Adhesion via Connector Molecules: The Many-Stitch Problem

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ABSTRACT: We study the fracture of adhesive junctions between two rubbers which are bound together by "connectors", i.e., polymer chains which are chemically identical to the rubbers. The "one-stitch" case in which each adhesive chain crosses the interface only once has been discussed previously. We focus here on the "many-stitch" case, in which each connector crosses the interface many times. We derive a dynamical equation for fracture. In the quasi-static limit, we find (to our surprise) that the fracture energy is not much larger than that in the one-stitch problem. For fast fracture propagation, viscous dissipations are significantly higher and chain scission may occur.

I. Introduction

The measured strength of good adhesive bonds[1] ($\sim 10^2$–10^3 J/m^2) is enormously larger than the Dupré work of separation (which, for van der Waals solids, would be in the range of 3×10^{-2} J/m^2). It is also much larger than what is required to break a plane of strong chemical bridges (~ 1 J/m^2). However, there is abundant evidence that suitable bridging molecules can provide a large enhancement of the adhesion energy. (1) Block copolymers AB play this role at the boundary between two (*glassy*) incompatible polymers: this has been measured and interpreted by Brown and co-workers.[2] (2) Grafted chains, or adhesion promoters, improve the adhesion between a solid and a *rubber*.[3]

Raphael and one of us have set up a qualitative model for the latter situation[4] in cases where the long connector molecule sets up a *single bridge* between the two sides (Figure 1). We call this the "one-stitch" problem. One example is obtained with a rubber A facing a hard solid S; long connectors C, grafted to the S surface, penetrate into A:C and A are assumed to be compatible. Another example is a pair of incompatible rubbers A and B, with an AB block copolymer at the interface.

We are interested here in a different problem shown on Figure 2, where two *identical* rubbers face each other. Connector molecules (C) are attached to one surface and invade both sides: this requires that C be chemically identical to the ambient rubber. We call this the "many-stitch problem".

Note that our connectors are attached only at one end (this is the "free" case as defined in ref 4). When it is chemically attached at both ends (the "bound" case), we have a completely different problem, which will be discussed elsewhere.

Do we get a stronger adhesive junction in the many-stitch situation (keeping the number of connectors/unit area fixed)? This is the question discussed here.

This paper is organized as follows. We start in section 2 with a review of the one-stitch case. In section 3, we study the parameters which characterize the weak junction in the many-stitch case and derive the dynamical equation for fracture. Sections 4 and 5 discuss the two limits of quasi-static and fast fracture propagation. We give some concluding remarks in section 6.

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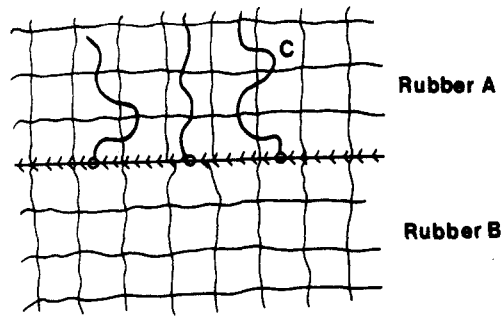

Figure 1. One-stitch case. Shown here is a rubber–rubber interface with connector molecules (C) grafted onto the surface of rubber B and penetrating into rubber A. Here each connector forms only one bridge across the interface.

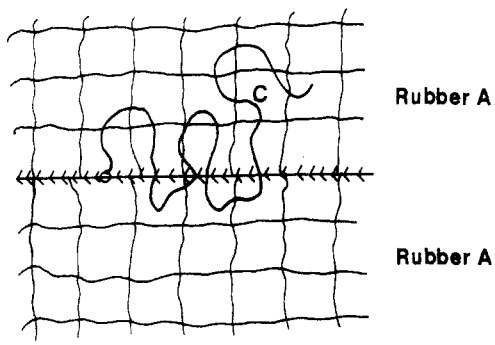

Figure 2. Many-stitch case. Here the connector molecule crosses the interface many times and forms multiple bridges. The grafted chain end is marked by a circle.

