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Role of Surface-Anchored Polymer Chains on the Adhesion of an Elastomer

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We study the adhesion between an elastomer of cross-link index, P, and a flat solid surface where polymer chains of polymerisation index, N, have been end-grafted. To understand the adhesive feature of such a system, one has to study both the origin of the grafted layer interdigitation with the network and the end-grafted chain extraction out of the elastomer when it separates from the solid surface. Both aspects are addressed here. We develop an analytical model that allows one to predict a critical surface grafting density, $\sigma^* \simeq P^{1/10}/N^{3/5}$, beyond which only the thermal fluctuations allow the layer to interdigitate with the elastomer. A review of the possible mechanisms of chain extraction is proposed.

Keywords: Adhesion; Elastomers; Polymers

1. INTRODUCTION

Surface-anchored polymer layers play an important role in adhesion because they can strengthen the interface [1,2]. The first key parameter is the degree of interdigitation between the surface layer and the bulk polymer system [3–5]. The adhesion promotion is related to the extraction of each penetrating anchored chain; therefore, a maximum in the density of penetrating chains is the condition for a maximum adhesion enhancement. When the facing polymer system is an elastomer, its elasticity can limit the penetration of the anchored

chains if the surface density is too high, resulting in a decrease of the adhesion [3]. In this respect, the first goal of this article is the determination of the critical surface density, σ^*, beyond which the interdigitation with the elastomer is weak. A second goal is to answer the other key question about the extraction mechanism responsible for the adhesion enhancement. An analysis based on Raphaël and de Gennes' early model is developed.

2. STUDY OF THE INTERDIGITATION

2.1. Total Penetration

We consider here the total penetration of grafted N-monomers chains in an elastomer with P monomers between cross links ($P < N$). The mean extension, L, of the chains can be obtained by minimizing the free energy of each penetrating chain. Classically, the elongation energy and the energy associated with the mean volume fraction gradient, ϕ_{av}/L (also called confinement energy), are taken into account. If σ is the dimensionless surface grafting density ($\sigma = a^2\Sigma$, where a is the typical size of a monomer), the average volume fraction occupied by the grafted layer is $\phi_{av} \simeq \sigma Na/L$ (see Figure 1a). A third term in the free energy is due to the elastic deformation of the network. De Gennes showed that the swelling free energy per volume unit is $E\phi^2$ ($E \simeq kT/a^3P$ is the elastomer elastic modulus), which gives the expression $(La^2/\sigma)(kT\phi_{av}^2/a^3P) \simeq kT(\sigma N^2a/LP)$ per grafted chain. The total free energy per grafted chain is thus (all numerical factors being ignored)

$$\frac{F_{tot}}{kT} \simeq \frac{L^2}{a^2N} + \frac{a^2N}{L^2} + \frac{\sigma N^2a}{PL}. \tag{1}$$

Two regimes exist. If the grafting density is smaller than $\sigma = P/N^{3/2}$, the swelling energy is small compared with the confinement energy, and the chains are Gaussian: $L \simeq aN^{1/2}$ and $F_{tot} \simeq kT$. On the other
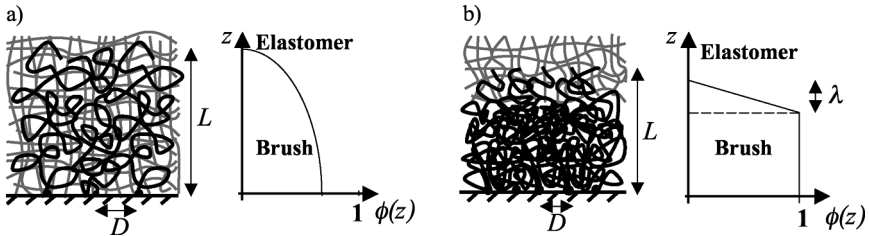

FIGURE 1 a) Total penetration regime and b) dry-brush regime.

hand, if $\sigma > P/N^{3/2}$, the confinement is weak and the chains are stretched: $L \simeq aN(\sigma/P)^{1/3}$, and $F_{tot} \simeq N(\sigma/P)^{2/3}kT$.

