Theory of Chain Pull-Out and Stability of Weak Polymer Interfaces. 1

L. Kogan, C.-Y. Hui,* and A. Ruina

Department of Theoretical and Applied Mechanics, Cornell University, Ithaca, New York 14850

Received June 27, 1995; Revised Manuscript Received March 4, 1996⊗

ABSTRACT: Polymer/polymer interfaces reinforced with block copolymers or grafted chains can fail by the pull-out of these chains. A number of constitutive models have been proposed in the literature to describe the pull-out of a single chain. In this paper, we use these models to construct a continuum theory of a weak interface, and we study the stability of such an interface subjected to a homogeneous deformation. We show tht if the perturbation contains a Fourier component with wavelength exceeding a critical value Λ_c, then the homogeneous deformation is unstable. The dependence of Λ_c on the geometry, the stiffness of the material outside the interface, and the pull-out models is derived. We also study the stress field near the tip of a preexisting interface crack using the different pull-out models.

1. Introduction

Interfaces of immiscible polymers are normally weak as there are few chains which can penetrate far enough into the interface to become entangled there. The fracture toughness of such an interface can approach its ideal work of adhesion $W = \gamma_1 + \gamma_2 - \gamma_{12}$, where γ_1 and γ_2 are the surface energy of polymers 1 and 2, respectively, and γ_{12} is the interfacial energy. It has been known for some time that some polymer additives, called compatibilizers, are capable of strengthening these interfaces—for example, an additive which dissolves in phase 1 but chemically reacts with the polymer in phase 2 to form a graft copolymer at the interface. Another type of compatibilizer is the diblock copolymer, a block of polymer miscible with polymer 1 (often polymer 1 itself) joined covalently to a block of polymer miscible with polymer 2.

The toughening mechanisms of interfaces reinforced using the above class of compatibilizers have been recently explored by a number of experiments using different incompatible systems of polymer glasses.[1−7] Concurrently, theoretical models have been proposed to explain the reinforcement effect of these block copolymers, and a failure mechanism map has been developed,[8−11] based in part on these models, which attempts to predict the mechanism of interface failure as N, the polymerization index of each block, and Σ, the number of block copolymer chains per unit area, are changed. Consistent with the prediction of the failure mechanism map,[3,4,10] the interface fails by crazing followed by chain scission when N and Σ are large, while fracture takes place by chain scission of the block copolymer at the joint when N is large and Σ is small. On the other hand, for block copolymers with at least one short block, chain pull-out is the mechanism for interface fracture when Σ is small (Washiyama et al.[5]).

There are fewer experimental studies with emphasis on the failure mechanisms of incompatible rubber/rubber interfaces reinforced with compatibilizers. In a series of papers,[12−15] a micromechanical model of interface deformation and failure was proposed based on chain pull-out. Specifically, Rubinstein et al.[14] and Ajdari et al.[15] developed a constitutive model describing the pull-out of a single chain using statistical physics and previous results on the diffusion of a polymer molecule entangled in its melt (the rubber network is treated as a highly entangled melt). The chains which are pull-out and the bulk rubber are assumed to be chemically identical. The force required for chain pull-out is derived for three different velocity regimes. Raphael and de Gennes[12] analyzed the propagation of a preexisting crack along an interface reinforced by a uniform distribution of chains using the aforementioned pull-out model. They showed that initiation of pull-out can occur if the stress on the interface exceeds a critical level σ^*. In Rubinstein et al.,[16] the pull-out model proposed by Raphael and de Gennes[12] and Ajdari et al.[15] is used to estimate the energy dissipation of an interface in which chains are pulled out uniformly, independent of their position along the interface. Concurrently, similar theoretical models of crack propagation based on chain pull-out at polymer/polymer interfaces were also developed by Xu et al.[10] Brown[17] has recently performed experiments in which a smooth lens-shaped slider made of a cross-linked siloxane (poly(methylsiloxane) or PDMS) rubber network is slid over a flat, smooth substrate coated with the glassy polymer, polystyrene (PS). The interface between the PDMS and PS was reinforced by a thin layer (about 18-nm thick) of PS−PDMS diblock copolymer. Brown[17] attempted to correlate his observations with the chain pull-out theory proposed by Rubinstein et al.[14] and Ajdari et al.[15] and found reasonable agreement when the sliding rate is less than 2 mm/s.

The implicit assumption previously made in the interpretation of experimental results (e.g., in Rubinstein et al.[14] and Ajdari et al.[15]) was that chain pull-out is spatially homogeneous (i.e., every chain is pulled out by the same amount independent of its position along the interface). In this work, we show that even for the case of a very simple geometry and loading (spatially homogeneous in the plane of the interface), slight imperfections (modeled as perturbations in the initial interface opening) may cause nontrivial failure modes. In fact, these modes usually take place in real experiments, because spatially homogeneous solutions are typically unstable and some imperfections (e.g., stress concentrations and defects along the interface) are always present in real systems.

A related problem is the adhesion of systems composed of two different materials. It is increasingly

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1996.

evident that a quantitative measure of adhesion can sometimes be obtained via the measurement of interfacial fracture toughness as shown by Brown[2] and Creton et al.[3] The concept of interfacial fracture toughness requires the presence of a preexisting interface crack that is large compared with the fracture process zone. Typically, cracks are introduced artificially in specimens designed for fracture toughness testing. Thus, the classical fracture mechanics approach ignores the problem of crack nucleation and damage evolution, assuming that the asymptotic state at which the interface fails is caused by the growth of preexisting cracks.

Two fundamental issues arise when a constitutive model (e.g., the pull-out model) is used to describe the motion of an interface. The first is the question of strength of an interface reinforced by compatibilizers on which separation and/or slip may occur. The second is the question of the stability of motion once separation or slip of the interface occurs.

The aim of this paper and the following paper in this issue (part 1 and part 2) is to study these two issues for an interface which fails by chain pull-out. In the analysis below, we assume that chain pull-out is one sided; e.g., the chain is grafted on one of the polymers. In particular, we focus on the connection between interface instability and the failure modes of the interface. For example, is it possible that the pull-out model leads to spatial localization manifested by the nucleation of cracks along the interface? If so, does the interface ultimately fail due to the growth of a few large cracks or by the coalescence of many small cracks? Furthermore, how do these different failure modes depend on the applied load, the stiffness of the loading machine, the initial spatial distribution of the imperfections, and the microstructural parameters describing chain pull-out? The novelty of this work is to show that the pull-out model developed by refs 12−16 can lead to a very complex motion of the interface (nucleation of cracks and interface failure) without the imposition of complex boundary conditions such as preexisting cracks. The key result is that the motion of an interface reinforced by a spatially homogeneous distribution of chains and subjected to a spatially homogeneous load is unstable, leading to the failure of the interface.

The issue of interface stability is studied in part 1 of this work. In part 2, the time evolution of the instability is studied by numerical integration of the governing equations for the special case of a planar interface between an elastic half-space and a rigid substrate. The elastic half-space is the elastic material occupying the infinite half-space exterior to the interface. The dependence of crack initiation and the failure modes of the interface on loading and microstructural parameters is then explored.

The plan of part 1 of this work is as follows: chain pull-out models for a single chain are reviewed; we then carry out a linear stability analysis of an interface reinforced by a spatially homogeneous distribution of chains and subjected to a spatially homogeneous load. In other words, we investigate the stability of the spatially homogeneous solution in which all chains are pulled out by the same amount, independent of their positions along the interface. The linear stability analysis is carried out for a variety of mechanical systems, e.g., a weakening planar interface between an elastic half-space and a rigid substrate. The elastic half-space can be replaced by other elastic systems such as an elastic strip, an elastic beam, or an elastic membrane

