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Adhesion between a Polymer Brush and an Elastomer: A Self-Consistent Mean Field Model

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ABSTRACT: The penetration of a polymeric brush into a cross-linked elastomer (chemically identical to the brush) is discussed theoretically, using a self-consistent mean field theory. The details of the microscopic interfacial structure of the system (thickness of the brush, free energy, profiles of elastomer and grafted chain volume fractions, distribution of free chain ends, and interdigitation length of the brush into the elastomer) are obtained. These results allow one to calculate the adhesion energy between a brush and an elastomer and to revisit the model of Brochard-Wyart *et al.* [*J. Phys. Chem.* **1993**, *98*, 9405]. The predictions of the new model are compared with some recent experimental reports (Creton *et al. Macromolecules* **1994** , *27*, 3174).

I. Introduction

Adhesion between a flat solid surface and a cross-linked elastomer is a technologically important problem. If the solid surface is bare, the adhesion energy G (the energy required to separate a unit area of a contact) is very small, comparable to the thermodynamic work of separation, i.e. smaller than 0.1 J m^{-2}. Mechanisms to improve adhesion may rely on interdigitation of molecules across the interface, often enhanced by the addition of a dopant *adhesion promoter*. A classical approach is to add chains that are tethered by one end to the solid surface.[1] The structure of the grafted layer is determined by two parameters: the dimensionless number of grafted chains per unit area ν and the polymerization index of the grafted chains N. At low surface coverage ν, the grafted chains do penetrate easily into the elastomer if they are chemically identical to it. Raphaël and de Gennes[2] have analyzed the contribution of the interdigitation between tethered chains and elastomer to the zero-rate fracture energy in terms of a pull out process. They predict that in many practical cases this contribution G_0 is given by[2−4]

$$G_0 \cong \Gamma N \nu \qquad (1)$$

where Γ is the surface tension of a melt of connector molecules.

Equation 1 is valid as long as the interdigitation between the tethered chains and the elastomer is total. However, theoretical studies on brushes in contact with a melt of short chains have shown that interdigitation between the liquid and the brush decreases with increasing grafting density of anchored chains ν[5−8] and can be ultimately lost; experimental studies confirm this fact.[9] On the other hand, de Gennes[10] has pointed out the strong analogy between a rubber and a melt of short chains. Using this analogy, Brochard-Wyart *et al.*[11] have shown that, because of partial interdigitation, G_0 does not vary linearly with ν: it reaches its maximum for $\nu \sim P^{-1/2}$ (where P denotes the chemical distance between cross-links in the elastomer).[12] However, their analysis utilizes a highly simplified Flory type argument which does not allow a quantitative description of the statistics of chains segments embedded in the elastomer: in general, probes of a brush that are localized in space, like density profiles of chain units or free ends, are not well represented by calculations based on Flory arguments. Recent theoretical developments in understanding polymer brushes, beyond free energy balance estimates, and under conditions of strong stretching lead to elegant and relatively simple theoretical results for a wide variety of brush properties and situations.[13] This more detailed picture is often called "parabolic brushes". The aim of this paper is to develop such a "parabolic brushes" like approach to describe the penetration of a brush into an elastomer and consequently to predict quantitatively the zero-rate fracture energy G_0. The paper is organized as follows. Section II reviews the Brochard-Wyart *et al.* model[11] for the interdigitation between a brush and a rubber. Section III is devoted to the "parabolic brush" like description of the penetration of a brush into an elastomer. It will be shown that, using appropriate reduced physical quantities, all equilibrium properties of the brush embedded in the elastomer can be described by two parameters: $\tilde{\nu} = (3\pi/4\sqrt{2})P^{1/2}\nu$ and $\beta = \alpha(\pi/2\sqrt{2})(P/N)$. ($\alpha$ is a numerical prefactor on the order of unity.) In this section the "motor" of interdigitation will be discussed in detail. Finally, in section IV, we calculate the zero-rate fracture energy G_0 and predict the maximum adhesion energy as well as the optimum surface coverage as a function of the physical parameters N, polymerization index of the anchored chains, and P, the chemical distance between cross-links in the elastomer. In the last section, the results are summarized and compared with some experimental data.

II. Interdigitation between a Brush and an Elastomer: The Brochard-Wyart *et al.* Model[11]

Consider a melt of grafted chains (polymerization index N) terminally attached to a flat solid surface (dimensionless number of grafted chains per unit area: ν). The brush is exposed to a network C chemically identical to the grafted chains (the chemical distance between cross-links in C is called P). We suppose in the following that $N^{1/2} < P < N$. The elastomer C has been cross-linked in the dry state. In this case, the swelling of the network by a volume fraction Φ of

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solvent costs the elastic energy per unit volume F_{el}:[10]

$$F_{\mathrm{el}} = \frac{1}{2}\frac{kT}{a^3}\frac{\Phi^2}{P} \tag{2}$$

kT is the thermal energy and a is the monomer size.

The corresponding shift in chemical potential for one monomer of a grafted chain is

$$\mu = a^3\frac{\partial F_{\mathrm{el}}}{\partial \Phi} = kT\frac{1}{P}\Phi \tag{3}$$

The brush is described by a Flory type approach. Denoting the thickness of the brush by h, the free energy of a grafted chain is written in the following form (all numerical coefficients are ignored):

$$F = kT\frac{h^2}{Na^2} + F_{\mathrm{el}} \tag{4}$$

The first term in eq 4 is the Gaussian deformation energy of the chain, and the second one is the swelling energy of the elastomer. Inserting the expression for the internal volume fraction of chains $\Phi = N\nu/h$ in eq 4 and minimizing F with respect to h lead to

$$h_{\mathrm{eq}} \cong Na\left(\frac{\nu}{P}\right)^{1/3} \tag{5}$$

This last expression is similar to the equilibrium thickness of a brush in a solvent of short chains.[5-8] Putting the equilibrium value of h in eq 4 gives the equilibrium free energy per chain:

$$F \cong kTN(\nu/P)^{2/3} \tag{6}$$

Using eqs 5 and 6 and the expression for Φ, the authors of ref 11 propose four regimes:

(i) $\nu < N^{-1}$: The grafted chains are not stretched and do not overlap (independent mushroom regime); the interdigitation is total.

(ii) $N^{-1} < \nu < PN^{-3/2}$: The mushrooms overlap, but the coils are still not stretched; interdigitation is fully allowed.

(iii) $PN^{-3/2} < \nu < P^{-1/2}$: The chains are stretched, and the interdigitation is not complete.

(iv) $\nu > P^{-1/2}$: Interdigitation is not allowed (it is easy to see that if the chains did penetrate into the elastomer, it would lead to a nonphysical result for the volume fraction: $\Phi > 1$).

The authors conjecture two states of partial interdigitation (regime iii). The first one corresponds to the case where each grafted chain inserts only n ($n < N$) monomers into the elastomer. However, it is possible to show that the constraint that n is the same for all chains is too strong and the corresponding "parabolic like" approach gives inconsistent results. In the second state of partial interdigitation proposed, only a fraction f of the chains penetrate into the rubber, while a fraction $(1 - f)$ does not and instead forms a passive layer between the solid and the rubber (see Figure 1). This second model is the basis of our approach developed in section III. The two important and subtle points of their analysis are the following:

(1) Each of the νf penetrating chains infiltrates n segments into the rubber, so that the embedded segments are not stretched; this leads to the relation $\nu f = Pn^{-3/2}$.

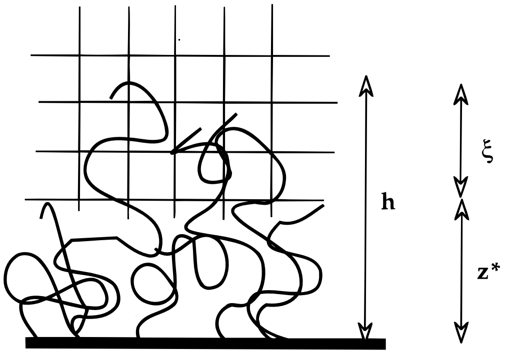

Figure 1. Cartoon of the partial interdigitation between a grafted brush and an elastomer. ξ is the interdigitation length, z^* is the thickness of the passive layer, and h is the total thickness of the brush.