Interestingly, this behavior is identical to the one of grafted chains interdigitating a P-monomer chain melt, because there is a perfect analogy between the swelling energy of the elastomer, $kT(\sigma N^2 a/LP)$, and the the Flory expression for osmotic free energy per grafted chain, $(La^2/\sigma)[kT(l - \phi_{av})ln(1 - \phi_{av})/a^3P] \simeq kT(\sigma Na/L - 1)(N/P)$, at small volume fraction, as pointed out by de Gennes [6]. However, even if the network swelling free energy seems to favor the penetration of the layer, for $L\phi_{av}^2$ is a decreasing function of L, it is always a positive energy, which will limit the penetration if ϕ_{av} is too high. This is not true in the melt case where the Flory–Huggins free energy is negative and where interdigitation is predicted until ϕ_{av} reaches 1 for $\sigma = 1/P^{1/2}$. Therefore, the analogy must break down above a critical grafting density. To determine this total penetration limit, we can approach the problem from the opposite limit, the very weak interdigitation at high grafting densities.

2.2. Dry Brush in Contact with an Elastomer

We consider the limit where the elastomer is in contact with a very dense grafted layer with almost no interdigitation, as Leibler and coauthors [7] did for what they called a "dry brush" in contact with a melt. In a dry-brush regime, the grafted layer interdigitates with the network only over a width λ, small compared with the thickness of the layer. Thus, this thickness is close to the minimum thickness $h_0 = \sigma Na$ (see Figure 1b). The free energy per grafted chain is still composed of three different terms. The mean elongation energy of chains, the lengths of which range between $h_0 - \lambda$ and $h_0 + \lambda$, is $F_{el}/kT \simeq \lambda^2/a^2N$ (where the constant term h_0^2/a^2N has been subtracted). The gradient term, which can be renamed as the interfacial term, is given by $F_{int}/kT \simeq a/\sigma\lambda$. The swelling energy is $F_{swell}/kT \simeq \lambda/\sigma aP$. Note that it is the opposite of the Flory–Huggins expression for the osmotic free energy in a melt. Therefore, as suspected from the beginning, the analogy breaks down at high σ, in the dry-brush regimes. The network swelling energy now goes against interdigitation and leaves the interfacial energy as the only term that drives interdigitation:

$$\frac{F_{dry}}{kT} \simeq \frac{\lambda^2}{a^2N} + \frac{a^2}{\sigma}\frac{1}{a\lambda} + \frac{a^2}{\sigma}\frac{\lambda}{a^3P}. \quad (2)$$

Again, two distinct dry-brush regimes can be distinguished. If $\sigma > N/P^{3/2}$, the network swelling energy is small compared with the

grafted chain elastic energy, and as for a melt, the interface width is $\lambda \simeq a(N/P)^{1/3}$ whereas the free energy per grafted chain is $F_{dry} \simeq kT/(N\sigma^2)^{1/3}$. There is a continuous transition at the grafting density $\sigma = 1/N^{1/2}$ between this regime and the total penetration regime corresponding to $\sigma < P/N^{3/2}$ for $P \geq N$. But if $\sigma < N/P^{3/2}$, the network swelling energy is large compared with the chain stretching energy, and $\lambda \simeq aP^{1/2} = \lambda_0$, which is the elastomer network mesh size. Note that there is no possible continuous transition of L and λ between this dry-brush regime and the total interdigitation regime corresponding to $\sigma > P/N^{3/2}$.

2.3. Transition

In an early work of Brochard–Wyart *et al.* [8], a partial penetration model was proposed to explain the transition from the total penetration at low grafting densities to the dry brush at high densities. It has been shown recently that the brush structure proposed in this model is unstable and that the transition is in fact a first-order transition at the critical surface grafting density (see Figure 2),

$$\sigma^* \simeq \frac{P^{1/10}}{N^{3/2}}, \tag{3}$$

where $F_{tot} = F_{dry}$ [9]. This limit is more realistic than the $1/P^{1/2}$ limit interdigitation grafting density predicted in Ref. [8]: σ^* is an increasing function of P, which is very intuitive, because the bigger P, the softer the elastomer and the easier the grafted chains can penetrate the network until they reach high volume fraction.

Because the chain length is finite, the thermal fluctuations allow the grafted layer to switch from the most stable state to the other, passing through partial penetration. Irregularities of the connector surface density may play an important role here.

