FEATURE ARTICLE

Adhesion Promoters

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Adhesion between a flat solid and a rubber is considerably increased by grafting chains (chemically identical to the rubber) on the solid surface. Similarly, a population of mobile chains dissolved into rubber can increase the strength of a rubber/rubber contact. A third (more recent) type of promoter is a "*Guiselin brush*", obtained by incubating certain polymer melts against a suitable solid. A major practical problem is to understand how the adhesive energy varies with the surface concentration σ of "connector molecules": very often, at high connector density, the strength goes down. We set up a theoretical picture of *polymer interdigitation*, covering most of the cases listed above. We also describe peeling measurements of the adhesion energy $G(\sigma)$ for Guiselin brushes (silica/PDMS/PDMS network). For the Guiselin brush, the statistical problem is much more complex. The main experimental result is the presence of a clear *maximum* in the plot of $G(\sigma)$.

I. Various Types of "Connector" Molecules

This paper is mainly concerned with the adhesion of rubbers. A first, major example concerns the contact between a rubber and a flat solid. If the solid surface is bare, the adhesion energy G (the energy required to separate a unit area of contact) is very small, comparable to the thermodynamic work of separation, i.e. smaller than 0.1 J/m². In practical adhesion problems, we need much larger values of G. This can be achieved by a number of methods.

(1) Grafted Chains. A classical approach amounts to attaching terminally certain polymer chains (the "connectors") on the solid surface. This actually leads to two distinct operation modes: *loose bridging*, where the connector end wanders into the rubber matrix (Figure 1a), and *chemical bridging*, where the connector end carries, for instance, a vinyl group and is ultimately bound to the rubber network (Figure 1b).

Let us first assume that the number of grafted chains per unit area v (or its dimensionless analog $\sigma = va^2$, where a is a monomer size) is small. Then, the grafted chains do penetrate easily in the rubber, if they are chemically identical to it. The adhesion energy for loose bridging has been analyzed by E. Raphaël;[1,2] the starting point is shown in Figure 2, where we see an advancing fracture with connector chains which are stretched up to a final length h_f. When the crack opening exceeds h_f, the connectors snap back to the solid surface and dissipate some energy: this is the leading contribution to G (at least in the limit of low fracture velocities; we always stay in this limit).

A central observation is that connectors can be pulled out only when the force acting on each of them is beyond a certain threshold f^*. There are two main contributions to f^*: (a) the van der Waals monomer/monomer attractions U_{vw} disfavor a molecular thread directly exposed to air and (b) the entropy of the thread is reduced.

E. Raphaël analyzed the combined effects of contributions a and b in a regime where $U_{vw} \leq kT$. He found that the force f^*
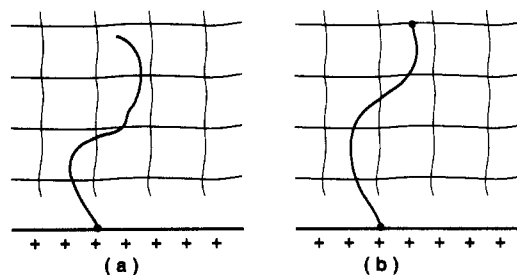
Figure 1. Grafted connectors between a solid and a rubber. In our entire discussion, the connector chain is assumed to be chemically identical to the rubber: (a) loose bridge; (b) chemical bridge.
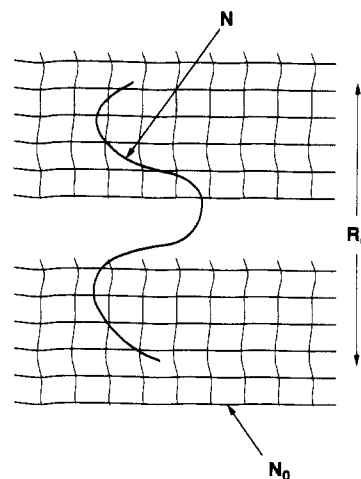

Figure 2. Mobile chain near the interface between two identical rubber blocks. Our entire discussion assumes that a single mobile chain is ideal; this is correct for $N < N_0^2$.

