Adhesion mechanisms at soft polymer interfaces

BY LILIANE LÉGER1,* AND COSTANTINO CRETON2

1Laboratoire de Physique des Solides, UMR 8502 CNRS—Université Paris Sud, Bâtiment 510, 91405 Orsay Cedex, France
2Laboratoire Physicochimie des Polymères et des Milieux Dispersés, UMR 7615 CNRS—ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

Based on several significant examples, we analyse the adhesion mechanisms at soft polymer interfaces with a special emphasis first on the role of connector molecules, that is, polymer chains bound to the interface and which transmit stress through a stretching and extraction mechanism, and second on the necessary relay that must be taken by additional dissipation mechanisms acting at larger scales if one wants to reach typical fracture toughnesses in the range of a few $10^2$ J m$^{-2}$. Examples of such bulk dissipation mechanisms will be discussed for interfaces between polymer melts and for pressure-sensitive adhesives in contact with a solid surface. We shall particularly point out the fact that the level of adhesion results from a competition between adhesive failure usually driven by both the interactions and the friction properties of the interface and bulk strong deformations which take place in the bulk of the adhesive layer. Controlling the friction properties of the interface then becomes a tool to finely tune adhesive properties.

Keywords: adhesion; soft polymers; connector molecules; pressure-sensitive adhesives; friction

1. Introduction: the paradox of adhesion

Adhesion phenomena are best exemplified when one intends to glue together two different solid parts in order to form an assembly. To do so, one usually deposits a liquid layer on the clean surface of one solid. The cleaning is quite important to ensure that the liquid wets the solid, and covers all asperities of the surface, which is almost always rough. Then the second solid is pressed against the liquid-covered surface. After some time, chemical reactions have taken place inside the liquid layer which has transformed into a solid that is able to sustain stresses. If the whole operation has succeeded, then both interfaces between the new solid-like glue layer and the solid parts are also able to sustain some stress. A way to quantify the result is to measure either the limiting stress the assembly can sustain before getting broken or the corresponding energy necessary to rupture the assembly.

* Author for correspondence (leger@lps.u-psud.fr).

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If one wants to model the process, and try to predict this energy of rupture, the easiest and naive way of thinking is to model the glue as a simple van der Waals liquid. As schematically presented in figure 1, if a tensile load is applied, the liquid layer will separate into two films with a liquid layer remaining in close contact with the solid surfaces (good wetting of the surface by the liquid) on each side of the broken contact. Two new interfaces between the liquid and air are thus created. The total energy per unit area necessary to produce these new interfaces is $W = 2\gamma$, where $\gamma$ is the surface energy of the liquid. For a van der Waals liquid, the order of magnitude of the surface tension is $\gamma = kT/a^2$, where $k$ is the Boltzmann constant; $T$ is the absolute temperature; and $a$ is a molecular size. This leads to $W \approx 0.1$ J m$^{-2}$ at most. This is much smaller than the typical fracture energies of an adhesive joint, usually in the range of a few 100 J m$^{-2}$ to a few 1000 J m$^{-2}$. Obviously, a van der Waals liquid is a poor glue.

One can imagine improving this ‘weak’ glue by adding stronger interactions between the molecules of the liquid, to render it more cohesive. A particularly strong interaction is provided by chemical covalent bonds, with a typical energy of rupture per bond of the order of 1 eV. Still in a naive approach, one can easily evaluate the energy necessary to open a fracture inside the adhesive layer as the energy of rupture of all bonds crossing the fracture plane. Per unit area of fracture, this energy is $G = \nu U_c$, where $\nu$ is the number of bonds per unit area and $U_c$ is the energy of rupture of one bond. With $U_c \approx 1$ eV, i.e. $1.6 \times 10^{-19}$ J, and one bond between each molecule, $\nu \approx 1/(0.3 \times 10^{-9})^2 = 1.1 \times 10^{19}$ m$^{-2}$, the corresponding energy of fracture increases to a few J m$^{-2}$ at most, again far below the practical adhesive strength encountered in adhesive joints.