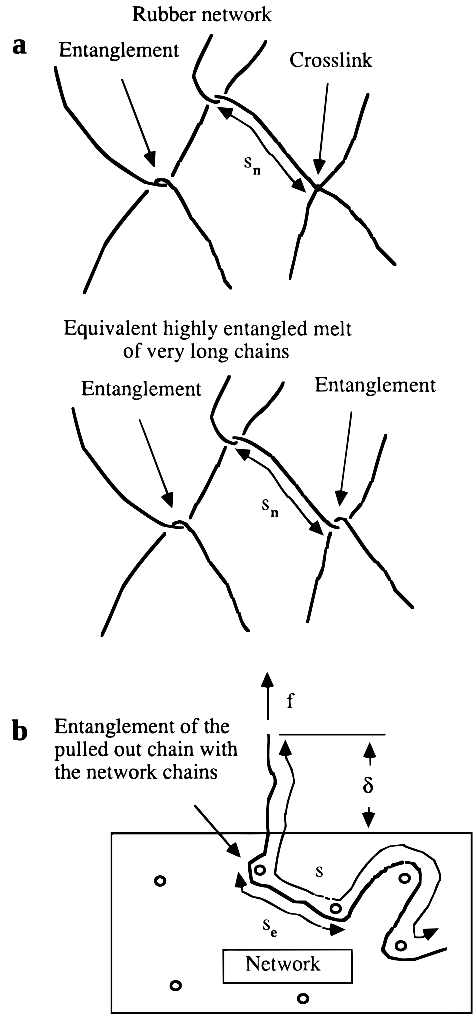

Figure 1. (a) Lightly cross-linked rubber network modeled as a highly entangled melt. The length of molecule strands between entanglements in the melt equals the length of molecule strands between topological constraints (cross-links and entanglements) in the rubber network, denoted as s_n. (b) Chain, entangled in the chemically identical, lightly cross-linked network (modeled as a highly entangled melt), pulled at one end with a force f that is larger than the critical value f^* below which chain pull-out cannot occur. δ denotes the distance of the chain end from the network. s is the total length of the chain; s_e is the length of the pulled out chain strand between its entanglements (denoted as circles) with the network chains. Since the network is treated as a highly entangled melt of very long chains (Ajdari et al.[15]) and the pulled out chain is assumed to be chemically identical to chains of the network, $s_e = s_n$ in a.

held taut at its ends by a tension T. The interface behavior assumed covers a whole family of constitutive laws describing the interface opening evolution. In the discussion, we investigate a crack propagation problem for the special case of an interface with preexisting cracks when the applied far-field stress is smaller than the interface threshold stress.

The following notations for citing equations will be used in this work. Equations in part 1 will be referred to as eq 1 *xx*, where *xx* is the equation number. For example, eq 1.12 is eq 12 in part 1. Likewise, eq 5 in part 2 will be referred to as eq 2.5.

2. Chain Pull-Out Model

The chain pull-out model developed by Raphael and de Gennes,[12] Ji and de Gennes,[13] Rubinstein et al.,[14] and Ajdari et al.[15] is schematically shown in Figure 1. In the model, the chain which is pulled out is imbedded in the chemically identical, lightly cross-linked rubber network which is modeled as a highly entangled melt (as was pointed out in Ajdari et al.,[15] a melt of very long chains behaves as a permanent network for a polymer chain being pulled out, Figure 1a). The average length of the molecule strands between entanglements in the melt is equal to the length of molecule strands between topological constraints (cross-links and entanglements) s_n in the rubber network. The number of constraints per unit volume is the same for the network and equivalent melt so that the short-time elastic properties of the network and the melt are identical. The chain is pulled at one end with a force f which is larger than the critical value f^* below which chain pull-out cannot occur. f^* is given by Raphael and de Gennes;[12] i.e.,

$$f^* \cong \frac{kT}{a}\sqrt{K_A} \qquad (1.1)$$

where a is the statistical segment length, T is the absolute temperature, and k is the Boltzmann constant. K_A is a material parameter which lies between 0 and 1 whose value depends on the properties of polymer chains and the environment, which is assumed here to be a poor solvent. Small values of K_A correspond to θ solvents; values of K_A close to 1 correspond to bad solvents, like air.

There are three possible regimes of pull-out, depending on the pull-out rate. In the analysis below, we assume that the pull-out rates correspond to the slow or fast regime. As was discussed by Raphael and de Gennes,[12] for slow and fast velocities, the pull-out force is proportional to the rate of pull-out, while for an intermediate range of pull-out rate, the force required for pull-out is essentially constant. Whenever possible, we will use the same notation as Raphael and de Gennes,[12] Ji and de Gennes,[13] Rubinstein et al.,[14] and Ajdari et al.[15]

Let δ denote the distance of the chain end from the network as the chain is pulled out by force f as shown in Figure 1b. Let Δ denote the distance of the chain end from the network as the chain is completely pulled out. As discussed by Raphael and de Gennes,[12]

$$\Delta = s\sqrt{K_A} \qquad (1.2)$$

where s is the total chain length. The factor $\sqrt{K_A}$ accounts for the fact that the chain is not fully stretched in the pull-out process. Let $\dot{\delta}(t,x)$ denote the time rate of change of δ; the force $f = f(\delta,\dot{\delta})$ for the chain pull-out is found to be

$$f = f^* + \frac{kT}{a^2}\frac{\tau_e}{\sqrt{K_A}}\, e^{[\mu(\Delta-\delta)]/[\sqrt{K_A}s_e]}\,\dot{\delta} \qquad (1.3a)$$

where τ_e is the relaxation time of a section of the pull-out chain between the entanglements and s_e is the length of the pull-out chain between entanglements. $\mu \approx 15/8$ is a constant. Equation 1.3a is valid only if $f > f^*$ (i.e., $\dot{\delta} > 0$) and $\delta < \Delta$. When $\delta = \Delta$, the chain is completely pulled out and the force f vanishes. Equation 1.3a is derived under the assumption that the rubber network is a melt of very long chains, chemically identical to the pull-out chain (which implies that $s_e = s_n$, Figure 1) and that the pull-out chain has at least one entanglement with the network (melt) molecules. An important characteristic of the pull-out chains imbedded in the network is their entanglement number, defined as an average number of entanglements of the pull-out chains with the molecules of the network, or formally as s/s_e (Figure 1b).

If we define the following constants,

$$B' = \frac{kT}{a^2}\frac{\tau_e}{\sqrt{K_A}} \qquad C = \frac{\mu}{\sqrt{K_A}s_e}$$

eq 1.3a becomes

$$f = f^* + B'e^{C(\Delta-\delta)}\dot{\delta} \qquad (1.3b)$$

Assuming that the chains are pulled out normally to the interface so that the tangential component of the pull-out force is zero, σ, the traction component normal to the planar interface, is related to the force f and Σ, the number of chains crossing a unit area of the interface, by $\sigma = f\Sigma$. Thus, the normal traction on the interface is related to the rate of chain pull-out and the remaining chain length $\Delta-\delta$ by

$$\sigma = \sigma^* + Be^{C(\Delta-\delta)}\dot{\delta} \qquad (1.3c)$$

Here $B = \Sigma B'$ and $\sigma^* = f^*/\Sigma$.

To summarize, at any instant in the loading history, either sticking, opening due to partial chain pull-out or opening due to complete chain pull-out (crack formation), can occur at a point $(x,0)$ on the interface. Conditions for these three states are as follows:

stick condition

$$\sigma < \sigma^* \qquad \dot{\delta} = \delta = 0 \qquad (1.4a)$$

opening conditions

(a) partial chain pull-out

$$\sigma = \sigma^* + Be^{C(\Delta-\delta)}\,\dot{\delta} \qquad \sigma > \sigma^* \text{ and } \Delta > \delta \qquad (1.4b)$$

(b) $\sigma = 0$

$$\delta \geq \Delta \qquad (1.4c)$$

At this point, we should mention that different versions of the above pull-out model exist in the literature.[10,12,15] These versions are sometimes approximations of eq 1.3a and are employed to simplify the solutions of boundary value problems. In some cases, additional features are added to eq 1.3a with the aim of improving the modeling of the pull-out process. Since considerable differences in the stress behavior near a crack tip can occur depending on which one of these models is used to study fracture, in the following, we shall give a brief description of these models and summarize the differences in the crack tip stress field predicted by these models for the case of a propagating crack. This summary will give a fracture mechanics perspective to the problem. It also sets the stage for the problem of crack nucleation and crack growth in such interfaces.

In the work of Ajdari et al.,[15] the term f^* in eq 1.3a is neglected so that the model for pull-out becomes

$$\sigma = \frac{kT}{a^2}\frac{\tau_e}{\sqrt{K_A}}\, e^{[\mu(\Delta-\delta)]/[\sqrt{K_A}s_e]}\dot{\delta} \qquad (1.5)$$

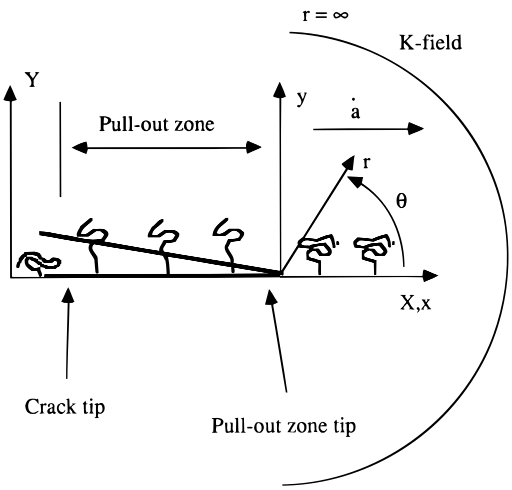

Figure 2. Plane strain crack, semiinfinite in length, propagating along the interface of two linearly elastic half-spaces with a steady-state velocity of $\dot{a}$ under small-scale yielding condition. The interface is reinforced by polymer chains. *(x,y)* is the Cartesian coordinate frame attached to the moving crack tip. The pull-out zone is defined as a region directly ahead of the crack tip in which interface opening is greater then zero but less than the critical value Δ; i.e., $\Delta > \delta(x,t) > 0$.