is, in fact, a geometric mean between both contributions,[1] namely,

$$f^* \cong (kTU_{vw})^{1/2}/a \tag{1}$$

For many practical cases, U_{vw} and kT are comparable, and we

can use the simplified form

$$f^* \sim U_{vw}/a \qquad (1')$$

The other important ingredient is the ultimate length, h_f, of the connectors. In the regime $kT \sim U_{vw}$, the chains are nearly fully extended:

$$h_f \cong Na \qquad (2)$$

where N is the polymerization index of the connectors. The energy G (in the low-velocity limit) is then simply the work (per unit area) performed to pull out the chains with a force f nearly equal to the threshold f^*:

$$G = \nu f^* h_f = \nu N f^* a$$

$$\cong \nu N U_{vw} \cong \sigma N \gamma \qquad (3)$$

where γ is the surface tension of a melt of connector molecules. The crucial factor in eq 3 is N: interdigitation leads to large enhancements of adhesion. The remaining problem is the choice of the surface density σ. To obtain strong adhesions, we wish to increase σ. But, clearly, when σ is very large, we are in danger of losing the interdigitation. The brush may segregate from the network. In section II (expanding upon the ideas of ref 3), we shall study what happens at relatively large grafting densities.

Let us briefly mention here the case of a brush with *chemical bridging* to the rubber. Here, we can understand the adhesion energy G following a classical argument by Lake and Thomas.[4] When the connectors are pulled out, each of their bonds has a stored elastic energy which is huge, comparable to a chemical binding energy U_x. After scission, the energy dissipated per connector is $\sim N U_x$ and

$$G \sim \nu N U_x \qquad (4)$$

Again, this is linear in N! If we compare the two estimates 3 and 4, we find a remarkable law:[1]

$$\frac{G_{\text{chemical}}}{G_{\text{loose}}}\bigg|_{V\to 0} \cong \frac{U_x}{U_{vw}} \qquad (5)$$

Typically, this ratio is on the order of 50. Early experiments by Ahagon and Gent,[5] using relatively short silane chains, between glass and a cross-linked p-butadiene, gave ratios on the order of 40.

(2) Mobile Chains between Two Rubber Blocks. Figure 2 describes the situation. Each mobile coil has a size $R_0 = N^{1/2}a$. The volume fraction occupied by the coils inside the rubber is ϕ. The connectors correspond to coils which are in a sheet of thickness $\sim R_0$ near the interfacial plane. Their superficial density is thus

$$\nu \sim \phi R_0/Na^3 \qquad (6)$$

Or, in dimensionless units

$$\sigma \cong \phi N^{-1/2} \qquad (7)$$

What is their impact on the adhesion energy G? At first, we note that each coil provides many connecting pieces between the two sides (a simple scaling estimate is $N^{1/2}$ pieces/coil). However, this is misleading. Adhesion with systems of this sort ("many stitch") was analyzed theoretically by Hong Ji:[6] he showed that, when the crack begins to open, very soon, most of the $N^{1/2}$ bridges zip out and that the effective strength of the
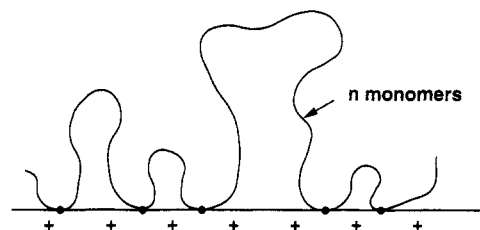

Figure 3. Idealized representation of a "pseudobrush". A number of overlapping chains are bound to the surface, but only one chain has been displayed. The number of contact points is on the order of $N^{1/2}$ (where N is the number of monomers per chain). The average length of the loops is $\bar{n} \sim N^{1/2}$, but some loops are much larger.

coil is still given by eq 3! Thus (omitting always all numerical coefficients)

$$G|_{V\to 0} = \phi N^{1/2} \gamma \qquad (8)$$

What is the maximum value of ϕ which can be achieved in practice? This was discussed in ref 3 and will be presented in section II.

