

ADHESION BETWEEN AN ELASTOMER AND A GRAFTED SURFACE

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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 substantially. This important problem has been recently considered by several authors in the case of a monodisperse "brush". In this article, we analyse the adhesion between a polydisperse brush and an elastomer, and we present some recent experiments conducted on polydimethylsiloxane - silica systems.

1 Introduction

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 elastomer^[1-3]. This "suction" process is expected to occur in an approximately planar *cohesive zone* directly ahead of the crack tip^[4].

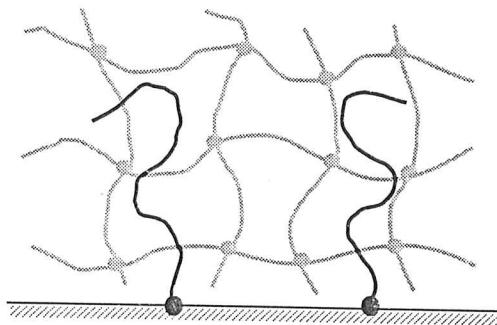


Figure 1. The interface between flat solid surface and a cross-linked elastomer is strengthened by the addition of chains (chemically identical to the elastomer) that are tethered by one end to the solid surface.

A number of models have been proposed to describe the process of chain pull-out and the relation between chain pull-out and interfacial toughness^[5-11]. In the model of Raphaël and de Gennes^[8-9], 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^[9-10]

$$G_0 - W \equiv kT N v \quad (1)$$

where v 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 $\sigma = v\alpha^2$, where α 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 Gennes^[12] and by Brochard-Wyart *et al.*^[13]. 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)^[12]. For a single N chain inside the elastomer, the Flory-type free energy can be written as

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

(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)^[14], 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 ^[12]. 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 a critical value $\Phi_1 = N_c/N$ ^[13]. The corresponding grafting density is $\sigma_1 = N_c/N^{3/2}$. 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 $n \equiv N_c^{2/3} \sigma^{-1}$ of monomers within the elastomer. As a result, $G_0 - W \approx kT n v$ 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 $\sigma \approx N_c^{-1/2}$. At that point, the interdigitation is lost and $G_0 - W$ falls off to zero^[15].

Experimentally, the formation of a dense polymer brush is a delicate chemical problem: one has to find a system in which the wall has no preferential interaction with the monomers of the chains, except the extremity to be grafted. An example of such a system has been worked out by P. Auroy *et al.*^[16], with $\alpha \approx$

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

hydroxylterminated polydimethylsiloxane (PDMS) chains end grafted on previously modified porous silica beads (by esterification of most of the silanol sites of the surface by pentanol molecules). Another and simpler way of forming dense surface anchored layers of polymer chains has been worked out by M. Deruelle *et al.*[17], through simultaneous adsorption and end grafting of PDMS on untreated silica surfaces. If the naturally oxidised surface of a silicon wafer is used, the layers can be analysed in details through reflectometry techniques such as X-Rays, neutrons reflectivity, or ellipsometry. The dry thickness h_0 of such layers, characterised by ellipsometry and X-Rays reflectivity, follows rather well the scaling law $h_0 \approx \alpha N^{1/2} \Phi_0^{7/8}$. When put into contact with a good solvent, these layers swell, but the thickness saturates at a value smaller than what would have been obtained with a purely end grafted layer made with the same chains, at the same surface density[18]. This is an experimental evidence that the structure of these simultaneously adsorbed and end grafted layers is different from that of a brush. In fact, due to the adsorption, these layers are made of loops, with a large polydispersity of loop sizes, reflecting the statistics of the chains in the reaction bath. The structure of such irreversibly adsorbed layers has been worked out by O. Guiselin[19], and they have been named pseudo-brushes, because they are analogous to highly polydisperse brushes of loops. Since, experimentally, pseudo-brushes are formed rather easily, it is of some importance to try to estimate the adhesion between a pseudo-brush and an elastomer. This will be done in Section 2. In Section 3 we present experiments conducted on polydimethylsiloxane - silica systems. The paper ends with some concluding remarks.

2 Adhesion between a polydisperse brush and an elastomer

In order to estimate the adhesion energy between a pseudo-brush and an elastomer, we will treat the pseudo-brush as a polydisperse brush of half loops. We assume the polydisperse brush to be characterized by the following distribution:

$$S(n) \approx \frac{\Phi_0^{7/8}}{a^2 n^{1/2}} \quad 1 < n < N \quad (3)$$

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 prepared by irreversible adsorption from a semi-dilute solution of volume fraction Φ_0 [19].

