}(\alpha/2)$, which is assumed to be a constant (see Figure 2). The problem of determining the deformation and stress distribution on the crack face is bypassed by this geometric assumption.[8]

One consequence of this assumption is that α is left as an undetermined constant. Specifically, the work done by the restraining traction per unit crack extension is

$$\int_0^\infty \sigma \, d\delta = \int_0^\infty \Sigma_b k_s \delta \, d\delta \tag{7}$$

It should be noted that (7) is the energy release rate for crack growth only if the normal stress is bounded there. If the normal stress is unbounded at the tip, then there can be an additional contribution to the energy release rate. For an interfacial crack, this additional energy is the same as the work (W_{ad}) needed to create two new surfaces, which for a cohesive crack is twice the surface energy (γ_s) of the material. Typically, the energy release rate for crack growth given by (7) is much larger than W_{ad}. The difficulty of evaluating (7) is that Σ_b is not a function of δ but a function of position. Specifically, (1), combined

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Table 1. Energy Release Rate for Crack Growth Calculated Using Different Models

model	energy release rate for crack growth G: long relaxation time or fast crack growth	energy release rate for crack growth G: short relaxation time or slow crack growth
rate independent (Lake and Thomas[11])	$\frac{\Sigma_o k_{max} E_a{}^2}{2(k_{max}\lambda)^2} + W_{ad}$	
Chaudhury et al.[7,8]	$\frac{\Sigma_o k_s (kT)^2}{2(k_s\lambda)^2}\left(\ln \frac{nkT}{\alpha V\tau_- k_s\lambda}\right)^2 + W_{ad}$	$\frac{\Sigma_o k_s(\alpha V\tau_-)^2}{n^2} + W_{ad}$
rate dependent with linear spring model	$\frac{\Sigma_o k_s (kT)^2}{2(k_s\lambda)^2}\left(\ln \frac{n\pi E^*}{4\Sigma_o k_s \tau_- V}\right)^2 + W_{ad}$	$W_{ad}\left(1 + \frac{16\Sigma_o k_s \tau_- V}{n\pi E^*}\right)$
rate dependent with nonlinear spring model[a]	$\Sigma_o w(0.9L_c) + \frac{\Sigma_o k_{max} L_c{}^2(\Delta_T - 0.9)^2}{2} + 17.1\Sigma_o k_o L_c{}^2(\Delta_T - 0.9) + W_{ad}\Delta_T =$ $0.9 - \frac{k_o}{k_{max}}\left(17.1 + \frac{2A}{3\lambda}\ln\frac{n\pi E^* L_c{}^2}{32G\tau_- V}\right)$	$W_{ad}\left(1 + \frac{16\Sigma_o k_o \tau_- V}{n\pi E^*}\right)$

[a] Note that in the limit of long relaxation time or fast crack growth, the formula for G based on the nonlinear spring model is implicit, that is, G has to be solved numerically.

with (3), can be written as

$$\frac{D\Sigma_b}{Dt} = V\frac{d\Sigma_b}{dx} = -\frac{n\Sigma_b}{\tau_-}\exp\left(\frac{k_s\lambda}{kT}\delta\right) \tag{8}$$

where the steady-state crack growth condition, $D/Dt = Vd/dx$ is used. Since δ is an increasing function of x, one can change the variable x to δ, resulting in

$$V\frac{d\Sigma_b}{d\delta}\frac{d\delta}{dx} = -\frac{n\Sigma_b}{\tau_-}\exp\left(\frac{k_s\lambda}{kT}\delta\right) \tag{9}$$

The chain density can be obtained by integrating (9) provided that $\alpha \equiv d\delta/dx$ can be determined. However, determining the crack opening requires the solution of all field equations, not just energy balance. By assuming that α is a constant,[8] (9) was integrated by Chaudhury et al.[7,8] without considering the spatial variation of δ.

On the basis of the above assumptions, Chaudhury et al.[7,8] showed that when the dimensionless parameter

$$\beta = \frac{nkT}{\alpha V\tau_- k_s\lambda} \ll 1 \tag{10}$$

the energy release rate for crack growth, G, is given approximately by

$$G \approx \frac{\Sigma_o k_s (kT)^2}{2(k_s\lambda)^2}(\ln\beta)^2 \tag{11}$$

The condition $\beta \ll 1$ corresponds to high crack speed or long relaxation time. Note that the unknown parameter α appears in the energy release rate expression. Explicit expression for the energy release rate was not given in refs 7 and 8 for $\beta \gg 1$, which corresponds to low crack speed or short relaxation time. In Appendix 2, we show that G in this limit is given by

$$G \approx \frac{\Sigma_o k_s (kT)^2}{(k_s\lambda)^2\beta^2} + W_{ad} = \frac{\Sigma_o k_s(\alpha V\tau_-)^2}{n^2} + W_{ad} \tag{12}$$

The kinetic expression for the energy release rate as provided by Chaudhury et al.[7,8] is an important step forward to estimating the interfacial fracture energies of rubbery solids. However, their treatments are incomplete and have certain inconsistencies in the strict sense of fracture mechanics. In this paper, we derive exact equations that govern the deformation and stress distributions on the crack faces. This formulation allows us to determine the relationship between crack growth rate and energy release rate, as well as the effective size of the cohesive zone and the crack-opening displacement, which were not considered in the previous treatment.[7,8] To make it simple, we focus mainly on the interfacial aspects of energy dissipation. The complete problem of viscoelastic fracture involving bulk and interfacial dissipation is considerably more complex, but they are the subjects of future research.

The plan of this paper is as follows: In section 2 we examine the assumptions of refs 7 and 8 with greater detail. We show that some of their assumptions are correct provided that certain modifications are made. On the basis of these modifications, we reformulate the problem for the special case of rate independent crack growth in section 3. This case is studied because it leads to the important result of Lake and Thomas by providing, at the same time, deeper insights into the rate dependent problem. In section 4, asymptotic results for the rate dependent cases are derived by modeling the chains as linear springs and, finally, in section 5, a cohesive zone model with nonlinear springs is introduced in order to remove some of the discrepancies in the linear spring model. Discussion and summary about these models are given in section 6.

Since four different models are studied in this work (rate independent, Chaudhury et al.[7,8] rate dependent linear spring model, and rate dependent nonlinear spring model), a table summarizing the key results is presented in Table 1. The definitions of the key symbols can be found in Appendix 1.

2. Examination of Assumptions

Assumption 1: k_s = Constant. Atomic force microscopy (AFM) has shown that the stiffness of polymer chains in extension increases with deformation.[8,15–18] AFM data can be fitted well using the persistence chain model[19]

$$F = \frac{kT}{A}\left[\frac{1}{4}\left(1 - \frac{\delta}{L_c}\right)^{-2} - \frac{1}{4} + \frac{\delta}{L_c}\right] \tag{13}$$

where L_c is the contour length of the chain and A is the persistence length, $L_c = nA$. For small chain extensions

$$F \approx \frac{3kT\delta}{2AL_c}, \qquad \delta/L_c \ll 1 \tag{14}$$

Thus, the spring constant for small deformation is

$$k_o = 3kT/2AL_c \tag{15}$$

The work needed to deform the chain from 0 to δ is

$$w = \frac{k_o\delta^2}{2}\left[\frac{2}{3} + \frac{1}{3}\left(\frac{\delta}{L_c}\right)^{-2}\left(1 - \frac{\delta}{L_c}\right)^{-1} - \frac{1}{3}\left(\frac{\delta}{L_c}\right)^{-1} - \frac{1}{3}\left(\frac{\delta}{L_c}\right)^{-2}\right] \tag{16}$$

Equation 16 shows that the work to break a chain is infinite unless a cutoff displacement is introduced. This is not surprising since the persistence chain model breaks down when $\delta/L_c > 0.9$ at $T \approx 300$ K. At room temperature, the energy stored in the chain at this point (i.e., $\delta/L_c \approx 0.9$) is very small. For example, in experiments,[7] the persistence length of poly(dimethylsiloxane) (PDMS) is about 0.3 nm. Taking $n = 150$, i.e., $L_c = 45$ nm, and $T = 300$ K, we find $k_o \approx 5 \times 10^{-4}$ N/m and $w \approx 4 \times 10^{-18}$ J at $\delta/L_c = 0.9$. In contrast, the energy just before chain failure occurs is roughly $nU \approx 10^{-16}$ J, where $U \approx 400$ kJ/mol is the energy to break a carbon−carbon bond. This is about 2 orders of magnitude greater than w. The energy needed to fail a unit area of surface is roughly $\Sigma_o nU$, where $\Sigma_o \approx 10^{18}/\text{m}^2$ is the initial number of load-bearing chains per unit area. Therefore, the entropic contribution to the fracture energy is insignificant in comparison with the enthalpic contribution. In light of the fact that the exact functional form of the force versus displacement relation is not known in the entire range of δ, we define an average stiffness by

$$k_s \equiv 2nU/L_c^2 \approx 2U/nA^2 \tag{17}$$

This average stiffness is consistent with the approach of Chaudhury et al.[7,8] For a PDMS chain with 150 units, $k_s = 0.1$ N/m, which is about 3 orders of magnitudes greater than k_o. Thus, the constant spring stiffness assumption will underestimate the stretch of the chains inside the cohesive zone. On the other hand, G will be off by 3 orders of magnitude if the lower stiffness is used. Finally, we note that k_s is inversely proportional to n, thus decreasing the degree of polymerization of the chain will increase the chain stiffness.