It is worth emphasizing that eq 8 is expected to work only in a low-velocity regime. At higher velocities, a completely different process becomes important, namely, the viscous relaxation of the mobile chains, far from the fracture tip. For instance, Ellul and Gent studied rubber blocks mixed with mobile chains of polyisobutylene[7] and found a considerable contribution of this type. (For a simple description of viscoelastic losses in fracture, see ref 8.)

(3) Pseudobrushes. When a silica surface is exposed to a melt of poly(dimethylsiloxane) (PDMS) for a sufficiently long time ($\sim$1 day), a certain amount of polymer becomes permanently bound to the solid. This amount is usually measured in terms of an "equivalent dry thickness" h. h is determined by washing out all the unbound polymer by a good solvent and then drying and measuring the residual weight. This has been done for various molecular weights by Cohen Addad and coworkers; they find[9]

$$h = \text{const } N^{1/2}a \qquad (9)$$

where N is always the number of monomers/chain. Equation 9 can be understood as follows: all the coils which touched the silica during incubation were within one radius of gyration of the surface. In this system, each coil is bound to the surface at many points (Figure 3). The surface density of chains is $\sigma = h/Na$.

When the polymer layer is again exposed to a good solvent, it swells; the basic theoretical picture for this form of swollen brush is due to O. Guiselin.[10] Among other things, he found the length distribution of the loops shown in Figure 3. He defines $a^{-2}\sigma(n)$ as the number of loops (per unit area), with a number of monomers $\geq n$. Two conditions define the structure of $\sigma(n)$:

(a) The total number of loops ($a^{-2}\sigma(1)$) is equal to the total number of chains per unit area ($a^{-2}\sigma$) multiplied by the average number of bridging sites/chains $\bar{p}$. A simple argument shows that $\bar{p} \sim N^{1/2}$. (In one coil volume, $\sim R_0^3$, we have an internal concentration N/R_0^3; the surface layer is a slice of volume R_0^2a.) Thus,

$$\sigma(1) \cong \sigma N^{1/2} \cong (h/Na)N^{1/2} \qquad (10)$$

where σ is always the total number of *chains* per area a^2.

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(b) The total number of *monomers* per unit area is

$$\sum_1^w a^{-2}(d\sigma/dn)n = h/a^3 \cong N^{1/2}a^{-2} \tag{11}$$

If we now look for a power law distribution

$$\sigma(n) = \sigma(1)n^{-x} \tag{12}$$

and impose the conditions of eqs 10 and 11, we find $x = 1/2$. Thus, a pseudobrush (or "Guiselin brush", as it is often called) is somewhat similar to a very polydisperse grafted layer; on the average, each polymer chain gives $N^{1/2}$ loops of length $\sim N^{1/2}$; but there are a few loops of size $\sim N$.

Another interesting aspect of the Guiselin brushes is that they can be prepared, not only from melts but also from semidilute solutions of PDMS in good solvents. If ϕ_0 is the original concentration of PDMS in the incubating bath, the equivalent dry thickness of the resulting brush is

$$h \cong N^{1/2}a\phi_0^{7/8} \tag{13}$$

Equation 13 has been established by various independent m e a s u r e - ments: neutron scattering,[11] ellipsometry, and X-ray reflectance.[12] This form follows from a simple picture, where all the chains in solution, which are within one radius of gyration $R(\phi_0)$ from the surface, get stuck. The classical scaling law for $R(\phi_0)$ is[13]

$$R(\phi_0) = R_0\phi_0^{-1/8} \tag{14}$$

and this brings us naturally to eq 13. Thus, the surface density σ of chains can be adjusted at will by varying ϕ_0:

$$\sigma = h/Na = N^{-1/2}\phi_0^{7/8} \tag{15}$$

What are the adhesive properties of a Guiselin brush, when it opposes a network of the same chemical composition? Experiments on this are described in section V.

