THE ADHESION BETWEEN ELASTOMERS

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I. INTRODUCTION

The phenomenon of *adhesion* concerns the interaction of two condensed phases brought into contact with each other. It involves a surprisingly large variety of materials - ranging from synthetic polymers to living cells and tissues. It is thought, for example, that the adhesive properties of external cellular membranes determine the main steps of an organism's development.

The complexity of the phenomenon of adhesion, as well as the diversity of materials capable of adhesive interaction, mean that a whole series of monographs would be required to constitute a comprehensive treatise. The purpose of this paper is more modest. We aim to present simple views on polymer adhesion to readers who are not familiar with this field. We choose to do so on a specific example, namely the adhesion between two cross-linked elastomers (a cross-linked elastomer consists of long, flexible chain-like molecules which are interconnected at various points by cross-links to form a molecular network; the polymer medium is locally fluid but the macroscopic flow of the material is prevented by the cross-links). This choice is motivated by a number of reasons: (a) the possibility of describing the fracture of the adhesive junction between the two elastomers in terms of a simple model, (b) the existence of controlled experiments that can be compared with the predictions of the model, (c) the possibility of introducing concepts that are of interest for other polymer adhesion problems, and, finally, (d) the fact that adhesion between elastomers is a technologically important field. Several texts on polymer adhesion are avaible (Wu, 1982; Kinloch, 1987; Lee, 1991; Vakula and Pritykin, 1991). A good reference for the results of the last few years is the review article by Brown (1991).

The problem we are interested in is represented on figure 1, where two chemically incompatible cross-linked elastomers A and B are in close contact. The interface between the two elastomers is strengthened by grafting some extra A chains (adhesion promoters) to the surface of the B elastomer. These chains - referred to as the *connectors* - cross the interface and penetrate into the bulk A elastomer. Note that since the two polymers (A) and (B) are incompatible, each connector crosses the interface only once. This situation is referred to as the one-stitch problem (Raphaël and de Gennes, 1992). The many-stitch problem has been investigated recently by Hong Ji and de Gennes (1993)). As a crack grows along the interface, the connectors are progressively pulled-out from the elastomer A. This suction process gives rise to a fracture energy that is larger than the work of adhesion W due to intermolecular interactions (typically of the van der Waals type). The aim of the present study is to analyze the effect of chain pull-out on the adhesion of the two elastomers.

The paper is organized as follows. Section II constitutes a brief introduction to linear elastic fracture mechanics. In section III we consider in detail the pull-out process.

Soft Order in Physical Systems, Edited by Y. Rabin
and R. Bruinsma, Plenum Press, New York, 1994

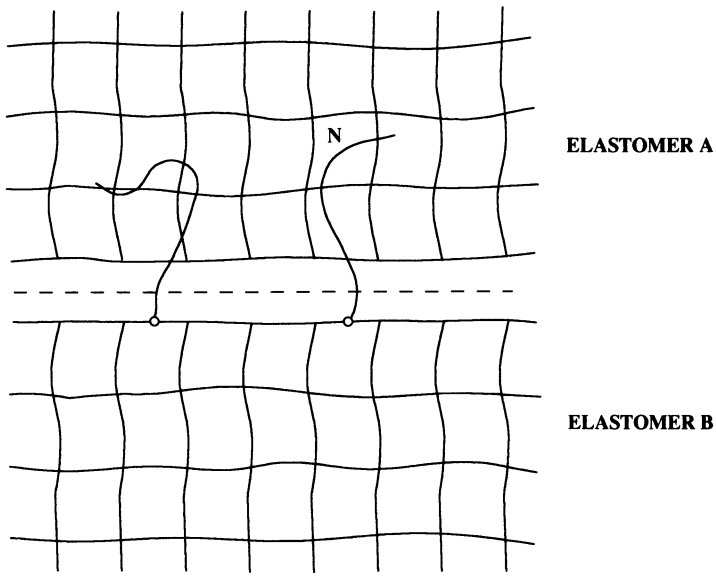

Figure 1. The interface between the two elastomers is strengthened by grafting some extra A chains (degree of polymerization, N) to the surface of the B elastomer.

The problem of a steadily growing crack along the interface between the two elastomers is analyzed in section IV. The paper ends with a discussion where comparison with the experimental results is made.