In Chaudhury et al.,[7,8] the spring constant and the relaxation time of bond dissociation are treated as fitting parameters to interpret data. Specifically, k_s and τ_- are determined by fitting (11) with $\alpha = 1$ on two sets of experiments on model systems. The first involves covalent bonding of a PDMS to glass via a coupling agent. The second case involves the hydrogen bonding interaction between plasma-oxidized PDMS and thin films of PDMS grafted onto a silicone wafer. According to Chaudhury et al.,[7,8] $\tau_- = 10^{13}$ s provides a good fit. Re-examining their data in Figure 8,[8] we found that $k_s = 0.12$ N/m and $\tau_- = 3 \times 10^{12}$ s provide a good fit to the data. Note that $k_s = 0.12$ N/m is consistent with that determined by (17).

Finally, the critical extension ratio where the persistence chain model breaks down is a function of absolute temperature. The critical stretch should vanish as the temperature approaches absolute zero. In this regime, entropic effects can be neglected and the chain stiffness can be taken as a constant, which we will denote by k_{max}. Note $k_{\text{max}} > k_s > k_o$.

Assumption 2: Definition of Crack Tip. Since the exponential function is always positive, (1) implies that chains will eventually break, no matter what the stress level is. In Chaudhury et al.,[7,8] the crack is modeled as semi-infinite, with its tip at the origin, i.e., $\delta(x{=}0) = 0$. This assumption leads to the following paradox: Since the normal stress directly ahead of the crack tip cannot be identically zero, chains outside the cohesive zone can be stretched and hence must break according to (1). Therefore, $\delta > 0$ for all $x < 0$, which contradicts the assumption that the crack tip is located at $x = 0$. In other words, unless there is a critical force below which no polymer chains can break, the crack tip cannot be properly defined.

One way of resolving this paradox is to note that the creation of new surfaces occurs against the attractive van der Waals forces. There is a maximum stress[20] associated with these forces, below which the surfaces cannot separate so that chain bridging cannot occur. Since the effect of these dispersive forces is not taken into account by the cohesive zone model, there exists a very small region about the crack tip where (1−4) fail. This means that the normal stress σ as the crack tip is approached from $x < 0$ will have a square root singularity of the form

$$\sigma = \frac{K_L}{(-2\pi x)^{1/2}}, \qquad x \to 0^- \tag{18}$$

where K_L is the local stress intensity factor. Crack growth occurs when the local energy release rate equals the work of adhesion, W_{ad}, i.e.

$$K_L^2/E^* = W_{ad} \tag{19}$$

It is possible to eliminate this singularity by including van der Waals interactions into the cohesive law, as will be shown below for the rate independent limit.

Assumption 3: Constant $\mathbf{d\delta/dx = \alpha}$. The assumption $d\delta/dx = \alpha$ violates a well-known result of Barenblatt,[21] who showed that the crack profile behind the crack tip must have the following forms (see Figure 3)

case I:

$$\delta = 8K_L x^{1/2}/(2\pi)^{1/2}E^* \qquad x \to 0^+ \tag{20}$$

case II:

$$\delta = \kappa x^{3/2} \qquad x \to 0^+ \tag{21}$$

where $\kappa = (16/3\pi E^*)\int_0^\infty(\mathrm{d}\sigma/\mathrm{d}x)(\mathrm{d}x/x^{1/2})$. For case I, the normal stress is discontinuous at the crack tip and has a singularity of the form given by (18). For case II, the normal

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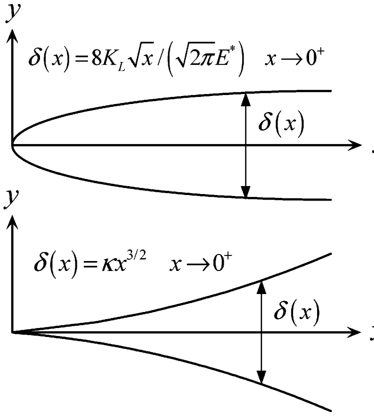

Figure 3. Two possible crack opening profiles. The top profile implies that there is energy flow to the crack tip, whereas there is no energy flow to the crack tip for the bottom profile.

stress is bounded and continuous at the crack tip. Case II is possible only for cohesive zone models that allow a positive cohesive stress at the crack tip. It has been shown[22] that a zero cohesive stress at the crack tip will lead to material interpenetration behind the crack tip. This is the case for cohesive zone models of the form $\sigma = \Sigma_b k_s \delta$ since $\delta = 0$ at the crack tip. Later we will show that it is possible to modify the cohesive zone model to obtain a continuous stress distribution by taking into account van der Waals or dispersive interactions.

3. Rate Independent Limit: Model of Lake and Thomas

It is instructive to consider the rate independent limit of (1), which reduces to the Lake and Thomas (LT) model.[11] A simple way to achieve this limit is to consider the regime of very low temperature. According to (1) and (2), the bond breaking rate at zero temperature is zero unless $-E_a = F\lambda$. Thus, one can define a "chain breaking force" as

$$F_{\max} = E_a/\lambda \tag{22}$$

The corresponding critical extenstion $\delta_{\max}$ is

$$\delta_{\max} = F_{\max}/k_{\max} \tag{23}$$

where $k_{\max}$ is the chain stiffness at very low temperature. In this case, entropic effects can be neglected entirely. The cohesive zone has finite length L since all chains are broken at $\delta = \delta_{\max} \approx L_c$. Since no chains are broken inside the cohesive zone, where $\delta < \delta_{\max}$, Σ_b becomes the areal density (Σ_o) of the load-bearing chains at zero temperature. The energetics in this case is simple; since Σ_o is a constant, eq 7 can be integrated. The work done by the cohesive stress per unit crack extension is

$$\int_o^{\delta_{\max}} \Sigma_o k_{\max} \delta \, d\delta = \frac{\Sigma_o k_{\max} {\delta_{\max}}^2}{2} \tag{24}$$

An interesting result not pointed out by Chaudhury et al.[7,8] is that (11) implies (24) for $kT/E_a \ll 1$; furthermore, this result is independent of the undetermined constant α. To show this, note that $kT/E_a \ll 1$ implies that

$$\ln \beta = \ln\left[\frac{n(kT)^2}{\alpha V h k_s \lambda} \exp\left(-\frac{E_a}{kT}\right)\right] \approx -\frac{E_a}{kT}\left(1 - \frac{2kT}{E_a} \ln \frac{kT}{E_a}\right)$$
$$\text{as } \frac{kT}{E_a} \to 0 \tag{25}$$

Substitution of (25) in (11) and setting $kT/E_a \to 0$ imply

$$G \to \frac{\Sigma_o k_s (kT)^2}{2(k_s \lambda)^2}\left[\frac{E_a}{kT}\left(1 - \frac{2kT}{E_a} \ln \frac{kT}{E_a}\right)\right]^2 = \frac{\Sigma_o k_s {E_a}^2}{2(k_s\lambda)^2} = \frac{\Sigma_o k_s {\delta_{\max}}^2}{2} \tag{26}$$

Note that G given by (26) is consistent with the LT theory provided that k_s defined by (17) is close to $k_{\max}$. In other words, k_s should not be treated as a fitting parameter in order to be consistent with the LT theory.

As mentioned earlier, the total energy release rate is given by

$$G = \frac{{K_L}^2}{E^*} + \frac{\Sigma_o k_{\max} {\delta_{\max}}^2}{2} \tag{27}$$

since the stress has a square root singularity governed by (18) at the crack tip. The additional energy release rate ${K_L}^2/E^*$ can be identified with the work of adhesion, W_{ad}, so that the total energy release rate is the sum of the work of adhesion and the energy required to stretch and break the polymer chains. The LT theory suggested that $k_{\max}{\delta_{\max}}^2/2 \approx nU$, which is significantly larger than W_{ad}/Σ_o.