It thus appears clear that adhesion mechanisms cannot be thought of only in terms of bond rupture and creation of new interfaces. These two processes do always take place when the adhesive assembly is ruptured, but they cannot, by themselves, explain the measured values of the fracture toughness. Much more energy has to be expended to rupture an adhesive joint than the energy of rupture of chemical bonds. This means that good adhesives are the materials able to dissipate energy before rupture when submitted to the mechanical loading of an adhesive test.
An important consequence is that the fracture toughness will, in general, depend on the mechanical test chosen to measure it.

A second also quite important consequence is that, in order to understand adhesion mechanisms, one has to go through the identification and the modelling of the different dissipation mechanisms involved in the rupture of the assembly under consideration. This is also the reason why most adhesives are polymers: these materials do provide efficient dissipation mechanisms.

The understanding of adhesion mechanisms at polymer interfaces has thus emerged as a major axis of research in recent years. An important notion is that of ‘connector molecules’, that is, polymer chains which are bound to an interface by chemical bonds or by physisorption, and which interact with the bulk polymer so that they act to transmit stress across the interface.

A second important notion is that of stress concentration leading to irreversibly deformed zones inside the materials, and thus to energy dissipation. This is quite classical in fracture mechanics. For example, when a crack propagates in an elastic material, the stress field tends to diverge at the crack tip. No material is able to sustain an infinite stress, and a plastically deformed zone appears at the crack tip. The energy necessary to form this plastically deformed zone is then irreversibly consumed when the fracture propagates. This energy per unit area of the open fracture is related to the work necessary to orient and extend polymer chains over a displacement which is comparable with the size of the plastically deformed zone. Both the size of the plastically deformed zone and the yield stress thus fix the energy necessary to propagate the crack. For an adhesive joint, we are faced with a very similar problem, complicated by the fact that now the two materials assembled to form the joint do not have the same mechanical properties. In order to describe the deformation field close to the interface, one needs to introduce conditions for the transmission of stresses through the interface, and thus understand, down to the molecular level, the relations between molecular organization and mechanical properties.

The case of assemblies between two glassy polymers (which most often are incompatible, which means that the assembly will usually delaminate spontaneously) in which the interface is reinforced by connector molecules made of diblock copolymers, each side of the diblock being compatible with one of the bulk polymers, has been particularly investigated during the past decade, and the adhesion mechanisms in such systems are now well identified (Creton et al. 2001a and references therein). In the present paper we rather focus on assemblies between soft polymers for which, surprisingly, much less is known. In a first part, we shall briefly present what has been predicted by P. G. de Gennes for the adhesive strength of an interface between a solid on which long flexible polymer chains have been grafted, and put into contact with a cross-linked elastomer made of the same polymer (Raphaël & de Gennes 1992). These predictions will be compared with experiments, and the notion of soft connector molecules will be illustrated. In a second step we shall discuss how connector molecules can develop due to partial interdiffusion at an interface between two molten polymers. This will lead to a discussion on how soft polymers can provide additional sources of energy dissipation when submitted to the mechanical loading of an adhesive test, and show how interfacial and bulk highly deformed zones interplay, highlighting the relations between adhesion and friction.
2. Stress transfer by one connector polymer molecule at solid–elastomer interfaces

Let us consider a smooth solid surface on which long polymer chains have been end grafted at sufficiently low grafting density so that they do not overlap (this is the so-called mushroom regime of grafting). When exposed to air, the polymer chains tend to collapse on the solid surface, as a result of the attractive van der Waals interactions between monomers and the underlying solid. If the same surface decorated with end-grafted polymer chains is put into contact with a polymer melt or a cross-linked elastomer of the same polymer, the chains tethered to the surface tend to interpenetrate into the bulk polymer through thermal fluctuations, in order to recover their equilibrium Gaussian conformation and gain entropy. What happens if one pulls off the elastomer as shown in figure 2a? Are the van der Waals interactions between monomers strong enough to maintain the surface grafted chain interdigitated into the bulk polymer and to stretch this surface chain? The question has been worked out by P. G. de Gennes (Raphaël & de Gennes 1992). The connector chains are indeed expected to be fully stretched inside the gap between the elastomer and the solid surface, as shown in figure 2b.

