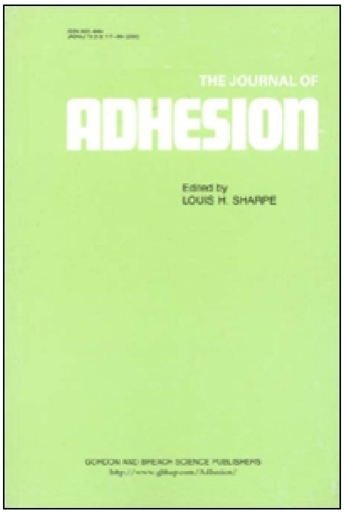

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Adhesion Between Rubbers and Grafted Solids*

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The adhesion energy, G (at low separation velocities), between a rubber and a solid surface, is expected to increase when flexible chains, chemically identical to the rubber, are attached to the surface. This can be set up with or without chemical binding of the chains to the rubber ("bound" chains or "free" chains).

1) For the "free" case, rupture is predicted to occur mainly in an adhesive mode. The calculated adhesion energy, G_a, has a maximum at a certain value of the grafting density, $\sigma = \sigma_2 = N_o^{-1/2}$ (where N_o is the number of monomers between cross links in the rubber).

2) For the "bound" case, we expect a linear increase of $G(\sigma)$ up to a value ($\sigma = \sigma_3$) where we switch from adhesive to cohesive rupture.

KEY WORDS: adhesion promoters; interfaces; adhesion energy; low separation velocity; flexible chains; interdigitation; "brush" of grafted chains; "sausage" model; "free" connectors; "bound" connectors

I. INTRODUCTION

To improve the adhesion between a soft rubber and a high energy surface, we often graft on the solid a certain number, ν, of flexible chains per unit area.[1] We expect more adhesion if the grafted chains interdigitate with the rubber, and this requires that there be no chemical difference between the two partners. But, even so, interdigitation may or may not occur, depending on the grafting density, ν, or of its dimensionless equivalent, σ (the fraction of surface sites on the solid which is grafted). When σ is too high, we may end up with a "brush" of grafted chains which does not mix very much with the rubber. In a previous note,[2] we had analysed qualitatively this interdigitation problem, but we had not fully understood the sequence of regimes. A modified version of this sequence is presented in section II.

The central problem is the prediction of adhesion energies, G (at least in a quasi static limit: very low separation velocities). Here, we have to distinguish two cases, displayed on Figure 1: the "free" case, where the grafted chain can slide out of the rubber without

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**Corresponding author.

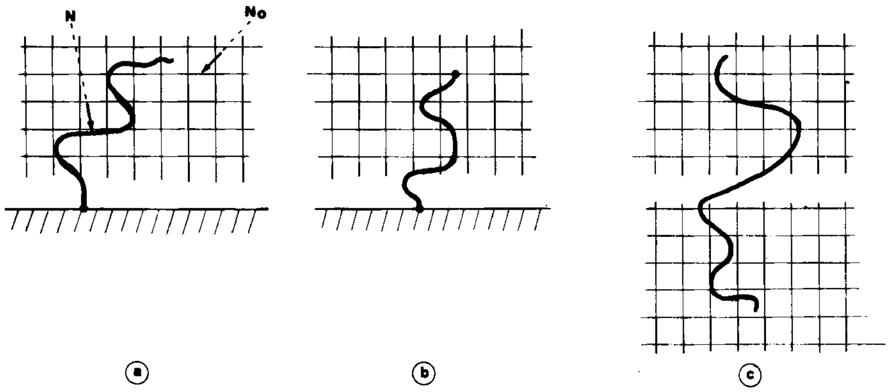

FIGURE 1 Various connector systems (a) "free" grafted chains (b) "bound" grafted chains (c) mobile connectors.

any chemical scission; and the "bound case", where chemical energies must be involved. Clearly, we gain by chemical binding, but how much? In the limit of low grafting density (small σ) where the grafted chains act independently, this has already been analysed:[3] the results have the following scaling form:

$$G_{\text{free}} = W_a(1 + N\sigma) \tag{1}$$

$$G_{\text{bound}} = W_a + W_b N\sigma \tag{2}$$

where N is the number of monomers per connector chain ; W_a is a reversible work of adhesion between the rubber and the bare solid, due to Van der Waals forces. On the other hand, $W_b = U_b/a^2$ describes the energy required to disrupt a dense array of chemical bonds (each bond giving an energy U_b, and occupying an area a^2). Typically, $a = 3\,\text{Å}$, $W_a \sim 30\,\text{mJ/m}^2$ and $W_b \sim 1\,\text{J/m}^2$.