Another variation is to replace the exponential in eq 1.3a by

$$e^{[\mu(\Delta-\delta)]/[\sqrt{K_A}s_e]} \rightarrow D'(\Delta - \delta) \quad (1.6)$$

where D' is a material constant.[12] In this case, the pull-out model has the form

$$\sigma = \sigma^* + D'(\Delta - \delta)\dot{\delta} \quad (1.7)$$

where D' is a material constant. Analyses are sometimes carried out by replacing $\Delta - \delta$ in eq 1.7 by δ so that eq 1.7 becomes

$$\sigma = \sigma^* + D'\Delta\dot{\delta} \quad (1.8)$$

Raphael and de Gennes[12] used the even simpler expression

$$\sigma = D'\Delta\dot{\delta} \quad (1.9)$$

in their calculation. Another version of the model used by Xu et al.[10] to study the pull-out of chains from polymer glasses is

$$\sigma = b(\Delta - \delta)(\dot{\delta} + \dot{\delta}^*) \quad (1.10)$$

where b and $\dot{\delta}^*$ are material constants such that $\sigma^* = b\dot{\delta}^*$. It should be noted that this model is purely phenomenological and was used to interpret experimental results.

All of the equations above assume that the condition $\dot{\delta} > 0$ is satisfied. Figure 2 shows a typical situation where these models are used to study crack propagation (Raphael and de Gennes[12]). A plane strain crack, semiinfinite in length, is assumed to propagate along the interface of two linearly elastic half-spaces with a steady-state velocity $\dot{a}$ under small-scale yielding condition. The interfaces are reinforced by chains which obey any of the pull-out laws stated in eqs 1.3 and 1.7−1.10. The steady-state condition implies that all field quantities are independent of time with respect to an observer moving with the crack tip; i.e., the material time derivative D/Dt at a fixed material point can be replaced by

$$D(...)/Dt = -\dot{a}(...)_{,x} \quad (1.11)$$

where the $(...)_{,x}$ denotes the partial derivative with x, and (x,y) are the coordinates of a point with respect to a Cartesian frame attached to the moving crack tip (Hui et al.[9]). The small-scale yielding condition (SSY) implies that the region of pull-out is small compared with typical specimen dimensions so that the crack is modeled as semiinfinite, with the remote Cartesian stress components σ_{ij} given by the asymptotic condition

$$\sigma_{ij}(r,\theta) \rightarrow K_I\hat{\sigma}_{ij}(\theta)/\sqrt{2\pi r} \qquad r \rightarrow \infty \quad (1.12)$$

where (r,θ) is the polar coordinate system attached to the moving crack tip. K_I is the mode I stress intensity factor and $\hat{\sigma}_{ij}(\theta)$ are universal functions describing the angular variation of the stress tensor far away from the crack tip.[18] As pointed out by Rice,[18] the stress intensity factor K_I uniquely characterizes the load sensed at the crack tip.

δ is a function of the position and time and is interpreted as the opening displacement of the interface crack. The region directly ahead of the crack tip where pull-out occurs is defined by $0 \le \sigma^* < \sigma_{yy}(x,y=0) \equiv \sigma(x)$ and is often called the cohesive zone. In this region, $\Delta > \delta(t,x) > 0$. In order to determine the dependence of the rate of crack growth on the applied loading K_I, a crack growth condition must be specified. A natural fracture criterion, consistent with the interface model, is that crack growth occurs when the condition $\delta = \Delta$ is satisfied at the physical crack tip located at $x = 0$. The location x^* where the condition

$$\sigma_{yy}(x^*,y=0) = \sigma^* \quad (1.13)$$

is defined as the tip of the cohesive zone. The existence of a finite cohesive zone tip is possible since

$$\dot{\delta} = 0 \quad \text{if} \quad \sigma(x) < \sigma^* \quad (1.14)$$

Note that the cohesive zone tip will not exist (it will be located at $x = \infty$) if $\sigma^* = 0$. It is a well-known result that a necessary condition for the stress to be continuous at x^* is $\delta_{,x}(x^*) = 0$ (Barenblatt[19]). The "," denotes partial derivative.

As pointed out by Fager et al.,[20] in rate-dependent problems, the stress field at the crack tip is not known a priori. For example, the interface pull-out models given by eqs 1.5, 1.8, and 1.9 all have the same velocity-dependent stress singularity at the crack tip at $x = 0$. It was shown by Fager et al.[20] that the stress singularity near the crack tip for an interface model of the form in eq 1.9 is

$$\sigma = M'(\dot{a})x^{-\theta(\dot{a})+1/2} \quad (1.15)$$

where $M'(\dot{a})$ is a function of the crack propagation rate and other material constants and $\theta(\dot{a}) = \frac{1}{\pi}\arctan(0,\pi)(-\pi/\dot{a})$.

By using this result, one can easily deduce that the stress singularity for the interface models given by eqs 1.5 and 1.8 is the same as eq 1.9, i.e., eq 1.15. This is easy to see for the case of eq 1.5, since the two interface models eqs 1.5 and 1.9 have the same asymptotic behavior near the crack tip; i.e., as $x \to 0^+$, eq 1.5 becomes

$$\sigma = \frac{kT}{a^2}\frac{\tau_e}{\sqrt{K_A}}\dot{\delta} \tag{1.16}$$

where we have used the fracture criterion $\delta = \Delta$. Consider the case of eq 1.8. There are two possibilities: (a) the stress is bounded at the crack tip and equals $\sigma^* > 0$ as $x \to 0^+$; (b) the stress σ or $\dot{\delta}$ is unbounded as $x \to 0^+$. If a is true, then the traction $\sigma_{yy}(x,y=0) \equiv \sigma(x)$ must have a jump discontinuity at $x = 0$. This is because $\sigma_{yy}(x,y=0) \equiv \sigma(x) = 0$ for all $x < 0$ as the crack is traction free. A well-known result in elasticity then implies that $\delta_{,x} = -\dot{\delta}/\dot{a}$ must have a logarithmic singularity at $x = 0$ (Timoshenko, Goodier[21]). By eq 1.8, this means that the stress as $x \to 0^+$ must be unbounded, which contradicts our original hypothesis a. Therefore, b must be true. If b is true, the interface material at small distances directly ahead of the crack tip must behave like eq 1.9. This means that the nature of singularity for eq 1.8 must be the same as eq 1.5.

Consider the interface models given by eqs 1.7 and 1.10. The stress $\sigma(x)$ as $x \to 0^+$ is bounded in these models as long as one imposes the fracture criterion $\delta = \Delta$ at $x = 0$. This is because the factor $\delta - \Delta$ goes to zero as $x \to 0^+$. The steady-state crack growth problem for an interface which behaves like eq 1.10 was solved by Xu et al.[10] As expected, this solution shows that the traction $\sigma(x) \to 0$ as $x \to 0^+$ so that the traction is continuous at the crack tip. For the case of 1.7, it is easy to see that the traction $\sigma(x) \to \sigma^*$ as $x \to 0^+$.

The above argument shows that using the interface model described by eq 1.4 would lead to the stress singularity given by eq 1.15. This singularity can be eliminated by modifying eq 1.4b to

$$\sigma = \sigma^* + B[e^{C(\Delta-\delta)} - 1]\dot{\delta} \qquad \sigma > \sigma^* \quad \text{and} \quad \Delta > \delta \tag{1.17}$$

Note that, since $e^{C\Delta} \gg 1$, the above modification has no significant effect on the pull-out model until pull-out is almost complete. Note that the interface model, eq 1.4, is based on the micromechanical model of chain pull-out, eq 1.1, which was derived under the assumption that each chain has at least one entanglement. This assumption is violated when the portion of the chain remaining in the network is shorter than its entanglement length s_e, i.e., in the end of the pull-out process. Indeed, the modifying factor $\Delta - \delta$ in eq 1.6 was introduced by Raphael and de Gennes[12] to overcome this difficulty. The modified pull-out model, eq 1.17, implies that $\sigma(x) \to \sigma^*$ as $x \to 0^+$.

To summarize, the pull-out models, eqs 1.4b and 1.5–1.10, discussed in this work have the general form

$$\dot{\delta} = 0 \qquad \sigma < \sigma^* \tag{1.18a}$$

$$\sigma = a\sigma^* + \phi(\delta/\Delta)\dot{\delta} \qquad \dot{\delta} > 0, \quad \delta < \Delta \tag{1.18b}$$

$$\sigma = 0 \qquad \delta > \Delta \tag{1.18c}$$

where a is either one or zero and ϕ is an arbitrary monotonically decreasing function of its argument and can be determined easily from eqs 1.4b and 1.5–1.10.