To get an idea of the transition from the dry brush to total penetration, one can study the behavior of a chain at the crack tip where the distance between the elastomer and the substrate, h, is fixed and of the order of h_0. The crack tip is filled with the dense grafted layer, and the interface width is of order λ_0. In such a situation, the free energy of the chain that partially penetrates the elastomer on n monomers (with $m = N - n$ monomers out) is

$$\frac{F}{kT} \simeq \frac{3}{2}\frac{a^2 m}{\lambda_0 h} + \frac{3}{2}\frac{h^2}{a^2 m} + n\left(\frac{\sigma}{P}\right)^{2/3} \tag{4}$$

The minimization gives $m = (h/a)/(a^2/\lambda_0 h - (\sigma/P)^{2/3})^{1/2}$, which is finite only for $\sigma < \sigma^*$. Thus, if $\sigma < \sigma^*$, the chain partially penetrates
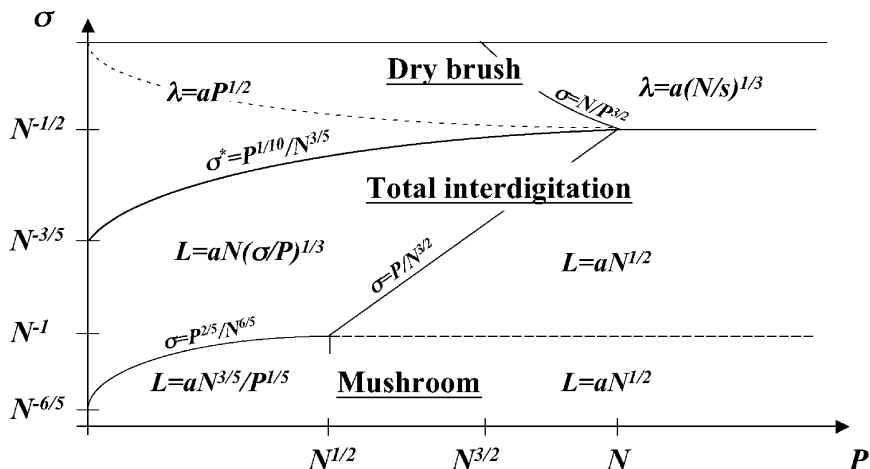
FIGURE 2 Interdigitation regimes of a grafted layer and an elastomer corresponding to various (σ, P) couples (σ is the surface grafting density adimentionalized with a, P is the number of monomers between cross links, and number of monomers per grated chain N is fixed). The dashed line in the left-hand-side dry-brush regime is the limit grafting density for interdigitation in the melt case.

the elastomer, and the m monomers remaining out are stretched ($h > am^{1/2}$), applying a force that tends to close the crack and extend the surface of the total penetration zone. If $\sigma > \sigma^*$, the chain does not penetrate the elastomer and the dry-brush domain grows.

Even before giving a detailed description of the dissipative pull-out mechanism that takes place at the fracture tip, we can straightforwardly relate the critical grafting density, σ^*, to the grafting density that gives the maximum adhesion enhancement, because it is the maximum surface density of penetrating chains one can reach. Because experimentally the relative adhesion enhancement, $\delta G = G(\sigma) - W$ (where W is the thermodynamic work of adhesion, and $G(\sigma)$ the measured adhesion energy), is a linear σ function at low σ [10–12], we can assume that $\delta G/W$ is of the form $\delta G/W = \alpha\sigma$ whenever the grafted layer is in a total interdigitation state (for a discussion of the form of α, see the following paragraphs). Experimental $\delta G(\sigma)$ data plots show a decrease at high σ, so we also assume that $\delta G/W$ is approximately nil when the layer is in a dry-brush state (only the fully penetrating chains participate in the adhesion enhancement). Then, taking into account the thermal fluctuations, we can write $\delta G/W$ as the thermodynamic average between the surface
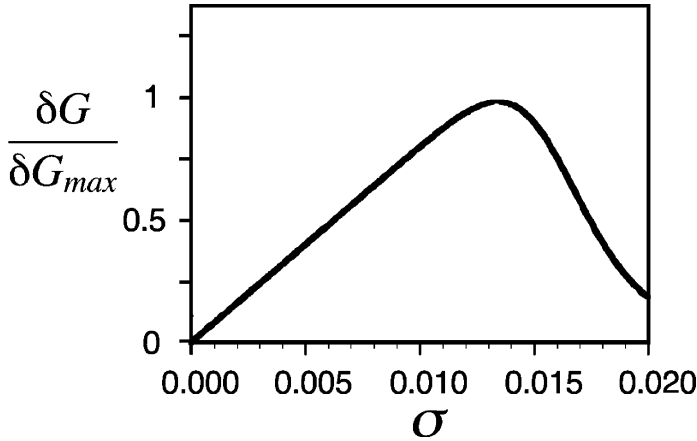
FIGURE 3 Theoretical prediction for adhesion enhancement ($N = 2300$ and $P = 230$).