In Chaudhury et al.,[7,8] neither the crack profile nor the cohesive zone length is determined. To determine these quantities, it is necessary to couple the deformation of the cohesive zone to the deformation of the elastic material outside. The problem is essentially that of a crack bridged by springs and has been investigated elsewhere.[23,24] Detailed formulation and results can be found in Appendix 3. The cohesive zone length L is found to be well approximated by

$$L \approx \frac{E^*}{4\pi \Sigma_0 k_{\max}} \frac{G}{W_{ad}} \tag{28}$$

Substitution of (27) into (28) gives

$$L \approx \frac{E^*}{4\pi\Sigma_0 k_{\max}}\left(1 + \frac{\Sigma_o k_{\max} {\delta_{\max}}^2}{2W_{ad}}\right) \approx \frac{E^* {\delta_{\max}}^2}{8\pi W_{ad}} \tag{29}$$

Thus, the length of the cohesive zone in the rate independent limit is directly proportional to the elastic modulus.

As discussed above, the undesirable feature of the above model, that the crack tip stress is unbounded, can be removed by including dispersive interaction in the cohesive zone model. Thus, the cohesive zone model $\sigma = \Sigma_o k_{\max} \delta$ can be replaced by

$$\sigma = \Sigma_o k_{\max} \delta + \sigma_{vdw} \tag{30}$$

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[24] Budiansky, B.; Amazigo, J. C.; Evans, A. G. *J. Mech. Phys. Solids* **1988**, *36*, 167.

where $\sigma_{\rm vdw} = \sigma_c \exp(-\delta/\delta_c)$ is the additional traction due to dispersive force. The material constant σ_c is the maximum stress that can be sustained by the interface, and δ_c is a characteristic decay distance. This model ensures the stress at the crack tip is bounded and positive so that material interpenetration cannot occur there. The energy release rate for fracture in this case is

$$G = \int_0^{\delta_{\max}} (\Sigma_o k_{\max}\delta + \sigma_{\rm vdw})\, {\rm d}\delta = \frac{\Sigma_o k_{\max}\delta_{\max}{}^2}{2} + \sigma_c\delta_c \quad (31)$$

where we have assumed that $\delta_{\max} \gg \delta_c$ so that the region where the van der Waals forces act is small compared with the region of chain bridging. Comparing (31) with (27), we note that the energy release rates of both cases are identical provided that $\sigma_c\delta_c = W_{\rm ad}$. It should be noted that the choice of $\sigma_{\rm vdw} = \sigma_c \exp(-\delta/\delta_c)$ is selected for mathematical convenience since it is well-known that the dispersion forces between van der Waals solids decay much slower than what an exponential function represents. However, it has been well-known that the solutions of fracture problems are insensitive to the form of the interaction potentials provided that the maximum stress and the work of adhesion are chosen to be approximately the same for these potentials.

The crack opening profile and the cohesive zone length associated with this modified cohesive zone model can be obtained by solving (A7) and (A8) in Appendix 3 with σ given by (30). Since the stresses are bounded, the condition $K_{\rm L} = 0$ has to be imposed in (A8) for this modified cohesive zone model. Our numerical results show that the cohesive zone lengths for both models are practically the same as long as $K_{\rm L}/K_{\rm A} \ll 1$ in the problem without dispersive interactions and $\delta_{\max} \gg \delta_c$. Similarly, the crack opening profiles for both models are identical except near the crack tip. This is to be expected, since the crack opening displacement in the absence of singularity is given by (21) instead of (20).

4. Formulation of the Rate Dependent Problem in an Elastic Material

The formulation of the rate dependent problem is essentially the same as that of the rate independent problem that is given in Appendix 3. In the rate dependent case, there is no definite δ above which all chains break; that is, there is always the possibility that some chains remain intact. Therefore, the cohesive zone length in the rate dependent case is infinite. In addition, since the density of chains Σ_b in the rate dependent case depends on the deformation, the cohesive stress $\sigma = \Sigma_b k_s \delta$ depends not only on δ but also onΣ_b. With these modifications, the governing equations are

$$K_{\rm L} = K_{\rm A} - \left(\frac{2}{\pi}\right)^{1/2} k_s \int_0^\infty \frac{\Sigma_b(x)\,\delta(x)\,{\rm d}x}{x^{1/2}} \quad (32)$$

$$\delta(x) = \frac{8K_{\rm A}}{(2\pi)^{1/2}E^*} x^{1/2} - \frac{4k_s}{\pi E^*}\int_0^\infty \Sigma_b\delta(x') \ln\left|\frac{x^{1/2} + x'^{1/2}}{x^{1/2} - x'^{1/2}}\right| {\rm d}x' \quad (33)$$

where $K_{\rm L} = (E^* W_{\rm ad})^{1/2}$. The density of load-bearing chains is determined using (8), i.e.

$$\frac{{\rm d}\Sigma_b}{{\rm d}x} = -\frac{n\Sigma_b}{\tau\_V} \exp\left(\frac{k_s\lambda}{kT}\delta\right) \quad (34)$$

To expedite the analysis, we introduce the following normalized variables:

$$\xi \equiv \frac{4\Sigma_o k_s}{\pi E^*} x'$$

$$\eta \equiv \frac{4\Sigma_o k_s}{\pi E^*} x$$

$$\hat{\delta} \equiv \frac{(E^*\Sigma_o k_s/2)^{1/2}\delta}{K_{\rm A}}$$

$$\hat{\Sigma}_b \equiv \Sigma_b/\Sigma_o \quad (35)$$

Distances from the crack tip are measured in units of $\pi E^*/4\Sigma_o k_s$, which is the stretch of a chain subjected to a force $\pi E^*/4\Sigma_o$. The opening displacement is normalized by$K_{\rm A}/(E^*\Sigma_o k_s/2)^{1/2}$, which is the opening of a traction free crack at a distance $\pi E^*/16\Sigma_o k_s$ from the crack tip. $\hat{\Sigma}_b$ is the normalized chain density and is less than or equal to 1. With this normalization, (32–34) become

$$f = 1 - \int_0^\infty \frac{\hat{\Sigma}_b(\xi)\,\hat{\delta}(\xi)\,{\rm d}\xi}{\xi^{1/2}} \quad (36)$$

$$\hat{\delta}(\eta) = 2\eta^{1/2} - \int_0^\infty \hat{\Sigma}_b(\xi)\,\hat{\delta}(\xi) \ln\left|\frac{\eta^{1/2} + \xi^{1/2}}{\eta^{1/2} - \xi^{1/2}}\right| {\rm d}\xi \quad (37)$$

$$\frac{{\rm d}\hat{\Sigma}_b}{{\rm d}\eta} = -b\hat{\Sigma}_b \exp(c\hat{\delta}) \quad (38)$$

where b, c, and f are dimensionless parameters defined by

$$b \equiv \frac{n\pi E^*}{4\Sigma_o k_s \tau\_V}$$

$$c \equiv \omega/f$$

$$\omega \equiv \frac{k_s\lambda(2W_{\rm ad}/\Sigma_o k_s)^{1/2}}{kT}$$

$$f \equiv (W_{\rm ad}/G)^{1/2} \quad (39)$$

The dimensionless parameter b^{-1} can be interpreted as the normalized crack speed and f^{-2} is the normalized energy release rate for crack growth. For a given material, the dimensionless constant ω is fixed, whereas c is proportional to the normalized energy release rate f^{-1}. Equations 36–38 imply that for a given material, the normalized crack speed is completely determined by the normalized energy release rate. Mathematically, we have

$$f^{-2} = G/W_{\rm ad} = h(b,\omega) \quad (40)$$

where h is a dimensionless function to be determined by the solution of (36–38). Integrating (38) and using the boundary condition $\hat{\Sigma}_b(0) = \Sigma_b(0)/\Sigma_o = 1$ gives

$$\hat{\Sigma}_b(\xi) = \exp[-b\int_0^\xi \exp[c\hat{\delta}(s)]\,{\rm d}s] \quad (41)$$

Substitution of (41) into (37) results in

$$\hat{\delta}(\eta) = \left[2\eta^{1/2} - \int_0^\infty \exp\left[-b \int_0^\xi \exp[c\hat{\delta}(s)]\, \mathrm{d}s\right]\hat{\delta}(\xi) \ln\left|\frac{\eta^{1/2} + \xi^{1/2}}{\eta^{1/2} - \xi^{1/2}}\right| \mathrm{d}\xi\right] \tag{42}$$

The normalized crack opening profile is determined by solving (42) subjected to the constraint (36).