The argument goes as follows. Assuming a partially extracted chain with $n$ monomers out of the elastomer, the free energy associated with that partial extraction, $e(h)$, for a gap $h$ between the solid and the elastomer is

$$e(h, n) = n\gamma a^2 + kTh^2/na^2$$

(2.1)

where $a$ is the monomer size. The first term on the r.h.s. of equation (2.1) represents the surface energy required to expose to air the $n$ extracted monomers. The second term is the elastic energy associated with the eventual stretching of the extracted portion of the chain. Minimizing that energy with respect to $n$ leads to

$$n(h) = \frac{h}{a} \left( \frac{\gamma a^2}{kT} \right)^{-1/2}$$

(2.2)
which means that the portion of chain inside the gap is indeed fully stretched \((n\) is proportional to \(h\)). The corresponding free energy is

\[
e_{\text{opt}}(h) = kT \frac{h}{a} \left( \frac{\gamma a^2}{kT} \right)^{1/2}.
\] (2.3)

There is thus a minimal force for a fibril to exist:

\[
f^* = \frac{d e_{\text{opt}}}{dh} = kT \frac{a}{a} \left( \frac{\gamma a^2}{kT} \right)^{1/2}.
\] (2.4)

The existence of such a minimal force has been confirmed experimentally on several systems \((\text{Brown 1993; Deruelle et al. 1994; Marciano 1995; Reiter et al. 1996})\). It is important to note that the force \(f^*\) is comparable with the force necessary to fully stretch a chain, \(kT/a\), and is also the force necessary to extract one monomer from the bulk polymer and expose it to air.

\(\text{(a) Case of a grafted surface}\)

Let us now consider a solid surface with \(n = \Sigma/a^2\) grafted chains per unit area \((\Sigma\) is the adimensional grafting density), in contact with a cross-linked elastomer \((\text{made of the same polymer})\). If a stress \(\sigma\) is applied as schematically presented in figure 2, the energy for opening a gap \(h\) is written

\[
G(h) = \left[ \frac{\Sigma}{a^2} kT \left( \frac{\gamma a^2}{kT} \right)^{1/2} - \sigma \right] h.
\] (2.5)

As long as the external stress \(\sigma\) remains smaller than the minimal stress to extract the chains

\[
\sigma^* = \frac{\Sigma}{a^2} kT \left( \frac{\gamma a^2}{kT} \right)^{1/2} = \frac{\Sigma}{a^2} f^*;
\] (2.6)

\(G(h)\) is minimal for \(h = 0\) and the crack does not open. As soon as the applied stress becomes larger than \(\sigma^*\), the crack opens. A zone with partially extracted and stretched chains forms at the crack tip.

The energy needed to propagate the crack at very low speed \((\text{quasi-static regime})\) is then the work of this minimum stress over a displacement corresponding to the length of the fully stretched connector chains, plus the energy of the two newly created interfaces, i.e.

\[
G_0 = W + \gamma \Sigma N,
\] (2.7)

where \(N\) is the number of monomers in the connector chains and using the approximation \(\gamma \approx kT/a^2\).

If the crack is forced to propagate at a finite velocity \(V\), additional dissipation due to friction between the extracted connector chain and the bulk elastomer has to be taken into account. This has been worked out in detail by Raphaël & de Gennes (1994), and the prediction is that the fracture energy is rapidly dominated by friction effects when the fracture velocity is increased, leading to

\[
G = G_0 \frac{V}{V^*}, \quad \text{with} \quad V^* = \frac{Ea^2}{3 \Sigma \xi_0 N},
\] (2.8)

where \(E\) is the elastic modulus of the elastomer and \(\xi_0\) is a monomer–monomer friction coefficient.

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A number of experimental investigations have been conducted in order to check the validity of these predictions (Creton et al. 1994; Tardivat 1998). We summarize below their main results, choosing the example of polydimethylsiloxane (PDMS) cross-linked elastomers in contact with silicon wafers on which PDMS chains of various length have been end grafted (Le´ger et al. 1999).

Typical data for the quasi-static propagation of the fracture at such interfaces are reported in figure 3. One can clearly see that things appear more complicated than predicted. Indeed the connector chains do promote adhesion, and the fracture energy can be strongly enhanced compared with the reversible work of adhesion $W = 43 \text{ mJ m}^{-2}$ for PDMS/PDMS contact. However, the efficiency of the connector chains does not increase monotonically with the surface grafting density as predicted by equation (2.7): the connector chains lose totally their aptitude to promote adhesion when too densely grafted at the interface. The next unexpected finding is that the adhesive strength of the interface highly depends on the cross-linking density in the elastomer.