We emphasize again that the exact coefficients in Eqs. (1) and (2) are not specified in our scaling analysis ; but they are expected to be of order unity.* If we compare the increments (ΔG) in G due to grafting, we find from Eqs (1,2) a remarkably simple result:

$$\Delta G_{\text{bound}} \sim \frac{W_b}{W_a} \Delta G_{\text{free}} \tag{3}$$

In the limit of very short connectors this ratio was confirmed by the classic experiments by Ahagon and Gent[1] on the adhesion between polybutadiene and glass, where the glass is grafted by relatively short silanes, which behave as adhesion promoters. Pure ethyl silanes are "free", while vinyl silanes, after cross linking *in situ*, are bound. The experimental G ratio is of order 35, as expected.

But there is a deeper aspect to Eq. (3)–namely, that the ratio should remain *independent of the connector length* (N) (provided that we stay in the low σ limit). We do not know of any systematic check of this property.

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*Also we simplified the results of Ref. 3 by assuming that typical Van der Waals energies are comparable with thermal energies (kT). This is indeed not bad at room temperatures.

All the discussion leading to Eqs. (1,2,3) is restricted to the limit of low grafting densities, σ. Our aim, in the present text, is to extend it, at least qualitatively, to all possible values of σ. The ultimate goal is to obtain a certain understanding of the adhesion energy, $G(\sigma)$, as a function of grafting density. This is done for the "free" case in section III, and for the "bound" case in section IV.

II. VARIOUS REGIMES OF INTERDIGITATION[2]

1) Unattached Connectors

The case at hand is shown on Figure (1 c). It is of some interest in the operation of paints, where latex particules in suspention build up contacts after solvent evaporation. These particles are based on a network, which contains, however, a certain small fraction of free chains: at the moment of contact, some of these chains will be shared between two particles, and play the role of transient connectors, as discussed in Ref. 2.

In this case, the mobile chains were present before the formation of the network, and their volume fraction can be large. In some other cases, a dry network is incubated in the presence of free chains. Then, what is the maximum concentration of mobile chains which the rubber will accept? To understand this, 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_o). Many authors have discussed the penetration (or non penetration) of the N chains into C, with very different results.[4,5] The crux of the matter is the *reference state* of the gel. If the network has been synthesised in the presence of the solvent, and then brought to the dry condition, it accepts chains readily. On the other hand, if the network has been synthesised in the dry state, the elastic energy for swelling ($1 \rightarrow 1 + \phi$) is (per unit volume) $F_{el} = 1/2\, E\phi^2$, where the elastic modulus is $E \sim kT/(N_o a^3)$. In the following, we concentrate on this last case.

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 of one mobile chain is:

$$\mu = a^3 N \frac{\partial}{\partial\phi}(F_{el}) = kT\frac{N}{N_o}\phi \tag{4}$$

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

$$\phi_e \cong N_o/N \tag{5}$$

This result is a simplified, qualitative version of the Flory theory of swelling by N chains. It may be of interest for adhesion studies between two rubber blocks which have been internally loaded (in the bulk) by mobile chains.[7] The "active region" has a thickness comparable with the coil size $R_o = N^{1/2} a$, on both sides of the contact.* Thus, the maximum surface density of connectors is:

$$\sigma_l = a^2 v_l \cong a^2 \frac{\phi_l}{N a^3} R_o = N_o / N^{3/2} \tag{6}$$

and this value of v(or σ) defines a maximum adhesion energy through Eq. (2). To go beyond this maximum, it would be necessary to incorporate mobile chains *before* curing the network.

2) Interdigitation Between a Brush and a Network

Let us analyse the structure of the brush inside the network by a self-consistent method of the Flory type.

a) The self-consistent picture: We write the free energy (F_1), per grafted chain, as the sum of an elastic contribution plus a swelling contribution:

$$\frac{1}{kT} F_1 = \frac{L^2}{N a^2} + \frac{N\phi}{N_o} \tag{7}$$

where L is the length of the brush, and $\phi = Na\sigma/L$ is the local volume fraction of grafted chains.

Equation (7) displays a remarkable similarity between our problem of grafted chains inside a network, and a chemical problem of grafted chains exposed to a melt of shorter chains:[8] if we choose N_o to be the length of these chains, the $1/N_o$ factor describes the Edwards' screening of interactions by the mobile chains.[11] Thus, we may say that a rubber matrix *screens out repulsions* between connector monomers, very much like a liquid with the same chain length. This observation will be useful later.