(2) $\nu(1 - f)$ chains are reflected at the interface between the passive layer and the elastomer; consequently, there is an interfacial energy of entropic origin which has the form

$$\gamma \simeq \frac{kT}{P^{1/2}a^2}(1 - f) \tag{7}$$

This interfacial energy is the cause, i.e. "motor" of the interdigitation.

The fraction of penetrating chains is obtained by minimization of the total free energy of the brush which is the sum of F and γ (eqs 6 and 7).

As a result, the interdigitation between the rubber and the grafted layer becomes incomplete as soon as the grafted chains are stretched ($\nu > PN^{-3/2}$). From this model, they predict the contribution of the interdigitation between tethered chains and elastomer to the zero-rate fracture energy $G_0 \cong \Gamma nf\nu$, this leads to

$$\begin{aligned} &\nu < PN^{-3/2} && G_0 \cong \Gamma N\nu \\ &PN^{-3/2} < \nu < P^{-1/2} && G_0 \cong \Gamma P^{2/3}\nu^{1/3} \\ &\nu > P^{-1/2} && G_0 = 0 \end{aligned} \tag{8}$$

III. Interdigitation between a Brush and an Elastomer: "The Parabolic Brush Model"

The parabolic brush model was developed independently by two groups.[14,15] The main results of this model for a brush swollen by a good (not too good) monomeric solvent are the following: (i) the conformations of different chains in the brush are not necessarily similar nor is a particular chain uniformly stretched; (ii) the density profile, rather than being a step function is instead parabolic.

The description of the brush consists of the conformations of the chains and such quantities as the monomer density $\Phi(z)$ at height z above the grafting surface, the local monomer chemical potential $\mu(z)$, and the density of free chain ends $\epsilon(z)$. These results are obtained by a solution of the one-dimensional self-consistent field (SFC) equation, in the strong stretching limit. This limit is relevant to long polymers, where the layer thickness h, the typical distance that chains are extended over, is much larger than the chain radius of gyration but is much less than the maximum extension of the chain. In this limit, a chain with a free end at height z_0 fluctuates only narrowly about its most favorable path $\mathbf{r}(n)$, where n runs from 0 for the free end to

N at the grafted end. In this case the path $z(n)$ of the chains obeys a "Newton's law" for the trajectory of a particle, if the variable n is interpreted as "time" and $U(z)$ as a potential energy:

$$\frac{\mathrm{d}^2 z}{\mathrm{d}n^2} = -\frac{\mathrm{d}U}{\mathrm{d}z} \tag{9}$$

with boundary conditions $z(0) = z_0$, $z(N) = 0$, and $(\mathrm{d}z/\mathrm{d}n)_{n=0} = 0$.

Then it is evident that for monodisperse chains, the potential $U(z)$ must be an equal-time potential, i.e., must give the same "time of flight" (chain length), for a particle starting from rest at any distance away from the grafting surface. That is $U(z)$ must be a harmonic-oscillator potential:

$$U(z) = -A + Bz^2 \tag{10}$$

The coefficient B determines the period of the oscillator, i.e. $B = \pi^2/(8N^2a^2)$. It is important to notice that this many-chain problem is solved exactly for *both the melt and the moderate density cases* by employing this "equal-time" argument:[16,17] *in both cases, the self-consistent potential is a harmonic oscillator potential.*[17]

Partial Interdigitation between the Brush and the Elastomer. We impose the condition that the monodisperse brush (polymerization index N) grafted to a flat solid surface (dimensionless number of grafted chains per unit area: ν) penetrates the elastomer C with an interdigitation length ξ ($\xi < h$, where h denotes the thickness of the brush) (see Figure 1). The interdigitation is total for $\xi = h$, whereas it is null for $\xi = 0$. For intermediate values of ξ, there is a partial interdigitation between the brush and the network. In this case, the brush is divided in two regions: For $0 < z < z^* = h - \xi$, the chains do not penetrate into the elastomer and form a passive dry layer in the melt state. For $z^* < z < h$, the chains penetrate into the elastomer and form a swollen layer. The free end of a chain can be located in the swollen layer ($z_0 > z^*$) as well as in the passive layer ($z_0 < z^*$). In both cases, the equal-time argument can be employed, so that the path of a chain is given by eq 9, with $U(z)$ being the "harmonic oscillator" potential of eq 10: *both layers of the brush (passive layer and swollen layer) are described by the same self-consistent potential.* In the passive layer $U(z)$ is fixed by the requirement that the volume fraction of grafted chains $\Phi = 1$. In the swollen layer $-U(z)$ equals the shift in chemical potential of a monomer embedded in the elastomer: $U(z) = -\mu(z)$, where $\mu(z)$ is given by eq 3. One can deduce the monomer volume fraction profile

$$\Phi(z) = 1 \qquad 0 < z < z^*$$

$$\Phi(z) = P(A - Bz^2) \qquad z^* < z < h \tag{11}$$

with

$$B = \frac{\pi^2}{8N^2a^2}$$

We introduce the following reduced quantities which allow a universal description of a brush in contact with an elastomer.

(1) reduced grafting density: $\tilde{\nu} = {}^3/_2 aN\sqrt{BP}\nu = (3\pi/4\sqrt{2})P^{1/2}\nu$

(2) reduced thickness of the brush: $\tilde{h} = \sqrt{BP}\mathrm{h} = (\pi/2\sqrt{2})(P^{1/2}/N)(h/a)$

(3) reduced interdigitation length: $\tilde{\xi} = \sqrt{BP}\xi = (\pi/2\sqrt{2})(P^{1/2}/N)(\xi/a) = x\tilde{h}$ where x is the length fraction of the brush embedded in the elastomer

(4) reduced thickness of the passive layer: $\tilde{z}^* = \sqrt{BP}z^* = (\pi/2\sqrt{2})(P^{1/2}/N)(z^*/a) = \tilde{h} - \tilde{\xi}$

The constant A in eqs 10 and 11 may be determined by demanding that the density profile $\Phi(z)$ has no discontinuity at $z = h$, but vanishes smoothly there:[14]

$$A = Bh^2 = \tilde{h}^2/P^2 \tag{12}$$

The thickness of the brush is computed by the mass conservation equation:

$$N\nu = \frac{1}{a}\int_0^h \Phi(z)\,\mathrm{d}z \tag{13}$$

Using eqs 11−13 leads to a relation between $\tilde{h}$, $\tilde{\nu}$, and $\tilde{\xi}$:

$$\tilde{h} = \frac{2}{3}\frac{\tilde{\nu}}{1 + \tilde{\xi}^2} + \tilde{\xi}\frac{1 + \tilde{\xi}^2/3}{1 + \tilde{\xi}^2} \tag{14}$$

Note that for $\tilde{h} = \tilde{\xi}$, eq 14 gives the classical relation between the thickness of a swollen brush and the grafting density: $\tilde{h}_{\mathrm{wet}} = \tilde{\nu}^{1/3}$. The case of the dry brush is already given by eq 14, with $\tilde{\xi} = 0$, and leads to $\tilde{h}_{\mathrm{dry}} = (2/3)\tilde{\nu}$.

Validity of the Model. Equation 11 shows that the density profile $\Phi(z)$ has a discontinuity at $z = z^*$: the interface between the two sublayers forming the brush (the passive layer and the swollen layer) is characterized by a concentration jump: $\Delta\Phi = \Phi(z^*-) - \Phi(z^*+) = 1 - \tilde{\xi}(2\tilde{h} - \tilde{\xi})$. The existence of the concentration jump is a mathematical consequence of the continuity of the self-consistent mean field acting on the grafted chains; physically, it follows the existence of an interfacial tension between the two sublayers of the brush, which will be discussed in detail in a following paragraph. The monomer volume fraction $\Phi(z)$ can never exceed 1; this is equivalent to the requirement that $\Delta\Phi > 0$. Using eq 14, this condition can be written

$$g_{\tilde{\nu}}(\tilde{\xi}) = \tilde{\xi}^4 - 4\tilde{\xi}\tilde{\nu} + 3 \geq 0 \tag{15}$$

The density profile is realizable if the inequality (15) is true. Computing the variation of the function $g_{\tilde{\nu}}(\tilde{\xi})$ gives the following results:

When $\tilde{\nu} < 1$, all possible values of the interdigitation length $\tilde{\xi}$ are allowed and $\Delta\Phi$ is always positive.