II. LINEAR ELASTIC FRACTURE MECHANICS

Let us consider a homogeneous, isotropic solid body. Under the action of applied forces, the solid body exhibit deformation. A point of initial position vector **r** (with components (x, y, z)) has, after the deformation, a new position $\mathbf{r}' = \mathbf{r} + \mathbf{u}$ where **u**(x, y, z) is the displacement field. The strain tensor u_{ik} is defined as (Landau and Lifshitz, 1986)

$$u_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} + \frac{\partial u_n}{\partial x_i}\frac{\partial u_n}{\partial x_k}\right) \tag{2.1}$$

(with $x_1 = x$, $x_2 = y$ and $x_3 = z$). In eqn (2.1) we have used the summation convention to suffixes occurring twice in an expression. Two neighboring points separated by a distance dl before the deformation are, after the deformation, separated by a distance dl' :

$$dl'^2 = dl^2 + 2\, u_{ik}\, dx_i\, dx_k \tag{2.2}$$

In the deformed body, internal stresses arise which tend to return the body to its original state. The force **F** per unit volume is given by

$$F_i = \partial\sigma_{ik}/\partial x_k \tag{2.3}$$

where σ_{ik} is the stress tensor.

For an linear elastic material the stress and strain tensors are related by (Hooke's law)

$$\sigma_{ik} = \frac{E}{1+\nu}\left(u_{ik} + \frac{\nu}{1-2\nu}u_{nn}\delta_{ik}\right) \tag{2.4}$$

where E is the Young's modulus and ν the Poisson's ratio.

Consider now the problem of a crack embedded in a linear elastic material (fracture mechanics within the confines of materials that obey Hooke's law is known as *linear elastic fracture mechanics*) . The crack extends in the negative x-direction with its tip at x = 0. The crack may be stressed in three different modes: (a) the cleavage or tensile-opening mode (mode I), (b) the in-plane shear mode (mode II), and (c) the antiplane shear mode (mode III), as depicted in figure 2. The superposition of the three modes describes the general case of loading. The mode I is technically the most important since it is the most commonly encountered and usually the one which most often results in failure (Kinloch, 1987). The following discussion will therefore be confined to this situation.

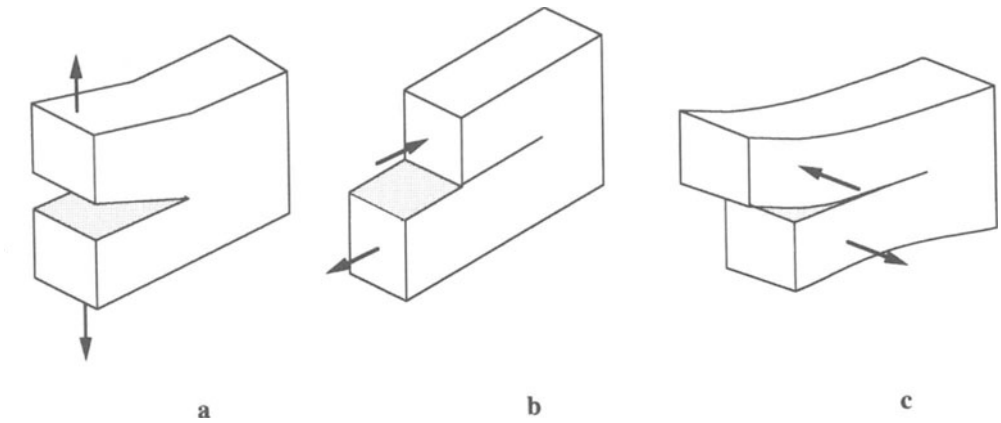

Figure 2. Modes of loading. (a) Cleavage mode: mode I. (b) In-plane shear mode: mode II. (c) Antiplane shear mode: mode III.

For a Mode I crack the tensile stress $\sigma(x) \equiv \sigma_{yy}(x,y = 0)$ and the crack displacement $u(x) \equiv u_y(x,y = 0)$ are respectively given by (Kanninen and Popelar, 1985)

$$\sigma(x) = \frac{K_I}{\sqrt{2\pi x}} \qquad x > 0 \tag{2.5}$$

$$\sigma(x) = 0 \qquad x < 0 \tag{2.6}$$

and

$$u(x) = \frac{4K_I}{E^*\sqrt{2\pi}}\sqrt{-x} \qquad x < 0 \tag{2.7}$$

$$u(x) = 0 \qquad x > 0 \tag{2.8}$$

The material parameter E* is given by E* = E for *plane stress* conditions and E* = E/(1 - ν^2) for *plane strain* conditions. These conditions are defined as follows:

$$\sigma_{zz} = 0 \qquad \text{plane stress} \tag{2.9}$$

$$\sigma_{zz} = \nu\,(\sigma_{xx} + \sigma_{yy}) \qquad \text{plane strain} \tag{2.10}$$

and $\sigma_{xz} = \sigma_{yz} = 0$ for both cases. In practice the state of stress near the crack tip varies from plane stress in a very thin specimen to plane strain near the center of a wide plate.