The loss of efficiency of the connector molecules at high grafting densities has been attributed to the rejection of the connector chains by the elastomer. Indeed, when the grafted surface is put into contact with the elastomer, the connector chains tend to penetrate into the elastomer in order to recover their Gaussian equilibrium conformation. They cannot do so without swelling the elastomer. There is thus an elastic energy penalty to be paid which obviously increases with the surface density of grafted chains. It can totally prevent the interdigitation process at large enough grafting density (Brochard-Wyart et al. 1994). It is,
however, not easy to correctly account for these effects, and it is only quite recently that a reasonable enough agreement between models and experiments has been obtained (Vilmin et al. 2004).

It is thus well admitted now that surface-anchored polymer chains can act as adhesion promoters and efficiently transmit stress through an interface. Van der Waals interactions between monomers are enough to maintain these connector chains stretched when one tries to separate the two partners of the assembly. The mechanisms by which the connector chains do promote adhesion are stretching and progressive extraction from the bulk material. After complete extraction, each connector chain relaxes its stretch and flattens down on the surface. The stretching energy is thus lost in the process, and has to be added to the energy of formation of the two new interfaces to permit the separation to occur. This additional energy can be viewed as the work of the force necessary to pull one connector chain out of the bulk material over the length of the extracted chain times the number of connector chains per unit area. The enhancement of adhesion energy compared with the thermodynamic work of adhesion is thus directly indicative of the degree of interdigitation of the tethered chains into the bulk polymer, as long as the fracture propagates slowly enough to remain in the quasi-static regime.

At finite velocities, additional dissipation has to be taken into account due to the friction between monomers in the bulk and in the extracted chains, and the adhesive strength becomes velocity dependent. The quantitative understanding of these velocity dependences, however, still remains under question; as shown in figure 4, the evolution of the fracture energy with the velocity of the advancing fracture appears correctly described by power laws over more than eight decades, with an exponent 0.08 much smaller than the predicted value of one. This discrepancy remains unexplained, and further experiments are certainly needed in order to fully establish the exact mathematical form of these velocity dependences (power law or logarithmic growth) and provide the correct interpretation.

Vilmin et al. (2004)
Let us come back to equation (2.7), and examine the order of magnitude of the adhesion enhancement produced by the connector chains. With a maximum grafting density in the range $\Sigma \approx 10^{-2}$ at most before the rejection from the elastomer becomes dominant, one can easily see that the number of monomers in the connector chains needs to be larger than $10^2$ if one wants that their contribution to adhesion starts to overcome the normal surface term $W$. For most typical polymers, this is the order of magnitude of the average number of monomers between entanglements. The connector chains need to be longer than an entanglement length to start promoting adhesion. However, unlike polymer glasses, where one entanglement is typically sufficient to obtain quite a large enhancement in fracture toughness (Creton et al. 2001a), the low friction force needed to extract polymer chains from an elastomer means that the adhesion enhancement effect keeps increasing very progressively as the connector chains become longer up to many entanglement lengths.

It is worthwhile to discuss now a similar and yet different case where chain interpenetration at the interface controls adhesion.

3. Polymer interfaces between polymer melts

Unlike the situation of tethered chains, where the connector chains can entangle with a polymer network with an identical chemical structure and $\Sigma$ and $N$ can be controlled independently, the structure of polymer interfaces between polymer melts is chiefly controlled by the interfacial width, that is, the average distance over which free chains can interpenetrate. If the two polymers are mutually immiscible, this interfacial width $w$ is controlled by the interaction parameter $\chi$ between the two polymers. The interfacial width $w$ and interfacial tension $\gamma_{12}$ between two immiscible polymers of infinite molecular weight are given by Helfand & Tagami (1971) and Jones & Richards (1999) as

$$w = \frac{a}{\sqrt{c \chi}},$$

$$\gamma_{12} = kT\rho a \sqrt{\frac{\chi}{6}} = \frac{kT\rho a^2}{6w},$$

where $a$ is the segment length; $c$ is a constant which has a value of 6 or 9 depending on whether the interface is in the weak or strong segregation limit; and $\rho$ is the density. If the molecular weight of the two polymers is not infinite, a correction factor increasing the interfacial width must be applied (Broseta et al. 1990). In essence, this means that the degree of interpenetration of polymer chains at the interface varies with the inverse of the square root of $\chi$. Since $a$ is of the order of the size of the monomer and the chain can be considered approximately Gaussian, the average number of monomers $A$ crossing the interface into monomer B is $\sim \chi^{-1}$, a result which has been extensively verified by neutron reflectivity.

