Interplay between Intermolecular Interactions and Chain Pullout in the Adhesion of Elastomers

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1. Introduction

The interface between two cross-linked elastomers can be strengthened by the addition of chains that cross the interface and are coupled by entanglement with the bulk elastomer (see Figure 1).[1] As a crack grows along the interface, the coupling chains are progressively pulled out from the material.[2] This "suction" process is expected to occur in an approximately planar *cohesive zone* directly ahead of the crack tip (see Figure 2).[3]

A number of models have been proposed to describe the process of chain pullout and the relation between chain pullout and interface toughness.[4-9] The models all predict that the toughness G increases linearly with crack speed when the speed is above a critical value, V^*. For $V \ll V^*$, $G = G_0$.

In the model of ref 8, the partially pulled-out chains are assumed to form single-chain fibrils. The minimization of the sum of the surface and stretching energies of these chains shows that there is a minimum force f^* required for a fibril to exist even at zero pullout rate. As the force on a chain that is being pulled out remains finite as $V \to 0$, the existence of a threshold toughness G_0 that is larger than the work of adhesion W due to intermolecular interactions (typically van der Waals type) is predicted. Due to an algebraic error, it was wrongly stated in ref 8 that G_0 was not a linear combination of W and the rate-independent limit of the pullout work [the error occurred in the derivation of the stress intensity factor equation (3.34)]. Here we reexamine in detail this important issue of the interplay between intermolecular interactions and chain pullout in the adhesion of elastomers.

2. Elastic Field

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 2). We assume that the two elastomers have similar elastic properties and describe the materials outside the interface as a linear elastic material with Young's modulus E and Poisson's ratio ν. If we assume the cohesive zone to be small compared with the crack length, the applied loading can be simulated by the prescription of the elastic K^A field far away from the tip[3]

$$\sigma^A(x) = K^A/(2\pi x)^{1/2}; \quad u^A(x) = \frac{4K^A}{E^*(2\pi)^{1/2}}(-x)^{1/2} \quad (1)$$

where σ^A and u^A are respectively the tensile stress and the crack displacement in the y-direction along $y = 0$ (K^A is the applied stress intensity factor). The material parameter E^* is given by $E^* = E$ for plane stress and $E^* = E/(1 - \nu^2)$ for plane strain. In the cohesive zone $0 < x < L + a$ (where a is a molecular size) the crack displacement $u(x)$ and the actual normal traction $\sigma(x)$ can be described in terms of a source function $\Phi(x)$ defined by:

$$\sigma(x) = \frac{(1-\nu)}{2}E^*\int_0^x dy\ \Phi(y)\ (x-y)^{-1/2} \quad (2)$$

$$u(x) = 2(1-\nu)\int_x^{L+a} dy\ \Phi(y)\ (y-x)^{1/2} \quad (3)$$

This formulation was first introduced by Cottrell[10] and recently reinvented and implemented by de Gennes.[5-7] It can be shown[11] that (2) and (3) are equivalent to the standard formulation relating the crack displacement $u(x)$ to the normal traction $\sigma(x)$ in the cohesive zone (see, e.g., ref 3)

$$u(x) = \frac{4K^A}{E^*(2\pi)^{1/2}}(L+a-x)^{1/2} - \frac{2}{\pi E^*}\int_0^{L+a} dt\ \sigma(t)\ \ln\left|\frac{(L+a-x)^{1/2}+(L+a-t)^{1/2}}{(L+a-x)^{1/2}-(L+a-t)^{1/2}}\right| \quad (4)$$

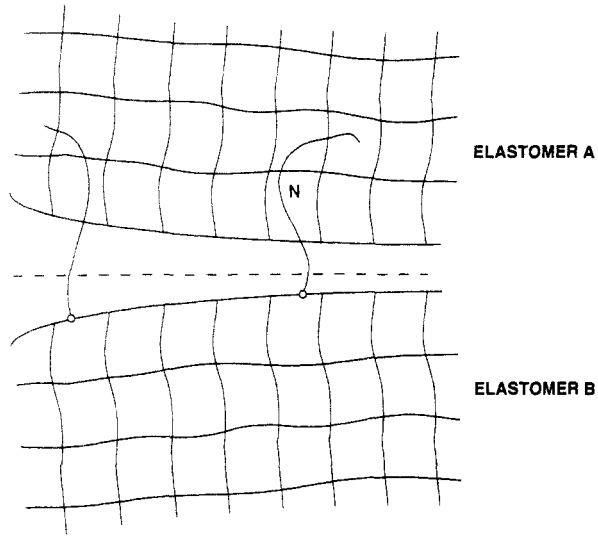

Figure 1. Interface between the two elastomers which is strengthened by grafting some extra chains (degree of polymerization, N) to the surface of the lower material. These chains cross the interface and penetrate into the upper elastomer. As the crack grows along the interface (from left to right), the coupling chains are progressively pulled out from the upper material.