The quantity K_I is referred to as the *stress intensity factor*. It is a function of the applied loading and the geometry of the cracked body. Since the level of K_I uniquely defines the stress field around the crack, Irwin (1964) postulated that the condition

$$K_I \geq K_{Ic} \tag{2.11}$$

represented a fracture criterion (i.e., fracture occurs when the value of K_I exceeds the critical value K_{Ic}). K_{Ic} is a material property and is often termed the *fracture toughness*.

Another approach to obtain a criterion for fracture was obtained by Griffith (1920) and is based on an energy balance. Consider a Mode I crack of area A embedded in a linear elastic material. Let us imagine an infinitesimal propagation of the crack by an amount dA. In this process, part of the elastic energy U stored in the system is released. The work done by the external applied forces is dW. Griffith's hypothesis is that fracture occurs if and only if the *strain energy release rate* $G_I = (dW - dU)/dA$ is larger than a critical value G_{Ic}

$$G_I \geq G_{Ic} \tag{2.12}$$

The critical value G_{Ic} is called the *fracture energy*, or the critical strain energy release rate. It is a material parameter.

As shown by Irwin (1964), a simple relationship exists between K_{Ic} and G_{Ic} :

$$G_{Ic} = (K_{Ic})^2/E^* \tag{2.13}$$

Thus a critical K_{Ic} criterion is equivalent to a critical G_{Ic} criterion.

III. CHAIN PULL-OUT PROCESS

As a crack grows along the interface between the two elastomers, the connectors are progressively pulled-out from the material (the connectors are assumed not to break, but to slip out by a viscous process). The aim of the present section is to describe in detail this pull-out process. Let us first consider what happens when the two elastomers are separated by a uniform air gap of thickness h (figure 3). We will come back to fracture propagation in section IV.

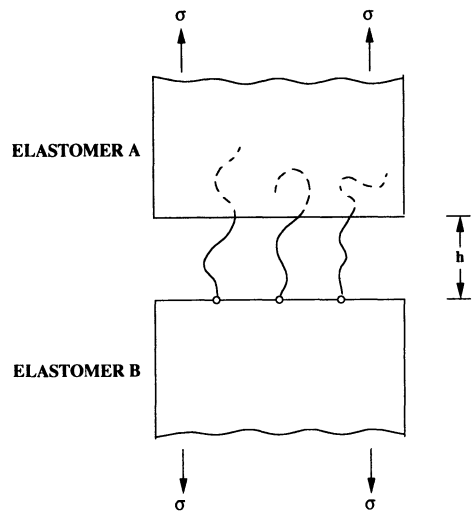

Figure 3. The two elastomers submitted to a uniform tensile stress σ.

The partially pulled-out chains are assumed to form single chain fibrils. The free energy e(h,n) of a fibril containing n monomers is given by

$$e(h,n) \cong \gamma_A a^2 n + kT \frac{h^2}{a^2 n} \tag{3.1}$$

The first term corresponds to the energy cost for exposing the n monomers to the air (a is a monomer size and γ_A is the interfacial energy between the bulk polymer A and the air). The second term in eqn (3.1) is a stretching term. Minimization of eqn (3.1) with respect to n gives

$$n(h) \cong \frac{h}{a} \left(\frac{\gamma_A a^2}{kT} \right)^{1/2} \tag{3.2}$$

Since in practice $\gamma_A a^2 \cong kT$, the fibril is almost fully stretched. The corresponding value of the free energy is

$$e(h) \cong kT \frac{h}{a} \left(\frac{\gamma_A a^2}{kT} \right)^{1/2} \tag{3.3}$$

Equation (3.3) shows that there is a minimum force f* required for a fibril to exist (Raphaël and de Gennes, 1992):

$$f^* \cong \frac{kT}{a} \left(\frac{\gamma_A a^2}{kT} \right)^{1/2} \tag{3.4}$$

Suppose that a uniform external tensile stress σ is applied to the elastomers (figure 3). The energy g_{area} per unit area (as a function of the distance h between the two elastomers) has the form shown on figure 4, where W denotes the thermodynamic work of adhesion of the two elastomers in the absence of connectors:

$$W = \gamma_A + \gamma_B - \gamma_{AB} \tag{3.5}$$

(W is due to intermolecular interactions, typically of the van der Waals type). For $h > a$, the energy $g_{area}(h)$ is linear (see eqn (3.3))

$$g_{area}(h) \cong \left[\Sigma \frac{kT}{a} \left(\frac{\gamma_A a^2}{kT} \right)^{1/2} - \sigma \right] h + (\text{const}) \qquad (h > a) \tag{3.6}$$

where Σ is the number of connectors per unit interface area. As long as σ is smaller than the critical stress

$$\sigma^* = \Sigma f^* \cong \Sigma \frac{kT}{a} \left(\frac{\gamma_A a^2}{kT} \right)^{1/2} \tag{3.7}$$

the energy g_{area} is minimal for $h = 0$ and the system remains closed. But as soon as σ becomes greater than σ^*, the energy minimum is at $h = +\infty$ and the system opens out. It is true that there remains an energy barrier but, in the fracture process to be discuss below, the fracture tip acts as a nucleation center and removes this barrier. Thus σ^* appears as a threshold stress for opening.