II. Partition Coefficient between a Melt and a Rubber[5]

Consider a melt of chains (N monomers/chain) exposed to a network C, chemically identical to the mobile chains (the chemical distance between cross-links in C is called N_0). Many authors have discussed the penetration (or nonpenetration) of the N chains into C, with very different results.[14,15] As emphasized long ago by Flory, the crux of the matter is the *reference state* of the network. If it has been cross-linked in the presence of a solvent, and then brought to the dry condition, it accepts chains readily. On the other hand, if it has been cross-linked in the dry state, the elastic energy for swelling (by a factor $1 + \psi$) is (per unit volume) $F_{el} = (1/2)E\psi^2$. Here, E, the elastic modulus, is $E \sim kT/(N_0a^3)$.

Let us now look at a volume fraction ϕ of mobile chains inside C. They impose a swelling $\psi = \phi$ and an elastic energy F_{el}. The corresponding shift in chemical potential for one mobile chain is

$$\mu = a^3N(\partial/\partial\phi)F_{el} = kT(N/N_0)\phi \tag{16}$$

and the partition coefficient (melt/C) is $k = \exp(-\mu/kT)$. We see that k becomes negligible above a concentration

$$\phi_1 = N_0/N \tag{17}$$

Equation 17 is nothing more than a simplified version of the Flory theory of swelling, with a particular choice of the reference state. A more precise version would amount to $\mu = kT[\ln \phi + N/N_0\phi]$ ($\phi \ll 1$), for which the approximate solution is $\phi \cong N_0/N \ln(N/N_0)$. In our rough estimates, we omit the logarithmic factors.

As pointed out in section I, this result is of interest for adhesion studies between two rubber blocks which have been internally loaded (in the bulk) by mobile chains. The "active region" has a thickness comparable to the coil size $R_0 = N^{1/2}a$, on both sides of the contact. Thus, the maximum two-dimensional density of connectors is

$$\sigma_l = a^2v_1 \cong a^2(\phi_1/Na^3)R_0 = N_0/N^{3/2} \tag{18}$$

and this value of v (or σ) defines a related adhesion energy through eq 3.

We emphasize again that the limit (eq 18) holds when the network has been cross-linked in the dry state. This differs from the Ellul–Gent experiments,[7] where the mobile chains were first mixed to the elastomer; then, in a second stage, the latter was cross-linked. The limit on ϕ, in this case, is set by the limited compatibility of the two partners.

III. Interdigitation between a Brush and a Rubber[5]

Let us return to Figure 1a and describe the brush by a self-consistent approach of the Flory type.[16] If the brush thickness is L, we can write the free energy per chain in the following form (ignoring all numerical coefficients):

$$F = kT(L^2/R_0^2) + F_{el} \tag{19}$$

The first term is the deformation energy of the coils. The second term is the swelling energy of the network, analyzed in section II. The internal concentration of grafted chains is here

$$\phi = Na^3/SL \tag{20}$$

where $S = v^{-1} = a^2\sigma^{-1}$ is the area per chain. Then, counted per chain, F_{el} is of the form (similar to eq 16)

$$F_{el} = a^3NE\phi \cong kT(N/N_0)\phi \tag{21}$$

Inserting eq 21 into 19 and optimizing the energy with respect to L, we find

$$L \cong Na(\sigma/N_0)^{1/3} \tag{22}$$

The factor N_0 in eqs 21 and 22 shows a remarkable similarity between brushes in a *network* and the (more classical) problem of brushes in a *solvent* of oligomers (N_0 units/oligomer) discussed in ref 16. In both cases, the matrix screens out the interactions between brush units. In the oligomer problem, screening takes place by an overall displacement of the short, mobile chains. In the network problem, it is performed by a slight deformation of the mesh, but the entropy effects are comparable.

Returning now to our discussion of eq 19, we ultimately find three regimes (Figure 4):

(a) When $\sigma < N^{-1}$, the grafted chains are not extended and do not overlap. We call this the "independent mushroom" regime.