When $\tilde{\nu} > 1$, $g_{\tilde{\nu}}(\tilde{\xi})$ is a decreasing function of $\tilde{\xi}$ ($\tilde{\xi}$ varies from 0 to its maximum value $\tilde{h}_{\mathrm{wett}}$) and it has a single zero $\tilde{\xi}_{\max}$. Consequently, for sufficiently high grafting density, there is a maximal value $\tilde{\xi}_{\max}$ of the interdigitation length, $\tilde{\xi}$. This maximum value is the single zero of the function $g_{\tilde{\nu}}$ between 0 and $\tilde{h}_{\mathrm{wett}}$.

Moreover, it can be shown that the physical condition that h is an increasing function of ξ is equivalent to the inequality (15).

These results disagree with the results of ref 11, and previous other results.[5,8] For $\nu > bP^{-1/2}$ (where $b = 3\pi/(4\sqrt{2})$ is a numerical prefactor), interdigitation between the brush and the rubber cannot be complete; however, partial interdigitation is allowed and, as expected, the maximal interdigitation length decreases with increasing surface grafting density. The discrepancy between the two models for this particular limiting coverage arises only because of the steplike density profile approximation of ref 11, which seems to be a too crude approximation for this problem.

Chain "Free Ends" Density Profile. We may write the monomer density profile $\Phi(z)$ in terms of the density of free chain ends $\epsilon(z)$:[14]

$$\Phi(z) = \int_z^h \frac{\epsilon(z')}{\sqrt{2B(z'^2 - z^2)}}\,dz' \qquad (16)$$

From eq 11, and after eq 16 is inverted by a Laplace transform, the end density $\epsilon(z)$ obeys

$$\epsilon(z) = \frac{z}{Na}\frac{1 - (\pi^2/8N^2a^2)(h^2 - z^{*2})}{\sqrt{z^{*2} - z^2}} + \frac{\pi^2 P}{4a^3N^3} z\left(\sqrt{h^2 - z^2} - \sqrt{z^{*2} - z^2}\right) \qquad z < z^*$$

$$\epsilon(z) = \frac{\pi^2 P}{4a^3N^3} z\sqrt{h^2 - z^2} \qquad z > z^* \qquad (17)$$

with h given by eq 14.

The free end density $\epsilon(z)$ exhibits a discontinuity at $z = z^*$, corresponding to the interface between the two sublayers of the brush. The natural scenario of interdigitation corresponds to a fraction f of the chains which penetrates, while a fraction $(1 - f)$ does not and forms a passive layer between the solid and the elastomer: this is the second type of interdigitation proposed by the authors of ref 11; the fraction f can be computed

$$f = \frac{1}{\nu}\int_{z^*}^h \epsilon(z)\,dz = \frac{1}{\tilde{\nu}}(2\tilde{\xi}\tilde{h} - \tilde{\xi}^2)^{3/2} \qquad (18)$$

Free Energy of the Brush. The free energy of the brush consists of two terms: the deformation energy of the coils and the swelling energy of the network.

Milner *et al.*[14] have shown that the free energy per unit area of a brush F_{brush} can be computed in a very simple way:

$$F_{\text{brush}} = kT\int_0^{\nu} -U(0)N\,d\nu' \qquad (19)$$

where $-U(0) = Bh^2$ (see eqs 10 and 12). In order to compute this energy, the brush is constructed by progressively adding chains. One has to calculate the free energy of a brush with a given grafting density and a given interdigitation length; thus, the integral (19) *must be evaluated at a constant fraction of interdigitation length x*. Equation 19 may be rewritten in reduced units:

$$F_{\text{brush}} = \frac{kT}{a^2}\frac{2\sqrt{2}}{\pi}\frac{N}{P^{3/2}}\tilde{F}_{\text{brush}}(\tilde{\nu},\tilde{\xi})$$

with

$$\tilde{F}_{\text{brush}}(\tilde{\nu},\tilde{\xi}) = \int_0^{\tilde{h}} \tilde{h}'^2 \left.\frac{\partial\tilde{\nu}'}{\partial\tilde{h}'}\right|_{x=\text{cte}} d\tilde{h}' \qquad (20)$$

From eqs 14 and 20, one gets

$$\tilde{F}_{\text{brush}}(\tilde{\nu},\tilde{\xi}) = \frac{2}{405}\frac{(3\tilde{\xi} + \tilde{\xi}^3 + 2\tilde{\nu})^2(4\tilde{\xi}^3 + 5\tilde{\nu} + 9\tilde{\nu}\tilde{\xi}^2)}{(1 + \tilde{\xi}^2)^3} \qquad (21)$$

Note that putting $\tilde{\xi} = \tilde{h}_{\text{wet}}$ or $\tilde{\xi} = 0$ in eq 21 gives respectively $\tilde{F}_{\text{brush}} = (2/5)\tilde{\nu}^{5/3}$ (free energy of a swollen brush) and $\tilde{F}_{\text{brush}} = (8/81)\tilde{\nu}^3$ (free energy of a dry brush).

It is straightforward to show, from eq 21, that F_{brush} is an increasing function of the interdigitation length ξ. In fact this result is obvious: interpenetrating a dry layer of grafted chains into an elastomer will cost an energy penalty; the grafted chains have to stretch more and the elastomer has to be swollen. It means that it is necessary to consider another contribution to the free energy of the brush in contact with an elastomer, which should be a decreasing function of the penetration length ξ to allow the interdigitation process.

Interfacial Energy of the Brush. A shown in a previous section, there is a discontinuity in concentration and free end density at the interface between the passive layer and the swollen layer: chains with free ends located at $z < z^*$ are reflected at the interface, which behaves as an noninterpenetrating wall for those chains. Ausserré has discussed the confinement of a polymer melt between two nonadsorbing plates.[18] Using a detailed lattice description of the configurations of the trapped chains, he has shown that the entropy loss per trapped chain is $\Delta S_1 = -\alpha k(Nl/D)$, where α is a numerical nonuniversal prefactor and D is the distance between the plates. All polymer configurational loss is localized in the interfacial layer of thickness l, where l is the correlation length for the polymeric system; in the case of a melt $l = a$. These results are in perfect agreement with de Gennes calculations[19] and Monte Carlo simulations[20] and allow one to understand that there is a confinement energy of entropic origin for grafted trapped chains in a melt state and that this energy is equivalent to a depletion interfacial tension $\gamma_1 = -Tv\Delta S_1/(al) = \alpha\kappa T/a^2$ with a correlation length $l = a$.