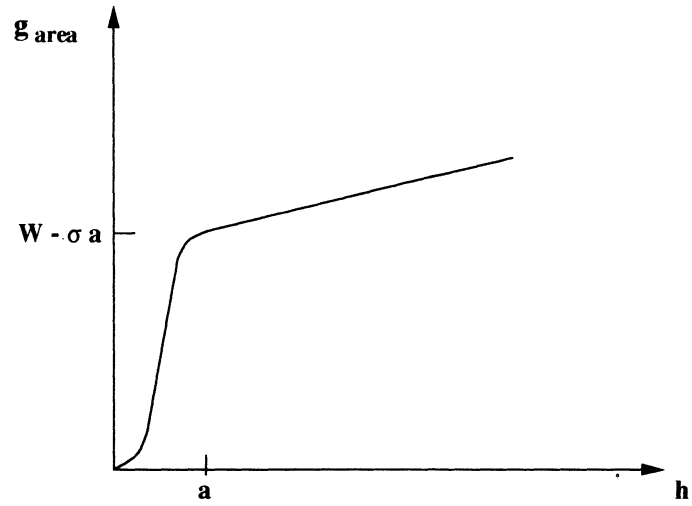

Figure 4. Energy per unit area as a function of the distance between the two elastomers.

For $\sigma > \sigma^*$, the connectors are progressively pulled-out of the elastomer. During this suction process, the energy is partly dissipated in viscous losses (caused by the slippage of the connectors in the elastomer) and partly stored in forming longer fibrils:

$$\sigma \, dh \cong [f_v \, ds + e'(h) \, dh] \, \Sigma \tag{3.8}$$

(e'(h) represents the derivative of e(h) with respect to h). Here $ds \cong (\gamma_A \, a/kT)^{-1/2} dh$ is the length of chain pulled-out when the distance between the two elastomers increased by dh and f_v is the friction force experienced by one connector

$$f_v \cong N \frac{h_f - h}{h_f} \zeta_0 \frac{ds}{dt} \tag{3.9}$$

In eqn (3.9), N is the degree of polymerization of the connector and ζ_0 is a monomer friction coefficient. The factor $(h_f - h)/h_f$ expresses the fact that the pull-out process becomes easier when only a small portion of the connector length remains to be pulled-out. For mathematical simplicity, we will hereafter ignore this correction. From eqns (3.7), (3.8) and (3.9) we arrive at the constitutive law

$$dh/dt = Q^{-1} (\sigma - \sigma^*) \qquad \sigma > \sigma^* \tag{3.10}$$

$$= 0 \qquad \sigma < \sigma^*$$

where

$$Q \cong \Sigma \, N \, \zeta_0 \, (\gamma_A \, a/kT)^{-1} \tag{3.11}$$

The suction process ends when the connectors are completely pulled-out of the elastomer. This occurs for $n(h) \cong N$ which corresponds to a maximal value of the opening

$$h_f \cong a \, N \left(\frac{\gamma_A \, a^2}{kT} \right)^{1/2} \tag{3.12}$$

IV. STEADY STATE CRACK GROWTH

IV.1. The Cohesive Zone

We now consider the problem of a steadily growing Mode I crack along the interface between the two elastomers. The crack extends in the negative x-direction with its tip at x = 0 (see figure 5). It propagates with a constant velocity V. We assume that the two elastomers have similar elastic properties and describe the materials outside the cohesive zone as a linear elastic material with Young's modulus E and Poisson's ratio ν.

The linear elastic analysis of section II predicts infinite stresses at the crack tip (eqn (2.5)). In reality, this divergence is relaxed by the dissipative pull-out process which takes place at the crack tip. The pull-out process is expected to occur in an approximately planar *cohesive zone* directly ahead of the crack tip. A thorough investigation of cohesive zone models can be found in Fager et al. (1991). See also Xu et al. (1991).

