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ADHESION BETWEEN A POLYDISPERSE POLYMER BRUSH AND AN ELASTOMER

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ABSTRACT

The interface between a flat solid surface and a cross-linked elastomer can be considerably strengthened by the addition of chains (chemically identical to the elastomer) that are tethered by one end to the solid surface. At high grafting densities these coupling chains may, however, segregate from the elastomer and the adhesion may drop considerably. This important problem has been recently considered by de Gennes *et al.* in the case of a monodisperse 'brush'. In this article we analyse the adhesion between a polydisperse brush and an elastomer, having in mind some very recent experiments by Marciano *et al.*

INTRODUCTION

The phenomenon of adhesion concerns the interaction of two condensed phases brought into contact with each other. It involves a surprisingly large variety of materials, ranging from synthetic polymers to living cells and tissues^{1,2}. Adhesion between a flat solid surface and a cross-linked elastomer is a technologically important problem (a cross-linked elastomer consists of long, flexible chain-like molecules that are interconnected at various points by cross-links to form a molecular network; the polymer medium is locally fluid, but the macroscopic flow of the material is prevented by the cross-links). The interface between the two materials can be strengthened by the addition of chains (chemically identical to the elastomer) that are tethered by one end to the solid surface. As a crack grows

along the interface, these coupling chains are progressively pulled-out from the elastomer³⁻⁵. This "suction" process is expected to occur in an approximately planar *cohesive zone* directly ahead of the crack tip⁶. A number of models have been proposed to describe the process of chain pull-out and the relation between chain pull-out and interfacial toughness⁷⁻¹³. In the model of Raphaël and de Gennes^{10,11}, the partially pulled-out chains are assumed to form single-chain fibrils. The minimization of the sum of the surface and stretching energies of these chains shows that there is a minimum force f^* required for a fibril to exist even at zero pull-out rate. As the force on a chain that is being pulled-out remains finite as $V \rightarrow 0$, the existence of a threshold toughness G_0 that is larger than the work of adhesion W due to intermolecular interactions (typically van der Waals type) is predicted. For many practical cases, the zero-rate fracture energy G_0 is given by^{11,12}

$$G_0 - W \cong kTN \nu \quad (1)$$

where ν is the number of coupling chains per unit interface area, N their polymerization index, and kT the thermal energy. In what follows we will often use the dimensionless grafting density $\sigma = \nu a^2$, where a is the monomer size.

Equation (1) is valid as long as the interdigitation between the coupling chains and the elastomer is total. For high σ values, however, the coupling chains may segregate (at least partially) from the elastomer and G_0 may reduce to W . This important problem has been recently considered by de Gennes¹⁴ and by Brochard-Wyart *et al.*¹⁵. The starting point of these studies is the analysis by de Gennes of the equilibrium between a melt of chains (N monomers per chain) and an elastomer cross-linked *in the dry state* (N_c monomers between cross-links)¹⁴. For a single N chain inside the elastomer, the Flory-type free energy can be written as

$$\frac{F}{kT} \cong \frac{R^2}{a^2 N} + \frac{a^3 N^2}{N_c R^3} \quad (2)$$

(all numerical factors being ignored). The first term represents the deformation energy of the chain (R is the coil radius). The

second term is the swelling energy of the elastomer. Since the free energy eqn (2) is identical to the free energy of a chain (N monomers) immersed in a melt of shorter, chemically identical chains (N_C monomers per chain)¹⁶, the N -chain conformation is the same in both situations. However, the volume fraction of monomers of the N chains within the elastomer is limited by the elastic energy of the elastomer to a value N_C/N ¹⁴. Similarly, a monodisperse brush* in contact with an elastomer is expected to fully interdigitate the network if the resulting volume fraction of monomers from the brush inside the elastomer, Φ , is smaller than an critical value $\Phi_1 \cong N_C/N$ ¹⁵. The corresponding grafting density is $\sigma_1 \cong N_C/N^{3/2}$. For $\sigma < \sigma_1$, $G_0 - W$ is a linear function of σ . For $\sigma > \sigma_1$, the interdigitation between the brush and the elastomer is only partial and each grafted chain has only a number $n \cong N_C^{2/3} \sigma^{-1}$ of monomers within the elastomer. As a result, $G_0 - W \cong kT n \nu$ increases more gradually with σ (like $\sigma^{1/3}$). In this regime, Φ is larger than Φ_1 and reaches a value of order 1 for $\sigma \cong N_C^{-1/2}$. At that point, the interdigitation is lost and $G_0 - W$ falls off to zero¹⁷.