This depletion energy is neglected in the "parabolic model", because all lateral configurations of the grafted chains are supposed to be Gaussian.[14] Only the chains whose free ends are located in the passive layer see the interface as a neutral wall; however, the interface is not solid, but diffuse, over a width $l = P^{1/2}a$. Thus, as first conjectured by Brochard-Wyart *et al.*,[11] the interfacial tension of the brush in contact with the elastomer can be tentatively written:

$$\gamma = \alpha\frac{kT}{a^2P^{1/2}}(1 - f) \qquad (22)$$

with f given by eq 18. Equation 22 may be written in reduced units:

$$\gamma = \beta\frac{kT}{a^2}\frac{2\sqrt{2}}{\pi}\frac{N}{P^{3/2}}\tilde{\gamma}(\tilde{\nu},\tilde{\xi})$$

$$\tilde{\gamma}(\tilde{\nu},\tilde{\xi}) = 1 - \frac{1}{\tilde{\nu}}\left[\frac{\tilde{\xi}}{1 + \tilde{\xi}^2}\left(\frac{4}{3}\tilde{\nu} + \tilde{\xi} - \frac{1}{3}\tilde{\xi}^3\right)\right]^{3/2} \qquad (23)$$

with

$$\beta = \alpha\frac{\pi}{2\sqrt{2}}\frac{P}{N}$$

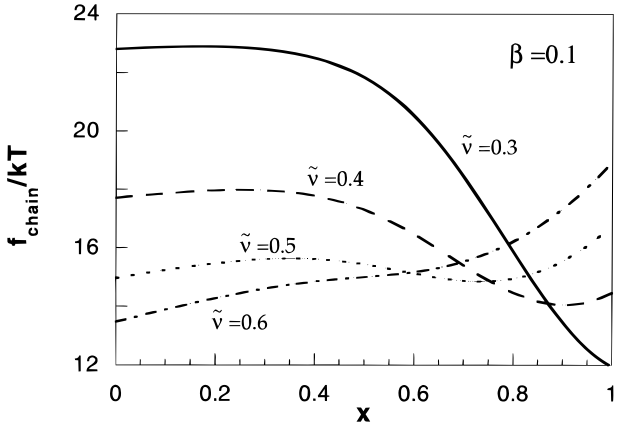

Figure 2. Variation of the average total free energy per grafted chain f_{chain} as a function of the interdigitation length fraction $x = \tilde{\xi}/h$, for $\beta = 0.1$ and several values of the reduced grafting density $\tilde{\nu}$.

The parameter β measures approximately the ratio between the interfacial energy γ of the brush and its "volume energy" F_{brush}. α is an unknown numerical factor, but on the order of unity. We will put $\alpha = 1$ in the following. By hypothesis, $N^{1/2} < P < N$, then $N^{-1/2} < \beta < 1$: *β is always a small parameter.*

As expected, the interfacial tension is a decreasing function of the interdigitation length: it favors interdigitation. The reduced interfacial tension $\tilde{\gamma}$ decreases between two extremal values: 1 (no interdigitation $\tilde{\xi} = 0$) and 0 (full interdigitation: $\tilde{\xi} = \tilde{h}$). Moreover, the slope of $\tilde{\gamma}$ at $\tilde{\xi} = 0$ is independent of $\tilde{\nu}$ and equals 0.

Equilibrium Structure of the Brush. The total free energy per unit area of the brush is $F = F_{\mathrm{brush}} + \gamma$ Equivalently, one has to compute the variations of the total reduced free energy as a function of $\tilde{\xi}$:

$$F = \frac{kT}{a^2}\frac{2\sqrt{2}}{\pi}\frac{N}{P^{3/2}}\tilde{F}(\tilde{\nu},\tilde{\xi}) \tag{24}$$

with

$$\tilde{F}(\tilde{\nu},\tilde{\xi}) = \tilde{F}_{\mathrm{brush}}(\tilde{\nu},\tilde{\xi}) + \beta\tilde{\gamma}(\tilde{\nu},\tilde{\xi})$$

where $\tilde{F}_{\mathrm{brush}}$, $\tilde{\gamma}$, and β are given by eqs 21 and 23.

The free energy per chain is $f_{\mathrm{chain}} = F/\nu$. From eq 24, f_{chain} writes

$$\frac{f_{\mathrm{chain}}}{kT} = \frac{3\pi\alpha}{4\sqrt{2}}\frac{\tilde{F}(\tilde{\nu},\tilde{\xi})}{\beta\tilde{\nu}} \tag{25}$$

Figure 2 shows the variation of f_{chain} (in kT units) with respect to the fraction $x = \tilde{\xi}/h$ of interdigitation length at several grafting densities $\tilde{\nu}$ and for $\beta = 0.1$ (this representation is strictly equivalent to the variation of $\tilde{F}(\tilde{\nu},\tilde{\xi})$ with respect to $\tilde{\xi}$ but more meaningful). One of the crucial points is that the slope at the origin (no interdigitation) is always positive:

$$\left.\frac{\partial\tilde{F}(\tilde{\nu},\tilde{\xi})}{\partial\tilde{\xi}}\right]_{\tilde{\xi}=0} = \frac{8}{27}\tilde{\nu}^2 \tag{26}$$

Thus, it ensues that, if one puts a dry layer of grafted chains in contact with an elastomer (adhesion experiment) and if the equilibrium state corresponds to partial or total interdigitation, the system has to jump over an energy barrier (corresponding to the maximum of $\tilde{F}(\tilde{\nu},\tilde{\xi})$) in order to reach this equilibrium state. In case the thickness of this barrier is much larger than kT per chain, the interdigitation process does not take place, for kinetic reasons. The existence of this energy barrier should have important consequences on adhesion enhancement. It will be discussed in a following section of this paper.

For low surface coverage of grafted chains, the minimum of the free energy corresponds to a total interdigitation ($\tilde{\nu} = 0.3$ in Figure 2). Note that full interdigitation is favored, even if the grafting density is much larger than $\nu = PN^{-3/2}$. It can be inferred that stretched chains can fully penetrate into the elastomer, contrary to the conjecture of ref 11. Upon progressively increasing the grafting density, the minimum of the free energy corresponds to a more partial interdigitation ($\tilde{\nu} = 0.4$ and $\tilde{\nu} = 0.5$ in Figure 2). The fraction of the penetration length x decreases smoothly with increasing $\tilde{\nu}$.

At some particular grafting density $\tilde{\nu}_{\mathrm{c}}(\beta)$, an instability occurs, and the minimum of the free energy corresponds to $\tilde{\xi} = 0$ (no interdigitation, $\tilde{\nu} = 0.6$ in Figure 2). For $\tilde{\nu} > \tilde{\nu}_{\mathrm{c}}$, the "no interdigitation" state remains the more favorable one. The threshold value $\tilde{\nu}_{\mathrm{c}}(\beta)$ is given by the equality between the free energy of the dry brush (no interdigitation) and the free energy of the more favorable partial interdigitation state (for $\beta = 0.1$, $\tilde{\nu}_{\mathrm{c}} = 0.505$). Another important feature is that the variation of $\tilde{\xi}$ causes f_{chain} to vary very slightly in the case; the minimum of f_{chain} corresponds to a state of partial interdigitation, for example f_{chain} undergoes a variation of 1 kT in the entire range of x for $\beta = 0.1$ and $\tilde{\nu} = 0.5$ (see Figure 2). *As a consequence, thermodynamic fluctuations of the interdigitation length and of all physical quantities related to it cannot be neglected and will play a crucial role, particularly in the case of partial interdigitation.* The effects of interdigitation length fluctuations on the adhesion energy will be discussed in detail in the following section.

Following a classical Landau–Ginzburg approach, we can predict all thermal average physical quantities of the system brush/elastomer, taking into account the Boltzmann statistical weight of each interdigitation length $\tilde{\xi}$ value: if M denotes a physical quantity (interdigitation length, thickness of the brush, adhesion energy, etc.), the observed value of M should correspond to the thermal average of M: $\langle M\rangle$, where

$$\langle M\rangle = \frac{\int_0^{\tilde{\xi}_{\max}(\tilde{\nu})} M(\tilde{\xi},\tilde{\nu})\exp\left[-\frac{f_{\mathrm{chain}}(\tilde{\xi},\tilde{\nu})}{kT}\right]\mathrm{d}\tilde{\xi}}{\int_0^{\tilde{\xi}_{\max}(\tilde{\nu})}\exp\left[-\frac{f_{\mathrm{chain}}(\tilde{\xi},\tilde{\nu})}{kT}\right]\mathrm{d}\tilde{\xi}} \tag{27}$$

where f_{chain}/kT is given by eq 25 and $\tilde{\xi}_{\max} = h_{\mathrm{wet}}(\tilde{\nu})$ if $\tilde{\nu} < 1$ and $\tilde{\xi}_{\max} = \mathrm{Min}[\mathrm{Zero}(g_{\tilde{\nu}})]$ if $\tilde{\nu} \geq 1$ (see eq 15).