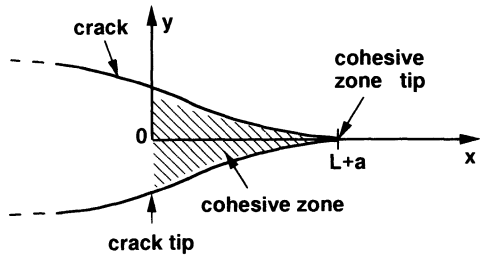

Figure 5. A schematic diagram of a cohesive zone ahead of a crack. The cohesive zone is defined by $0 < x < L+a$, where a is a molecular size.

The adhesive junction between the two elastomers is an example of a *weak adhesive junction* (de Gennes, 1989a). When a fracture propagates along such a junction, the dissipation tends to be localized in a thin ribbon ahead of the crack tip.

If we assume the cohesive zone $0 < x < L + a$ to be small compared with the crack length, the applied loading can be simulated by the prescription of the elastic K † field far away from the crack tip

$$\sigma(x) = \frac{K}{\sqrt{2\pi x}} \qquad x >> L + a \tag{4.1}$$

$$u(x) = \frac{4K}{E^*\sqrt{2\pi}}\sqrt{-x} \qquad x << 0 \tag{4.2}$$

The elastic field associated with the cohesive zone can be described in terms of a source function $\Phi(x)$ (with $0 < x < L + a$) defined by:

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† For notational simplicity, the subscript Ic of K_{Ic} and G_{Ic} will be systematically dropped throughout the remainder of this article.

$$\sigma(x) = \frac{(1-\nu)}{2} E^* \int_0^x dy\, \Phi(y)\,(x-y)^{-1/2} \qquad x > 0 \qquad (4.3)$$

$$= 0 \qquad x < 0$$

$$u(x) = 2(1-\nu) \int_x^{L+a} dy\, \Phi(y)\,(y-x)^{1/2} \qquad x < L + a \qquad (4.4)$$

$$= 0 \qquad x > L + a$$

This formulation was first introduced by Cottrell (1969) and recently implemented by one of us (de Gennes, 1989a, 1989b). It can be shown (Hui and Raphaël, 1993) that eqns (4.3) and (4.4) are equivalent to the standard formulation

$$u(x) = \frac{4K}{E^*\sqrt{2\pi}} \sqrt{L + a - x}$$

$$- \frac{2}{\pi E^*} \int_0^{L+a} dt\, \sigma(t)\, \mathrm{Ln} \left| \frac{\sqrt{(L + a - x)} + \sqrt{(L + a - t)}}{\sqrt{(L + a - x)} - \sqrt{(L + a - t)}} \right| \qquad (0 < x < L + a) \qquad (4.5)$$

(see e.g. Fager et al., 1991)

For $x >> L + a$, eqn (4.3) should reduce to eqn (4.1). The source function $\Phi(x)$ therefore satisfies

$$K - \sqrt{\pi/2}\,(1-\nu)\, E^* \int_0^{L+a} dy\, \Phi(y) = 0 \qquad (4.6)$$

Knowing K, the fracture energy G of the interface may be derive from the Irwin equation (2.13)

$$G = \frac{K^2}{2\mu(1+\nu)} \qquad \text{plane stress} \qquad (4.7a)$$

$$G = \frac{(1-\nu)\, K^2}{2\mu} \qquad \text{plane strain} \qquad (4.7b)$$

where μ is the shear modulus, $\mu = E/\,2(1 + \nu)$.

In order to determine the source function $\Phi(x)$, we distinguish two regions within the cohesive zone. For $0 < x < L - a$, we adopt the constitutive law eqn (3.10) relating the opening rate $dh/dt = 2\, du/dt$ and the normal stresses acting on the cohesive zone. Inserting eqns (4.3) and (4.4) into eqn (3.10) and assuming plain strain conditions we obtain the fundamental equation (de Gennes, 1990)

$$\int_0^x dy\, \Phi(y)\,(x-y)^{-1/2} - \sigma^*/\mu = \lambda \int_x^{L+a} dy\, \Phi(y)\,(y-x)^{-1/2} \qquad (0 < x < L - a) \qquad (4.8)$$

where the eigenvalue λ is defined by

$$\lambda = V/V^* \tag{4.9}$$

$$V^* = \frac{\mu}{2(1-\nu)Q} \cong \frac{\mu}{2(1-\nu)\Sigma N \zeta_0}\left(\frac{\gamma_A a}{kT}\right) \tag{4.10}$$

Equation (4.8) is an integral equation for the source function $\Phi(x)$. It must be supplemented by the boundary conditions

$$\sigma(x = L - a) = \sigma^* \tag{4.11}$$

$$2u(x=0) = h_f \tag{4.12}$$

For $L - a < x < L + a$, we assume that $\Phi(x)$ is unaffected by the connectors (Raphaël and de Gennes, 1992). Since in the absence of connectors the fracture energy is simply given by W, we have

$$\Phi(x) = \left[\frac{W}{4\pi\mu a^2(1-\nu)}\right]^{1/2} \qquad (L - a < x < L + a) \tag{4.13}$$