3. Linear Stability Analysis and Crack Nucleation

Consider the planar interface between a rigid half-space and a linearly elastic system which we assume to be an elastic half-space. This geometry is illustrated in Figure 3. The chains can be pull-out only from the upper half-plane (e.g., these chains are grafted on the material of the lower half-plane). To simplify the mathematics, we will assume that the deformation is at most two dimensional. For the case of an elastic half-space, the deformation is either in-plane stress or plane strain. At time $t = 0$, a uniform stress σ_∞ is applied to the elastic component as illustrated by Figure 3. Since chains are assumed to be pulled out normally to the interface, we seek solutions where the shear traction on the interface $y = 0$ is identically zero.

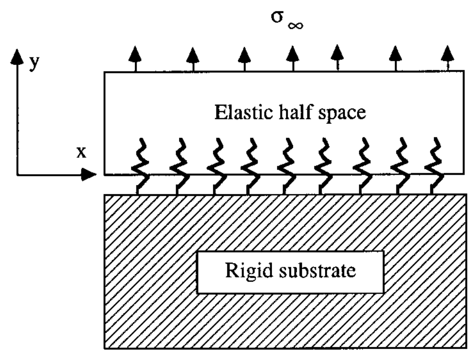

Figure 3. Planar interface between a rigid half-space and an elastic half-space. A uniform stress σ_∞ is applied to the elastic half-space. This figure shows the homogeneous solution where the chains are pulled out uniformly in space.

Specifically, we seek solutions for an elastic half-space occupying the upper half-plane, whose boundary (i.e., $y = 0$) is subjected to the conditions specified by eq 1.18. The governing equation for the stress field in the upper half-plane is the biharmonic equation

$$\nabla^4\Psi = 0 \tag{1.19}$$

where Ψ is the Airy stress function. The stresses σ_{ij} (i, $j = 1, 2$) in the upper half-plane $y > 0$ are related by Ψ by

$$\sigma_{ij} = \delta_{ij}\nabla^2\Psi - \Psi_{,ij}$$

where ∇^2 is the 2D Laplacian operator and δ_{ij} the Kronecker delta. The boundary conditions are

$$\Psi_{,xy}(t,x,0) = \Psi_{,xy}(t,x,\infty) = \Psi_{,yy}(t,x,\infty) = 0$$

$$\Psi_{,xx}(t,x,\infty) = \sigma_\infty \tag{1.20a}$$

$$\dot{\delta}(t,x,0) = 0 \qquad \text{for} \quad \Psi_{,xx}(t,x,0) < \sigma^* \tag{1.20b}$$

$$\Psi_{,xx}(t,x,0) = a\sigma^* + \phi(\delta/\Delta)\dot{\delta} \qquad \text{for} \quad \Psi_{,xx}(t,x,0) > \sigma^* \quad \text{and} \quad \Delta > \delta \tag{1.20c}$$

$$\Psi_{,xx}(t,x,0) = 0 \qquad \text{for} \quad \Delta \le \delta \tag{1.20d}$$

where a "," denotes partial derivative. The initial conditions are

$$\delta(0,x,0) = \epsilon g(x) \tag{1.20e}$$

where $g(x)$ is some given functions, $0 \le g(x) \le \Delta$, and ϵ is a constant, which controls the amplitude of the initial interface opening displacement. Equation 1.20a expresses the condition that the only nonvanishing stress as $y \to \infty$ is the spatially uniform normal traction σ_{yy}. Equation 1.20b enforces the condition that the interface

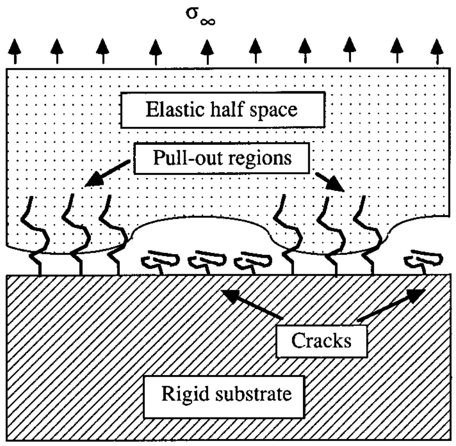

Figure 4. Elastic half-space bonded to a rigid half-space. A homogeneous traction normal to the interface, $\sigma_\infty > \sigma^*$, is applied to the elastic half-space at infinity. Cracks and pull-out zones are formed along the interface. Cracks are traction free as the chains are completely pulled out in the crack regions.

is intact when $\sigma_{yy} < \sigma^*$, whereas the amount of pull-out at a spatial point x is given by the pull-out model, eq 1.18, when $\sigma_{yy} > \sigma^*$ and $\Delta > \delta$. Finally, the formation of crack is expressed by eq 1.20d.

Although the governing PDE, eq 1.19, is linear and elliptic, the boundary condition on the interface $y = 0$ is nonlinear and time dependent. Furthermore, both the displacement $\delta(x,t)$ and the normal traction $\sigma(x,t) \equiv \sigma_{yy}(x,y=0,t) = \Psi_{,xx}(x,y=0,t)$ are unknown on the interface.

The simplest solution to problem eq 1.20 can be obtained by considering the case where $\sigma_\infty < \sigma^*$. In this case, the solution is spatially homogeneous with $\delta = 0$ on the interface. For example, if the elastic system is the upper half-space, the solution of eq 1.20 corresponds to a uniform straining of an elastic half-space attached to a frictionless rigid substrate. Thus, the strength of the interface can be defined as σ^*.

The more interesting case is when $\sigma_\infty > \sigma^*$. In this case, the pull-out force can vary along the interface once opening occurs. Physically, we expect that the solution is very sensitive to initial conditions. These solutions correspond to the formation of cracks and pull-out zones along the interface, as schematically shown in Figure 4 for the case of the elastic half-space.

We shall identify the opening of the interface with $\delta(t,x)$. At any instant in time t, the normal traction $\sigma(t,x)$ on the interface can be decomposed into two parts, due to the linearity of the elastic system; i.e.,

$$\sigma = \sigma_\infty + \sigma^{\text{elastic}}$$

The first term σ_∞ corresponds to a spatially homogeneous solution for which stresses are uniform in the elastic system (i.e., $\sigma_{yy} = \sigma_\infty$, and all other in-plane stress components equal zero) as shown in Figure 3. The second term σ^{elastic} equals minus the normal traction on the surface of the elastic system due to the surface displacement $\delta(t,x)$; it can be found by solving a boundary value problem, i.e., eq 1.19 subjected to traction-free conditions at infinity and with the displacement on $y = 0$ given by $\delta(t,x)$ when the elastic system is an elastic half-space. Since the mechanical system outside the interface is linearly elastic, σ^{elastic} is a linear operator acting on $\delta(t,x)$, and it can be found using the theory of elasticity. For the case of elastic half-space loaded in plane strain,

$$\sigma^{\text{elastic}}(\delta(t,x)) = \frac{G}{\pi(1-\nu)} \int_{-\infty}^{\infty} \frac{\delta_{,\xi}(t,\xi)}{\xi - x}\, d\xi \qquad (1.20f)$$

where G is the shear modulus and ν is Poisson's ratio of the half-space. For the case of plane stress, σ^{elastic} is given by eq 1.20f with ν replaced with $\nu/(1-\nu)$.

According to eq 1.18, the time evolution of the interface opening during pull-out ($\sigma > \sigma^*$ and $\delta < \Delta$) is given by

$$\dot{\delta} = 0 \qquad \sigma < a\sigma^*$$

$$\sigma_\infty + \sigma^{\text{elastic}}(\delta(t,x)) = a\sigma^* + \phi(\delta(t,x)/\Delta)\dot{\delta}(t,x) \qquad \dot{\delta} > 0, \quad \delta < \Delta$$

$$\sigma_\infty + \sigma^{\text{elastic}}(\delta(t,x)) = 0 \qquad \delta > \Delta \qquad (1.21a)$$

where $\dot{\delta}(t,x) \equiv \partial/\partial t\ \delta(t,x)$. From now on, we shall omit arguments of these functions as long as it does not lead to confusion.