The fluctuations of $\langle M\rangle$ can be evaluated by calculating the square root of the variance:

$$\Delta\langle M\rangle = \sqrt{\langle M^2\rangle - \langle M\rangle^2} \tag{28}$$

The mean value $\langle M\rangle$ at a fixed surface coverage $\tilde{\nu}$ depends only on two terms: $\tilde{\nu}$ and β. The use of the reduced quantities allows one to predict a universal equilibrium structure of brushes in contact with an elastomer.

Analytical calculations of the average state are unfortunately impossible. However, the numerical calculations are easy to do. In Figure 3a–c, the computed average values $\langle\tilde{\xi}\rangle$, $\langle x\rangle$, and $\langle\tilde{h}\rangle$ are plotted as a function

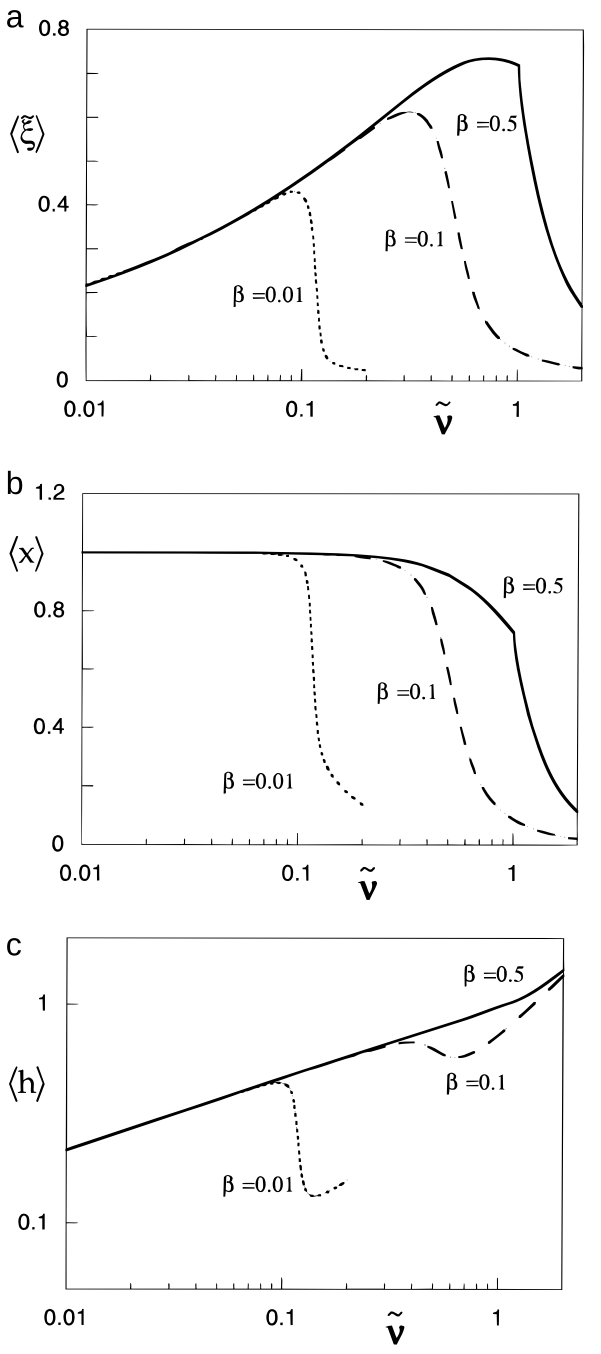

Figure 3. Average interdigitation length (IIIa), average interdigitation length fraction (IIIb), and average thickness of the grafted brush (IIIc) as a function of the grafting density. All variables are in reduced units.

of the reduced grafting density $\tilde{\nu}$ for a large interval of the parameter β.

Figure 3c shows on a log−log scale, that the thickness of the brush lies between two limiting values: for low surface coverage, full interdigitation, $\langle\tilde{h}\rangle = \tilde{h}_{\mathrm{wet}} = \tilde{\nu}^{1/3}$ and for high surface coverage, no interdigitation, $\langle\tilde{h}\rangle = \tilde{h}_{\mathrm{dry}} = (2/3)\tilde{\nu}$. (One can see in this figure, for the case $\beta = 0.1$, the two corresponding limiting straight lines with slopes respectively equal to $^1/_3$ and 1.) It is interesting to notice that the thickness of the brush decreases abruptly around the threshold value $\tilde{\nu}_c(\beta)$: embedded chains begin to be expelled from the elastomer and the brush deswells abruptly, this effect is important only for low values of β, for which the fluctuations play a minor role.

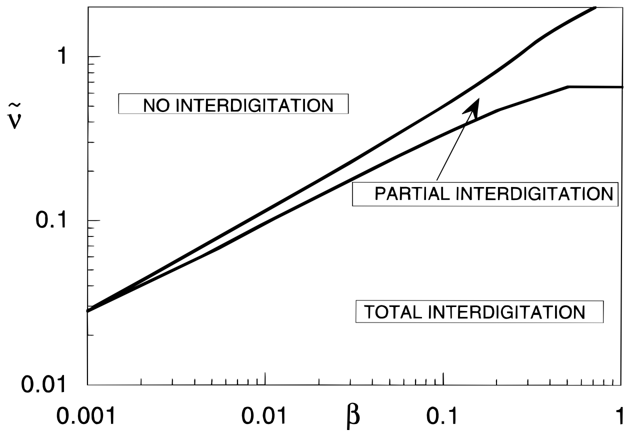

Figure 4. $(\beta, \tilde{\nu})$ diagram of the interdigitation state between a brush and an elastomer (log−log scale).

Figure 3b shows that the width of the $\tilde{\nu}$ range of partial interdigitation ($0 < x < 1$) increases with increasing β. In this range of partial interdigitation the thickness of the brush $\langle\tilde{h}\rangle$ is a nonmonotone function of $\tilde{\nu}$; this behavior arises from the competition between two competing effects: deswelling of the brush due to the decrease of the interdigitation and increase of the brush thickness due to the enhancement of chain stretching. Both opposite effects occur by increasing the surface coverage of grafted chains. For $\beta < 0.2$, the first effect dominates, whereas the second one dominates for $\beta > 0.2$.

Figure 3a shows that for all values of β, the average interdigitation length $\langle\tilde{\xi}\rangle$ reaches its maximum at the surface coverage, beyond which the interdigitation ceases to be total.

We can quantify the notion of "interdigitation state" of the system brush/elastomer by computing the grafting density of the minimum of f_{chain} with respect to $\tilde{\xi}$; it is depicted in Figure 4 in a $(\beta,\tilde{\nu})$ diagram (log−log scale). There are three domains: (no interdigitation, partial interdigitation, and total interdigitation). The calculated threshold value $\tilde{\nu}_c(\beta)$, beyond which the instability occurs is the separation line between the "no interdigitation" domain and "the partial interdigitation" domain in Figure 4. It exhibits a remarkable scaling law behavior (for $\beta < 0.2$), i.e. $\tilde{\nu}_c \cong \beta^{2/3}$. Converting this result to natural units gives $\nu_c \cong P^{1/6}N^{-2/3}$. This result differs significantly from previous models which predict $\nu_c \cong P^{-1/2}$.[5,8] The second curve plotted in Figure 4 is the separation line between the total interdigitation domain and the partial interdigitation domain. This line defines another threshold value $\tilde{\nu}_T(\beta)$, beyond which the minimum of the free energy ceases to correspond to total interdigitation. For $\beta < 0.2$, $\tilde{\nu}_T(\beta)$, varies roughly as a power law of β: $\tilde{\nu}_T \cong \beta^{1/2}$, and is practically insensitive to the variations of β, for $\beta > 0.5$. Again converting this result to natural units gives $\nu_T(\beta) \cong N^{-1/2}$ for $\beta < 0.1$ and $\nu_T(\beta) \cong P^{-1/2}$ for $\beta > 0.5$. $\nu_T(\beta)$ is always higher than $PN^{-3/2}$; this means that *stretched grafted chains can fully penetrate into the elastomer.*

IV. Adhesion Energy Elastomer/Brush

Analytical Calculation of the Zero-Rate Fracture Energy. In case of partial interdigitation, only the segments of chains embedded in the elastomer will contribute to the adhesion energy.[10,11] By analogy with eq 1, the contribution G_0 of the interdigitation between the grafted chains and the elastomer to the zero-rate fracture energy is given by

$$G_0(\xi,\nu) = \Gamma \int_{z^*}^{h} N(z)\, \epsilon(z)\, \mathrm{d}z \tag{29}$$

with

$$N(z) = \frac{2N}{\pi} \arccos\left[\frac{z^*}{z}\right]$$

The free end density $\epsilon(z)$ is given by eq 17 and $N(z)$ denotes the number of monomers embedded in the elastomer for a chain whose free end is located at $z > z^*$. $N(z)$ is obtained by integration of eq 9.