(b) When $N^{-1} < \sigma < \sigma_l$, the mushrooms overlap, but the coils are still not extended. Interdigitation is still fully allowed.
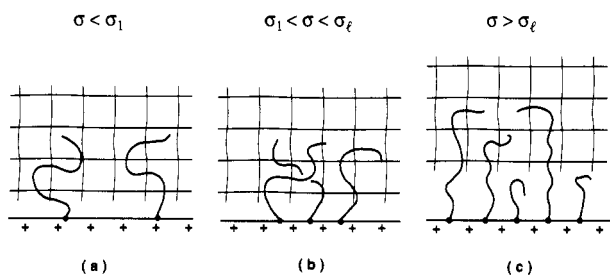
Figure 4. Three regimes for a brush exposed to a rubber: (a) separate mushrooms; (b) overlapping mushrooms; (c) partial interdigitation.
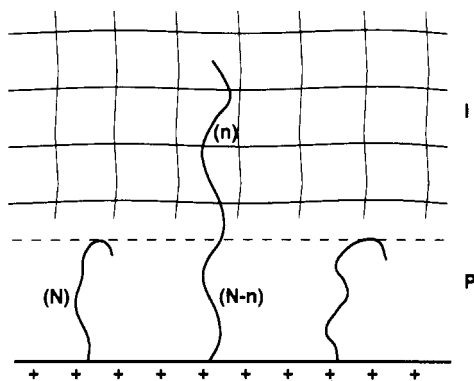

Figure 5. Partial interdigitation between a grafted brush and a rubber: (I) interdigitated region; (P) passive layer. A fraction f of the chains penetrates into I.

(c) When $\sigma > \sigma_l$, we have a "brush" with extended chains. Here, σ_l is still given by eq 18! And, by using eqs 16 and 20, our reader can check that the interdigitation is complete only for $\sigma < \sigma_l$.

What happens beyond that point? There are many possibilities:

(1) One of us (F. Brochard-Wyart) proposed a state of partial interdigitation, where each connector inserts only $n(<N)$ monomers into the network. The number n is such that $\sigma = \sigma_1(n)$; That is

$$n = N(\sigma_1/\sigma)^{2/3} = N_0^{2/3}\sigma^{-1} \qquad (23)$$

The resulting adhesion energy is

$$G = vf^*na \sim \sigma^{1/3} \qquad (24)$$

It is an increasing function of σ.

(2) Another type of partial interdigitation corresponds to a fraction f of the chains which penetrate, while a fraction $(1 - f)$ does not penetrate at all and forms a passive layer between the solid and the network (Figure 5). If each penetrating chain infiltrates n segments into the rubber, the threshold condition is now

$$\sigma f = \sigma_1(n) \equiv N_0/n^{3/2} \qquad (25)$$

The thickness h of the passive layer is given by

$$h/a = \sigma(1 - f)N + \sigma f(N - n) \qquad (26)$$

and f must be obtained through a minimization of the free energy F (per unit area). This F contains two contributions:

(a) Each of the σf penetrating chains is just at threshold and has an energy $\sim kT$ due to network swelling.

(b) The interface between the passive layer and the network has a certain surface energy, because a number $\sigma(1 - f)$ of chains are reflected there. If the interface was sharp, this would
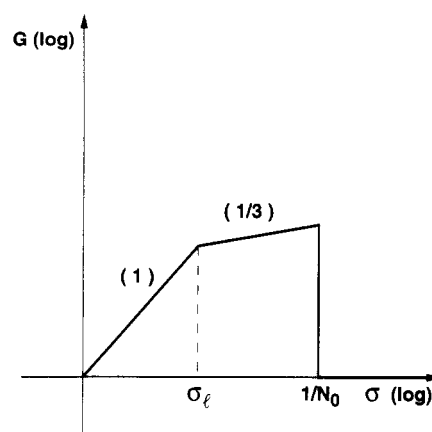

Figure 6. Theoretical plot for the adhesion energy (at very low velocities) of a brush/network pair as a function of the reduced grafting density σ.