We assume that $\sigma^{\text{elastic}}(\delta)$ is a linear integral operator acting on δ,x,

$$\sigma^{\text{elastic}}(\delta) \equiv \sigma^{\text{elastic}}[\delta_{,x}]$$

According to eq 1.20f, this is true for the case of elastic half-space. Under this assumption, eq 1.20a can be normalized. Specifically, if we define

$$t' = \frac{\sigma_\infty - \sigma^*}{\phi_0 x_0}\, t$$

$$x' = \frac{\sigma_\infty - \sigma^*}{G_0 x_0}\, x$$

$$u(t',x') = \frac{\delta(t,x)}{x_0}$$

$$\tilde{\phi}(u) = \frac{1}{\phi_0} = \frac{1}{\phi_0}\, \phi\left(\frac{x_0}{\Delta}\, u\right)$$

$$\tilde{\sigma}^{\text{elastic}}(u) = \frac{1}{\sigma_\infty - \sigma^*}\, \sigma^{\text{elastic}}(\delta) \qquad (1.21b)$$

where x_0 has dimensions of length (length scale of the system), G_0 has dimensions of stress (effective stiffness of the elastic component), and ϕ_0 has dimensions of stress/rate (effective friction coefficient of the pull-out law), eq 1.21a becomes

$$\dot{u} = 0 \qquad \sigma < a\sigma^*$$

$$\tilde{\sigma}^{\text{elastic}}(u) + 1 = \tilde{\phi}(u)\, \frac{\partial u}{\partial t'} \qquad \dot{u} > 0, \quad u < \frac{\Delta}{x_0}$$

$$\tilde{\sigma}^{\text{elastic}}(u) + \frac{\sigma_\infty}{\sigma_\infty - \sigma^*} = 0 \qquad u < \frac{\Delta}{x_0} \qquad (1.21c)$$

3.1. Spatially Homogeneous Solution, $\sigma_\infty > \sigma^*$. A spatially homogeneous solution ($\sigma^{\text{elastic}} = 0$ for all x

and t, $g(x) = 0$) exists. In general, the homogeneous solution $\delta_0(t)$ is obtained by integrating eq 1.18b; i.e.,

$$(\sigma_\infty - a\sigma^*)t = \Delta \int_0^{\delta_0(t)/\Delta} \phi(\eta)\, \mathrm{d}\eta \qquad (1.22a)$$

For the special case of $\phi(\delta/\Delta) = Be^{C(\Delta-\delta)}$ (see eq 1.4b), the opening displacement $\delta(t,x) = \delta_0(t)$ on the interface is found by integrating eq 1.22a; i.e.,

$$\delta_0(t) = -\frac{1}{C}\ln\left(1 - \frac{\sigma_\infty - \sigma^*}{Be^{C\Delta}}Ct\right) \qquad (1.22b)$$

This solution indicates that all chains on the interface are pulled out by the same amount and the interface fails simultaneously when $\delta_0(t) = \Delta$, i.e., when

$$t = \frac{(1 - e^{-\Delta C})Be^{C\Delta}}{C(\sigma_\infty - a\sigma^*)}$$

3.2. Crack Nucleation. Consider a special case when the elastic component of the system is the elastic half-space loaded in plane strain, as shown in Figure 3, and the chain pull-out law is given by eqs 1.4a–c. We normalize time, spatial coordinate, and interface opening respectively by setting

$$x_0 = \frac{1}{C} \quad G_0 = \frac{G}{1-\nu} \quad \phi_0 = Be^A$$

in eq 1.21b. A is defined by

$$A = C\Delta = \mu\frac{s}{s_e} \approx \frac{15}{8}\frac{s}{s_e} \qquad (1.23a)$$

where G is the shear modulus and ν is Poisson's ratio of the elastic half-space.

This yields

$$t' = \frac{(\sigma_\infty - \sigma^*)C}{Be^A}t$$

$$x' = \frac{(\sigma_\infty - \sigma^*)C(1-\nu)}{G}x$$

$$u(t',x') = \frac{A}{\Delta}\delta(t,x)$$

$$\tilde{\phi}(u) = e^{-u}$$

$$\tilde{\sigma}^{\mathrm{elastic}}(u) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{u_{,\xi'}(t',\xi')}{\xi' - x'}\,\mathrm{d}\xi' \qquad (1.23b)$$

Note that G for an elastomer is given by

$$G = \frac{\rho RT}{M_n} = \frac{\rho RTa}{s_n M_0}$$

where ρ is the density of the elastomer, M_n is the molecular weight of the elastomer chain strands between constraints, and s_n is the length of the elastomer chain strands between constraints. Recall that the constitutive model of the chain pull-out is based on the assumption that $s_e = s_n$ so that the normalization of the spatial coordinate is independent of s and s_e:

$$x' = \frac{(\sigma_\infty - \sigma^*)\mu M_0 x(1-\nu)}{\sqrt{K_A}\rho RTa}$$

With these normalized variables, the governing equations of the interface opening become

$$\tilde{\sigma}^{\mathrm{elastic}}(u) + 1 = e^{-u}\frac{\partial u(t',x')}{\partial t'} \qquad u < A \qquad (1.24a)$$

$$\tilde{\sigma}^{\mathrm{elastic}}(u) + \frac{\sigma_\infty}{\sigma_\infty - \sigma^*} = 0 \qquad u \geq A \qquad (1.24b)$$

$$u(t=0,x') = \epsilon'\tilde{g}(x') \qquad (1.24c)$$

where $\epsilon' = A\epsilon$, $\tilde{g}(x') = g(x)/\Delta$, and ϵ is the amplitude of the initial perturbation; i.e.,

$$\delta(t=0,x) = \epsilon g(x) \qquad (1.24d)$$

where $0 \leq g(x) \leq \Delta$.

Using this normalization, the homogeneous solution with $g(x) = 0$ becomes

$$u_0 = -(\log(1 - t')) \qquad (1.24e)$$

so that the failure of the interface occurs at $u_0 = A$; i.e., $t' = 1 - e^{-A}$.

The normalization used, eq 1.23, is based on the assumption that the elastic component of the system is the elastic half-space. For other elastic systems, a similar normalization can be found, resulting in normalized equations similar to eq 1.24. The assumption $\sigma^{\mathrm{elastic}}(\delta) \equiv \sigma^{\mathrm{elastic}}[\delta_{,x}]$ may be relaxed. The resulting form of the linear operator $\tilde{\sigma}^{\mathrm{elastic}}$ and expression for x' will depend on each particular system.

We define crack nucleation as follows:

Crack nucleation is said to occur at time T_c and at location $x_c(T_c)$ is $u(t<T_c,x) < A$ for all x and $u(t=T_c,x_c) = A$.

The normalized equations, eqs 1.24a–d, allow simplification of the crack nucleation problem, since these equations depend only on the material parameter A and the initial perturbation. To investigate the dependence on A, let $u(t,x;\epsilon')$ be the solution of eq 1.24a subjected to the initial condition eq 1.24c. Let $u_{\max}(T,\epsilon')$ be the maximum value of $u(t,x;\epsilon')$ at time $t = T > 0$ for a fixed value of ϵ':

$$u_{\max}(T,\epsilon') = \max_x [u(T,x;\epsilon')] = u(T,x_{\max}(T,\epsilon'))$$

where $x_{\max}(T,\epsilon')$ is defined as a value of spatial coordinate at which the maximum of the interface opening is achieved. Note that crack nucleation cannot occur if $A > u_{\max}(T,\epsilon')$. Clearly, if we *choose* $A = u_{\max}(T,\epsilon')$, then crack nucleation occurs at time T at $x_{\max}(T,\epsilon')$. Thus, the dependence of crack nucleation on the material parameters A and ϵ can be studied by finding the maximum of the solution of eq 1.24a at each moment of time.

3.3. Stability of the Homogeneous Solution. The stability of the interface subjected to homogeneous far-field loading (before the crack nucleation) is analyzed by investigating the linear stability of homogeneous solution, eq 1.22, with respect to the perturbations of the initial conditions given by eq 1.24c.

The stability analysis depends on the functional form of the chain pull-out law but does not depend on the specific form of the elastic operator $\tilde{\sigma}^{\text{elastic}}$. The stability analysis given below is valid for the class of interfaces which can be characterized by the dimensionless equations eq 1.21c, i.e., for systems with a wide range of possible elastic components and with the functional form of the pull-out law given by eq 1.18. The stability analysis is carried out in the regime $\sigma_\infty > \sigma^*$ and $u < A$ so that the second equation in eq 1.18 is the only relevant equation governing the deformation of the interface.

Recall that the second equation in eq 1.21a can be written in dimensionless form

$$\dot{u}\tilde{\phi}(u) = 1 + \tilde{\sigma}^{\text{elastic}}(u) \tag{1.25}$$

where u, $\tilde{\phi}(u)$, and $\tilde{\sigma}^{\text{elastic}}(u)$ are defined by eq 1.23b for the special case of an elastic half-space. In eq 1.25 and in the equations below, we will omit primes in the notation for the normalized spatial and temporal coordinates unless otherwise specified. The weakening of the interface is modeled by the assumption that $\tilde{\phi}(u)$ is a positive monotonically decreasing function of u. This implies that $u_0(t)$ is a monotonically increasing function of time. The spatially homogeneous solution will be denoted by $u_0(t)$ (e.g., $-(\log(1 - t))$ for the special case of $\tilde{\phi}(u) = e^{-u}$; see eqs 1.23b and 1.24e).