Returning now to eq. (7), and minimizing the energy with respect to L, we arrive at:

$$L = Na \left(\frac{\sigma}{N_o} \right)^{1/3} \tag{8}$$

b) The "sausage" model: It is of interest, at this point, to give a slightly more local picture for the state of the grafted chains in the brush (Fig. 2)–based on our earlier work on N chains confined in a tube filled with shorter (N_0) chains.[12] We can think of one (N) chain is being composed of a sequence of subunits (or sausages), each of length l and diameter $D = a\sigma^{-1/2}$, where D is the distance between grafting points.

Inside one sausage we have a certain number of monomers (g) from the N chain. On scales smaller than l, the grafted chain is ideal, and thus:

$$l^2 = g a^2 \tag{9}$$

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*In our discusion, all microscopic sizes (e.g., the monomer size) are represented by one length, a.

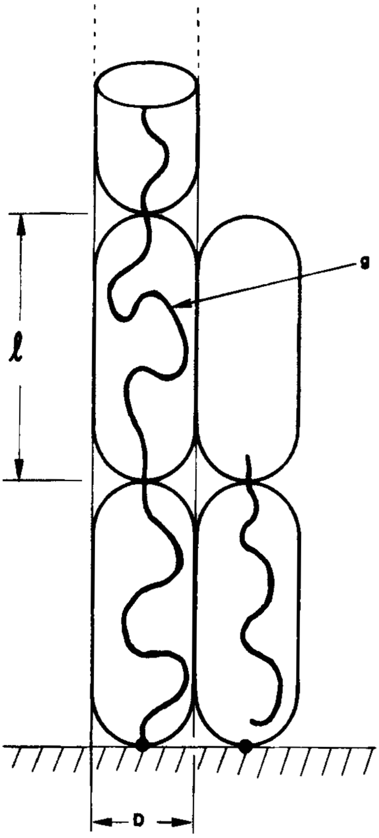

FIGURE 2 The "sausage" model for a grafted brush interdigitated with a rubber network. Within each sausage, the grafted chain behaves as an ideal chain confined inside a tube of diameter $D = \nu^{-1/2}$ (the distance between grafting points).

The concentration, ϕ, is such that a sausage is just at the invasion threshold defined by Eq. (5), replacing N by g:

$$\phi \equiv \frac{ga^3}{lD^2} = \frac{N_o}{g} \tag{10}$$

Combining Eqs. (9) and (10), we arrive at:

$$l = a\left(\frac{N_o}{\sigma}\right)^{1/3} \tag{11}$$

$$g = \left(\frac{N_o}{\sigma}\right)^{2/3} \tag{12}$$

and we can check that the total length $L = (N/g)l$ coincides with Eq. (8). The whole picture holds when $g < N$ or equivalently:

$$\sigma > \sigma_l = N_0/N^{3/2} \tag{13}$$

Note that this lower limit coincides with Eq. (6) for mobile connectors.

The sausage model discussed here is very primitive–as pointed out to us by E. Raphaël and by a referee. In actual fact, adjacent chains from the brush do overlap their sausages to some extent. The resulting analysis* is much more complex; but the results of interest for us (Eqs. 8 and 13) are not altered (the Flory model of Eq. (7) would, in fact, be sufficient for our purposes). But the sausage picture gives a valuable, simple insight.

c) The upper interdigitation limit: The screened Flory model, with interdigitated chains, will hold up to a certain limit, where the rubber becomes expelled. In the langage of Ref. 8, there will be a crossover to a "dry brush" when the internal concentration, ϕ, becomes of order unity. Returning to Eq. (10), we see that this corresponds to $g = N_o$ and to a certain limiting value of σ, which we call σ_2:

$$\sigma_2 = N_o^{-1/2} \tag{14}$$

For $\sigma > \sigma_2$, all interdigitation disappears. This has been discussed in more detail (for the analog case of a liquid matrix made of N_o chains) by C. Ligoure,[9] M. Aubouy and E. Raphaël.[10]

d) A list of regimes for grafted brush against rubber: The various situations obtained upon increasing the surface density σ are summarized in Figure 3.

α – At very low densities $\sigma < \sigma_l \equiv N^{-1}$, we have independent "mushrooms".

β – When $\sigma_1 < \sigma < \sigma_l$ (where σ_l is given in Eq. (6)), the mushrooms overlap, but the grafted chains do not stretch: this is due to the screening effect of the rubber matrix.

γ – When $\sigma_l < \sigma < \sigma_2 \equiv N_o^{-1/2}$, we expect a stretched brush, with "sausages", as shown on Figure 2. We still expect good interdigitation.