give an energy $\gamma_0 \sim kTa^{-2}$. But, we expect the interface to be diffuse, over a width $\sim N_0^{1/2}a$, corresponding to the network size. As usual in polymer interfaces, the energy γ should be proportional to (thickness)$^{-1}$: we are thus led to the conjecture

$$\gamma \sim (kT/N_0^{1/2}a^2)(1 - f) \qquad (27)$$

and to an overall energy F of the form

$$a^2(F/kT) = \sigma f + N_0^{-1/2}(1 - f) \qquad (28)$$

Near the onset of partial interdigitation $(\sigma \sim \sigma_1(N))$ we have

$$\sigma N_0^{1/2} \sim \sigma_1 N_0^{1/2} \cong (N_0/N)^{3/2} \qquad (29)$$

We constantly assume that $N \gg N_0$. Then, for σ only slightly smaller than σ_1, the slope dF/df in eq 28 is negative, and the optimum should correspond to $f = 1$, i.e. to the Brochard-Wyart proposal. On the other hand, at higher σ values $(\sigma \sim N_0^{-1/2})$ the slope would become positive, and the system prefers $f = 0$. Interdigitation then disappears completely. This prediction is described in Figure 6. It is supported by an analogy: as already pointed out after eq 22, there is (for our purposes) a certain similarity between a network and a liquid of short chains (length N_0). The statistics of a brush exposed to such a liquid has been studied in ref 16 and more recently by C. Ligoure[17] and M. Aubouy and E. Raphaël.[18] The limit which all authors find for interdigitation turns out to be exactly the same $(\sigma \sim N_0^{-1/2})$.

IV. Adhesion Elastomer/Pseudobrush

(1) **Experiments.** We have prepared series of pseudobrushes formed by simultaneous adsorption and end grafting of $\alpha - \omega$ hydroxy-terminated poly(dimethylsiloxane) (PDMS) (narrow fractions, weight average molecular weight in the range 20 000–700 000) on the naturally oxidized (silica) surface of silicon wafers. The measured dried thickness of these layers obeys the scaling law of eq 13, with $a = 5.5$ Å.[12]

These PDMS layers were then put into contact with a ribbon of cross-linked PDMS (average molecular weight between crosslinks M_0 in the range 10 000–70 000) for at least 2 days. After this time, the adhesive strength of the interface elastomer/pseudobrush was tested, using a 90° peel test conducted at very low velocity (50–500 Å/s). The details of the experimental setup will be reported elsewhere.[19] Typical results for the energy (per unit area) necessary to break the junction at a velocity 50 Å/s are reported in Figure 7 as a function of ϕ_0, for a series of pseudobrushes formed with PDMS of molecular

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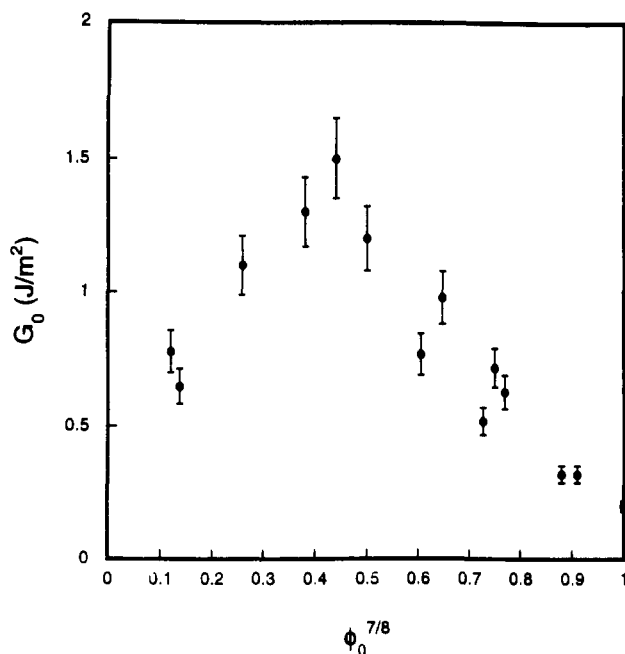*J. Phys. Chem., Vol. 98, No. 38, 1994* **9409**