Using the appropriate reduced units and the mass conservation equation (13), $G_0(\xi,\nu)$ can be written in a simpler way:

$$G_0(\xi,\nu) = \frac{2\sqrt{2}}{\pi}\Gamma \frac{N}{P^{1/2}} \tilde{G}_0(\tilde{\xi},\tilde{\nu}) \tag{30}$$

with

$$\tilde{G}_0(\tilde{\xi},\tilde{\nu}) = \frac{2}{3}\, \frac{\tilde{\xi}^2(\tilde{\nu} + \tilde{\xi})}{1 + \tilde{\xi}^2}$$

Now, the average value $\langle \tilde{G}_0(\tilde{\nu})\rangle$, as well as the thermal fluctuations $\Delta\langle \tilde{G}_0(\tilde{\nu})\rangle$, can be calculated by putting the value of $G_0(\xi,\nu)$ (eq 30) into eqs 27 and 28, respectively.

Kinetics Barrier. As pointed out in the previous section, if the equilibrium structure of the system brush/elastomer corresponds to a partial or total interdigitation state, the system has to jump over an energy barrier in order to reach this equilibrium structure (see Figure 2). The value of the energy barrier per chain is defined by $\Delta U = \mathrm{Max}[f_{\mathrm{chain}}(\tilde{\nu},\tilde{\xi})] - f_{\mathrm{chain}}(\tilde{\nu},0)$, where f_{chain} is given by eq 25. In the case where the energy barrier ΔU is much larger than kT, the system cannot explore all values of the interdigitation length in a reasonable time, so that adhesion should be very weak. In order to evaluate numerically this effect we have chosen the following criterion: if $\Delta U/kT > 1$, the interdigitation is not allowed and the effective interdigitation length $\tilde{\xi}_{\mathrm{eff}} = 0$. Numerical calculations done with a large set of parameter β show that kinetics effects are relevant only for low values of β, i.e. $\beta < 0.015$ or equivalently $N > 75$ P; it corresponds to a system with a large asymmetry between the polymerization index of the connector molecules N and the chemical distance between the cross-links of the elastomer P. For many practical cases the parameter β is not so small, and kinetics effects can be neglected.

Adhesion Energy: Numerical Results. In Figure 5, the calculated zero-rate fracture energy $\langle \tilde{G}_0\rangle$ in reduced units is plotted as a function of the reduced surface coverage $\tilde{\nu}$ for a width range of the parameter β. In all cases, $\langle \tilde{G}_0\rangle$ exhibits a maximum at an optimum surface coverage $\tilde{\nu}_{\mathrm{opt}}$ which increases as a function of β. In the total interdigitation domain ($\tilde{\nu} < \tilde{\nu}_{\mathrm{T}}(\beta)$), $\langle \tilde{G}_0\rangle = 2/3\nu$, equivalent to eq 1.[2] For low values of β ($\beta < 0.3$), the maximum adhesion energy occurs in the total interdigitation domain, whereas it occurs in the partial interdigitation domain for higher values of β. Note that the optimum surface coverage $\tilde{\nu}_{\mathrm{opt}}$ coincides with the surface coverage of maximum interdigitation length (Figure 3a). Finally note also, that adhesion can occur for $\tilde{\nu} > 1$ in slightly asymmetric systems ($\beta > 0.3$). In the inset of Figure 5, $\langle \tilde{G}_0\rangle$ as well as the fluctuations of the adhesion energy $\Delta\langle \tilde{G}_0\rangle$ (represented by the "error bars" centered around $\langle \tilde{G}_0\rangle$ with height equal to $\Delta\langle \tilde{G}_0\rangle$) are plotted as a function of $\tilde{\nu}$ for $\beta = 0.175$. It clearly shows that fluctuations are very important in case of partial interdigitation ($\tilde{\nu} > \tilde{\nu}_{\mathrm{T}}(\beta)$).

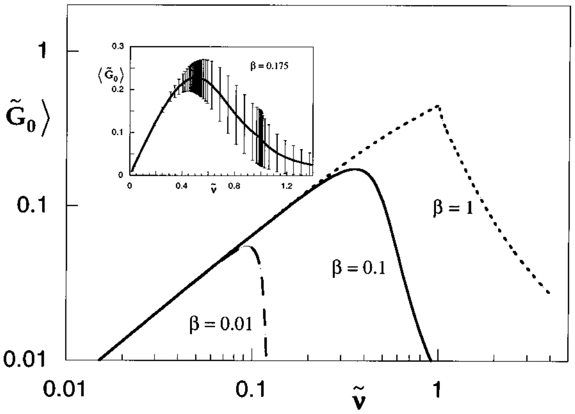

Figure 5. Variation of the average zero-rate fracture energy $\langle \tilde{G}_0\rangle$ (reduced units) as a function of the grafting density $\tilde{\nu}$ (reduced units) for several values of β (log−log scale). Inset: $\langle \tilde{G}_0\rangle$ and fluctuations $\Delta\langle \tilde{G}_0\rangle$ ("error bars") as a function of $\tilde{\nu}$ for $\beta = 0.175$ (linear scales).

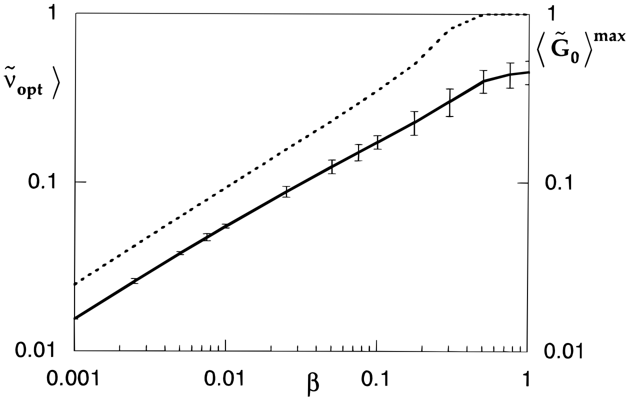

Figure 6. Plot of the maximum adhesion energy $\langle \tilde{G}_0\rangle^{\mathrm{max}}$ (full line) and the corresponding fluctuations ("error bars") versus β. Plot of the optimum grafting density (corresponding to the maximum zero-rate fracture energy) as a function of β (dotted line).

The two important characteristics of the system brush/elastomer, the zero-rate maximum adhesion energy $\langle \tilde{G}_0\rangle^{\mathrm{max}}$, as well as the thermodynamic fluctuations $\Delta\langle \tilde{G}_0\rangle^{\mathrm{max}}$ and the corresponding optimum surface coverage $\tilde{\nu}_{\mathrm{opt}}$ are plotted as a function of β in Figure 6 (master curve). For $\beta < 0.3$, $\tilde{\nu}_{\mathrm{opt}}(\beta)$ and $\langle \tilde{G}_0\rangle^{\mathrm{max}}$ exhibit a power law dependence on β: $\langle \tilde{G}_0\rangle^{\mathrm{max}} \cong \beta^{1/2}$ and $\tilde{\nu}_{\mathrm{opt}} \cong \beta^{0.57}$. For $\beta > 0.3$, $\tilde{\nu}_{\mathrm{opt}}(\beta)$ and $\langle \tilde{G}_0\rangle^{\mathrm{max}}$ are almost independent of β. Note also the important fluctuations of $\langle \tilde{G}_0\rangle^{\mathrm{max}}$ at high β.