For strongly immiscible polymer pairs, this number will vary from a few monomers to 30–50 monomers, a value well below the average number of monomers between entanglements $N_e$. However, if $\chi < 1/N_e$, that is, weakly
immiscible polymer pairs, entanglements can form at the interface and one expects these entanglements to affect adhesion between the two polymer melts.

Experimentally, measuring the adhesion between two polymer melts is challenging, since the materials are soft and highly viscoelastic and in practice it is only relevant for highly entangled polymer melts which respond as viscoelastic solids at the test temperature and strain rate.

In this case, the work of fracture of interfaces between polymer melts can be measured with a probe test (Gent & Kim (1990) and Schach et al. (2007) for short contact times) or a peel test (Hamed (1981) and Hamed & Shieh (1983) for long contact times). Provided that the test is properly executed to decouple interfacial effects from large-scale bulk effects, the practical work of adhesion $W_{\text{adh}}$ can be measured. A systematic study has recently been performed for increasingly interpenetrated interfaces between high-molecular-weight polymers of various degrees of immiscibility (Broseta et al. 1990). The key result of these experimental studies is that the adhesion energy between two polymer melts increases strongly with increasing interpenetration depth as shown in figure 5. This result was qualitatively expected since the formation of entanglements at polymer interfaces invariably increases their mechanical strength. However, with an average molecular weight between entanglements of the order of 3 kg mol$^{-1}$ for the polymers used in the study leading to average distances between entanglements of the order of 30–50 Å, this quantitative correlation has shown that several entanglements are needed to recover the bulk strength of the weakest of the two bulk materials.

It is worthwhile to note that the absolute values of $W_{\text{adh}}$ measured here are much larger than the values obtained for tethered chains of figure 3. This is because for these experiments the bulk materials are highly viscoelastic polymer melts; the contribution of viscoelastic dissipation cannot be neglected as will be discussed in more detail below (§4). Nevertheless, the adhesion energy remains highly sensitive to the interfacial structure, in this case the interpenetration length.

Figure 5. Adhesion energy $W_{\text{adh}}$ of interfaces between PB420K-H and different polymers as a function of the interpenetration width at the interface $w$. The horizontal dashed line represents the cohesive fracture energy of PB420K-H. Adapted from Schach et al. (2007).
This result should be compared with equivalent studies performed on interfaces between glassy polymers (Schnell et al. 1998; Brown 2001; Benkoski et al. 2002, 2003; Silvestri et al. 2003) which showed that one entanglement distance or less is typically sufficient to recover bulk strength.

It is also interesting to note that, as in the case of tethered chains, chain interpenetration dominates the adhesive behaviour, regardless of surface energetics. If one tries to apply the classic equation for the thermodynamic work of adhesion between two different surfaces to this case, the prediction of $W_{\text{adh}}$ is clearly at odds with the results of figure 5.

(a) Kinetics of strength build-up

If the two polymers are identical, they will mutually interdiffuse until the interface vanishes. However, because the dynamics of long polymer chains is slow, this healing of the interface is not instantaneous and the interdiffusion distance is controlled by kinetics (Stamm et al. 1991; Karim et al. 1994). Based on figure 5, one would expect the work of adhesion to reach a plateau value when the interpenetration is of the order of a few entanglements. The most accessible diffusion time for a linear polymer is the terminal relaxation time $\tau_d$ which characterizes a displacement of the centre of mass of a distance of the order of the polymer coil.

In a series of well-controlled experiments (Schach & Creton submitted), Schach et al. showed that the contact time where the work of adhesion reaches a plateau scales linearly with the terminal relaxation time of the polymer (figure 6). Of course, these results hold for simple linear monodisperse polymers. Practical situations often involve polydisperse or branched polymers, and for

Figure 6. Value of $W_{\text{adh}}$ as a function of contact time for three different SBR linear monodisperse polymers. Molecular weights are given in the inset and reptation times are 13, 140 and 1140 s, respectively, for the three molecular weights. The tests were performed at room temperature at a probe velocity of 100 $\mu$m s$^{-1}$. Adapted from Schach & Creton (submitted).
weakly immiscible polymers may combine thermodynamics and kinetics. Nevertheless, the important aspect to keep in mind is the importance of chain interpenetration at interfaces for adhesion between polymer melts.