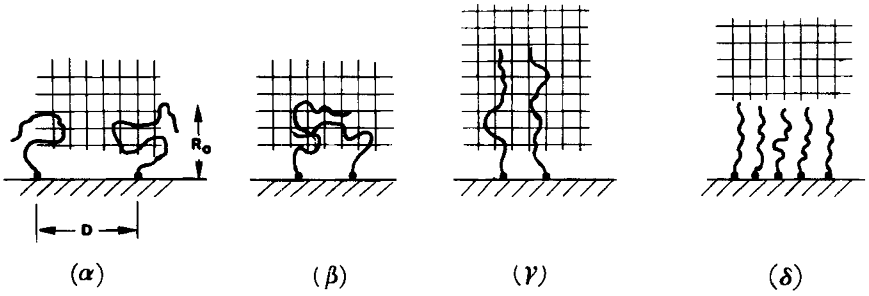

FIGURE 3 Various regimes for a grafted brush facing a rubber network: (α) separate mushrooms (β) overlapping mushrooms (γ) stretched chains (see also Fig. 2) (δ) segregated brush.

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*M. Aubouy, E. Raphaël, to be published.

In Ref. 2, we had mentioned a different possibility, where the last sausage interdigitated, while the rest of the chain segregated out of the rubber. But a comparison of energies shows that the completely interdigitated brush is more stable.

δ – For $\sigma > \sigma_2$, we expect no interdigitation.

III. "FREE" CONNECTORS: ESTIMATE OF THE ADHESION ENERGY

1) Interdigitated Regime ($\sigma < \sigma_2$)

For this regime of total penetration, the adhesion energy, G, has been discussed in Ref. 3: the net result is Eq. (1), giving an energy which increases linearly with σ. It may be useful to rederive Eq. (1) briefly at this point. The underlying picture of rubber/solid separation is shown on Figure 4. To extract one connector chain from the rubber, a certain threshold force f^* is required. This force results from two effects: a) when a monomer is pulled out in thin air, it loses a certain Van der Waals energy, U_v, which came from contacts with adjacent rubber monomers. b) the connector chain, when pulled out, it taut and has lost a certain entropy, ΔS, corresponding to a free energy $\Delta S\, kT \sim kT$. In the following discussion, we shall simplify this by noting that kT and U_v are usually comparable at room temperature. Then we can write simply:

$$f^* \sim U_v/a \tag{15}$$

where a is a monomer size. The other crucial parameter is the final size, h_f, of the taut connectors when they are very close to snapping out of the rubber. This is of order:

$$h_f = Na \tag{16}$$

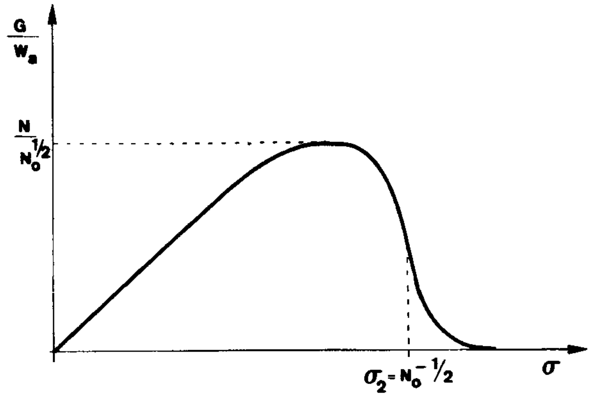

FIGURE 4 Qualitative plot of adhesive energy G *versus* grafting density σ in the "free" case. This plot holds provided that the cohesive rupture energy of the rubber is higher than the maximum G_{max}.

At low separation velocities, the force applied to the connectors is very nearly equal to the threshold value, f^*. The energy, ΔG, due to the connectors is simply the work done by this force ($f^* h_f$) multiplied by the number of connectors per unit area:

$$\Delta G_{\text{free}} = \nu f^* h_f = \nu U_v N \tag{17}$$

and this is equivalent to Eq. (1).

2) The Maximum Adhesion Energy

When we reach values of σ near σ_2, the inner concentration in the brush, ϕ, becomes of order unity, and the interaction term in Eq. (7) must be rewritten in a more general form (as in Ref. 8. Also, the adhesion energy must be corrected, as first pointed out by E. Raphaël. We should replace Eq. (1) by:

$$G_{\text{free}} - W_a = W_a N \sigma (1 - \phi) \tag{1'}$$

where the factor $(1 - \phi)$ describes the fact that each connector is seeing only $(1 - \phi)$ adjacent monomers of the matrix. The detailed forms which result from these modifications are discussed in a forthcoming note by E. Raphaël. Here, at our scaling level, we mainly emphasize the value of G at the maximum. When $\sigma \sim \sigma_2$, from Eq. (1′), we expect a maximum:

$$G_{\max}^{\text{free}} \cong W_a N / N_o^{1/2} \tag{18}$$

This can represent a considerable gain in adhesion. The general shape of $G(\sigma)$ is shown on Figure 4. Let us emphasize, finally, that Eq. (18) holds only for the *adhesive* mode: at very large N, we may switch to cohesive rupture.* This will be discussed in more detail in the next section.