It is instructive to estimate the order of magnitudes of the parameters b and c as well as the length $\pi E^*/4\Sigma_o k_s$ used to scale the distance from the crack tip. At room temperature ($T = 300$ K), $k_s = 0.1$ N/m. Following Chaudhury et al.,[7,8] we assume $n = 150$, $\lambda = 10^{-10}$ m, $\Sigma_o = 2.5 \times 10^{18}$ m^{-2}, $E^* = 1$ MPa, 10^{-6} s $\leq \tau_- \leq 10^{13}$ s, and 10^{-10} m/s $\leq V \leq 1$ m/s, we find $E^*/\Sigma_o k_s \approx 10^{-11}$ m. Thus $\eta = 1$ corresponds to 0.1 Å from the crack tip. Also

$$b \approx \frac{10^{-9}}{\tau\_V} \tag{43}$$

A lower bound for b at room temperature is obtained by substituting the longest relaxation time $\tau_- = 10^{13}$ s and the highest crack speed $V = 1$ m/s in (43). This lower bound is found to be 10^{-22}. An upper bound for b is obtained by choosing the shortest relaxation time $\tau_- = 10^{-6}$ s and the slowest crack rate $V = 10^{-10}$ m/s; in this case, $b \approx 10^7$. Thus, $10^{-22} \leq b \leq 10^7$ and $c \approx 10G^{1/2}$. Since1 $< G <$ 100 J/m^2, $1 < c < 100$.

As experiments[7,8] are carried out in the regime where $b \leq 10^{-10}$, numerically solving the nonlinear integral eq 42 is practically impossible. In the following, we present asymptotic solutions in this regime. This asymptotic solution is based on the energy conservation integral of Rice,[25] which states that

$$G = \Sigma_o k_s \int_0^\infty \hat{\Sigma}_b \delta\, \mathrm{d}\delta + W_{ad} \tag{44}$$

Thus, G can be evaluated if $\hat{\Sigma}_b$ is known. In general, $\hat{\Sigma}_b$ can only be determined by solving the integral eq 42. However, for $b \ll 1$, this difficulty can be avoided by noting that (38) can be rewritten as $\mathrm{d} \ln \hat{\Sigma}_b/\mathrm{d}\eta = -b \exp(c\hat{\delta})$. Since the logarithmic function varies very slowly, practically all the chains are broken when $b \exp(c\hat{\delta}) > 1$. Using the definition of c and $\hat{\delta}$, we note

$$c\hat{\delta} = \frac{k_s \lambda L_c}{kT} (\delta/L_c) = C\Delta \tag{45}$$

where $C = (k_s\lambda L_c/kT)$ and $\Delta = \delta/L_c$. At room temperature, $\lambda L_c/kT \approx 10^3$ so that $C \approx 10^3 k_s$.

Figure 4 plots $b \exp(C\Delta)$ versus the stretch ratio $\Delta = \delta/L_c$ for several values of b with $C = 10^2$. Notice that for small b, the transition from $\mathrm{d} \ln \hat{\Sigma}_b/\mathrm{d}\eta \ll 1$ to $\mathrm{d} \ln \hat{\Sigma}_b/\mathrm{d}\eta \gg 1$ is extremely sharp. This means that a good approximation is to assume

$$\hat{\Sigma}_b = 1 \qquad \Delta < \Delta_T$$
$$\hat{\Sigma}_b = 0 \qquad \Delta > \Delta_T \tag{46}$$

where Δ_T is a normalized critical opening displacement determined by the condition $b \exp(C\Delta) = 1$, i.e.

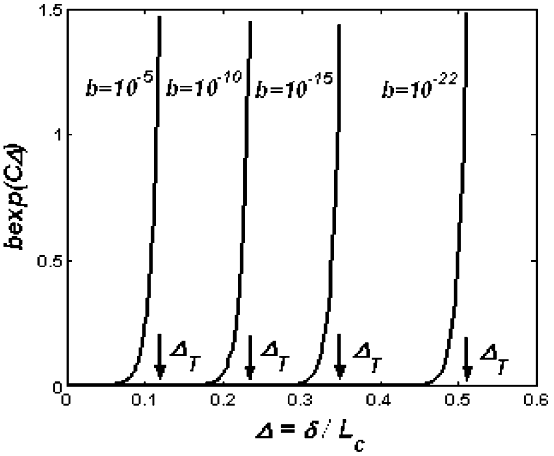

Figure 4. Dependence of rate of chain breakage on the stretch ratio for different b values. $b^{-1} = 4\Sigma_o k_s \tau_- V/n\pi E^*$ is the normalized velocity of crack propagation. $C = k_s\lambda L_c/kT$, $\Delta = \delta/L_c$ is the normalized crack opening displacement. Δ_T (see (47)) corresponding to different b values is indicated.

$$\Delta_T = \frac{\ln(1/b)}{C} \tag{47}$$

Substituting (46) in (44), a good approximation to the energy release rate is

$$G = \Sigma_o k_s L_c^2 \int_0^{\Delta_T} \Delta \mathrm{d}\Delta + W_{ad} = \frac{\Sigma_o k_s (kT)^2}{2(k_s\lambda)^2}\left(\ln \frac{n\pi E^*}{4\Sigma_o k_s \tau\_V}\right)^2 + W_{ad} \tag{48}$$

Equation 48 is similar to the expression derived by Chaudhury et al.[7,8] (see eq 11), i.e.

$$G = \frac{\Sigma_o k_s (kT)^2}{2(k_s\lambda)^2}\left(\ln \frac{nkT}{\alpha V \tau\_k_s \lambda}\right)^2 \tag{49}$$

However, the new expression (48) does not contain the undetermined parameter α as in (49). Indeed, the two energy release rate expressions are identical if $kT/\alpha\lambda$ in (49) is replaced by $\pi E^*/4\Sigma_o$.

There is, however, an inconsistency associated with the assumption of constant spring stiffness. The Δ_T values corresponding to different values of the normalized velocity b^{-1} for $k_s = 0.1$ N/m are shown in Figure 5. We note that, even for the smallest $b = 10^{-22}$, all the chains would have been broken by the time $\Delta = \delta/L_c \approx 0.5$. In reality, since $\Delta_T < 0.9$, the load-bearing chains are not close to being fully stretched, therefore, the actual energy stored in the chains should be given by $\Sigma_0 w$ instead of (48), where w is defined as (16). In other words, both the expressions (48) and (11) overestimate the energy release rate! Of course, one can choose a smaller k_s (e.g., $k_s < 0.01$ N/m) so that C is smaller. This gives $\Delta_T > 0.9$; however, the energy release rate is underestimated since k_s is smaller than that given by (17).

The fact that the chain density drops abruptly from Σ_o to 0 for $b \ll 1$ implies that there is a one-to-one correspondence between the rate independent LT solution and the present one. Indeed, the two problems are identical as long as the cohesive zone length in the LT problem is considered to be a function of the crack speed. Indeed, (48) implies that

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(25) Rice, J. R. *Appl. Mech. Trans. ASME* **1968**, *90*, 379.

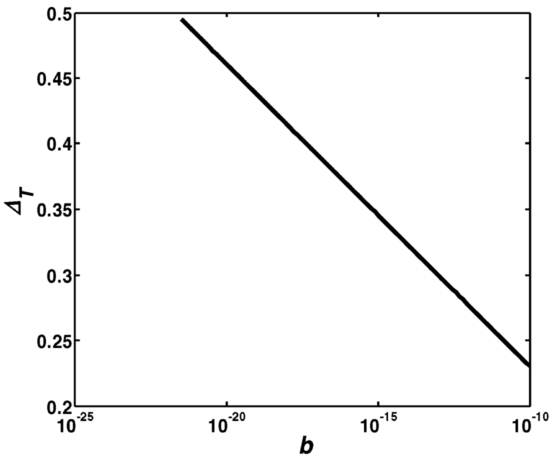

Figure 5. Normalized critical opening displacement Δ_T vs normalized velocity b. Even for the smallest $b = 10^{-22}$, all the chains would have been broken when $\Delta = \delta/L_c \approx 0.5$.

$$G/W_{ad} = \frac{\Sigma_o k_s (kT)^2}{2(k_s\lambda)^2 W_{ad}}\left(\ln \frac{n\pi E^*}{4\Sigma_o k_s \tau\_V}\right)^2 + 1 \approx \frac{\Sigma_o k_s (kT)^2}{2(k_s\lambda)^2 W_{ad}}\left(\ln \frac{n\pi E^*}{4\Sigma_o k_s \tau\_V}\right)^2 \quad (50)$$