In this letter we analyse the related but somewhat different problem of the adhesion between a polydisperse brush and an elastomer.

ADHESION BETWEEN A POLYDISPERSE BRUSH AND AN ELASTOMER

Having in mind some recent experiments by Marciano *et al.* (see Conclusion), we assume the polydisperse brush to be characterized by the following distribution:

$$S(n) \cong \frac{\phi_0^{7/8}}{a^2 n^{1/2}} \quad 1 < n < N \quad (3)$$

where $S(n)$ is the number (per unit area) of chains made of more than n monomers ($1 < n < N$). This distribution is reminiscent of the 'pseudo-tail' distribution calculated by Guiselin in the case of

* A layer of polymer chains grafted at one end onto a solid surface is usually referred to as a 'brush'.

a layer prepared by irreversible adsorption from a semi-dilute solution of volume fraction ϕ_0 ¹⁸.

Let us first recall some useful results concerning the behavior of a polydisperse brush (described by the length distribution eqn (3)) exposed to a melt of mobile chains (degree of polymerization N_C , with $N^{1/2} < N_C < N$) ^{19,20}. (a) In the regime $\phi_0 > N_C^{-1/3}$, the mobile chains penetrate into the brush to a distance from the wall that corresponds for the tethered chains to the index

$$s \equiv N_C \phi_0^{7/4} \quad (4)$$

(the n -th monomers of all tethered chains larger than n are supposed to be located at the same distance from the surface) ¹⁸⁻²⁰. Note that s is an increasing function of N_C : decreasing the length of the melt chains increases the stretching of the brush and therefore increases the mixing by providing more volume for the melt. (b) There exists a threshold value of ϕ_0 below which the excluded volume interactions cease to be relevant at the brush extremity ^{19,20}. This threshold value is given by $\phi_{0T} \equiv (N_C/N)^{8/7}$ (see also ref.14). For $\phi_0 = \phi_{0T}$, the number of chains per unit area is of the order of $a^{-2}(N_C/N)$ and the average volume fraction of chains of the brush inside the interdigitation zone is of the order of N_C/N .

We now consider what happens when the polydisperse brush is exposed to an elastomer (N_C monomers between cross-links, with $N^{1/2} < N_C < N$). By analogy with the monodisperse brush, we make the conjecture that the network elasticity starts to restrict the interdigitation when $\phi_0 = \phi_{0T}$. The use of this criterion is strengthened by the fact that it is also the point when the average volume fraction of brush chains in the network is of the order of N_C/N .

We now consider the situation $\phi_0 > \phi_{0T}$ where we expect partial interdigitation: as a result of the brush polydispersity, long enough chains will penetrate into the elastomer while short ones will not. In order to describe qualitatively this partial interdigitation regime, we assume that the number of chains per unit area that enter the network is locked at its value for $\phi_0 = \phi_{0T}$, that is at $a^{-2}(N_C/N)$. One can thus define an index m such that the

number (per unit area) of chains of more than m monomers is given by $a^{-2}(N_c/N)$:

$$m \equiv (N/N_c)^2 \phi_0^{7/4} \quad (5)$$

The novel feature of the polydisperse brush compared to the monodisperse brush is that we now have two independent mechanisms leading to partial interdigitation: the 'melt mixing effect', which imposes the cutoff s , and the elastomer elasticity, which imposes the cutoff m . According to the relative value of s and m (eqns (4) and (5)), two cases must be considered. As long as s is larger than m , that is for $N_c > N^{2/3}$, it is plausible to assume that the elastomer behaves like a melt of N_c chains and penetrates into the brush to a distance from the wall that corresponds to the index s . According to eqn (1), the adhesion energy G_0 is then given by

$$G_0 - W = kT \int_s^N dn \left(- \frac{dS(n)}{dn} \right) (n - s) \quad (6)$$

The integral appearing in eqn (6) corresponds to the number of monomers present in the elastomer (see eqn (1)). Using eqn (4), we get

$$G_0 - W \equiv \frac{kT}{a^2} N^{1/2} \phi_0^{7/8} \left[1 - \phi_0^{7/8} (N_c/N)^{1/2} \right]^2 \quad (7)$$