II. One-Stitch Problem

A complete discussion of this problem can be found in ref 4. Here we shall review the main points. All numerical prefactors are ignored. We begin by considering the threshold stress for an adhesive junction to open up. For this purpose, we write down the free energy of one polymer bridge between two blocks of rubbers separated at a distance h (see Figure 3):

$$\Delta F_0 = n(h)\,\gamma_A a^2 + \frac{h^2}{n(h)\,a^2} kT \qquad (2.1)$$

The first term is the energy cost for exposing a linear chain to air (γ_A is the surface tension of the bulk polymer). The second term is entropic. In practice, for our purpose, $\gamma_A a^2 \sim kT$. The optimum of eq 2.1 occurs then for

$$h \sim n(h)a \qquad (2.2)$$

i.e., for strongly extended connectors. The free energy is

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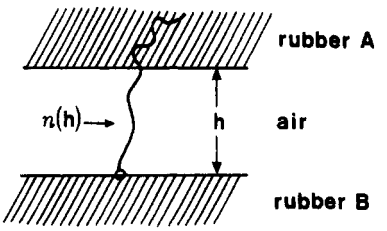

Figure 3. Polymer bridge between two rubber blocks separated at a distance h.

$$\Delta F_0 \sim kTn(h) \sim kT(h/a) \tag{2.3}$$

The threshold force to pull out one adhesive chain is

$$f_0^* = \frac{\mathrm{d}(\Delta F)}{\mathrm{d}h}\bigg|_{h=0} \cong \frac{kT}{a} \tag{2.4}$$

For the one-stitch problem, each adhesive chain forms only one bridge after the junction opens. Assuming the average separation between grafted chain ends is D, we arrive at the threshold stress:

$$\sigma_0^* = \frac{f_0^*}{D^2} = \frac{kT}{aD^2} \tag{2.5}$$

The fracture of adhesive junctions is accompanied by the adhesive chains being progressively sucked out of the rubber. During the suction process, the energy is partly dissipated in the viscous loss caused by the friction between adhesive molecules and the rubber and partly stored in forming polymer bridges. Assuming a stress $\sigma > \sigma_0^*$ at the junction, from balance of work we have

$$\sigma\,\mathrm{d}h = \sigma_0^*\,\mathrm{d}h + \frac{f}{D^2}\mathrm{d}s \tag{2.6}$$

Here $\mathrm{d}s$ is the length of chain sucked out when the distance between the two rubbers increases by $\mathrm{d}h$. From eq 2.2, we have

$$\mathrm{d}s = a\,\mathrm{d}n(h) \cong \mathrm{d}h \tag{2.7}$$

and f is the friction force experienced by one adhesive chain:

$$f = N\zeta_1 \frac{\mathrm{d}s}{\mathrm{d}t} \tag{2.8}$$

where ζ_1 is the friction coefficient for one monomer and $N\zeta_1$ is the total tube friction coefficient.

Finally, from eqs 2.6–2.8, we arrive at the dynamical equation for the one-stitch case:

$$\sigma - \sigma_0^* = Q_0 \frac{\mathrm{d}h}{\mathrm{d}t} \tag{2.9}$$

where $Q_0 \equiv \zeta_1/D^2$ is defined as the junction friction coefficient.

The suction process stops when the adhesive chain is completely pulled out of the rubber. This occurs when $n(h) = N$ which corresponds to a maximum opening:

$$h_f \cong Na \tag{2.10}$$

We are now ready to discuss fracture propagations. In linear fracture mechanics, a crack has a parabolic shape and is characterized by a divergent stress at the crack tip[5] (Figure 4):

$$\sigma(x) = \begin{cases} 0 & x < 0 \\ \dfrac{K}{(2\pi x)^{1/2}} & x > 0 \end{cases} \tag{2.11a}$$

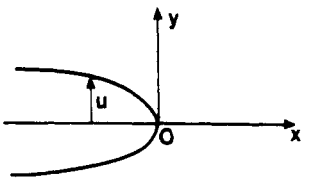

Figure 4. Geometry of fracture in a linear elastic medium.

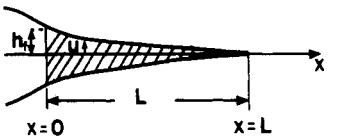

Figure 5. Adhesive fracture of a weak junction. The suction process of connector molecules starts at the yielding point ($x = L$) and ends at the maximum opening point ($x = 0$).

$$u(x) = \begin{cases} 2(1-\nu)\dfrac{K}{\mu}\left(\dfrac{|x|}{2\pi}\right)^{1/2} & x < 0 \\ 0 & x > 0 \end{cases} \tag{2.11b}$$

where μ is the shear modulus, ν the Poisson ratio, and K the stress intensity factor. As shown by Irwin, the fracture energy G is quadratic in K (assuming type-I load):[5]

$$G = K^2/\mu \tag{2.12}$$

G is measured directly through a "peeling test" for adhesion.[1]