The length of the cohesive zone can be estimated using (28), i.e.

$$L \approx \frac{E^*(kT)^2}{8\pi(k_s\lambda)^2 W_{ad}}\left(\ln \frac{n\pi E^*}{4\Sigma_o k_s \tau\_V}\right)^2 \quad (51)$$

The regime which corresponds to very slow crack growth rate or short relaxation time is characterized by the condition $b \gg 1$. For large normalized crack velocity, b, the relation between crack growth rate and applied stress intensity factor or energy release rate can be determined using (36). Using (41), (36) becomes

$$f = 1 - \int_0^{\infty} \exp[-b \int_0^{\xi} \exp[c\hat{\delta}(s)]\, ds] \frac{\hat{\delta}(\xi)}{\xi^{1/2}}\, d\xi \quad (52)$$

Watson's Lemma[26] states that the asymptotic behavior of the integral in (52) for $b \gg 1$ is dictated by the behavior of $\hat{\delta}(\xi)$ as $\xi \rightarrow 0$. The behavior $\hat{\delta}(\xi)$ as $\xi \rightarrow 0$ is given by (20). Applying Watson's Lemma, (52) becomes

$$f \approx 1 - 2f \int_0^{\infty} \exp(-b\xi)\, d\xi = 1 - \frac{2f}{b} \quad (53)$$

Substitute $f = (W_{ad}/G)^{1/2}$ in (53) and noting that $b \gg 1$, we have

$$G \approx W_{ad}(1 + 4b^{-1}) \quad (54)$$

Since $b \propto V^{-1}$, G is a linear function of the crack speed. As the crack growth rate goes to zero, the energy release rate approaches the intrinsic work of adhesion. It is instructive to compare our result with the prediction of eq 12. Equation 12 predicts that G should increase with the square of the crack growth rate, whereas (54) implies that G should increase linearly with the velocity. This discrepancy is due to the fact that, in the short relaxation time or slow crack growth regime, chains are broken everywhere except those closed to the crack tip. Thus, the solution in this regime is very sensitive to the crack tip profile. As mentioned in the Introduction, the crack profile (i.e., a plane wedge) assumed by Chaudhury et al.[7,8] is incorrect. This oversight leads to a different prediction of G versus V. However, it should be noted that it is very difficult to perform experiments that satisfy the condition $(G - W_{ad})/W_{ad} \ll 1$.

The length of the cohesive zone L can be estimated by noting that the strong decay of the exponential function implies that most of the contribution to $\hat{\Sigma}_b$ in (41) occurs in the region $\xi \le 1/b$ or $x \le \pi E^*/4b\Sigma_o k_s$. Indeed, a good approximation for $\hat{\Sigma}_b$ in the limit of $b \gg 1$ is $\exp(-b\xi)$ for sufficiently small ξ. Therefore, if we assume that the interface fails when $\hat{\Sigma}_b = 0.01$, the approximate length of the effective cohesive zone becomes

$$L = \frac{2\pi E^*}{4\Sigma_o k_s b} \ln(10) \approx 3.6 \frac{E^*}{\Sigma_o k_s b} \quad (55)$$

for very slow crack speed or small relaxation time.

5. Nonlinear Spring Model

The inconsistency appearing in the linear spring model shows a need for the usage of a nonlinear spring model, which describes the stretching of the polymer chain from its initial state to final failure. Since there is no closed form analytic model for the spring stiffness, we assume that the spring force is a function only of the stretch $\Delta \equiv \delta/L_c$ and the absolute temperature

$$F = \tilde{F}(\Delta, T) \quad (56)$$

To be specific, we assume the following functional form for the spring force: For $\Delta \le 0.9$, F is given by the persistence chain model (13), and for $\Delta \ge 0.9$, F is a linear function of Δ, i.e.

$$\begin{aligned} F &= k_0 L_c (1 - \Delta)^{-2}\left[1 - \frac{3}{2}\Delta + \frac{2}{3}\Delta^2\right]\Delta \\ &\Delta \le 0.9 \\ F &= k_{max} L_c (\Delta - 0.9) + F(\Delta{=}0.9) \\ &\Delta \ge 0.9 \end{aligned} \quad (57)$$

where k_{max} is the maximum spring stiffness that can be several orders of magnitude higher than k_0. For example, if $k_{max} = 1$ N/m, then $\hat{k}_{max} \equiv k_{max}/k_0 = 2000$. Note also that we implicitly assume that $T \approx 300$ K since the critical stretch ratio where the persistence chain model breaks down is 0.9.

The governing equations in this case are

$$K_L = K_A - \left(\frac{2}{\pi}\right)^{1/2} \int_0^{\infty} \frac{\Sigma_b(x)\, F(x)\, dx}{x^{1/2}} \quad (58)$$

$$\delta(x) = \frac{8K_A}{(2\pi)^{1/2} E^*} x^{1/2} - \frac{4}{\pi E^*} \int_0^{\infty} \Sigma_b(x')\, F(x') \ln \left|\frac{x^{1/2} + x'^{1/2}}{x^{1/2} - x'^{1/2}}\right| dx' \quad (59)$$

$$\frac{d\Sigma_b}{dx} = -\frac{n\Sigma_b}{\tau\_V} \exp\left(\frac{F\lambda}{kT}\right) \quad (60)$$

For nonlinear stiffness, L_c is an additional length scale. Let us introduce the normalized variables

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[26] Carrier, G. F.; Krook, M.; Pearson, C. E. *Functions of a Complex Variable, Theory and Technique*; McGraw-Hill: New York, 1966.

$$\xi = \frac{32G}{\pi E^* {L_c}^2} x'$$

$$\eta = \frac{32G}{\pi E^* {L_c}^2} x$$

$$\gamma = \frac{\Sigma_o k T L_c}{8G\lambda}$$

$$\rho = \frac{n\pi E^* {L_c}^2}{32G\tau\_V}$$

$$\hat{F} = F\lambda/kT$$

$$\hat{\Sigma}_b = \Sigma_b/\Sigma_0 \quad (61)$$

where ξ and η are normalized distances from the crack tip, $\hat{F}$ is the normalized force on a chain, and ρ is a normalized velocity. The dimensionless parameter γ is a measure of the effect of the spring force on the local stress intensity factor. This normalization allows us to reduce eqs 58−60 to

$$f = 1 - 2\gamma \int_0^\infty \frac{\hat{\Sigma}_b(\xi)\, \hat{F}(\Delta(\xi))\, d\xi}{\xi^{1/2}} \quad (62)$$

$$\Delta(\eta) = \eta^{1/2} - \gamma \int_0^\infty \hat{\Sigma}_b(\xi)\, \hat{F}(\xi) \ln\left|\frac{\eta^{1/2} + \xi^{1/2}}{\eta^{1/2} - \xi^{1/2}}\right| d\xi \quad (63)$$

$$\hat{\Sigma}_b(\eta) = \exp(-\rho \int_0^\eta \exp(\hat{F}(\Delta(\xi)))\, d\xi) \quad (64)$$

where $f = (W_{ad}/G)^{1/2}$. Theoretically, for a given f, one can determine Δ and the normalized crack velocity ρ by solving (62)−(64).

Let us estimate the order of magnitude of the normalized crack velocity ρ. Using $\tau_- = 10^{13}$ s, $L_c = 45$ nm, and $n = 150$, we found $\rho = (3 \times 10^{-21}/GV)$. Note that $k_{max} = 1$ N/m is an upper bound for the spring stiffness for a chain of length $n = 150$.[8] Since 1 J/m^2 < G < 10^2 J/m^2, and experiments which involve covalent interactions are carried out with velocities between 10^{-7} and 10^{-10} m/s, $10^{-16} < \rho < 10^{-11}$. Furthermore, $10^{-3} \leq \gamma \leq 1$.