4. Additional bulk dissipation for soft adhesives

Let us come back again to equation (2.7). Even if the connector chains are longer than a distance between entanglements, their contribution to adhesion enhancement can hardly reach more than 10 or 20 times $W$, because increasing the length of the connector chains imposes to decrease their grafting density to remain in the non-overlapping grafting regime. The stretching and extraction mechanism thus appears efficient to permit the transmission of stresses across the interface, but it cannot, by itself, provide adhesion energies larger than a few J m$^{-2}$, at low velocity for the propagation of the fracture. This clearly means that in order to reach adhesion toughness in the range of a few 10 J m$^{-2}$, one needs first an interface able to transmit stresses (which can be done by connector chains) and, second, the relay of additional dissipation mechanisms acting at other length scales than the molecular distances in the immediate vicinity of the interface. Such additional dissipations may be provided by the deformation of the highly viscoelastic material which constitutes a soft adhesive. We examine now a few examples in which we do understand how to manipulate these viscoelastic dissipations inside the adhesive layer.

(a) Failure of interfaces between viscoelastic layers and solid surfaces

A detailed analysis of the strain field inside an adhesive layer in the vicinity of the peel front has been conducted by Amouroux et al. (2001) in the case of acrylic tapes in contact with silicone elastomers containing variable amounts of silica-like nanoparticles (MQ resins in the silicones’ nomenclature; Amouroux et al. 2001) in order to modulate the adhesion energy. In a peel test, the mechanical loading of the soft adhesive layer is rather complex, and contains both tensile and shear contributions (Kaelble 1974). Amouroux et al. (2001) have clearly shown that depending on the aptitude of the interface to sustain shear stresses (and not only mode one opening stresses as discussed when describing the role of connector chains in adhesion enhancement) two different failure modes of the interface can appear. If the interface fails because it can only support weak shear stresses, interfacial slip develops close to the peel front, and the adhesive strength is dominated by the friction between the adhesive and the substrate due to this localized slip motion. If, on the contrary, the interface is able to sustain the shear stresses associated with the peel force, the whole adhesive layer is sheared, and the adhesive toughness is dominated by the viscoelastic losses associated with these deformations inside the whole adhesive layer. The adhesive strength is then larger than in the case of failure due to interfacial slip because the volume of adhesive inside which the deformations are noticeable becomes large, inducing a large dissipation. The velocity or strain rate dependences of these two processes (interfacial friction and bulk shear deformation) are quite different, which means that, first, the transition between failure modes when one progressively increases the interfacial friction depends on the peel velocity and, second, that very weak modifications in the interfacial friction may lead to significantly different adhesive energies at high enough peel velocities (Amouroux et al. 2001).
While this effect is present independent of the geometry used, detailed studies were done in the probe test geometry, which fixes the boundary conditions of the deformation and imposes, schematically, a controlled change in distance between two parallel and confined plates which separate from each other at a constant velocity (Shull & Creton 2004). In the specific case of pressure-sensitive adhesives (PSAs) detached from cross-linked silicone layers, the PSA is approximately 100 \( \mu \text{m} \) thick and deposited on a rigid glass slide while the silicone layer deposited on a cylindrical moving probe is only 1 \( \mu \text{m} \) thick and acts simply as a boundary condition.

A variety of rather complex microscopic deformation mechanisms are observed experimentally in this geometry: from simple interfacial failure, where a crack propagates at the interface, to cavitation or bulk fingering followed by fibrillation, where larger deformations of the adhesive are achieved (Shull & Creton 2004). In all these cases, the debonding process is determined by the coupling of bulk and interfacial properties of the material.

If a linear elastic model is considered for the deformation of the adhesive, the growth of a defect initially present at the interface between the thick elastic layer and the rigid surface depends on the competition between two different simpler mechanisms: the resistance to the interfacial propagation of a crack, which is governed by the critical energy release rate \( G_c \), and the resistance to bulk deformation, determined by the elastic modulus of the elastic layer \( E \) (see figure 7). The term \( G_c \) depends on the interfacial structure (resistance to slippage, chain interpenetration and interfacial interactions) and on the dissipation mechanisms close to the interface.