Figure 5 shows the adhesive failure of a weak junction. The central assumption here is that the singularity associated with a crack line is spread out over the entire junction. This is quantified by a distribution of sources $\varphi(x)$. The stress field $\sigma(x)$ and the junction opening $U(x)$ are obtained by the principle of superposition:[3]

$$\sigma(x) = \begin{cases} 0 & x < 0 \\ \mu\int_0^x \varphi(\xi)|x-\xi|^{-1/2}\,\mathrm{d}\xi & x > 0 \end{cases} \tag{2.13a}$$

$$u(x) = \begin{cases} 2(1-\nu)\int_x^L \varphi(\xi)|\xi - x|^{1/2}\,\mathrm{d}\xi & x < L \\ 0 & x > L \end{cases} \tag{2.13b}$$

At a large distance ($x \gg L$), eq 2.13 reduces to eq 2.11 for a pointlike source, yielding the stress intensity factor:

$$\int_0^L \phi(\xi)\,\mathrm{d}\xi = \frac{1}{(2\pi)^{1/2}}\frac{K}{\mu} \tag{2.14}$$

In the weak junction model, one uses the above expressions for $\sigma(x)$ and $u(x)$ in the dynamical equation for the junction. This leads to an eigenequation which needs to be supplemented with proper boundary conditions. One then solves for the eigenfunction $\varphi(x)$ and derives $\sigma(x)$ and $u(x)$. Using eq 2.14 one finds K and subsequently the fracture energy G.

In the one-stitch problem, assuming steady-state fracture propagations of velocity V, the dynamical equation (eq 2.9) has the form

$$\sigma - \sigma^* = Q_0 \frac{\mathrm{d}h}{\mathrm{d}t} = -Q_0 V \frac{\mathrm{d}u}{\mathrm{d}x} \tag{2.15}$$

Inserting eq 2.13 into eq 2.15, one obtains an eigenequation

$$\int_0^x \phi(\xi)\,|x-\xi|^{-1/2}\,\mathrm{d}\xi - \sigma_0^*/\mu = \lambda\int_x^L \phi(\xi)\,|\xi - x|^{-1/2}\,\mathrm{d}\xi \tag{2.16}$$

where λ is the eigenvalue:

$$\lambda \equiv (1-\nu)Q_0(V/\mu) = V/V_0^* \tag{2.17}$$

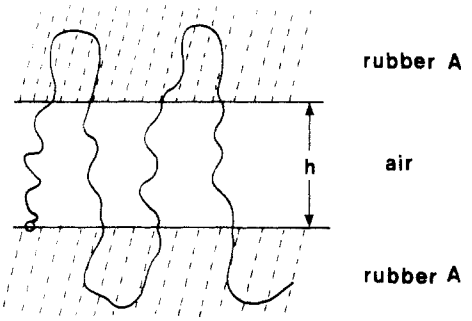

Figure 6. Multiple "stitches" formed by one connector between two rubbers separated at a distance h.

V_0^* is a characteristic velocity:

$$V_0^* \cong \mu/Q_0 \tag{2.18}$$

The boundary conditions are

$$\sigma(L) = \sigma_0^* \tag{2.19a}$$

$$u(0) = h_f \tag{2.19b}$$

It turns out that eq 2.17 with boundary conditions (eq 2.19) has an exact solution of the form[6]

$$\varphi(x) = \frac{\sigma_0^*}{\mu}\frac{\cos \pi\epsilon}{\pi}x^{-[(1/2)+\epsilon]}(L-x)^{\epsilon} \tag{2.20}$$

with

$$\tan(\pi\epsilon) = \lambda = V/V_0^* \tag{2.21}$$

From this solution we may derive the fracture energy G and the junction length L

$$G \cong \sigma_0^* h_f \frac{\tan(\pi\epsilon)}{\epsilon} \tag{2.22a}$$

$$L \cong \frac{\mu h_f}{\sigma_0^*}\frac{\tan(\pi\epsilon)}{\epsilon} \tag{2.22b}$$

with the limiting behaviors

$$G = \begin{cases} G_0 \cong \sigma_0^* h_f & V \ll V_0^* \\ \sigma_0^* h_f \dfrac{V}{V^*} \cong G_0 \dfrac{V}{V^*} & V \gg V_0^* \end{cases} \tag{2.23}$$

and

$$L = \begin{cases} L_0 \cong \dfrac{\mu h_f}{\sigma_0^*} & V \ll V_0^* \\ \dfrac{\mu h_f}{\sigma_0^*}\dfrac{V}{V^*} \cong L_0 \dfrac{V}{V^*} & V \gg V_0^* \end{cases} \tag{2.24}$$