Figure 7. Experimental results for the adhesion energy between pseudobrushes formed from PDMS of molecular weight 242 370 and a PDMS elastomer (molecular weight between cross-links $M_c = 10\ 250$ measured through 90° peel tests at 50 Å/s, for series of pseudobrushes formed at various volume fractions of polymer in the reaction bath Φ_0.
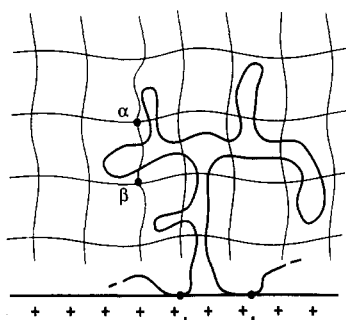

Figure 8. The "cactus". One loop of a pseudobrush (IJ), when penetrating a network, builds up a conformation where every "gate" (for instance the $\alpha\beta$ gate) is used at least twice; this imposes a strong reduction in entropy.

weight 242 370 ($I = M_w/M_n = 1.10$) and an elastomer with $M_0 = 10\ 250$. The most remarkable feature is the existence of a maximum in the adhesive strength of the elastomer/pseudobrush interface, when ϕ_0 is increased. This is in good qualitative agreement with what has just been predicted in section III for the brushes, with an interdigitation, and thus an adhesion energy vanishing at high σ. A pseudobrush is, however, much more complicated to describe than a brush, and we do not have yet a theory for this case.

(2) Theoretical Aspects. A pseudobrush is not really equivalent to a polydisperse brush. A major feature is the "cactus effect" displayed in Figure 8. When a loop with m monomers and fixed attachment points (I and J) attempts to interdigitate with the network, its conformations are strongly restricted, and there is an entropy loss:

$$\Delta S_{\text{cactus}} \sim \beta m/N_0 \tag{30}$$

where β is a numerical factor of order unity. The net result is that most loops with $m > N_0$ *should not enter at all*. The only pieces which enter freely are the two ends of the chain. From

this argument, one would naively expect a rather weak adhesion $G(\sigma)$: the number $\tilde{\sigma}$ of loops of length $\geq m$ which are allowed to enter is now

$$\tilde{\sigma} = \sigma m^{-1/2} \tag{31}$$

rather than $\sigma(N/m)^{1/2}$.

The adhesion energy should then be given by

$$G/2\gamma \cong \int_{N_0}^{N} \mathrm{d}m(\sigma m^{-3/2})m \cong \sigma N^{1/2} \tag{32}$$

(rather than σN for a simple brush). Equation 32 would hold for full interdigitation. Ultimately, at high σ, eq 32 would be cut off, possibly again at $\sigma = N_0^{1/2}$, as in simple brushes. The adhesion energies measured in the PDMS experiments appear somewhat too high to be described by eq 32.

V. Concluding Remarks

At the crude level of scaling laws, we begin to have a certain perception of the main controlling factors for rubber adhesion in the presence of adhesion promoters, or "connector molecules".

(1) For rubber/rubber contacts, strengthened by mobile chains, the history of the rubber is crucial: if it has been cross-linked prior to the insertion of mobile chains, the maximum concentration of connectors should be severely limited, and short connectors are preferable, as seen from eqs 3 and 18.

(2) For simple grafted layers, we predict a regime of partial interdigitation, where the adhesion energy increases very slowly with the grafting density. At higher surface concentrations ($\sigma > N_0^{-1/2}$), the brush should not interdigitate any more. All this should be amenable to experiments, possibly by using block copolymers rather than grafted chains.

(3) With a typical model system such as PDMS against silica, the most readily available situation corresponds to the Guiselin brush. Our peeling data on these brushes show an interesting maximum in $G(\sigma)$. However, no complete theory is available yet for this case.

(4) There are other limitations to our discussion, such as the following:

(a) Rubber/rubber contacts (or latex/latex contacts) will be, in practice, extremely sensitive to the polydispersity of the mobile connectors. This can, in fact, be taken into account rather easily in our picture.

(b) We have not incorporated the possibility of chemical scission for the connectors. In fact, our discussion of section I shows that, for most loose systems, the force on the connectors (at low velocity) is $f^* \cong U_{vw}/a$, where U_{vw} is a van der Waals energy. This is far below the chemical rupture forces $f_x \sim U_x/a$. Thus, in the low-velocity regime, scission is indeed negligible for loose systems of unbranched connectors.

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