Consider a spatially inhomogeneous solution $u(t,x)$ which is a perturbation of the homogeneous solution $u_0(t)$; i.e.,

$$u(t,x) = u_0(t) + \epsilon u_N(t,x) + O(\epsilon^2)$$

where $\epsilon > 0$ is a small parameter. Linearization of eq 1.25 leads to the following equation for $u_N(t,x)$:

$$\dot{u}_N(t,x)\tilde{\phi}(u_0) = \tilde{\sigma}^{\text{elastic}}(u_N) - \dot{u}_0\tilde{\phi}'(u_0)u_N \tag{1.26}$$

Let $u_x(x,\kappa)$ be an eigenfunction of the linear operator $\tilde{\sigma}^{\text{elastic}}$, and let $\lambda(\kappa)$ be the associated eigenvalue; i.e.,

$$\tilde{\sigma}^{\text{elastic}}(u_x(x,\kappa)) = \lambda(\kappa)u_x(x,\kappa) \tag{1.27}$$

For the geometry we consider in this work, it is easy to verify that the eigenfunctions in space are of the form $u_x(x,\kappa) = e^{i\kappa x}$. It is important to note that the eigenfunctions $u_x(x,\kappa)$ are the boundary values of functions $u_x(x,y,\kappa)$ that satisfy the governing equations in the elastic system. For example, for the case when the elastic system is an elastic half-space bonded to a rigid substrate, $u_x(x,y,\kappa)$ is the vertical component of the normalized displacement field and can be derived from a stress function Ψ that satisfies the biharmonic equation (see eq 1.19). In particular,

$$\lim_{y\to 0^+} u(x,y,\kappa) = u_x(x,\kappa) \tag{1.28}$$

In other words, $\lambda(\kappa)$ and $u_x(x,\kappa)$ are determined by solving the differential equations governing the elastic system. Physically, they represent periodic spatial perturbations with a wavelength $2\pi x_0(\sigma_\infty - \sigma^*)/(G_0|\kappa|)$. For the case of an elastic half-space, the normalization, eq 1.23b, leads to $\lambda(\kappa) = -|\kappa|$.

The general solution of eq 1.26 subjected to the boundary condition eq 1.24 is obtained by first seeking time-dependent eigenfunctions of the governing equations in separable form; i.e.,

$$u_N(t,x,y) = u_x(x,y,\kappa)u_t(t,\kappa) \tag{1.29}$$

On the interface $y = 0$,

$$u_N(t,x,y=0) = u_N(t,x) = u_x(x,\kappa)u_t(t,\kappa) \tag{1.30}$$

By substitution of eq 1.29 into eq 1.26, we obtain the following equation on $u_t(t)$:

$$\frac{d}{dt}\log(u_t(t,\kappa)) = \left(\lambda(\kappa) - \frac{\tilde{\phi}'(u_0)}{\tilde{\phi}(u_0)}\right)\dot{u}_0 \tag{1.31}$$

where $\tilde{\phi}'(u_0) \equiv (d/du)\tilde{\phi}(u)|_{u=u_0}$. Note that since $u_0(t)$ is a monotonically increasing function of time, there is a one-to-one correspondence between $u_0(t)$ and t. This observation allows us to consider $u_t(t)$ as a function of $u_0(t)$. Thus, eq 1.31 can be rewritten in the form

$$\frac{d}{du_0}\log(u_t(u_0,\kappa)) = \left(\lambda(\kappa) - \frac{\tilde{\phi}'(u_0)}{\tilde{\phi}(u_0)}\right) \tag{1.32a}$$

Equation 1.32a may be solved for u_t as a function of u_0, resulting in

$$u_t(u_0) = \exp\left\{\int_0^{u_0}\left(\lambda(\kappa) - \frac{\tilde{\phi}'(u_0)}{\tilde{\phi}(u_0)}\right)du_0\right\} = \tilde{\phi}(0)e^{\lambda(\kappa)u_0 - \log(\tilde{\phi}(u_0))} = \tilde{\phi}(0)\frac{e^{\lambda(\kappa)u_0}}{\tilde{\phi}(u_0)} \tag{1.32b}$$

From eqs 1.29 and 1.32b, it is clear that the growth and decay of a periodic perturbation of normalized wavelength $2\pi/|\kappa|$ depends on the sign of $\lambda(\kappa) - \tilde{\phi}'(u_0)/\tilde{\phi}(u_0)$. This motivates us to define the following stability conditions:

The inhomogeneous term $u_N(t,x,y) = u_x(x,y,\kappa)u_t(t,\kappa)$, resulting from the perturbation in initial condition, is instantaneously stable (decaying) at time t if

$$\frac{d}{du_0}\log(u_t(u_0,\kappa))|_{u_0=u_0(t)} < 0 \tag{1.32c}$$

Conversely, $u_N(t,x,y) = u_x(x,y,\kappa)u_t(t,\kappa)$ will be called instantaneously unstable (growing) if

$$\frac{d}{du_0}\log(u_t(u_0,\kappa))|_{u_0=u_0(t)} > 0 \tag{1.32d}$$

It is clear that $\text{sgn}((d/du_0)\log(u_t(u_0,\kappa))|_{u_0=u_0(t)})$ is determined entirely by $\lambda(\kappa)$ (which depends on the elastic system) and the properties of $\tilde{\phi}(u)$ (which depends on the interface model).

Using eq 1.32b and the principle of superposition, the exact solution of eq 1.26 subjected to arbitrary initial perturbation $u_N(u_0(t=0),x)$ is

$$u_N(u_0,x) = \tilde{\phi}(0)\int_{-\infty}^{\infty} u_N(u_0(t=0),\kappa)e^{i\kappa x}\frac{e^{\lambda(\kappa)u_0}}{\tilde{\phi}(u_0)}\,d\kappa \tag{1.33a}$$

where

$$u_N(u_0(t=0),\kappa) = \frac{1}{2\pi}\int_{-\infty}^{\infty} u_N(u_0(t=0),x)e^{i\kappa x}\,dx \tag{1.33b}$$

is the Fourier transform of $u_N(u_0(t=0),x)$.

We define a normalized critical wavelength of the imposed perturbation

$$\tilde{\Lambda}_c(u_0) = \frac{2\pi}{\kappa_c(u_0)}$$

by

$$\frac{d}{du_0}\log(u_t(u_0,\kappa))\bigg|_{u_0=u_0(t),\kappa=\kappa_c(u_0)} = 0 \qquad (1.34)$$

By eq 1.31, the critical wavelength $\tilde{\Lambda}_c(u_0)$ can be determined from

$$\lambda(\kappa_c(u_0)) = \frac{\tilde{\phi}'(u_0)}{\tilde{\phi}(u_0)} \qquad (1.35a)$$

Equations 1.32, 1.33, and 1.35 imply that initial perturbations with

$$\lambda(\kappa(u_0)) > \lambda(\kappa_c(u_0)) = \frac{\tilde{\phi}'(u_0)}{\tilde{\phi}(u_0)} \qquad (1.35b)$$

are instantaneously unstable. Note that $\lambda(\kappa)$ is always negative ($\lambda(\kappa) = -|\kappa|$ for the case of an elastic half-space) and small absolute values of $\lambda(\kappa)$ correspond to "long waves" or, equivalently, to small absolute values of κ. Although the function $\lambda(\kappa)$ depends on the elastic component outside the interface, the qualitative behavior is identical for a wide variety of elastic systems.

To explore the role of stiffness of the elastic half-space on the stability of the homogeneous solution, we turn to the normalization, eq 1.21b. The relation

$$x' = \frac{\sigma_\infty - \sigma^*}{G_0 x_0}\, x$$

implies that the stiffer the loading system the larger $G_0/(\sigma_\infty - \sigma^*)$ is and the longer the physical wavelength

$$\Lambda_c = \tilde{\Lambda}_c \frac{G_0 x_0}{\sigma_\infty - \sigma^*}$$

needed for instantaneous linear instability is.