Since the experiments on covalent interactions are carried out in the regime of $\rho \ll 1$, we focus our analysis in this regime. Similar to our previous analysis, $\hat{\Sigma}_b(\xi) \approx 1$ as long as $\rho \exp \hat{F} \ll 1$. According to (57) and (15)

$$\begin{aligned} &\hat{F} = q(1-\Delta)^{-2}\left[1 - \frac{3}{2}\Delta + \frac{2}{3}\Delta^2\right]\Delta \\ &\Delta \leq 0.9 \\ &\hat{F} = q\hat{k}_{max}(\Delta - 0.9) + 17.1q \\ &\Delta \geq 0.9 \end{aligned} \quad (65)$$

where $q = 3\lambda/2A$. Taking $\lambda \approx 10^{-10}$ m and $A \approx 3 \times 10^{-10}$ m, q is found to be about 1/2. The strong decay of the exponential function and the rapid increase of the stiffness near $\Delta \approx 1$ imply that the transition from $\hat{\Sigma}_b = 1$ to $\hat{\Sigma}_b(\xi) = 0$ is very sharp. This transition occurs at $\Delta = \Delta_T$ defined by

$$\rho \exp \hat{F} = 1 \quad (66)$$

Thus, $\hat{\Sigma}_b = 1$ for $\Delta < \Delta_T$ and $\hat{\Sigma}_b = 0$ for $\Delta > \Delta_T$. The sharpness of this transition is illustrated by considering the case of $\hat{k}_{max} = 2000$, which is an upper bound for $\hat{k}_{max}$. At $\Delta = 0.9$, $\hat{F} = 17.1q = 8.6$, $\exp \hat{F} = 5.4 \times 10^3$. This means that for $\rho < 2 \times 10^{-4}$, it is possible for Δ_T to exceed 0.9, a necessary condition for increasing the interfacial energy release rate. The increase in energy release rate is very sensitive on $\hat{k}_{max}$. This is because $\hat{F}$ increases from $17.1q$ to $\hat{F} = 17.1q + 0.1q\hat{k}_{max}$ in the interval $0.9 \leq \Delta \leq 1$. For $k_{max} = 1$ N/m or $\hat{k}_{max} = 2000$, $\exp \hat{F}$ increases from 5.4×10^3 at $\Delta = 0.9$ to 1.4×10^{47} at $\Delta = 1$! For $k_{max} = 0.1$ N/m or $\hat{k}_{max} = 200$, $\exp \hat{F}$ increases from 5×10^3 to 1.1×10^8. In the first case (i.e., $k_{max} = 1$ N/m), even for the smallest $\rho = 10^{-16}$, $\rho \exp \hat{F} = 10^{31}$! Thus practically all chains fail before Δ reaches 1. For the second case (i.e., $k_{max} = 0.1$ N/m), most chains are intact until $\Delta = 1.2$. It is important to note that, with the constant stiffness assumption, Δ_T (~0.5) for the second case is much less than 0.9. In other words, the energy stored in a chain before it fails is completely entropic and the energy release rate should be given by $\Sigma_0 w$ (see (16)) instead of (11) or (48). The nonlinear spring model removes this difficulty.

The energy release rate to propagate a crack at the speed V is

$$G \approx \frac{\Sigma_o k_o {L_c}^2}{q} \int_0^{\Delta_T} \hat{F}(\Delta)\, d\Delta + W_{ad} \quad (67)$$

By contrast, the energy release rate in the rate independent limit (i.e., LT model) is

$$G_{LT} = \frac{\Sigma_o k_o {L_c}^2}{q} \int_0^{\Delta_f} \hat{F}(\Delta)\, d\Delta + W_{ad} = \Sigma_o n U + W_{ad} \quad (68)$$

where $\Delta_f \equiv \delta_{max}/L_c$ with δ_{max} defined in (23). Indeed, the argument above implies that for typical velocities and material parameters, the energy release rate is much lower than G_{LT}, which is consistent with the experimental data.[8] To see this, let us use the expression of Δ_T as in eqs 65 and 66; thus

$$\hat{k}_{max}(\Delta_T - 0.9) + 17.1 = -q^{-1} \ln \rho \quad (69)$$

for $\Delta_T > 0.9$. At room temperature, the maximum value of the right-hand side of (69) is about $-2 \ln(10^{-16}) \approx 74$. For $\hat{k}_{max} = 2000$, Δ_T must be less than 1. This means that the energy release rate cannot exceed the LT model. Thus, for all practical purposes, G_{LT} is an upper bound for G. For sufficiently small ρ so that $\Delta_T > 0.9$

$$G \approx \frac{\Sigma_o k_o {L_c}^2}{q} \int_0^{0.9} \hat{F}\, d\Delta + \frac{\Sigma_o k_{max} {L_c}^2 (\Delta_T - 0.9)^2}{2} + 17.1 \Sigma_o k_o {L_c}^2 (\Delta_T - 0.9) + W_{ad} \quad (70)$$

where Δ_T is determined by (69). The first term is the stored entropic energy $\Sigma_0 w$ (see (16)). The last term is typically on the order of 60 mJ for van der Waals solids and can be neglected in comparison with the rest. For$\Delta_T < 0.9$, (70) should be replaced by

$$G \approx \frac{\Sigma_o k_o {L_c}^2}{q} \int_0^{\Delta_T} \hat{F}\, d\Delta + W_{ad} \quad (71)$$

Figure 6 plots $G^{1/2}$ vs $\log_{10} V$ for the case of interfacial toughness being governed by the covalent bonds. The experimental data (square symbols), as obtained from Chaudhury et al.,[7,8] are fitted with eqs 48, 49, and 70. The fit using (48) is obtained using $k_s = 0.117$ N/m,$\tau_- = 2.1 \times 10^{12}$ s and $\lambda = 0.12$ nm. The fit using (49) is obtained using $k_s = 0.123$ N/m, $\tau_- = 3 \times 10^{12}$ s, $\alpha = 1$, and $\lambda = 0.1$

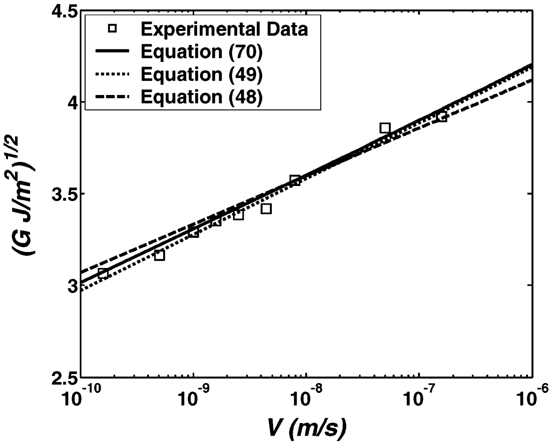

Figure 6. Comparison of three predictions of the energy release rate with experimental data.

nm, whereas the fit using (70) is obtained using $k_{\max} = 0.1$ N/m, $\tau_- = 3 \times 10^9$ s, and $q = 0.56$. In contrast to (48) and (49), many choices of ($k_{\max}$, λ, τ_-) can be found to fit the data well using (70).

As can be seen from Figure 6, all three equations (48), (49), and (70) can be used to fit the data well. Physically, (49) contains an unknown parameter α which cannot be a constant. Both (48) and (49) underestimate the critical stretch required to propagate a crack, while (70) removes the discrepancy. However, (70) is much more complicated than (48), since Δ_T involves G and thus (70) is an implicit expression of G. The reason the linear model (48) agrees well with the nonlinear model (70) even though k_s and k_o are very different is due to the fact that most of the energy stored in a chain is accumulated when the chain is close to being fully stretched. The spring constant in this regime is much closer to k_s. Since in practice it is difficult to measure the crack opening displacement, (48) can be used instead of (70) as long as the spring constant k_s is consistent with (17). In view of the above analysis, it is a bit surprising that the energy release rate obtained from (49) does not vary too much from those obtained from the more exact analysis. This is somewhat a fortuitous situation arising from the fact that as α in (49) appears within a logarithmic expression. The situation is however very different with short relaxation time or slow crack growth, i.e., when the fracture energy varies linearly with crack velocity.

Finally, we comment on the regime of short relaxation time that is characterized by $\rho \gg 1$. Substituting (64) into (62) gives

$$f = 1 - 2\gamma \int_0^\infty \frac{\exp(-\rho \int_0^\eta \exp(\hat{F}(\Delta(\xi)))\,\mathrm{d}\xi)\hat{F}(\Delta(\xi))\,\mathrm{d}\xi}{\xi^{1/2}} \tag{72}$$

As in the previous case, the asymptotic behavior of the integral in (72) is dictated by the behavior of $\hat{F}$ as $\Delta \to 0$, as is given by (20)−(21). The calculations are essentially the same as before, and the result is still given by (54), provided that k_s in b is replaced by k_o. This is not surprising, since the chains at the tip are barely stretched. Indeed, the use of k_s overestimates the stiffness of these chains by about 3 orders of magnitude.