Examples. In the previous subsection, all predictions concerning adhesion have been given in reduced units: this permits a universal description of the adhesion phenomenon between a brush and an elastomer. However, the use of natural units is more meaningful, in order to illustrate the predictions of this model.

Typically, the chemical distance P lies within the range (50, 1000), and the polymerization index of end-functionalized chains (forming the brush) is less than 10^4; in fact it is very difficult (and consequently expensive) to synthesize long end-functionalized chains ($N > 1000$). Moreover, the formation of stretched brushes is a very slow process,[21] and it is certainly not easy to

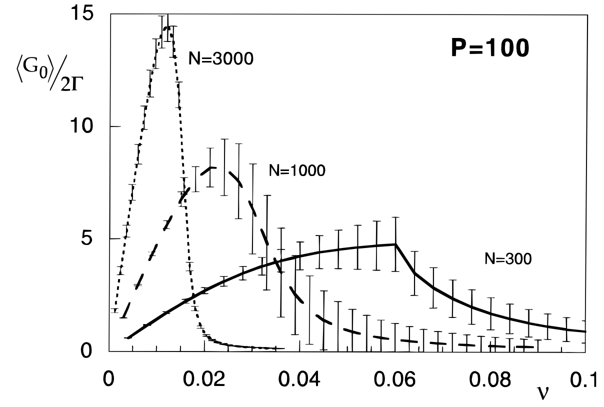

Figure 7. Variation of the zero-rate fracture energy and its fluctuations (dimensionless units) as a function of the grafting density (number of grafted chains/a^2) for an elastomer with a chemical distance between cross-links $P = 100$ and several polymerization indexes N for the grafted brush.

obtain dry brushes with high grafting surface density for long chains.

In the absence of interdigitation between the brush and the elastomer, the zero-rate adhesion energy is just the Dupré work of separation of two identical polymers, i.e. twice the surface tension of a melt of chemically identical polymers: 2Γ (for simplicity we have assumed that the brush and the elastomer are chemically identical). A convenient measure of the adhesion efficiency of the brush is the ratio $G_0/2\Gamma$. A significant enhancement adhesion requires that $G_0/2\Gamma \gg 1$.

An example of the adhesion efficiency of grafted brushes is depicted in Figure 7: the ratio $\langle G_0\rangle/2\Gamma$ is plotted as a function of the surface density of grafted chains ν (dimensionless units) for an elastomer with a chemical distance between cross-links $P = 100$ and various indexes of polymerization of grafted chains N. The numerical value of the unknown prefactor α in eq 22 has been fixed at 1.

First of all, the longer the grafted chains, the larger is the maximum adhesion energy. Note, however, that for very long grafted chains ($N = 3000$ in this case), a large adhesion efficiency needs very stretched chains (in order to obtain $\langle G_0\rangle/2\Gamma = 14.5$, one needs $\nu = 10^{-2} = 17PN^{-3/2}$); thus it is not obvious that such stretched brushes can be easily obtained. Another interesting feature is depicted for the case $N = 300$: the adhesion energy is slightly dependent on the grafting density and for these shortest chains the adhesion efficiency is very weak ($G_0/2\Gamma < 5$) and the fluctuations are very important.

Figure 8a shows the maximum adhesion energy $\langle G_0\rangle^{\max}/2\Gamma$ and the optimum corresponding area density ν_{opt} for a brush of grafted chains with polymerization index $N = 1000$ as function of chemical distance between cross-links in the elastomer. The more important message of this figure is that both $\langle G_0\rangle^{\max}/2\Gamma$ and ν_{opt} are *weakly* sensitive to the variations of P. Two regimes can be distinguished: $P < 250$, the maximum adhesion corresponds to a total interdigitation ν_{opt}, and $P > 250$, the maximum adhesion corresponds to a partial interdigitation.

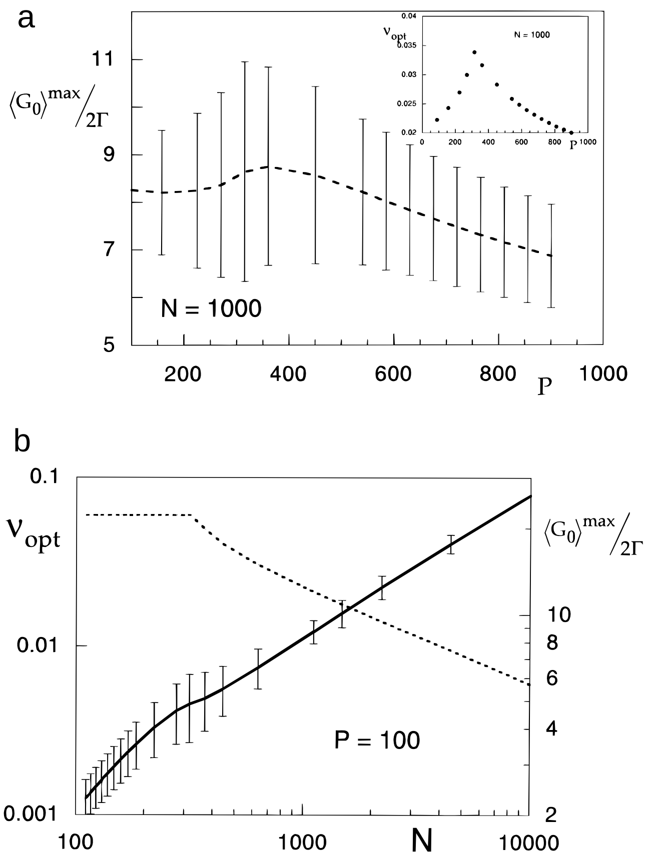

Figure 8. (a) Variation of maximum zero-rate fracture energy in dimensionless units (full line) and corresponding optimum grafting density ((number of grafted chains/a^2), inset) for a brush with polymerization index $N = 1000$ as a function of the chemical distance between cross-links P of the elastomer. (b) Variation of maximum zero-rate fracture energy in dimensionless units (full line) and corresponding optimum grafting density ((number of grafted chains/a^2), dotted line) for an elastomer with chemical distance between cross-links P, as a function of the polymerization index N of the grafted brush.

In Figure 8b $\langle G_0\rangle^{\max}/2\Gamma$ and ν_{opt} are plotted as function on N for an elastomer of chemical distance between cross-links $P = 100$: the two important features are that $\langle G_0\rangle^{\max}/2\Gamma$ varies roughly as $N^{1/2}$ and that ν_{opt} is independent of N in the partial interdigitation state ($N < 250$) and varies roughly as $N^{-0.43}$, in the total interdigitation state ($N > 250$).