VI.2. The Quasi-Static Limit

Let us first consider the quasi-static limit $V \to 0$. For $\lambda = 0$, equation (4.8) reduces to

$$\int_0^x dy\, \Phi(y)\,(x-y)^{-1/2} = \sigma^*/\mu \tag{4.14}$$

which leads to

$$\Phi(x) = \frac{\sigma^*}{\pi\mu x^{1/2}} \qquad 0 < x < L_0 - a \tag{4.15}$$

(the subscript 0 in L_0 refers to the limit $V \to 0$). Using eqns (4.6), (4.13) and (4.15) the applied stress intensity factor in the quasi static limit is found to be

$$K_0 = 2\sqrt{2/\pi}\,\sigma^*\left(L_0^{1/2} + \frac{1}{2}B^{1/2}\right) \tag{4.16}$$

where

$$B = \frac{\pi\mu W}{(1-\nu)(\sigma^*)^2} \tag{4.17}$$

(we have neglected terms of order a/L_0).

The length $L_0 + a$ of the cohesive zone can be determined by using the boundary condition eqn (4.12)

$$h_f = 4(1 - \nu) \int_0^{L_0+a} dy\, \Phi(y)\, y^{1/2} \tag{4.18}$$

Inserting eqns (4.13) and (4.15) into eqn (4.18) and again neglecting a compared with L_0, we obtain

$$h_f = 4\left[\frac{W(1 - \nu)}{\pi \mu}\right]^{1/2} L_0^{1/2} + \frac{4(1 - \nu)}{\pi \mu} \sigma^* L_0 \tag{4.19}$$

Equation (4.19) can be rewritten as

$$A = L_0 + B^{1/2} L_0^{1/2} \tag{4.20}$$

where

$$A = \frac{\pi \mu h_f}{4(1 - \nu) \sigma^*} \tag{4.21}$$

Using eqns (4.7), (4.16) and (4.20) the zero-rate fracture energy, G_0, is found to be (plain strain)

$$\begin{aligned} G_0 &= \frac{(1 - \nu)(K_0)^2}{2\mu} \\ &= \frac{4(1 - \nu)(\sigma^*)^2}{\pi \mu}\left[\frac{B}{4} + B^{1/2} L_0^{1/2} + L_0\right] \\ &= \frac{4(1 - \nu)(\sigma^*)^2}{\pi \mu}\left[\frac{B}{4} + A\right] \end{aligned} \tag{4.22}$$

Hence (Brown et al., 1993):

$$G_0 = W + h_f \sigma^* \tag{4.23}$$

The zero-rate fracture energy G_0 is therefore larger than the thermodynamic work of adhesion W. This result is nontrivial since one would expect the pull-out contribution to the fracture energy to vanish when the crack propagation rate goes to zero. In fact, as explained in section III, there is a minimum force f* (eqn (3.4)) required for a fibril to exist, even at zero pull-out rate. As the force on a chain that is being pulled-out remains finite as $V \to 0$, the existence of a zero-rate fracture energy G_0 that is larger than the work of adhesion W is expected.

Equation (4.23) can also be proven by calculating the work done against stresses in the cohesive zone (Rice, 1968; Brown et al., 1993)

$$G_0 = \int_0^{h_f} \sigma\, dh = -\int_0^{L_0+a} \sigma(x)\left(\frac{dh}{dx}\right) dx \tag{4.24}$$

Now, assuming plane strain, we have from eqns (4.3), (4.4), (4.13) and (4.15) :

$$\sigma(x) = \sigma^* \tag{4.25}$$

for $0 < x < L_0 - a$, and

$$\sigma(x) = \sigma^* + \frac{E}{2(1+\nu)}\left[\frac{W}{4\pi\,\mu\,a^2\,(1-\nu)}\right]^{1/2} 2[x - (L_0-a)]^{1/2} \tag{4.26}$$

$$\frac{dh}{dx} = -4(1-\nu)\left[\frac{W}{4\pi\,\mu\,a^2\,(1-\nu)}\right]^{1/2} [(L_0+a) - x]^{1/2} \tag{4.27}$$

for $L_0 - a < x < L_0 + a$. Combining eqns (4.24)-(4.27) we obtain

$$G_0 = h_f\,\sigma^* + \frac{2W}{\pi a^2}\int_{L_0-a}^{L_0+a} dx\,[x - (L_0-a)]^{1/2}\,[(L_0+a) - x]^{1/2}$$

$$= h_f\,\sigma^* + W \tag{4.28}$$

i.e., we recover eqn (4.23).