6. Discussions and Summary

Our analysis shows that when $b \gg 1$ (short relaxation time or slow crack growth), the energy release rate increases linearly with crack speed and scales with the work of adhesion, i.e.

$$G \approx W_{\mathrm{ad}}\left(1 + \frac{16\Sigma_o k_o \tau_- V}{n\pi E^*}\right) \tag{73}$$

In this regime, the resistance to crack growth is mainly due to dispersive forces. Equations of the form

$$G = W_{\mathrm{ad}}(1 + \Psi(V,T)) \tag{74}$$

have been proposed by Gent and Schultz[2] as well as Andrews and Kinloch[1] to interpret interface crack growth data. Maugis and Barquins[4] studied the adhesion between a rigid indenter and a thick, nearly incompressible polyurethane elastomer. The relation between G and V obtained by them has the following form

$$G \approx W_{\mathrm{ad}}[1 + (V/V^*)^{0.6}] \tag{75}$$

where $W_{\mathrm{ad}} \approx 0.08$ J/m^2 and $V^* = 22$ nm/s. The second terms in both (74) and (75) are usually attributed to viscoelastic losses, whereas in our case the energy loss is due to rate dependent chain scission.

For long relaxation time ($b \ll 1$), we have shown that all three expressions (48), (49), and (70) can be used to fit experimental data. In addition, the spring stiffness and the activation length used to fit data do not vary much from one expression to another. However, (49) contains a parameter α which cannot possibly be a constant. Since (49) can be written in the form $G^{1/2} = A \ln V + B$, α has no effect on the slope of the resulting line in a log plot. The value of α, however, affects the intercept which is used to determine the relaxation time. Our analysis shows that $kT/\alpha\lambda$ in (49) should be replaced by $\pi E^*/4\Sigma_o$. Therefore, within the limitation of the constant spring stiffness assumption, (48) should be used instead of (49). It is demonstrated that both expressions underestimate the critical stretch required to propagate a crack. Equation 70, which is obtained using a nonlinear theory, does not suffer from this limitation. At very low temperatures, the rate dependent theory approaches the LT model (27).

In the regime of long relaxation time, the energy release rates do not scale with the work of adhesion. Indeed, the energy release rate is approximately independent of W_{ad}. It is often thought that relation of the form given by (74) is universal. Our result provides an exception to this rule.

Finally, we comment on the size of the cohesive zone. Consider first the rate independent limit where the cohesive zone length is given by (28). Using $k_s = 0.1$ N/m, $\Sigma_o = 10^{18}$ m^{-2}, $E^* = 1$ MPa, $G = 10^2$ J/m^2, and $W_{\mathrm{ad}} = 60$ mJ/m^2, L is found to be 1.3 nm. The size of the cohesive zone in the rate dependent case, which can be estimated using (51), is even smaller than 1.3 nm since the corresponding energy release rate is smaller than the rate independent case. Thus, the characteristic length scale of the energy dissipation zone surrounding the crack tip turns out to be on the order of 1 nm.

That dissipation occurs in such an extremely small region cannot be attributed entirely to the fact that the material is elastic. For example, Gent and Lai[3] reported peel data on thin sheets of elastomers which are adhered together by C−C or S−S interfacial bonds. Even though these elastomers are viscoelastic, the effective size of the dissipative zone was estimated to be on the order of 0.1−10 Å^3. The size of these dissipative zones was also computed by Rahul Kumar et al.[27] using a finite element model. In these computation models, local failure of the

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(27) Rahul Kumar, P.; Jagota, A.; Bennison, S. J.; Saigal, S.; Muralidhar, S. *Acta Mater.* **1999**, *47*, 4164.

interface is modeled using a rate independent cohesive zone model. The size of the viscous dissipation zone was again found to be on the order of 10^{-11} m for peel velocities that showed significant increase in fracture toughness.

A possible explanation of this paradox was offered by a recent work of Hui et al.[28] They pointed out that in soft materials where the modulus is much less than the stress required to break bonds, the crack blunts before it can propagate. The blunted zone provides an additional length scale that is absent in a theory based on small strains. Within the blunted zone the material is highly stretched and therefore other dissipative mechanisms can take place (e.g., cavitation) which cause further increases in the energy release rate. Clearly such deformation mechanisms are not considered in our model.

There are obvious limitations to our model. To simplify the mathematics, small strain theory is used throughout the analysis. However, it should be noted that the theory of Johnson, Kendall, and Roberts (JKR), which is also based on small strains, has been very successful in quantifying the contact mechanics of soft materials.[29] Therefore, although the details of deformation near the crack tip may not be captured by the small strain theory, the relationship between the crack growth rate and the energy release rate is much less affected by the small strain approximation. As pointed out by Chaudhury et al.,[7,8] the transition state theory of Tobolsky and Eyrings[30] was based on the assumption that the transition state and the ground state are in thermal equilibrium, which is incorrect. The correct formulation was given by Kramers[31] who showed that bonds at ground energy state cross the energy barrier by a diffusion process either in the spatial or in the energy coordinate. In addition, the assumption of a transition state having a fixed transition length λ is also flawed. As demonstrated by Kausch[13] and Evans,[14] the transition state is modified by the force so that λ cannot be regarded as a constant. As pointed out by Chaudhury et al.,[7,8] these are the reasons why the activation energy E_a which corresponds to a relaxation time of 3×10^{12} s is about 151 kJ/mol, which is considerably smaller than the dissociation energy (454 kJ/mol) of a siloxane bond. Therefore, both the transition length λ and E_a must be treated as adjustable parameters in our model. Finally, we have not considered the effect of bulk viscoelastic deformation, which is a very important source of energy dissipation in polymeric materials. In general, there are two relaxation time scales, one is of the interface and the other is of the bulk. To simplify our analysis, we chose to study an elastomeric system so that the bulk dissipation could be avoided. It is possible that the interfacial and bulk relaxation processes are similar in some cases, in which WLF transform could work. This may be the case with some of the results published by Gent,[9,10] where the energy release rate follows the WLF superposition principle. There are, however, indications that one relaxation time may not adequately describe some of the situations[32] and that if the interface relaxes too fast, bulk viscoelastic deformation may not amplify interfacial fracture energy.[8] All these subtleties deserve careful analysis, which is the subject of our future studies.

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Appendix 1. Symbols

Σ_b	number of load-bearing polymer chains per unit area
Σ_o	number of load-bearing polymer chains per unit area at zero temperature
F	force on a typical chain
k_s	average spring constant
k_o	spring constant for small deformation
k_{max}	average spring constant at low temperature
n	number of units of a polymer chain
λ	activation length of bonds
A	persistence length
L_c	contour length of the chain, $L_c = nA$
k	Boltzmann constant, $k = 1.38 \times 10^{-23}$ J/K
h	Planck's constant, $h = 6.63 \times 10^{-34}$ J·s
T	absolute temperature
τ_-	relaxation time of bond dissociation
E_a	activation energy of bond dissociation
E	Young's modulus of the elastomer
ν	Poisson's ratio of the elastomer ≈1/2
L	cohesive zone length
$\delta(x)$	opening displacement in the cohesive zone as a function of distance (x) from the crack tip
V	steady-state crack velocity
K_A	applied stress intensity factor
K_L	local stress intensity factor
G	energy release rate required for crack growth
W_{ad}	work of adhesion.
$w(\delta)$	work needed to stretch a chain from its relaxed state to δ

Appendix 2

Asymptotic Behavior of the Energy Release Rate of Chaudhury et al.[7,8] When $\beta \gg 1$. Since $d\delta/dx = \alpha$, Σ_b can be obtained by integrating (9), which results in eq A1, i.e.

$$\Sigma_b = \Sigma_o \exp\left[-\beta\left(\exp\left(\frac{k_s\lambda}{kT}\,\delta\right) - 1\right)\right] \tag{A1}$$

where we have imposed the condition $\Sigma_b = \Sigma_o$ at $\delta = 0$. The energy release rate G is obtained by substituting (A1) into (7), i.e.

$$G = \Sigma_o k_s \int_0^\infty \delta \exp\left[-\beta\left(\exp\left(\frac{k_s\lambda}{kT}\,\delta\right) - 1\right)\right] d\delta \tag{A2}$$

Introduce the new variable $u = \exp((k_s\lambda/kT)\delta)$ or $\delta = (kT/k_s\lambda) \ln u$, (A2) becomes

$$\frac{\Sigma_o k_s (kT)^2}{2(k_s\lambda)^2}\, e^{\beta} \int_1^\infty \exp(-\beta u)\, d(\ln u)^2 \tag{A3}$$

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(28) Hui, C.-Y.; Jagota, A.; Bennison, S. J.; Londono, J. D. *Proc. R. Soc. London, Ser. A* **2003**, *459*, 1489.

(29) Johnson, K. L., Kendall, K., Roberts, A. D., *Proc. R. Soc. London, Ser. A* **1971**, *324*, 301.

(30) Tobolsky, A, Powell, R. E., Eyring, H. In *Chemistry of Large Molecules*; Burk, R. E., Grummitt, O., Eds.; Interscience Publishers: New York, 1943.