V. Summary and Discussion

Comparison with Experiments. The effects of polymeric brushes on the adhesion of elastomers has been recently investigated by Brown[22] and by Creton, Brown, and Shull,[23] using the JKR technique. A thin layer of polystyrene−polyisoprene diblock copolymer was placed at the interface between a polystyrene-coated substrate and a polyisoprene cross-linked lens. The zero-rate fracture energy G_0 was measured as function of the area density of copolymer present at the interface. One of the experiments[23] used PI brushes with three different polymerization indexes ($N = 588$, $N = 882$, and $N = 2205$) and an elastomer with a not well-controlled chemical distance between cross-links P but varying between $P = 43$ and $P = 75$. The Dupré work of adhesion of two PI surfaces is $2\Gamma = 0.064$ J/m^2. The monomer length a is obtained from the radius of gyration of the PI block:[23] $a \simeq 0.66$ nm independent of N, as expected. In Figure 9a−c, we have plotted the predicted values of $G'_0 = \langle G_0\rangle + 2\Gamma$ (J/m^2) as well as the thermodynamic fluctuations $\Delta\langle G_0\rangle$ as a function of the area density of copolymers $\Sigma = \nu/a^2$ (chains/nm^2) together with the experimental points of ref 23 (circles). We have omitted the experimental points $\Sigma = 0$ (in this case the adhesion energy should correspond to the

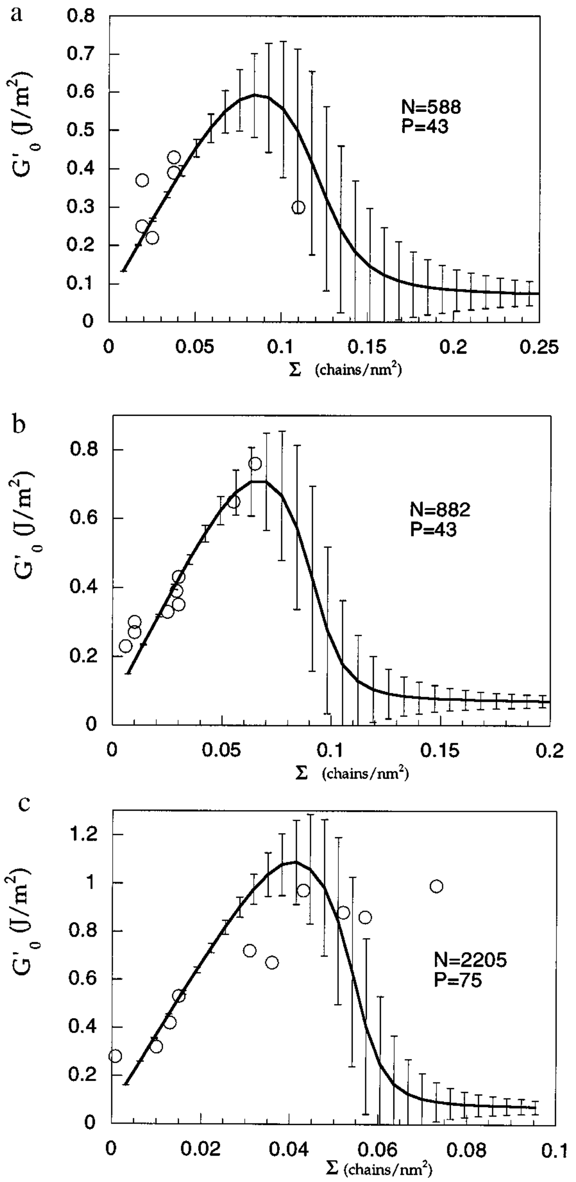

Figure 9. Comparison between the experimental values of the zero-rate fracture energy (figure 4 of ref 23) and the predictions of the model: (a) $N = 588$; (b) $N = 882$; (c) $N = 2205$. (circles) experimental points; (full line) model; (error bars) theoretical fluctuations. $a = 0.66$ nm; Dupre work of a PI interface, 0.064 J/m^2; X axis, area density of grafted chains (chains/nm^2); Y axis, threshold toughness G'_0 (J/m^2). Note that there is only one fitting parameter: $\alpha = 1.5$ (eq 22).

Dupré work of a PS/PI interface: 0.12 J/m^2). *Note that there is only one adjustable parameter, the unknown parameter* α *(eq 22) in the theoretical calculations. For all three sets of experimental data, we used the same value* $\alpha = 1.5$. For each value of N, we have tested the two extremal experimental values of P ($P = 43$ and $P = 75$) and select the better one for the fit; however, this is not a very sensitive parameter, whereas the value of a is a very sensitive one. There is good *quantitative* agreement between the theory and experiments, except for one experimental point ($\Sigma = 0.073$ chains/nm^2, and $N = 2205$) which cannot be explained by the model, even if the inaccuracy of the measurement inherent in the technique (the measured value G'_0 is obtained by an extrapolation of the zero-rate velocity) could explain the discrepancy between the theory and the experiment. Finally, one needs more experimental results in order to test the validity of the model, and a direct measurement of the interdigitation length, using for instance neutron scattering experiments with labeled grafted chains, may allow a more accurate measurement of the interdigitation.

Conclusion. The present model of interdigitation between a brush and an elastomer is based on the original model of ref 11, and the predictions are in qualitative agreement with those of ref 11. However, a quantitative description of the adhesion between a brush and elastomer requires a quantitative description of the statistics of chain segments embedded in the elastomer, which was the aim of the present paper, using "the parabolic model" to describe the brush in contact with an elastomer.[14] Moreover the present model attempts to evaluate quantitatively the "motor" for the interdigitation phenomenon: the interfacial energy of depletion. Consequently, both descriptions are significantly different from a quantitative point of view, in particular, the threshold values of area densities for the interdigitation domains, the variations of the adhesion energy as a function of area density and the maximum expected adhesion energies and corresponding optimum surface coverages are deeply affected by the detailed description of chains statistics. The major difference between the two models lies in this: in ref 11, the authors postulate that stretched chains cannot *fully* penetrate into an elastomer. This assumption implies a simple relation between the area surface density of grafted chains, the fraction of embedded chains, and the average number of embedded segments per penetrating chain, from which the adhesion energy is calculated. In the present paper, such an assumption is not needed and the relationship between the three former parameters is obtained self-consistently; as a result, it appears that real brushes (i.e. *stretched grafted* chains) are able to fully penetrate into the elastomer; the adhesion energy is calculated by taking into account the Boltzmann weight of all available brush configurations. The importance of fluctuations of the interdigitation length and their consequences on the adhesion energy are clearly revealed by this model.

The principal limitation of results presented in the present paper would seem to be that they are only valid under the condition of strong stretching of chains in the brush ($\nu \gg PN^{-3/2}$), in fact, it is not true as regards the predicted adhesion energy, because at low surface coverage ($\nu \ll PN^{-3/2}$), the adhesion energy is given by eq 1 (an expression which is valid for isolated grafted chains), but as shown in this paper, this expression remains valid even for surface coverages much larger than this threshold value; so, it is possible in principle to predict the zero-rate adhesion energy between a layer of grafted chains and an elastomer of the same chemical composition, whatever the number of grafted chains per unit area.

From a theoretical point of view, the present simple analytical model has several weaknesses.

(i) The expression of the swelling energy of the elastomer (eqs (2 and 3) is oversimplified: logarithmic corrections have been neglected. However, an alternative expression for the swelling energy of the elastomer cannot be a simple free energy of mixing $F_{\text{mix}} = (kT/P)(1 - \phi)\ln(1 - \phi)$. This expression has been used in the parabolic like approach of the brush in contact with a melt of short chains:[6] it is rather easy to show that this approach predicts a total interdigitation between the brush and the elastomer whatever is the polymerization index and the area density of grafted chains, but in this model the Gaussian stretching energy of the short chains which penetrate into the brush is neglected; this approximation is clearly incorrect at high grafting density. In the present model, the phenomenon of progressive exclusion of the elastomeric chains from the brush prevents this problem.

(ii) The expression of the interfacial energy of the brush (eq 22) is tentative, and the prefactor α is unknown. However, it allows a clear understanding of the interdigitation process and agrees with theoretical studies on the confinement of molten chains.[18−20] An alternative expression of the interfacial energy has been recently proposed[24] in the context of adhesion between two dry copolymer brushes: $\gamma \cong \Sigma kTh^2/N$, which is directly deduced from the confinement energy of an ideal isolated chain between two plates.[25] However, this expression is not correct in the case of a melt of confined chains:[18,19,26] the entropy of confinement is rather entirely localized in the surface layer.

As shown in ref 27, the values of the adhesion energy at finite crack velocities are intimately related to the adhesion energy at zero crack velocity; the present results should be useful to reconsider more quantitatively the length of junction as well as the fracture energy at finite crack velocity.

Finally, this model could be used in the context of the wetting behavior of thin polymer films on layers of chemically identical grafted molecules.[28]

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