Equations 2.23 and 2.24 are the main predictions for the one-stitch problem. At zero velocity (quasi-static limit), the situation is equivalent to the Dugdale model for crazing in fracture mechanics.[5] The stress distribution is uniform over the entire junction. It is thus clear that the fracture energy G_0 is no other than the work to pull out chains at a constant stress σ_0^* over a distance h_f. Above a characteristic velocity V_0^*, viscous loss dominates and both the fracture energy G and the junction length L increase linearly with the fracture velocity.

III. Many-Stitch Problem

The situation is shown in Figure 6. A chain is grafted by one end onto the surface of rubber B. Assuming the chain is equally compatible with both rubbers, it makes many "stitches" across the interface. When the junction is closed ($h = 0$), the average number of stitches one chain makes is on the order of $B(0) \sim N^{1/2}$ since the chain is ideal on large length scale due to screening.[7] The average number of monomers on the loop between two consecutive stitches is $L(0) \sim N^{1/2}$. Now assume the junction is open at a constant separation h; each stitch forms one polymer bridge, with its length given by $n(h)$ in eq 2.2. The number of bridges one chain makes is a decreasing function of h. Suppose that the time scale involved here is short so that tube configurations in each loop remain roughly unchanged. Then the conservation of the total number of monomers on the chain requires

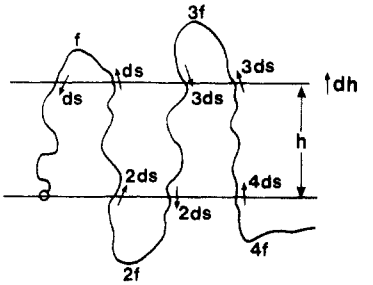

Figure 7. Schematic illustration of the chain pullout process in the many-stitch case. It shows motions of monomers along one connector chain when the distance between the two rubbers is increased by dh.

$$B(h)\, n(h) + B(h)\, N^{1/2} = N \tag{3.1}$$

This type of counting was introduced first as the "block and tackle" problem by Mc Leish et al.[8] in connection with certain crazing processes.

From eqs 2.2 and 3.1, we find the number of bridges per chain at separation h:

$$B(h) = \frac{N}{N^{1/2} + h/a} \tag{3.2}$$

The free energy of the chain is

$$\Delta F/kT = B(h)\, \Delta F_0/kT = \frac{N}{1 + (a/h)N^{1/2}} \tag{3.3}$$

The threshold force on one chain when the junction opens is

$$f^* = \left.\frac{\mathrm{d}(\Delta F)}{\mathrm{d}h}\right|_{h=0} \cong N^{1/2}\frac{kT}{a} \cong N^{1/2} f_0^* \tag{3.4}$$

which is much larger than that in the one-stitch case because more bridges need to be formed.

Assuming the average distance between grafted chain ends is D, one has the threshold stress:

$$\sigma^* = \frac{f^*}{D^2} \cong \frac{kT}{aD^2}N^{1/2} = N^{1/2}\sigma_0^* \tag{3.5}$$

The chain is pulled out completely when $n(h) \sim N$, giving

$$h_f \cong Na \tag{3.6}$$

which is the same as in the one-stitch case.

Consider now the dynamical process of chain pullout, as shown in Figure 7. Assume that, during a time interval dt, the two rubbers are pulled apart by a distance dh. Starting from the grafted end, the first loop experienced a friction force f:

$$f = \zeta_1 N^{1/2}\frac{\mathrm{d}s}{\mathrm{d}t} \tag{3.7}$$

where $\mathrm{d}s \cong \mathrm{d}h$ (eq 2.7). The second loop, however, must deliver a length of 2ds during the same time interval in order to maintain the bridge configuration in between.

Thus the friction is also twice as strong: $2f$. By the same argument, the friction force on the third loop is $3f$, and so on and so forth. The loop friction increases linearly along the chain counting from the grafted end. As we will see later, this is the origin of the drastic enhancement of viscous loss in the many-stitch problem.