VI.3. Propagation at Finite Velocity

We now consider the steady state propagation of the crack at a finite velocity V. In order to simplify the discussion, we will assume that $h_f\,\sigma^* >> W$. We can then ignore the contribution of the intermolecular forces to the fracture energy (see eqn (4.23)) and eqns (4.8) and (4.11) reduce to

$$\int_0^x dy\,\Phi(y)\,(x-y)^{-1/2} - \sigma^*/\mu = \lambda \int_x^L dy\,\Phi(y)\,(y-x)^{-1/2} \qquad (0 < x < L) \tag{4.29}$$

$$\sigma(x = L) = \sigma^* \tag{4.30}$$

It turns out that the system (4.29)-(4.30) has an exact solution of the form (Fager et al., 1991)

$$\Phi(x) = \mu^{-1}\,\sigma^*\,\frac{\cos\pi\varepsilon}{\pi}\,x^{-[(1/2)+\varepsilon]}\,(L-x)^{\varepsilon} \tag{4.31}$$

with

$$\tan(\pi\varepsilon) = \lambda \tag{4.32}$$

The length L of the cohesive zone can be determined by using eqn (4.4) and the boundary condition (4.12)

$$4(1-\nu)\int_0^L dy\,\Phi(y)\,y^{1/2} = h_f \tag{4.33}$$

Using eqn (4.31) we get

$$L = \frac{\pi \mu h_f}{4(1-\nu)\sigma^*} \frac{1}{\Gamma(1+\varepsilon)\Gamma(1-\varepsilon)} \frac{1}{\cos\pi\varepsilon} \tag{4.34}$$

with the limiting behaviors

$$L = \frac{\pi \mu h_f}{4(1-\nu)\sigma^*} \qquad V = 0 \tag{4.35}$$

$$= \frac{\pi \mu h_f}{4(1-\nu)\sigma^*} \frac{2}{\pi} \frac{V}{V^*} + \ldots \qquad V >> V^* \tag{4.36}$$

In eqn (4.34), $\Gamma(x)$ is the usual gamma function (see e.g. Abramowitz and Stegun, 1970). The fracture toughness K satisfies (see eqn (4.6))

$$\sqrt{\pi/2} \frac{E}{(1+\nu)} \int_0^L dy\, \Phi(y) = K \tag{4.37}$$

Using eqn (4.31) we obtain

$$K = \frac{2\sqrt{2}\,\Gamma(1+\varepsilon)}{\Gamma(\frac{1}{2}+\varepsilon)} \sigma^* L^{1/2} \tag{4.38}$$

From eqns (4.7), (4.31) and (4.38) the fracture energy G is found to be

$$G = h_f \sigma^* \frac{\Gamma(1+\varepsilon)}{\Gamma(1-\varepsilon)\,[\Gamma(\frac{1}{2}+\varepsilon)]^2} \frac{\pi}{\cos\pi\varepsilon} \tag{4.39}$$

with the limiting behaviors

$$G = h_f \sigma^* \qquad V = 0 \tag{4.40}$$

$$= h_f \sigma^* \frac{\pi}{2} \frac{V}{V^*} + \ldots \qquad V >> V^* \tag{4.41}$$

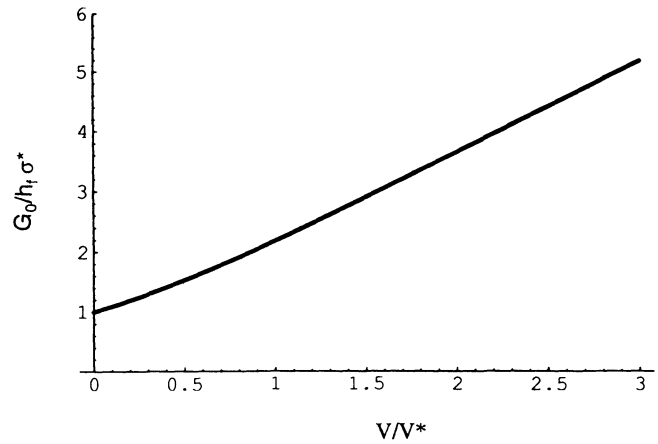

Figure 6. Plot of $G/h_f \sigma^*$ versus V/V^*.

Figure 6 represents the behavior of $G/h_f \sigma^*$ as a function of the ratio V/V^*. It is important to notice that the slope of the curve at the origin, s(0), is non zero: $s(0) = (4 \ln 2)/\pi \cong 0.88$, and does not differ greatly from the slope at infinity, $s(\infty) = \pi/2 \cong 1.57$. Thus, the curve does not exhibit a plateau for $V < V^*$ and it might be difficult to determine the value of V^* just by looking for a crossover in the curve behavior (this point has emerged from discussions with L. Léger; see also Xu et al. 1991). An more reliable way to determine V^* would be to look for the velocity at which $G \cong 2.19\ h_f \sigma^*$.