\( G_c/E \) represents an elastic length, related to the displacement that can be applied to the adhesive before failure occurs (Crosby et al. 2000; Webber et al. 2003). For real viscoelastic adhesives, the situation is more complex since at large strains, these materials are typical strongly non neo-hookean (Roos & Creton 2005). \( G_c(v) \) and \( E(\omega) \) will depend also strongly on the crack propagation rate (Josse et al. 2004).
and strain rate. However, the concept of a ratio between mostly interfacial viscoelastic dissipation and bulk elasticity remains valid and an approximate rate-dependent value of $G_c/E$ can still be qualitatively used to predict the growth pattern of an initial defect (Creton et al. 2001b; Shull & Creton 2004).

Several regimes are observed in practice and the shapes of the stress–strain curves obtained with probe tack tests are shown in figure 8. For values of $G_c/E$ smaller than the thickness of the adhesive film, the critical stress at which an initial defect, analogous to that depicted in figure 9, starts to expand is determined mainly by $G_c$ and the initially present defects will propagate at the interface so that an adhesive failure occurs before an extensive deformation of the materials is possible. Such an example is shown in figure 9. In that situation, for viscoelastic materials, $G_c$ can be written as (Maugis & Barquins 1978; Shull et al. 1998)

$$G_c = G_0 (1 + \varphi (aTv)),$$

where $G_0$ is the limiting value of the energy release rate at low propagation rates and $\varphi (aTv)$ is a multiplicative factor representing the viscoelastic dissipation. In this regime, therefore, increasing the interfacial interactions or increasing the dissipative properties of the adhesive results in an increase in the adhesion energy.

For values of $G_c/E$ much larger than the thickness of the film, cavities grow mainly into the bulk of the layer, forming a foam as the walls between cavities are extended into fibrils. At larger strains, corresponding to the fibrillation regime, the

Figure 8. Schematic of the different stress–strain curves that can be observed as a function of the values of $G_c/E$ for (a) interfacial cracks and (b) fibrils.
behaviour of the adhesive is dominated by a competition between viscoelastic extension of the cavity walls and adhesive failure that causes the detachment from the substrate. In this case, the adhesion energy depends primarily on the nonlinear elastic properties of the material (Creton et al. 2005), and is not very sensitive to $G_c$.

Therefore, one often observes a transition from a regime dominated by the dissipative properties of the adhesive (controlling $G_c$) and described in the work of Amouroux et al. (2001), to a regime where there is a coupling between the nonlinear extension and the resistance to slippage at the interface.

This transition can be described with the following qualitative argument: if $G_c(v)$ increases, the interfacial crack slows down for a given applied normal stress. Simultaneously, if the adhesive has a pronounced softening in its stress–strain curve, the deformation of the walls between the cavities when the adhesive layer detaches from the surface can increase nonlinearly for a given applied stress. The combination of both effects leads to a much greater fibril extension before detachment as shown in figure 10 for a soft acrylic adhesive detached from a series of silicone elastomers prepared with increasing silica nanoparticle content leading to increasing values of $G_c(v)$.

Since soft adhesives are weakly cross-linked materials, they almost always soften above a certain level of deformation due to the orientation of the entanglements in the direction of the tensile stress. In uniaxial tension, most

Figure 9. (a–d) Images from above of the progressive propagation of interfacial cracks at the interface between a viscoelastic layer and a solid surface. Time is progressing from (a) to (d).
PSAs can be represented by a Mooney–Rivlin model combined with the Gent model (Gent 1996) to account for the strain hardening at large strains. This can be written as

\[ \sigma_N = 2 \left( C_1 + \frac{C_2}{\lambda} \right) \frac{1}{(1 - J_1/J_m)} \left( \lambda - \frac{1}{\lambda^2} \right), \]

with \( J_1 = \lambda^2 + (2/\lambda) - 3 \).