The total energy dissipation is the sum of dissipation of all loops:

$$dE_v(h) = \sum_{m=1}^{B(h)} mf\, m\, ds = (\sum_{m=1}^{B(h)} m^2) f\, ds \cong \frac{1}{3}B(h)^3 f\, ds \quad (3.8)$$

assuming that $B(h) \gg 1$.

Since the areal density of adhesive chains is $1/D^2$, we can write down the balance of work:

$$\sigma\, dh = \frac{1}{D^2}[d(\Delta F) + dE_v] \quad (3.9)$$

Combining eqs 3.2, 3.3, 3.5, 3.7–3.9, and 2.7, wre obtain the dynamical equation for the many-stitch problem:

$$\sigma - \frac{\sigma^*}{(1 + h/h^*)^2} = \frac{Q}{(1 + h/h^*)^3}\frac{dh}{dt} \quad (3.10)$$

where $Q \equiv \zeta N^2/(3D^2) \cong NQ_0$ is the new junction friction coefficient, and $h^* \equiv aN^{1/2}$ is the new characteristic length.

In comparison with the one-stitch case, we may make the following comments:

(1) The threshold stress $\sigma^* \cong N^{1/2}\sigma_0^*$ is much higher, since typically $N \sim 10^2$–10^4.

(2) The new junction friction coefficient $Q \cong NQ_0$ is very large, implying strong dissipations in the suction process.

(3) There exists a new length scale h^*. When $h < h^*$, the density of the polymer bridges stays roughly constant and frictions are high. When $h > h^*$, both the density of the bridges and frictions are significantly reduced.

IV. Quasi-Static Limit

We first consider the limit of quasi-static fracturing. Take $v = 0$ in eq 3.10, the dynamical equation reduces to a simple form:

$$\sigma - \frac{\sigma^*}{(1 + h/h^*)^2} = 0 \quad (4.1)$$

Since $h^* \ll h_f$, over a large part of the junction we have $h > h^*$, and the dynamical equation may be approximated by

$$\sigma - \sigma^*[h^*/h]^2 = 0 \quad (4.2)$$

Equation 4.2 is not valid for $x = L$ ($h = 0$) because of the boundary condition $\sigma(L) = \sigma^*$. We must introduce a cut-off length $L' < L$ which defines the validity range of eq 4.2 $0 < x < L'$ and

$$h(L') \cong h^*$$

$$\sigma(L') \cong \sigma^* \quad (4.3)$$

(Later we will find that L' is very close to L and eq 4.2 is a good approximation for the entire junction.)

In the weak junction model where $\sigma(x)$ and $h(x)$ are given by the source function $\varphi(x)$ as in eq 2.13, eq 4.2 has an approximate scaling solution of the form

$$\varphi(x) \cong \varphi_0(L - x)^{-3/2} \quad (4.4)$$

Since from eq 2.13a

$$\sigma(x) \cong \mu\int_0^x \varphi(\xi)(x - \xi)^{-1/2}\, d\xi$$

$$\cong \mu\varphi_0(L - x)^{-1}[\int_1^{L/(L-x)} u^{-3/2}(1 + u)^{1/2}\, du] \quad (4.5)$$

For x not too close to the origin ($x = 0$), the integral in the bracket varies slowly and $\sigma(x)$ is dominated by the $(L - x)^{-1}$ term. Hence approximately

$$\sigma(x) \cong \mu\varphi_0(L - x)^{-1} \quad (4.6)$$

From eq 2.13b we obtain

$$h(x) \cong \int_x^{L'} \varphi(\xi)\,(\xi - x)^{1/2}\, d\xi \cong \varphi_0\left[\frac{L - x}{L - L'}\right]^{1/2} \quad (4.7)$$

The constants φ_0 and L' are determined by the boundary conditions in eq 4.3; we find

$$\begin{cases}\varphi_0 \cong h^* \\ L - L' \cong \mu h^*/\sigma^*\end{cases} \quad (4.8)$$