V. DISCUSSION

In the preceding two sections we have presented a simple model for the adhesion between two cross-linked elastomers in the presence of connectors. The model predicts that when the crack velocity tends to zero, the fracture energy takes the simple form (eqn (4.23))

$$G_0 \cong W + (\gamma_A a^2) N \Sigma \tag{5.1}$$

The model also predicts that the fracture energy increases linearly with the crack velocity when the velocity is well above a critical value V^* (eqns (4.10) and (4.41)).

What is the situation on the experimental side? Ellul and Gent (1984, 1985) have shown that the incorporation of free chains into a cross-linked network increased significantly the fracture energy of interfaces between cross-linked elastomers at finite crack growth rates, but had no effects at very low rates. More recently, Reichert and Brown (1993) placed a known amount of diblock copolymer at the interface between cross-linked polyisoprene and polystyrene. Using a peel test they found that, at the pull-out rate they used, the presence of block copolymer increased the fracture energy by up to a factor 5. The pros and cons of peel tests are reviewed by Brown (1993). An alternative test is the JKR test (after Johnson, Kendall and Roberts, 1971) in which an elastic spherical cap is pushed against a flat plate. The contact area is a function of the applied load, the radius of curvature and the elastic moduli of the cap, and the thermodynamic work of adhesion W between the two materials. If the load is released, the contact area will decrease with time and the measured work of adhesion can be interpreted as the fracture energy G (Brown, 1993).

The effects of chain pull-out on the adhesion of elastomers has been recently investigated by Brown (1993) and by Creton, Brown and Shull (1993) using the JKR technique. A thin layer of polystyrene-polyisoprene diblock copolymer was placed at the interface between a polystyrene coated substrate and a polyisoprene cross-linked lens. Over the whole range of crack speeds investigated (10^{-10} - 10^{-7} m/s), the presence of the copolymer produced a large increase in the fracture energy G. This increase is believed to be due to the pull-out of the polyisoprene chains of the diblock from the bulk cross-linked polyisoprene. At low crack speeds the fracture energy of the interface G was found to increase linearly with velocity from a threshold value G_0. At higher crack speeds, a transition occurred after which the G increased at a much lower rate, which could be attributed to viscoelastic bulk losses. The measured value of G_0 was in good agreement with the predictions (5.1). Furthermore, G_0 increased linearly with the areal density of copolymer present at the interface, Σ, and monotically with the degree of polymerization of the polyisoprene chains, N. This agrees well with the predictions of the model presented in sections III and IV. The observed value of V^* seems, however, to be much lower than the prediction (4.10). In his preliminary study, Brown (1993) suggested that this might be caused by the polyisoprene chains forming multiple stitches. Indeed, as shown by Hong Ji and de Gennes (1993), if each connector crosses the interface many times, G_0 is not altered but V^* is reduced by a factor N from the value obtained in the single-stitch case. According to Creton et al. (1993), this suggestion seems rather unlikely to be correct. Another explanation for the low observed value of V^* has been proposed by Creton, Brown and Shull (1993). It is based on a very recent model of Rubinstein *et* al. (1993) for the problem of slip between a solid surface with attached grafted chains and a cross-linked elastomer. Rubinstein et al. predicted that at very low velocity the friction is due to a

balance between chain stretching and chain relaxation and is considerably larger than the standard Rouse friction. According to Creton et al. (1993), a similar augmentation of the friction should occur in their case, leading to a significant reduction of V* (see eqn (4.10)).

Quite recently, Marciano, Hervet and Léger (1993) have conducted peel tests on a system made of a thin ribbon of elastomeric polydimethylsiloxane (PDMS) brought into contact with a flat silicon wafer grafted with PDMS chains. The internal structure of the grafted PDMS layer (i.e. the loop and tail distribution) was adjusted by varying the polymer concentration in the reaction bath, f. From peel force measurements at very low velocity (50 Å/s), Marciano et al. estimated G_0. They found that G_0 (as a function of f) exhibited an optimum† around $f \approx 30\%$. The occurence of an optimum can be qualitatively understood by noting that at low f the number of connectors is rather small whilst at high f the number of connectors is high but they penetrate into the network with difficulty (Marciano et al., 1993). More theoretical work will be required to understand quantitatively the penetration of the connectors into the network and the corresponding fracture energy (O'Connors and McLeish, 1993).

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