The three material constants of this model are \( C_1, C_2 \) and \( J_m \) but \( J_m \) and \( C_1 \) are not really independent, since they are both physically related to the presence of chemical cross links. When \( \lambda \approx 1 \), one recovers linear elasticity with Young’s modulus given by \( E = 6(C_1 + C_2) \) while at large strains the stress increases owing to the finite extensibility characterized by \( \lambda_{\text{max}} \approx (J_m + 3)^{1/2} \). In the affine model, the extension where strain hardening sets in should be of the order of \( \sqrt{N_c}/2 \), where \( N_c \) is the average degree of polymerization of the chain and is inversely proportional to \( C_1 \); therefore for \( \lambda_{\text{max}} \gg 1 \), \( \lambda_{\text{max}} \approx C_1^{-1/2} \) and \( J_m \approx 1/C_1 \). This result of course relies on a simple interpretation of rubber elasticity of ideal networks but gives a general idea that it is not possible to have a vanishing value of \( C_1 \) and a low value of \( J_m \).

With \( C_2 \approx 5C_1 \) and \( J_m \approx 100 \), typical (Lindner et al. 2006) of PSAs, the effective stiffness of the material obtained from equation (4.2) decreases by a factor of 10 between \( \lambda = 1 \) and 2. Therefore, if the detachment strain reaches about \( \varepsilon = 1 \), a large increase in the deformation of the layer is expected even with a modest increase in interfacial friction.

This strong nonlinear coupling between resistance to friction and nonlinear extension occurs for intermediate levels of \( G_c/E \) when both \( G_c \) and the nonlinear constitutive equations are important. On the one hand, for low values of \( G_c/E \), the practical work of adhesion is dominated by interfacial dissipation and depends chiefly on \( G_0 \) and slightly on the dissipative properties of the adhesive.

Figure 10. Maximum deformation before detachment for an acrylic viscoelastic adhesive on different surfaces with increasing values of MQ nanoparticles and hence increasing values of \( G_0 \). The different curves correspond to different probe velocities.
On the other hand, at high values of $G_c/E$, the adhesion energy is controlled by the extension process of the fibrils and the detachment stress depends then mainly on the value of $J_m$ in equation (4.2).

5. Conclusions

We have shown that the adhesion mechanisms at soft polymer interfaces could be understood in terms of relays of dissipation mechanisms acting at different length scales, from molecular to macroscopic. The first step is to provide an interface able to sustain stress. Connector molecules, that is, polymer chains firmly attached to the interface and well interdigitated into the bulk polymer (either on one side of the interface if the soft polymer is in contact with a solid wall, or on both sides in the case of polymer–polymer interfaces), are able to play that role and to promote adhesion. They do act as adhesion promoters because when one tries to propagate a fracture at the interface they resist against being extracted from the bulk polymer, as a result of cohesive interactions between monomers. They are thus stretched, and when they finally get extracted as the fracture propagates, their elastic stretching energy is lost when they relax their stretching and flatten on the surface. Monomer–monomer van der Waals interactions are enough to permit this mechanism to develop, but it becomes important in the fracture toughness only if the grafted chains are long enough, typically longer than several average distances between entanglements. This dissipation mechanism at molecular scales is by far insufficient to produce an interfacial fracture toughness in the range of a few 10 J m$^{-2}$ or more typical of pressure-sensitive adhesives. In order to reach such a level of adhesion, one needs additional dissipation mechanisms to become active. We have shown that bulk deformations in a viscoelastic material could efficiently be used to do so, and that competitions between interfacial failure and large extensional deformations in the bulk adhesive were finally determining the fracture toughness. If one wants to modulate adhesion, one then needs to manipulate the surface properties of the system in order to prevent interfacial failure and induce strong deformations in a large volume of the material. Then the fracture energy strongly depends on the viscoelastic properties of the adhesive, and on the velocity of fracture.

A totally different route has emerged recently, based on attempts to mimic some aspects of the easy and efficient way insects and lizards are able to reversibly and efficiently stick on any surface, due in particular to the patterning of their fingers and toes at micro- or nanometric scales. Systematic studies do show that producing the equivalent of micrometric connectors by micropatterning the substrate (made of PDMS elastomer) can provide an efficient way of finally controlling adhesion (Ghatak et al. 2004; Crosby et al. 2005; Lamblet et al. 2007). This is another promising route, which could provide adhesion modulation totally driven by the mechanical properties of the substrate and the geometry of the patterns, and only weakly depending on the exact chemical nature of the adhesive.

References


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Adhesion mechanisms at polymer interfaces


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