(31) Kramers, H. A. *Physica* **1940**, *VII* (4), 284.

(32) Thanawala, S. K.; Chaudhury, M. K. *Langmuir* **2000**, *16*, 1256.

With the change of variable $v = u - 1$, (A3) can be rewritten as

$$G = \frac{\Sigma_o k_s (kT)^2 \beta}{2(k_s \lambda)^2} \int_0^{\infty} [\ln(1 + v)]^2 \exp(-\beta v)\, dv \quad (A4)$$

The asymptotic behavior of the integral $\int_0^{\infty}[\ln(1 + v)]^2 \exp(-\beta v)\, dv$ for $\beta \gg 1$ can be obtained using Watson's Lemma,[26] i.e.

$$\int_0^{\infty} [\ln(1 + v)]^2 \exp(-\beta v)\, dv \approx \frac{2}{\beta^3} \qquad (A5)$$

$$\beta \gg 1$$

Combining (A4) and (A5) yields $G \approx \Sigma_o k_s (kT)^2/(k_s\lambda)^2\beta^2$.

Appendix 3

Crack Profile and Length of Cohesive Zone in the Limit of Lake and Thomas. The displacement δ_s due to the restraining spring traction σ acting on the crack face is

$$\delta_s(x) = -\frac{4}{\pi E^*} \int_0^{\infty} \sigma(x') \ln \left| \frac{x^{1/2} + x'^{1/2}}{x^{1/2} - x'^{1/2}} \right| dx' \quad (A6)$$

The total crack opening displacement $\delta(x)$ is the sum of the opening displacement due to the remote applied K_A field (5) and the closing displacement due to the restraining spring force (A6), i.e.

$$\delta(x) = \frac{8K_A}{2\pi^{1/2}E^*} x^{1/2} - \frac{4}{\pi E^*} \int_0^{L} \sigma(x') \ln \left| \frac{x^{1/2} + x'^{1/2}}{x^{1/2} - x'^{1/2}} \right| dx' \quad (A7)$$

where L is the cohesive zone length. As shown by Barenblatt,[21] the stress at the crack tip has a square root singularity given by (18), where

$$K_L = K_A - \left(\frac{2}{\pi}\right)^{1/2} \int_0^{L} \frac{\sigma(x')\, dx'}{x'^{1/2}} \qquad (A8)$$

In the rate independent limit, $\sigma = \Sigma_o k_{max} \delta$ inside the cohesive zone. Equation A7 becomes

$$\delta = \frac{8K_A x^{1/2}}{(2\pi)^{1/2}E^*} - \frac{4\Sigma_o k_{max}}{\pi E^*} \int_0^{L} \delta(x') \ln \left| \frac{x^{1/2} + x'^{1/2}}{x^{1/2} + x'^{1/2}} \right| dx' \quad (A9)$$

Now we normalize the distance from the crack tip using the cohesive zone length. The opening displacement is normalized by $8K_A L^{1/2}/(2\pi)^{1/2}E^*$, which is essentially the opening of a traction free crack at a distance L behind the crack tip. The normalized variables are

$$\bar{\delta} = \frac{(2\pi)^{1/2}E^*\delta}{8K_A L^{1/2}}, \qquad X = x/L \qquad (A10)$$

Using (A10), (A9) becomes

$$\bar{\delta} = X^{1/2} - \chi \int_0^{1} \bar{\delta}(X') \ln \left| \frac{X^{1/2} + X'^{1/2}}{X^{1/2} - X'^{1/2}} \right| dX' \quad (A11)$$

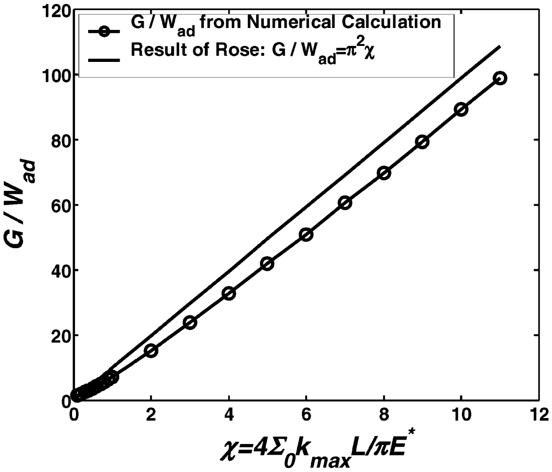

Figure 7. Relation between G/W_{ad} and the normalized cohesive zone length χ. Circles (lower curve) represent numerical solutions. The upper curve is the approximate solution given by (A14).

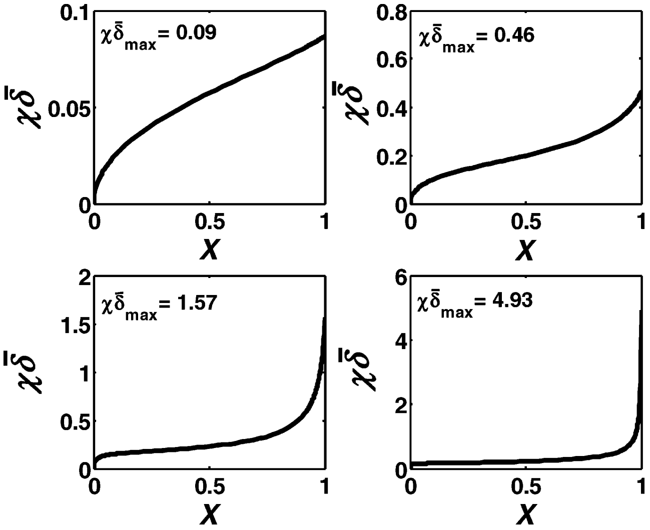

Figure 8. Normalized crack opening profiles versus normalized distance behind crack tip for different $\chi\bar{\delta}_{max}$.

where χ is the normalized cohesive zone length defined by

$$\chi = \frac{4\Sigma_o k_{max} L}{\pi E^*} \qquad (A12)$$

In normalized form, (A8) is

$$f = 1 - 2\chi \int_0^{1} \frac{\bar{\delta}(X')\, dX'}{X'^{1/2}} \qquad (A13)$$

where $f \equiv K_L/K_A = (W_{ad}/G)^{1/2}$. Ideally, the crack opening profile and the cohesive zone length should be obtained by numerically solving the linear integral equation (A11) in conjunction with (A13) and the fracture condition $\delta(L) = \delta_{max}$. In this case, χ and f are treated as unknowns. In practice, it is much easier to solve the integral equation (A11) with a known value of χ which allows f and $\bar{\delta}_{max} = [(2\pi)^{1/2}E^*\delta_{max}/8K_A L^{1/2}]$ to be determined. The dependence of the normalized cohesive zone length χ on f is shown in Figure 7. For most elastomers, $10 \le f^{-2} < 10^4$, so that $f \ll 1$. For small f, an asymptotic result due to Rose[23] can be used to determine the cohesive zone length. The result is

$$L \approx \frac{E^*}{4\pi\Sigma_0 k_{\max}} \frac{G}{W_{\mathrm{ad}}} \tag{A14}$$

Equation A14, which provides a good approximation for *L*, is also plotted in Figure 7. The relative error of our numerical results and Rose's approximation is within 10%. Finally, we note that eqs 27 and A14 imply that

$$f^{-2} = 1 + 4\pi^2(\chi\bar{\delta}_{\max})^2 \tag{A15}$$

In other words, f, χ, and $\bar{\delta}_{\max}$ are related. This relationship is verified by our numerical results.

Plots of normalized crack opening displacements $\chi\bar{\delta}$ versus distance behind the crack tip are shown in Figure 8. Here, the normalized crack opening $\chi\bar{\delta}$ is used instead of $\bar{\delta}$ since

$$\chi\bar{\delta} = \frac{\delta}{2\pi}\left(\frac{\Sigma_o k_{\max}}{2W_{\mathrm{ad}}}\right)^{1/2} \tag{A16}$$

is a crack opening displacement normalized by a displacement that depends only on material parameters.

The results in Figure 8 show that the crack opening profile is sensitive to $\chi\bar{\delta}_{\max}$. As $\chi\bar{\delta}_{\max}$ increases, the region where significant chain stretching occurs is concentrated to the edge of the cohesive zone away from the crack tip. According to (A16), for fixed $\delta_{\max}$ and $k_{\max}$, $\chi\bar{\delta}_{\max}$ depends only on $(\Sigma_o/W_{\mathrm{ad}})^{1/2}$. This means that large areal chain density and small work of adhesion cause the stretching of chains to be concentrated at the cohesive zone edge.

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