Equation (7) predicts the existence of a maximum in the adhesion energy as ϕ_0 increases (see Fig. 1). This maximum occurs for $\phi_0 = (N/9N_c)^{4/7}$. Note that since ϕ_0 cannot exceed 1, the maximum disappears if N is larger than $9N_c$.

We now consider the opposite case $N_c < N^{2/3}$. Since m is now larger than s , we expect the elastomer to penetrate into the brush less deeply than a melt of N_c chains. If one postulates that the penetration is controlled by the index m , the adhesion energy G_0 is then given by

$$G_0 - W = kT \int_m^N dn \left(- \frac{dS(n)}{dn} \right) (n - m) \quad (8a)$$

$$\cong \frac{kT}{a^2} N^{1/2} \phi_0^{7/8} \left[1 - \phi_0^{7/8} (N^{1/2}/N_C) \right]^2 \quad (8b)$$

Equation (8b) predicts the existence of a maximum in the adhesion energy as ϕ_0 increases. This maximum occurs for $\phi_0 = (N_C/3N^{1/2})^{8/7}$. Note that since ϕ_0 cannot exceed 1, the maximum disappears if N is smaller than $N_C^2/9$.

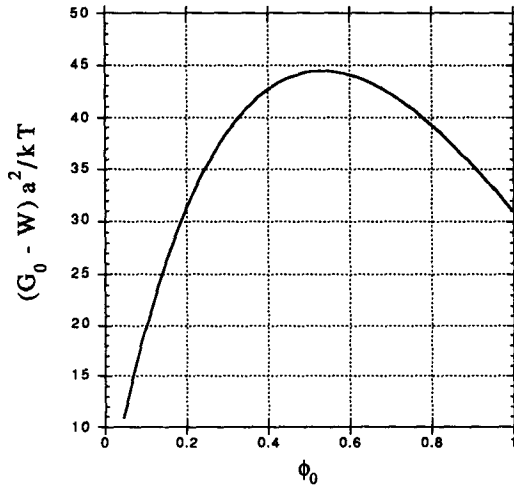


Fig. 1. Plot of $(G_0 - W)a^2/kT$ versus ϕ_0 for $N = 3 \cdot 10^4$ and $N_C = 10^4$ according to eqn (7) .

According to eqns (7) and (8), the maximal value of the curve $G_0 - W$ versus ϕ_0 varies *non monotonically* with N_C (see Fig. 2):

$$\frac{a^2}{kT} (G_0 - W)_{\max} \cong (4/3^3) N_C \quad \text{for } N^{1/2} < N_C < N^{2/3} \quad (9)$$

and

$$\frac{a^2}{kT} (G_0 - W)_{\max} \cong (4/3^3) N N_c^{-1/2} \quad \text{for} \quad N^{2/3} < N_c < N \quad (10)$$

This non monotonic behavior is our central result. From eqns (9) and (10), one finds that $(G_0 - W)_{\max}$ is optimum for $N_c \cong N^{2/3}$ where it takes the value $(4/3^3)kTa^{-2}N^{2/3}$. Equations (9) and (10) are valid for relatively small values of N . For a more complete discussion, see Appendix.