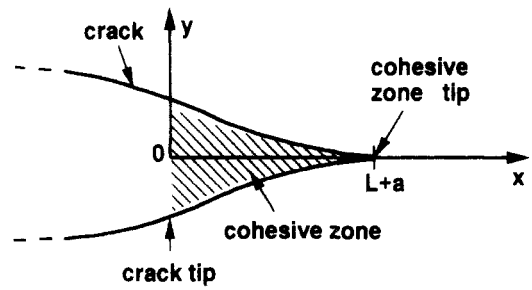

Figure 2. Schematic diagram of a cohezive zone ahead of a crack. The cohesive zone is defined by $0 < x < L + a$, where a is a molecular size. In the rate-independent limit, the normal traction is equal to σ^* in the region $0 < x < L - a$. In the region $(L-a, L+a)$, intermolecular interactions contribute to the normal traction which is given by (20).

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The source function $\Phi(x)$ satisfies[7]

$$K^A - (\pi/2)^{1/2}(1-\nu)E^* \int_0^{L+a} dy\, \Phi(y) = 0 \quad (5)$$

Knowing K^A, the fracture toughness G of the interface may be derived from the Irwin equation[12]

$$G = (K^A)^2/E^* \quad (6)$$

3. Constitutive Equation and Threshold Toughness

To determine the source function $\Phi(x)$, we adopt the following constitutive law relating the opening displacement $h = 2u$ and the normal stresses acting on the cohesive zone[8]

$$dh/dt = Q^{-1}(\sigma - \sigma^*) \qquad \sigma > \sigma^* \quad (7)$$

$$dh/dt = 0 \qquad \sigma < \sigma^* \quad (8)$$

where σ^* is the threshold stress below which pullout does not occur, i.e., $\sigma^* = f^*\Sigma$. f^* is the minimum force required for a fibril to exist (see the Introduction), and Σ is the number of connecting chains per unit interface area. The physical basis of f^* and of the friction coefficient Q is explored in detail in ref 8. Imposing that $\sigma(x=L-a) = \sigma^*$, we obtain, for the case of plane strain and in the rate-independent limit[8]

$$\Phi(x) = \frac{\sigma^*}{\pi\mu x^{1/2}} \qquad 0 < x < L - a \quad (9a)$$

$$\Phi(x) = \left[\frac{W}{4\pi\mu a^2(1-\nu)}\right]^{1/2} \qquad L - a < x < L + a \quad (9b)$$

where $\mu = E/2(1+\nu)$ is the shear modulus. Using (5) and (9), the applied stress intensity factor in the rate-independent limit is found to be

$$K^A{}_0 = 2(2/\pi)^{1/2}\sigma^*(L^{1/2} + (1/2)B^{1/2}) \quad (10)$$

where

$$B = \frac{\pi\mu W}{(1-\nu)\sigma^{*2}} \quad (11)$$

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

The length $L + a$ of the cohesive zone can be determined by using the boundary condition

$$h_f = 4(1-\nu)\int_0^{L+a} dy\, \Phi(y)\, y^{1/2} \quad (12)$$

where $h_f = 2u(x=0)$ is the maximal opening of the cohesive zone. h_f is proportional to the length of the pulled-out chains.[8] Using (9) and again neglecting a compared with L, we obtain

$$h_f = 4\left[\frac{W(1-\nu)}{\pi\mu}\right]^{1/2} L^{1/2} + \frac{4(1-\nu)}{\pi\mu}\sigma^* L \quad (13)$$

Equation 13 can be rewritten as

$$A = L + B^{1/2}L^{1/2} \quad (14)$$

where

$$A = \frac{\pi\mu h_f}{4(1-\nu)\sigma^*} \quad (15)$$

Combining (6), (10), and (14), the threshold toughness G_0 is found to be

$$G_0 = \frac{(1-\nu)(K^A{}_0)^2}{2\mu} = \frac{4(1-\nu)(\sigma^*)^2}{\pi\mu}\left[\frac{B}{4} + B^{1/2}L^{1/2} + L\right] = \frac{4(1-\nu)(\sigma^*)^2}{\pi\mu}\left[\frac{B}{4} + A\right] \quad (16)$$

Hence

$$G_0 = W + h_f\sigma^* \quad (17)$$

We therefore conclude that G_0 is the sum of W and the rate-independent limit of the pullout work $h_f\sigma^*$.

Equation 17 can also be proven by calculating the work done against stresses in the cohesive zone[13]

$$G = \int_0^{h_f} \sigma\, dh = -\int_0^{L+a} \sigma(x)\left(\frac{dh}{dx}\right) dx \quad (18)$$

Now, assuming plane strain, we have from (2), (3), and (9):

$$\sigma(x) = \sigma^* \quad (19)$$

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

$$\sigma(x) = \sigma^* + \frac{E}{2(1+\nu)}\left[\frac{W}{4\pi\mu a^2(1-\nu)}\right]^{1/2} 2[x - (L-a)]^{1/2} \quad (20)$$

$$\frac{dh}{dx} = -4(1-\nu)\left[\frac{W}{4\pi\mu a^2(1-\nu)}\right]^{1/2}[(L+a) - x]^{1/2} \quad (21)$$

for $L - a < x < L + a$. Combining (18)–(20), we obtain

$$G_0 = h_f\sigma^* + \frac{2W}{\pi a^2}\int_{L-a}^{L+a} dx\, [x - (L-a)]^{1/2}[(L+a) - x]^{1/2} = h_f\sigma^* + \frac{2W}{\pi a^2}\frac{\pi a^2}{2} = h_f\sigma^* + W \quad (22)$$

i.e., we recover that G_0 is indeed the sum of W and the rate-independent limit of the pullout work $h_f\sigma^*$.

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