adhesion of a total interdigitation layer and a dry brush:

$$\frac{\delta G}{W} = \alpha\sigma \frac{\exp\left[-F_{tot}/kT\right]}{\exp\left[-F_{tot}/kT\right] + \exp\left[-F_{dry}/kT\right]}$$
$$= \alpha\sigma \frac{\exp\left[(1 - (\sigma/\sigma^*)^{5/3})1/\sigma P^{1/2}\right]}{1 + \exp\left[(1 - (\sigma/\sigma^*)^{5/3})1/\sigma P^{1/2}\right]}. \qquad (5)$$

The thermal fluctuations smooth the total interdigitation–dry brush transition, giving an adhesion curve that nicely reproduces the experimental curves [9,11,12]: the maximum surface adhesion energy is reached for $\sigma \simeq \sigma^*$, and then δG decreases over the characteristic grafting density range $\sigma^*(P/N)^{3/5}$ (see Figure 3). The predicted position, σ^*, of the maximum of the adhesion is in good agreement with the experiments [9], unlike $1/P^{1/2}$.

   Still, the extraction mechanism needs to be understood to determine the dependence of the parameter α on N and P, the aim being the determination of the best parameters σ and N that optimize the adhesion of an elastomer of reticulation index P.

3. EXTRACTION MECHANISM

The dominant model of chain extraction has been developed by Raphael and de Gennes [13] from the idea that the extracted chains prefer to stay inside the elastomer than be in contact with the air
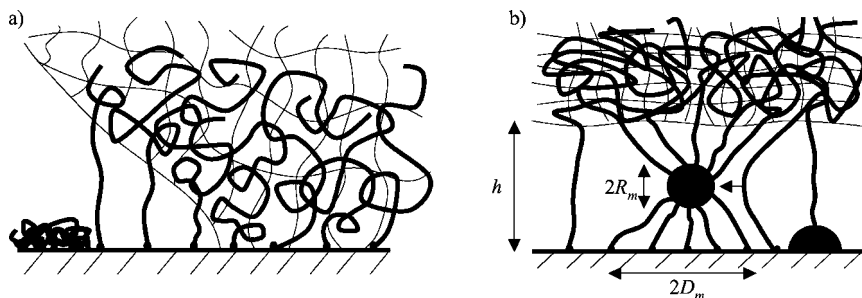
FIGURE 4 a) Raphaël and de Gennes' model for chain extraction, and b) micelle formation. On the right-hand side, a chain aggregating on the substrate is represented.

(see Figure 4a). Thus, the chains are fully stretched between the substrate and the elastomer until the height of the fracture exceeds $h = KaN$ ($K = \sqrt{\gamma a^2/kT}$ is of order unity and γ is the surface tension of the polymer). Then, the chains collapse on the substrate, and the free energy, $N\gamma a^2$, per chain is lost. The predicted adhesion enhancement is $\delta G = \sigma N\gamma$.

Though a linear increase of δG with σ is in agreement with the experimental data, the N dependence is not always observed [10,11,14].