Equation 1.35 implies that $\kappa_c(u_0)$ can change with time (or, equivalently, with u_0). If we define $\psi(u_0) \equiv \log(\tilde{\phi}(u_0))$, then eq 1.35a becomes $\lambda(\kappa_c(u_0)) = (d/du_0)\ \psi(u_0) \equiv \psi'(u_0)$; i.e.,

$$\lambda(\kappa_c(u_0)) = \frac{d}{du_0}\psi(u_0) \equiv \psi'(u_0) \qquad (1.36)$$

Since $\lambda(\kappa)$ is a monotonic decreasing function, eqs 1.36 and 1.35b imply that $\kappa_c(u_0)$ will grow with time if $\psi''(u_0) < 0$ and decay if $\psi''(u_0) > 0$. Physically this means that if $\psi''(u_0) > 0$, then the critical wavelength increases as time increases so that perturbations that were unstable at an earlier time may die out. If $\psi''(u_0) < 0$, then perturbations that were originally stable may start to grow. The only case in which κ_c is independent of time, i.e., $\kappa_c(u_0) = $ constant, is when $\psi''(u_0) = 0$, which is equivalent to

$$\frac{\tilde{\phi}'(u_0)}{\tilde{\phi}(u_0)} = \text{constant} \qquad (1.37)$$

i.e., $\tilde{\phi}(u_0)$ is an exponential function, and this is exactly

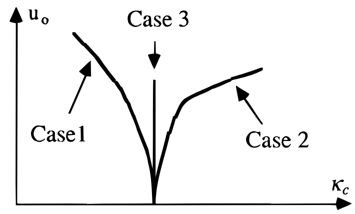

Figure 5. Dependence of the critical wave number κ_c on time (homogeneous interface opening) shown schematically for three possible cases: case 1, $\psi''(u_0) > 0$; case 2, $\psi''(u_0) < 0$; case 3, $\psi''(u_0) = 0$, where $\psi(u_0) \equiv \log(\tilde{\phi}(u_0))$.

the model used by Ajdari et al.[15] to describe chain pull-out at low rates. Thus, the critical wavelength being independent of time is a uniqe property of the exponential weakening law. These results are summarized in Figure 5.

For the special case of the exponential weakening law (system governed by eqs 1.23b and 1.24a), the instability condition, eq 1.35a, becomes $\kappa_c = 1$. In the dimensional form, the critical wavelength is

$$\Lambda_c = \frac{2\pi G\Delta}{A(1-\nu)(\sigma_\infty - \sigma^*)} \approx \frac{8\pi s_e}{15\epsilon_\infty} \qquad (1.38)$$

where $\epsilon_\infty = [(1-\nu)(\sigma_\infty - \sigma^*)]/2G$ is a homogeneous far-field strain and s_e is the length of the chain strand between entanglements. The definition of A is given by eq 1.23a.

4. Discussion

There are two ways to explain why perturbations with sufficiently long wavelengths are unstable. The first way is to think of the elastic half-space as a complex loading machine. The compliance of this machine can be obtained by superimposing a small sinusoidal perturbation on the homogeneous interface opening displacement. It is easy to see that the compliance of the machine increases with the wavelength Λ of the perturbation. Indeed, a straightforward dimensional analysis shows that the compliance scales with Λ/G, where G is the shear modulus of the elastic half-space. If the compliance of the loading machine is smaller than the compliance of the interface, the homogeneous solution is stable and the perturbation decays to zero with time. However, if the machine is more compliant than the interface, the homogeneous solution becomes unstable with respect to the imposed perturbation. The derivation in the previous section is a rigorous justification of this explanation. A second intuitive but less formal explanation is to think of a crack as a *special* case of a spatial perturbation on an otherwise perfect interface. Clearly, the longer the crack, the more likely the interface is to fail.

The result of the linear stability analysis above indicates that the motion of an infinite interface under a far-field fixed load is always linearly unstable with respect to perturbation of the initial conditions (or boundary conditions) if the perturbation has Fourier components with sufficiently long wavelengths (see eqs 1.33a and 1.35b). In a typical experiment, the dimension of the interface is sufficiently large with respect to the mean chain spacing, and therefore, the interface can be approximated by the continuum model. If the dimension of the interface is much larger than the critical wavelength, then since random perturbations have all wavelengths present in their Fourier decomposition, the homogeneous mode of interface deformation studied above is unstable and could lead to an erroneous prediction if it is used to quantify experimental observations. Obviously, the best way to avoid instabilities is to make sure that the sample dimension is less than the critical wavelength of the system. This sample size can be estimated using eqs 1.35a and 1.23b. For instance, consider the case of an elastic half-space and exponential weakening law, the polymer chains and the network being polystyrene at 175 °C with $M_e \approx$ 20 000 and $a \approx 7$ Å (Ajdari et al.[15]). Since s_e for this case is approximately 200a, the critical wavelength estimated using eq 1.38 is $\Lambda_c \approx 2 \times 10^{-7}\ m/\epsilon_\infty$. If $\epsilon_\infty =$ 0.01, $\Lambda_c \approx 20\ \mu$m, so the sample dimension should be less than 20 μm. As we can see, this number depends on the entanglement length and on the level of applied load. The latter is the easiest one to control.

Most of the analysis in this work focuses on the case when $\sigma_\infty \geq \sigma^*$. What happens when $\sigma_\infty < \sigma^*$? We show in the Appendix that for the case of $\sigma_\infty < \sigma^*$, the interface can fail only if preexisting cracks are present. We also estimate the critical stress intensity factor for the growth of a preexisting crack.

It should be noted that, while the linear analysis presented in the previous sections allows us to obtain a useful criterion for the initiation of instabilities of the interface, it does not describe the evolution of the interface close to failure, as well as the formation of cracks and crack growth. These questions are addressed in part 2 of this work by numerically integrating the nonlinear equations.

In the analysis above, the interface is between an elastic half-space and a rigid substrate. The quantitative results we obtained can be extended to a variety of elastic loading systems. For example, the elastic half-space can be replaced by an elastic slab, an elastic beam, a membrane, etc. The only change in the analysis is the replacement of the linear operator $\tilde{\sigma}^{\text{elastic}}(u)$ defined by eq 1.20f to one that is appropriate to the elastic system being studied. Also, the normalization, eq 1.21b, may need modification.

Likewise, the rigid half-space in our model of the interface can be replaced by other elastic systems, e.g., an elastic half-space. In the special case when the upper and lower half-spaces have identical elastic moduli and the initial conditions are symmetric with respect to the x axis, the results of our analysis are directly applicable. If the half-spaces have different elastic moduli or if the initial conditions are not symmetric, our analysis has to be modified. However, we expect these systems to exhibit the same qualitative features as observed for the system we considered in this work.

The linear stability analysis presented in this work assumes that the deformation of the elastic component is at most two dimensional. Our results can also be generalized to the case when the deformation of the elastic component is three dimensional. Specifically, consider the special case when the elastic component is an elastic half-space undergoing a three-dimensional deformation. In this case, the eigenfunctions $u_{\mathbf{r}}(\mathbf{r},\kappa)$ of the elastic operator $\tilde{\sigma}^{\text{elastic}}$ are defined by

$$\tilde{\sigma}^{\text{elastic}}(u_{\mathbf{r}}(\mathbf{r},\kappa)) = \lambda(\kappa)u_{\mathbf{r}}(\mathbf{r},\kappa)$$

where $\mathbf{r}$ is the normalized position vector in the plane of the interface and κ is the wave vector. These eigenfunctions are plane harmonic waves in the plane of the interface; i.e.,

$$u_{\mathbf{r}}(\mathbf{r},\kappa) = e^{i\kappa\cdot\mathbf{r}}$$

The isotropy of the half-space implies that $\lambda(\kappa)$ depends only on the magnitude of the wave vector. Thus, the dependence of the eigenvalue on the wave number is the same as in the plane strain case; i.e.,

$$\lambda(\kappa) = -|\kappa|$$

We therefore concluded that, for this particular three-dimensional case, a general perturbation of the homogeneous solution is instantaneously unstable if the Fourier decomposition of the imposed perturbation contains plane waves with wavelengths exceeding the critical value given by eqs 1.34 and 1.38.