The junction length L is determined by the condition $h(0) = h_f$:

$$L \cong N(\mu h^*/\sigma^*) = \mu h_f/\sigma_0^* \quad (4.9)$$

(We see that $(L - L')/L \sim N^{-1} \ll 1$.) The stress intensity factor is

$$K \cong \mu\int_0^L \varphi(\xi)\, d\xi \cong (\sigma^* h^*/\mu)^{1/2} \quad (4.10)$$

and finally the fracture energy is given by the Irwin relation:

$$G \cong K^2/\mu \cong \sigma^* h^* \cong \sigma_0^* h_f \quad (4.11)$$

From eqs 4.8 and 4.10, we find that the fracture energy G and the junction length L are both close to those in the one-stitch case (see eqs 2.23 and 2.24). This means that we do not get improved adhesion in the many-stitch case when the fracture velocity is low. This point is clear once we realize that, for very slow fracture, viscous loss is negligible. External work all goes into stretching the connector molecules which should be the same in both the one-stitch and many-stitch cases. In fact, we may arrive at this conclusion without even solving the dynamical equation since

$$G \cong \int_0^{h_f} \sigma\, dh \cong \int_0^{h_f} \sigma^*(1 + h/h^*)^{-2}\, dh \cong \sigma^* h^* \cong \sigma_0^* h_f \quad (4.12)$$

On the other hand, we are left with many unsolved problems related to the integral equations. Do we have a simple additivity between the thermodynamic work W and the connector work $\sigma_0^* h_f$ when they are comparable? In the one-stitch problem the conclusion is *negative*: there is no simple additivity.[4] In the many-stitch case the problem is even more complex: we do not know the answer.

V. Fast Fracture with Chain Scissions

Assume steady-state fracture propagations with velocity V. From eq 3.10, the dynamical equation has the form

$$\frac{\sigma}{\mu} - \frac{\sigma^*}{\mu(1 + u/h^*)^2} = -\frac{V}{V^*}\frac{1}{(1 + u/h^*)^3}\frac{du}{dx} \quad (5.1)$$

Here $V^* \cong \mu/Q \cong N^{-1}V_0^*$. The characteristic velocity is significantly lower than in the one-stitch case because of the large frictions in the chain pullout process. The junction is more sensitive to the increase of velocity. Viscous dissipations start to dominate the fracture process in a much lower velocity range than in the one-stitch problem.

This dynamical equation is a highly nonlinear integral equation. The exact solution is not available currently. However, for fast fracture propagation, the dominant process is likely the chain scissions at the crack tip ($x = 0$) because of high stress concentrations. There are two factors which suggest that this might be the case. In the first place, the characteristic stress σ^* is high, leading to great stress concentrations. Second, the characteristic velocity V^* is very low, making the ordinary experimental velocity deep inside the fast fracture regime ($\lambda \equiv V/V^* \gg 1$).

For simplicity, assume that chain scissions occur at $h_0 < h^*$. Then over the entire junction we have $h < h^*$, and we may approximate the nonlinear dynamical equation with a simple form

$$\frac{\sigma}{\mu} - \frac{\sigma^*}{\mu} = -\frac{V}{V^*}\frac{du}{dx} \tag{5.2}$$

which is formally the same as the dynamical equation for the one-stitch problem (eq 2.15). The solution to this equation is known and is given in eqs 2.20 and 2.21. The new set of boundary conditions is

$$\begin{cases}\sigma(0) = \sigma_\chi \\ \sigma(L) = \sigma^*\end{cases} \tag{5.3}$$

where σ_χ is the critical stress at which chain scission occurs.

From the solution for the source function $\varphi(x)$ in eqs 2.20 and 2.21, one may derive the stress distribution near the crack tip ($x \ll L$):

$$\sigma(x) \cong \sigma^*(L/x)^{1/2} \tag{5.4}$$

Here we have assumed that $V \gg V^*$, such that $\epsilon \cong 1/2$ (from eq 2.21). L is the junction length:

$$L = \frac{\mu h^*}{\sigma^*}\frac{V}{V^*} = L^*\frac{V}{V^*} \tag{5.5}$$

where $L^* \equiv \mu h^*/\sigma^*$.

The stress distribution in eq 5.4 must have a cutoff at $x = d$, where d is the average distance between polymer bridges. In the one-stitch case $d \cong D$, where D is the distance between grafted chain ends. Here we have $d \cong DN^{-1/4}$ because each chain makes $\sim N^{1/2}$ bridges instead of just one. The maximum stress at the junction tip is then

$$\sigma_{max} = \sigma(d) \cong \sigma^*(L/d)^{1/2} \tag{5.6}$$

For chain scission to occur, this must be at least the same as the scission stress σ_χ. This leads to the scission criteria:

$$\sigma_\chi \cong \sigma^*(L/d)^{1/2} \tag{5.7}$$

Inserting the expression for L in eq 5.5 into this criteria, one obtains the scission velocity:

$$V_s \cong V^*\left(\frac{\sigma_\chi}{\sigma^*}\right)^2\frac{d}{L^*} \tag{5.8}$$