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 $N^{1/2} < N_c < N$)^[20-21]. (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)^[19-21]. 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^[20-22]. This threshold value is given by $\Phi_{0T} \equiv (N_c/N)^{8/7}$ (see also Ref.12). For $\Phi_0 \equiv \Phi_{0T}$, 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 with more than m monomers is given by $a^{-2}(N_c/N)$:

$$m \equiv (N_c/N)^2 \Phi_0^{7/4} \quad (5)$$

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 of the brush present in the elastomer (see eqn (1)). Using eqn (4), we get^[23]

$$G_0 - W \approx \frac{kT}{a^2} N^{1/2} \Phi_0^{7/8} \left[1 - \Phi_0^{7/8} (N_c/N)^{1/2} \right]^2 \quad (7)$$

Equation (7) predicts the existence of a maximum in the adhesion energy as $\Phi_0^{7/8}$ increases. This maximum occurs for $\Phi_{0\max}^{7/8} = (N/9N_c)^{1/2}$ and $(G_0 - W)_{\max} = kT a^{-2} N^{1/2} (4/9) \Phi_{0\max}^{7/8}$. 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^[23]

$$\begin{aligned} G_0 - W &= kT \int_m^N dn \left(-\frac{dS(n)}{dn} \right) (n-s) \\ &\approx \frac{kT}{a^2} N^{1/2} \Phi_0^{7/8} \left[1 - \Phi_0^{7/8} (N^{1/2}/N_c) \right]^2 \end{aligned} \quad (8)$$

Equation (8) predicts the existence of a maximum in the adhesion energy as $\Phi_0^{7/8}$ increases. This maximum occurs for $\Phi_{0\max}^{7/8} = N_c/(3N^{1/2})$ and $(G_0 - W)_{\max} = kT a^{-2} N^{1/2} (4/9) \Phi_{0\max}^{7/8}$. Note that since Φ_0 cannot exceed 1, the maximum disappears if N is larger than $N_c^2/9$.

It is worth noting that eqns (7) and (8) can be rewritten as^[24]

$$\frac{G_0 - W}{(G_0 - W)_{\max}} = \frac{9}{4} \frac{\Phi_0^{7/8}}{\Phi_{0\max}^{7/8}} \left(1 - \frac{1}{3} \frac{\Phi_0^{7/8}}{\Phi_{0\max}^{7/8}} \right)^2 \quad (9)$$

According to eqns (7) and (8), the maximal value of the curve $G_0 - W$ versus $\Phi_0^{7/8}$ varies non monotonically with N_c :

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

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

From eqns (10) and (11), one finds that $(G_0 - W)_{\max}$ is optimum for $N_c \cong N^{2/3}$ where it takes the value $(4/3^3) kT a^{-2} N^{2/3}$ [25].

3 Experiments

Systematic experiments on polydimethylsiloxane - silica systems have been undertaken using the pseudo-brushes presented at the end of Section 2^[24][26-28]. Narrow fractions of PDMS chains (α - ω hydroxyl terminated, M_w in the range 20 000 to 700 000, $M_w/M_n = 1.1$) were used at volume fractions Φ_0 ranging from 5 to 100%, to form the layers on the upper surface of silicon wafers.

Two mechanical tests have been developed to extract the adhesion energy: 90° peel tests, conducted on an especially built machine allowing for very low velocities (5 nm/s to 10 mm/s) and the J.K.R. test^[29] in which a small elastomer lens is pressed against the substrate; measuring the area of contact as a function of the applied load yields both the adhesion energy and the elastic modulus of the elastomer. Details of the experimental set up and of the results are reported in reference^{[24][26]} for the peel test and in references^{[27][28]} for the JKR test. In order to minimise as much as possible bulk dissipation in the elastomer in the peel test, we have used silk reinforced thin ribbons (200 nm thick), and checked both the thickness and the width dependence of the measured peel force.

On Fig. 2 we have reported the measured adhesion energies obtained at very low velocity (5 nm/s) deduced from peel tests (Fig. 2a) and from J.K.R. tests (Fig. 2b), on layers formed at fixed molecular weight and increasing Φ_0 . In both cases, a maximum in the evolution of the adhesion energy as a function of the surface density of chains, $\sigma \approx \Phi_0^{7/8}$, is clearly visible. On Figure 2a, results obtained with two different elastomers (molecular weights between cross links respectively 10 400 and 24 000) seem to indicate that the position of the maximum is not strongly affected by N_c , the polymerisation index between crosslinks, while the adhesion energy at the maximum increases with N_c . Surprisingly enough, the layers with the higher σ (obtained by adsorption and grafting from a polymer melt) do not provide large adhesion energy.