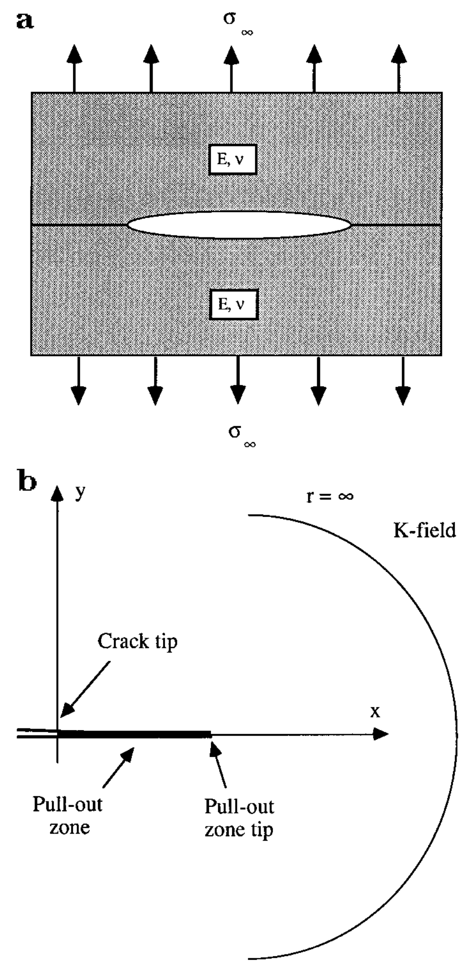

Figure 6. (a) Preexisting interface crack of length 2a between two identical elastic half-spaces with Young's modulus E. The loading is a uniform tension σ_∞ normal to the interface applied at $y = \pm\infty$ with $\sigma_\infty < \sigma^*$. The interface is reinforced with chains that satisfy eq 1.18 with $a = 1$. (b) Pull-out zone ahead of a preexisting crack along the interface between two identical elastic half-spaces. The size of the pull-out zone in front of the crack tip is small compared to the crack length so that the crack can be modeled as semiinfinite (small-scale yielding condition[18]). (x,y) is the Cartesian coordinate frame attached to the crack tip. The tip of the pull-out zone propagates with time so that the length of the pull-out zone $L(t)$ increases.

Acknowledgment. C.-Y. Hui is supported by the Materials Science Center at Cornell, which is funded by the National Science Foundation (DMR−MRL Program). We acknowledge Professor E. J. Kramer for valuable discussions.

Appendix

To be specific, consider the interface model, eq 1.18. It is easy to see that the interface is stable with respect to all perturbations with amplitude less than Δ since no pull-out can occur (i.e., $\dot{\delta} = 0$) unless $\sigma_\infty > \sigma^*$. This means that, for the case of $\sigma_\infty < \sigma^*$, the interface can fail only if preexisting cracks are present.

Consider a preexisting crack of length $2a$ lying along the interface between two identical elastic half-spaces with Young's modulus E and Poisson's ratio ν as shown in Figure 6a. The interface is reinforced with chains that satisfy eq 1.18 with $a = 1$. A uniform normal traction $\sigma_{yy} = \sigma_\infty$ is applied at $y = \pm\infty$ at $t = 0^+$. We want to determine the condition for crack initiation. In the following, we assume that the pull-out zone is small compared to the crack length $2a$ so that the small-scale yielding condition applies as illustrated in Figure 6b.

At $t = 0^+$, the stress field is given by the elastic solution since pull-out cannot occur instantaneously. This means that the stress field has a square-root singularity at the crack tip at $t = 0^+$, resulting in an infinite pull-out rate at the crack tip. The pull-out model implies that stress relaxation must occur for $t > 0$ as chain pull-out occurs in the region $(0,L(t))$ directly ahead of the crack tip. The size of this region $L_0 = L(t{=}0^+)$ at $t = 0^+$ is determined by the condition

$$K_I/\sqrt{2\pi L} = \sigma^*$$

i.e.,

$$L_0 = \frac{(K_I/\sigma^*)^2}{2\pi}$$

Note that no pull-out has yet occurred in L_0 at $t = 0^+$. For $t > 0$, the stress field ahead of the crack tip must be nonsingular, since the crack opening rate at the crack tip must be finite for $t > 0$. Note that, by definition, $\sigma > \sigma^*$ for all x and t in $(0,L(t))$.

Let us assume that the applied stress intensity factor K_I is sufficiently small so that the crack remains stationary. The pull-out zone will increase in size as the normal stress σ inside $(0,L(t))$ relaxes to its equilibrium value $\sigma = \sigma^*$. The final size of the pull-out zone L_∞ can be calculated exactly using the Dugdale model; i.e.,

$$L_\infty = \frac{\pi(K_I/\sigma^*)^2}{8} \tag{1.39}$$

The assumption of a stationary crack implies that the crack opening displacement at the crack tip δ_{COD} must be less than Δ for all times. We anticipate that this can happen only if the applied stress intensity factor K_I is less than some critical value K_{IC}. An upper bound for K_{IC}, K_{IC}^{ub}, may be estimated by setting the crack opening displacement of the Dugdale model to Δ and is found to be

$$K_{IC}^{ub} = (\sigma^*\Delta E^*)^{1/2} \tag{1.40}$$

The condition $K_I \leq K_{IC}^{ub}$ is necessary in order for the crack to remain stationary. It is also sufficient. To see this, we assume that crack initiation occurs at $t_i > 0$ so that the crack opening displacement at t_i is equal to Δ. The energy release rate G_I at initiation is

$$\frac{{K_I}^2}{E^*} = G_I = -\int_0^{L(t_i)} \sigma(\xi)\, d\delta(\xi) > -[\int_0^{L(t_i)} \sigma^*\, d\delta(\xi)] = \sigma^*\Delta = \frac{(K_{IC}^{ub})^2}{E^*} \tag{1.41}$$

where $E^* = E/(1 - \nu^2)$. This means that crack growth cannot occur if $K_I < K_{IC}^{ub}$. This means that $K_{IC} = K_{IC}^{ub}$.

Since $K_{IC} = K_{IC}^{ub}$, the crack is stationary as long as $K_I < K_{IC}^{ub}$ and the pull-out zone will grow until it reaches its equilibrium length L_∞. If $K_I > K_{IC}$, crack growth will occur before stress relaxation is complete. The condition $K_I \leq K_{IC} = (\sigma^*\Delta E^*)^{1/2}$ can be used to obtain an expression for the critical length of the preexisting crack. For example, for a plane strain crack of length $2a$ in an infinite elastic medium subjected to a uniform tensile stress σ_∞ at $y = \pm\infty$, the critical crack length a_c is

$$a_c = \frac{\sigma^*\Delta E^*}{\pi {\sigma_\infty}^2} \tag{1.42}$$

This completes the analysis for the case of $\sigma_\infty < \sigma^*$.

References and Notes

(1) Brown, H. R.; Deline, V. R.; Green, P. F. *Nature* **1989**, *341*, 221.
(2) Brown, H. R. *Macromolecules* **1989**, *22*, 2859.
(3) Creton, C.; Kramer, E. J.; Hui, C. Y.; Brown, H. R. *Macromolecules* **1992**, *25*, 3075.
(4) Washiyama, J.; Kramer, E. J.; Hui, C. Y. *Macromolecules* **1993**, *26*, 2928.
(5) Washiyama, J.; Creton, C.; Kramer, E. J.; Xiao, F.; Hui, C. Y. *Macromolecules* **1993**, *25*, 6011.
(6) Xiao, F.; Hui, C.-Y.; Washiyama, J.; Kramer, E. J. *Macromolecules* **1994**, *27*, 4382.
(7) Dai, C.-A.; Diar, B.; Dai, K.; Ober, C. K.; Kramer, E. J.; Hui, C.-Y.; Jelinski, L. W. *Phys. Rev. Lett.* **1995**, *74*, 2837.
(8) Brown, H. R. *Macromolecules* **1991**, *24*, 2752.
(9) Hui, C. Y.; Ruina, A.; Creton, C.; Kramer, E. J. *Macromolecules* **1992**, *25*, 3948.
(10) Xu, D. B.; Hui, C. Y.; Kramer, E. J.; Creton, C. *Mech. Mater.* **1991**, *11*, 257.
(11) Sha, Y.; Hui, C. Y.; Kramer, E. J.; Ruina, A. *Macromolecules* **1995**, *28*, 2450.
(12) Raphael, E.; de Gennes, P. G. *J. Phys. Chem.* **1992**, *96*, 4002.
(13) Ji, H.; de Gennes, P. G. *Macromolecules* **1993**, *26*, 520.
(14) Rubinstein, M.; Ajdari, A.; Leibler, L.; Brochard-Wyart, F.; de Gennes, P. G. *C. R. Acad. Sci. II* **1993**, *316*, 317.
(15) Ajdari, A.; Brochard-Wyart, F.; de Gennes, P. G.; Leibler, L.; Viovy, J. L.; Rubinstein, M. *Phys. A* **1994**, *204*, 17.
(16) Rubinstein, M.; Leibler, L.; Ajdari, A. *Polym. Prepr.* **1994**, *35*, 628.
(17) Brown, H. R. *Science* **1994**, *263*, 1411.
(18) Rice, J. R. In *Fracture*; Leibowitz, L., Ed.; Academic: New York, 1968; Vol. 2, p 191.
(19) Barenblatt, G. I. *Adv. Appl. Mech.* **1962**, *7*, 59.
(20) Fager, L.-O.; Bassani, J. L.; Hui, C.-Y.; Xu, D.-B. *Int. J. Fract.* **1991**, *52*, 119.
(21) Timoshenko, S. P.; Goodier, J. N. *Theory of Elasticity*, 3rd ed.; McGraw-Hill: New York, 1970.

MA950907V