Assuming that the energy associated with breaking one chemical bond of the chain is U_χ, then $\sigma_\chi \cong U_\chi/ad^2$ and $\sigma^* \cong kT/ad^2$. Hence $(\sigma_\chi/\sigma^*)^2 \cong (U_\chi/kT)^2$ and we have

$$V_s \cong V^*N^{-1/4}\left(\frac{U_\chi}{kT}\right)^2\frac{D}{L^*} \tag{5.9}$$

Typically, we have $U_\chi \sim 2$ eV and $U_\chi/kT \sim 10^2$. Take connector molecules with $N \sim 10^3$ and assume that they are grafted at an average separation of $D \sim 10^2$ Å between chain ends. Usually V_0^* is of order 10^{-3} m/s and $V^* \sim N^{-1}V_0^* \sim 10^{-6}$ m/s. The typical shear modulus of rubbers is of order $\mu \sim 10^5$ J/m; this gives $L^* \sim 10^2$ Å. Inserting these values into eq 5.9, one finds the order of magnitude of the scission velocity $V_s \sim 1$ cm/s. This is comparable to the peeling velocities in conventional peeling tests.[9]

For fracture with velocities above V_s, both the fracture energy G and the junction length L reach saturated values. From eq 5.6, we find

$$L_s \cong D\left(\frac{\sigma_\chi}{\sigma^*}\right)^2 N^{-1/4} \cong D\left(\frac{U_\chi}{kT}\right)^2 N^{-1/4} \sim 10\ \mu m \tag{5.10}$$

and

$$G_s \cong \frac{\sigma^{*2}L}{\mu} \cong G^*N^{3/4} \sim 10^3\ J/m^2 \tag{5.11}$$

where $G^* \equiv U_\chi^2/\mu a^2D^3 \sim 10$ J/m^2.

We must caution here that our analysis does not predict the actual onset velocity for chain scission, since we assumed that scission occurs for $h_0 < h^*$, whereas they may happen earlier. However, eq 5.9 does provide an upper bound for the onset velocity of chain scission.

Similarly, one may study the possibility of chain scissions in the one-stitch problem. In general, one finds a higher scission velocity with a much lower fracture energy in comparison with the many-stitch case. For example, the analysis above gives a scission velocity of order $V_s \sim 1$ cm/s with fracture energy $G_s \sim 10^3$ J/m^2. In the corresponding one-stitch problem, one finds that $V_s \sim 10$ cm/s and $G_s \cong G^* \equiv U_\chi^2/\mu a^2D^3 \sim 10$ J/m^2. One interesting feature here is that the saturated fracture energy G_s, which corresponds to the ultimate strength of the junction, does not depend on the molecular weight of the connector molecules N. In the many-stitch problem, $G_s \cong G^*N^{3/4}$ increases with N.

To test for chain scissions experimentally, one may first look for signs of saturation of fracture energy with increasing velocity, as is predicted in eq 5.11. A different, but more definitive, test could be obtained by washing off the residue of adhesives after the peeling test and measuring the molecular weight of the residual chains by gel permeation chromatography. A reduced value over the original molecular weight would be clear evidence for chain scissions. Of course, one could also invoke certain chemical tests, such as the detection of remaining free radicals.

VI. Concluding Remarks

(1) One remarkable prediction emerging from eq 4.11 is that the many-stitch conformation should *not* enhance the adhesive energy $G(V \to 0)$ (except possibly by a change of numerical prefactors): with an equal surface density of connectors, the one-stitch system is just as good as low velocity).

(2) At high velocities, we are able to make a (tentative) prediction only in a regime where the chains break. This in turn leads to eq 5.11 where the fracture energy is proportional to the square of the chemical energy U_χ. There is a superficial similarity between this result and a formula due to Brown for the toughness of glassy polymers.[2]

The analogy is not very deep: in regards to the distance between connectors, Brown has $G \sim D^{-4}$ where eq 5.11 has D^{-3}. But in both cases we end up with very high adhesion.

(3) We should keep in mind that, with a relation such as eq 3.10 in the slow limit ($dh/dt \to 0$), the stress σ is a decreasing function of the opening h, and this may lead to instabilities.

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