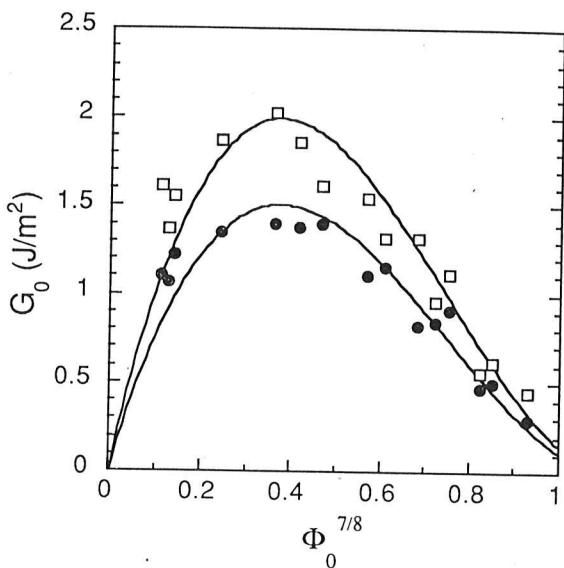


Figure 2a. Measured adhesion energy G_0 as a function of the surface density of the chains in the surface layers (proportional to $\Phi_0^{7/8}$) from peel experiments performed at a velocity $V = 50 \text{ nm s}^{-1}$ for elastomers with $M_c = 10000$ (filled symbols) and $M_c = 24000$ (open symbols), and chains in the surface layers with a molecular weight 412000. The full lines are just guides for the eyes.

4. Concluding remarks

The remarkable experimental features presented in the preceding section are 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.*[13] 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 unity[13]. 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.

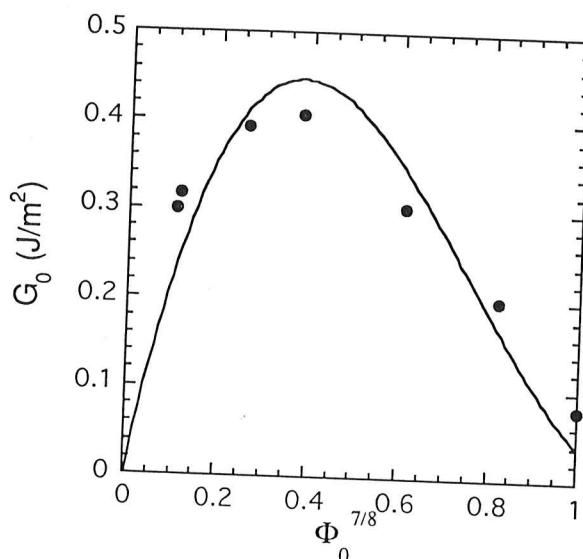


Figure 2b. Measured adhesion energy G_0 as a function of the surface density of the chains in the surface layers from JKR experiments at $V=10 \text{ nm s}^{-1}$ for elastomers with $M_c=10000$ and chains in the surface layers with a molecular weight 412000. The full lines is just a guide for the eyes.

A model taking the cactus effect into account has been recently proposed[24]. This model also leads to the form of eqn (9) but with $\Phi_{0\max}^{7/8}=1/3$ and $(G_0-W)_{\max}=kT\alpha^{-2}N^{1/2}(4/9)\Phi_{0\max}^{7/8}$. All the experimental results obtained with peel tests are reported on Figure 3, along with the master curve eqn (9).

The challenge is at present to obtain sufficiently accurate data to test further the validity of these descriptions. This implies controlling as far as possible the quality and the reproducibility of the elastomers, as the local elasticity in the interdigitated region is the key parameter which limits or allows the connectors to be efficient. A strong advantage of the J.K.R. test is to allow simultaneous measurements of the adhesion energy and of the elastic modulus. It thus reveals to be a unique tool and

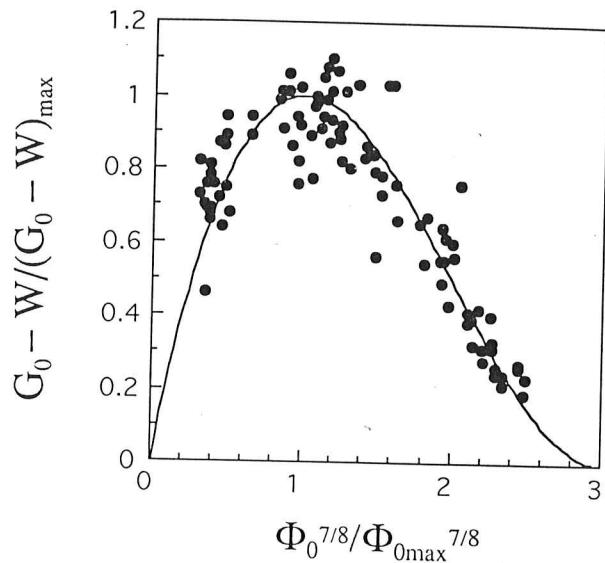


Figure 3. $\frac{G_0 - W}{(G_0 - W)_{\max}}$ as a function of $\Phi_0^{7/8} / \Phi_{0\max}^{7/8}$: experimental results and master curve eqn (9).

should allow a better understanding of the molecular mechanisms at the origin of the enhancement of the adhesion energy between a solid and an elastomer through connector molecules.

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SHORT AND LONG CHAINS AT INTERFACES

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