3.1. Micelles

An objection to Raphaël and de Gennes' model has been raised by Ligoure [15]: if the distance h between the substrate and the elastomer is larger than $h^* = 2Ka/\sigma$, the pulled-out chains can form stable micelles of any size. Thus, the chain extraction would be accelerated by the formation of very large micelles, giving a complete extraction of the chains before $h = KaN$, as soon as the grafting density exceeds $1/N$. Then, the adhesion would not be enhanced much by the presence of the grafted chains. Although we agree that micelles would be stable for $h > h^*$, we think that it is important to consider the kinetics of their formation. The growth rate of a micelle depends on the time it takes for each new chain to join the micelle. To reach a micelle, each new chain, initially isolated and stretched between the substrate and the elastomer, must extract itself further from the elastomer (see Figure 4b). In this respect, each new micelle-forming chain must go through a state of energy, F_{gap}, higher than the energy, F_i, of the initial stretched state. If the energy gap, $\delta F = F_{gap} - F_i$, is larger than kT, the time for a new chain to join

a micelle will be very large ($\tau \sim \exp{(\delta F/kT)}$) and the micelles will not have the time to grow during the unsticking of the elastomer. Ligoure has shown that the radius of a micelle involving m chains is $R_m = am/2\pi K$, which is small compared with the distance, $D_m = a(m/\pi\sigma)^{1/2}$, between the center of the micelle and the farther chains, as long as $m < \pi K^2/\sigma$ (see Figure 4b). Assuming $m < \pi K^2/\sigma$, let us consider the formation of an m-micelle, with $h > h^* > D_m > R_m$. The energy gap for a new chain to join the micelle is

$$\delta F(R_m) = 2\frac{a\gamma}{K}\left(\sqrt{h^2 + 4(D_m - R_m)^2} - h\right) \simeq K\frac{am}{h\sigma}kT. \qquad (6)$$

Therefore, the kinetics of the formation of large micelles (with more than $N/2$ monomers per chain, which would reduce the adhesion promotion), is very slow if $\sigma < K^{3/2}/N^{1/2}$, which is larger than σ^*. Hence, one does not expect large micelles to appear spontaneously if the fracture between the elastomer and the substrate has a finite velocity. A similar analysis can be applied to the hypothetical formation of bundles [16–18]. Note that this discussion assumes that micelles are formed by the aggregation of individual chains. Other kinetic pathways, such as the coalescence of small micelles into larger ones, should in principle also be considered. Although we believe that the energy gaps associated with these pathways will remain large, this point should be studied further.

3.2. Aggregation onto the Substrate

As shown in the previous section, micelle formation is rather unlikely to induce chain extraction. However, another form of spontaneous chain extraction is conceivable. Indeed, it might be more favorable for a partially pulled-out chain to be in contact with the solid substrate rather than to stay into the elastomer. The spontaneous extraction of a pulled-out chain depends on surface energies of the system. A chain that would collapse on the substrate would form a small drop (see Figure 4b) whose shape depends on the spreading parameter of the polymer on the substrate $S = \gamma_{SG} - (\gamma + \gamma_{SL})$ (where γ_{SG}, γ, and γ_{SL} are, respectively, the substrate–air, polymer–air, and polymer–substrate surface energy). If the spreading parameter is positive (total wetting), the liquid drop prefers to spread onto the substrate rather than be in the bulk. On the other hand, if S is negative, the energy of a drop deposited onto the substrate is higher than its energy in the bulk, and it does not spread. Therefore, a pulled-out grafted chain will spontaneously collapse on the substrate if $S > 0$, whereas it can

stay a very long time stretched between the substrate and the elostomer if $S > 0$.

Finally, Raphaël and de Gennes' model should hold in the nonwetting situations, as confirmed in [10], but not in the total wetting situations. In this latter situation, the adhesion enhancement should be lower, but not lower than $\delta G = \sigma P \gamma$, as the chain extraction always involves a deformation of the elastomer over a mesh size around the extraction point. Note that the adhesion enhancement would be even more velocity dependent in this case. These hypothesis could explain the discrepancies between these models and some experimental results, as well as P dependence of the adhesion enhancement, which is sometimes observed [11,14].

4. CONCLUSION

We have developed a scaling analysis from which we obtain the limit surface grafting density beyond which almost no interdigitation occurs. This limiting connector surface density, $\sigma^* \simeq P^{1/10}/N^{3/5}$, apparently also corresponds to the grafting density for the maximum adhesion. Several extraction mechanisms are addressed, and we show that only in a nonwetting situation is Raphaël and de Gennes' prediction of an adhesion enhancement proportional to N valid. Additional work is needed to understand the adhesion promotion in a total wetting situation.

ACKNOWLEDGMENTS

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