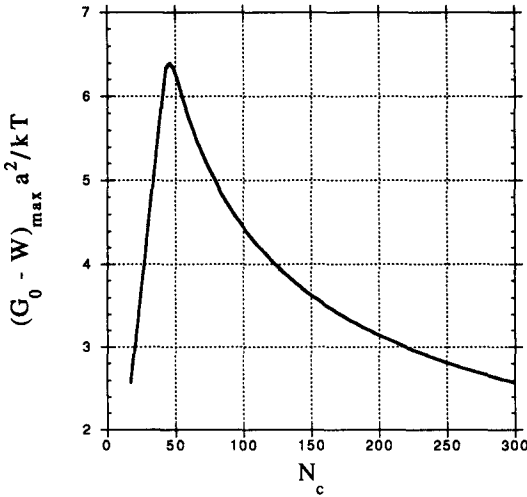


Fig. 2. Plot of $(G_0 - W)_{\max} a^2 / kT$ versus N_c for $N = 3 \cdot 10^2$ according to eqns (9) and (10). Near the maximum, the curve has been smoothed in order to avoid an unphysical discontinuity of the slope.

CONCLUDING REMARKS

Quite recently, Marciano and Léger²² have conducted peel tests on a system made of a thin ribbon of elastomeric polydimethylsiloxane (PDMS) brought into contact with a flat silicon wafer on which PDMS chains had previously strongly adsorbed. The internal structure of the PDMS layer - which experimentally²³ seems to be well described by the model of Guiselin¹⁸ for irreversible adsorption (eqn (3)) - was adjusted by varying the polymer concentration in the reaction bath, ϕ_0 . From peel force measurements at very low velocity (5 nm/s), Marciano

and Léger have estimated the zero-rate fracture energy G_0 . They found that G_0 (as a function of ϕ_0) exhibits a maximum. This remarkable feature is in qualitative agreement with the theoretical predictions of section 2. In fact, the experimental system is more complicated since one deals with loops rather than individual chains. According to Brochard-Wyart *et al.*¹⁵, when a loop (with fixed attachment points on the solid surface) of length $2n$ interdigitates into the elastomer, its conformations are strongly restricted. The corresponding entropy loss is given by $\Delta S \equiv \beta(2n/N_C)$, where β is a numerical factor of order unity¹⁵. This effect, referred to as "the cactus effect", is absent when one considers the penetration of two distinct chains of length n into the elastomer. More theoretical and experimental work will therefore be required to understand quantitatively this important issue.

* * *

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APPENDIX

Equations (9) and (10) were established assuming $N/9 < N^{2/3}$ (i.e. $N < 729$). If $N/9 > N^{2/3}$, these equations should be respectively replaced by

$$\frac{a^2}{kT} (G_0 - W)_{\max} \equiv (4/3^3) N_C \quad \text{for} \quad N^{1/2} < N_C < 3N^{1/2} \quad (11a)$$

$$\equiv N^{1/2}[1 - N^{1/2}N_C^{-1}]^2 \quad \text{for} \quad 3N^{1/2} < N_C < N^{2/3} \quad (11b)$$

and

$$\frac{a^2}{kT} (G_0 - W)_{\max} \equiv N^{1/2}[1 - (N_C/N)^{1/2}]^2 \quad \text{for} \quad N^{2/3} < N_C < N/9 \quad (12a)$$

$$\equiv (4/3^3) N N_C^{-1/2} \quad \text{for} \quad N/9 < N_C < N \quad (12b)$$

From eqns (11) and (12), one finds that $(G_0 - W)_{\max}$ is optimum for $N_C \equiv N^{2/3}$, where it takes the value $kT a^{-2} N^{1/2} [1 - N^{-1/6}]^2$.

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DISCUSSION

N° 1 - ENDRES - Can you see the fibres between substrate and rubber by any microscopic technique ?

RAPHAEL - In the model of ref.10, the partially pulled-out chains are assumed to form single-chain fibrils. I think that it would be quite difficult to observe these fibrils directly with conventional microscopic techniques.

N° 2 - WILLIAMS - Do you assume in this model that N is smaller than an entanglement length ? Can you reach a regime where you make knots ?

RAPHAEL - In the model of ref.10, it is assumed that the connectors slip out from the elastomer by a viscous process. In this simple picture, the entanglement length does not come into play. If the crack propagates at high velocity, the pull-out process is quite rapid and this might lead to the formation of knots.