IV. ADHESION WITH BOUND CONNECTORS

We now turn to the situation of Figure 1b where all connector chains are chemically bound to the network. At low grafting densities, σ, the solid-rubber interface is the weak partner, and we expect Eq. (2) to hold. But, if we increase σ, we reach a point where the cohesive rupture energy G^{coh} is smaller than the prediction of Eq. (2).

A scaling estimate for G^{coh} can be derived from the Lake-Thomas argument.[13] Near the fracture plane, the rubber chains which have to be cut occupy a thickness $e_o = N_o^{1/2} a$. The volume concentration of rubber chains is $1 / N_o a^3$, and this surface concentration is:

$$\nu_o = a^{-2} N_o^{-1/2} \tag{19}$$

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* We are indebted to L. Vovelle for pointing this out of us.

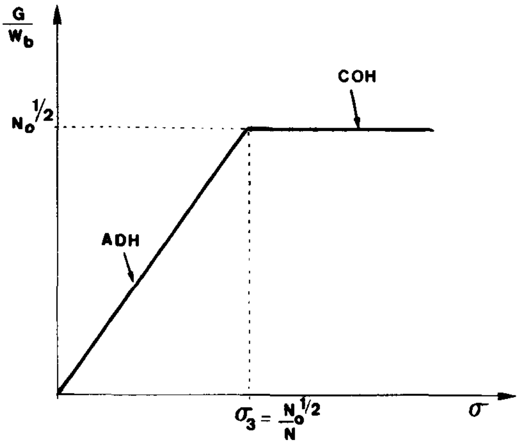

FIGURE 5 Adhesion energy *versus* grafting density, σ, in the "bound" case.

We expect a cohesive fracture energy (at low velocities) of the form:

$$G^{\mathrm{coh}} = \nu_o U_b N_o \tag{20}$$

where U_b is a chemical bond energy, or equivalently using Eq. (19):

$$G^{\mathrm{coh}} = W_b N_o^{1/2} \tag{21}$$

Comparing this with Eq. (2), we see that G^{coh} becomes smaller than G_{bound} at a grafting density:

$$\sigma_3 = \frac{N_o^{1/2}}{N} \tag{22}$$

The inequality $G^{\mathrm{coh}} > G_{\mathrm{bound}}$ does not strictly impose a switch from adhesive rupture to cohesive rupture: as suggested to us by a referee, the correct criterion may be close to minimum stress, rather than minimum energy. However, for our systems, the structure of the relation between applied stress and G is the same (within coefficients) for both modes: thus, at our scaling level, we are inclined to think that mode switching is reasonably described by Eq. (22). Then we conclude that there is no practical interest in grafting densities above σ_3. The corresponding plot of adhesion energy *versus* grafting density is shown on Figure 5.

V. GENERAL CONCLUSIONS

All the present work is very tentative, and restricted to a simple limit: very low velocities, negligible contributions of far field viscoelastic losses to the adhesion, etc. But within these limits, some predictions emerge for grafted systems.

1) *For "free" connectors*, the rupture is usually expected to hold in the adhesive mode; the optimal grafting density is $\sigma \sim \sigma_2 = N_o^{-1/2}$, giving $G \sim W_a N N_o^{-1/2}$.

However, if the connectors are extremely long ($N > N_o W_b / W_a$), we may switch to cohesive rupture (Eq. (21)). But this, in practice, appears as an infrequent event.

2) *For "bound" connectors*, rupture should occur in the adhesive mode for $\sigma > \sigma_3 = N_o^{-1/2} N^{-1}$. Above this crossover point, we expect cohesive rupture.

Our main result is, thus, to define approximate optimums for the grafting density: σ_2 for the free case and σ_3 for the bound case. But, once again, we emphasize that our discussion is limited to very low separation velocities, V: at a certain limit, V_1 for instance, in the "free" mode, connectors may start to break chemically. We hope to return to these more general situations in the future.

On the experimental side, experiments on silicone rubbers facing grafted silica surfaces are under way in the group of L. Léger. As of now, they show very weak adhesion–possibly because the times for interdigitation are very long.

Acknowledgements

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