

## Fracture and Adhesion of Soft Viscoelastic Materials and Gels

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In the last tens years considerable progress has been made in understanding which molecular features and material properties control the adhesion of soft materials. One of the interesting results coming out from this work is the fact that dissipative mechanisms at the molecular level such as molecular friction, but also network defects or non permanent bonds, could significantly enhance the fracture toughness of soft polymer based materials. Conversely for tough materials, a fine control of the non linear elastic properties of the materials could influence both adhesive and fracture resistance.

### Introduction

Adhesion is generally associated with molecular interactions at interfaces and often to strong chemical bonds. However for soft materials the major contribution to adhesive forces is often simply provided by van der Waals forces and strong covalent bonds are most of the time absent. On the other hand the low elastic modulus of these materials means that they are easily deformed even for relatively weak interfacial interactions[1].

The case of soft materials fracture is a little different, since to give the material its solid-like character and prevent flow, some strong bonds are necessary and need to be broken to fracture the material. However, typically a small concentration of strong bonds are diluted in a majority of weak bonds and a significant deformation of the material (and hence reorganization of the weak bonds) is necessary to break the strong bonds. How to maximize this energy dissipation when fracturing the strong bonds remains an open problem.

Macroscopically what is often measured is either the practical work of adhesion which is a macroscopic measure of the energy dissipated in the material upon debonding from a rigid interface, or the fracture toughness  $G_c$  which is the energy per unit area to fracture the material. For soft materials both of these values typically involve large strains in the materials and viscoelastic dissipation. In practice however two contributions to the fracture or adhesion energy should be considered: an elastic contribution, which is due to elastic energy initially stored in the material and then rapidly dissipated upon fracture. This is the macroscopic analogous of the well-known Lake-Thomas argument[2] where the threshold fracture energy of an elastomer is directly associated with the amount of energy stored in all the bonds of a polymer chain before fracture. Following this argument, the more compliant the material and the more energy can be stored (and released irreversibly upon fracture) and the higher the fracture toughness. However such a model has limitations since it predicts that an infinitely soft material would be infinitely tough. Clearly a second mechanism, limiting the volume where elastic energy is irreversibly dissipated upon fracture is needed. At lower deformation rates for bonds which are further away from the crack tip, viscosu dissipation by molecular friction becomes an important dissipative factor since the dissipative volume can become important. This is the so-called linear viscoelastic theory of fracture which predicts well the dissipation occurring during dynamic crack propagation far from the crack tip[3].

The challenge for theorist is to couple both approaches into one. We will not present here a new theory but some recent experimental results focusing on the energy dissipation mechanisms and their relationship to material properties.

## Adhesion

A very versatile test for the evaluation of adhesive properties of soft materials is the probe test where a hard flat-ended probe is put in contact and subsequently removed from a soft adhesive layer[4]. Depending on the type of adhesive and the strength of adhesive interactions two types of mechanisms are observed. Experiments on the debonding of soft adhesives have shown that the relative importance of one or the other mechanism is controlled by the ratio between resistance to interfacial crack propagation and elastic modulus. For high values of  $G_d/E$ , interfacial crack propagation does not occur over large scales, multiple cracks are nucleated and blunt creating a foamed fibrillar structure which is significantly tougher. On the other hand for low values of  $G_d/E$ , cracks can propagate over large distances and eventually coalesce causing a fracture of the bond without extensive deformation of the adhesive material[5].

Although this approach is qualitatively very useful it has some inherent limitations due to the fact that it has been developed for linear elastic materials and that it assumes that all energy dissipated during crack propagation is essentially dissipated very close to the crack tip. It is possible however to adapt the concept to viscoelastic materials with some approximations. The value of  $G_c$  for an interface between a soft rubber and a hard surface can be expressed as a function of the type[6]:

$$G_c = G_0 \left( 1 + \frac{\nu}{\nu^*} \right)^n \quad (1)$$

where the second term accounts for viscoelastic dissipation. The simplest way to characterize the dissipative character of a material in the linear regime is to use the dissipation factor  $\tan \delta$ . In this case equation 1 can be rewritten as

$$G_c \approx G_0 \tan \delta(\omega) \quad (2)$$

And the the ratio  $G_d/E$  could then be approximated by

$$\frac{G_c}{E} \approx G_0 \frac{G''}{(G')^2} \quad (3)$$

In order to check the validity of these concepts for soft adhesives, we have tested the adhesion of two materials with an identical chemical structure but varying rheological properties (the materials are acrylic soft polymers with different amounts of gel fraction). In order to test mainly the interfacial crack propagation mechanism we have used as adherends a series of silicone release liners with varying compositions controlling therefore the interfacial component  $G_0$  of adhesion.

The adhesion energy of the two adhesives and their values of  $G''/(G')^2$  are shown on figure 1. Clearly the material that has a low value of  $G''/(G')^2$  has a much lower work of adhesion on these silicone surfaces regardless of the absolute value of  $G_0$  (which increases with increasing amount of MQ resin incorporated in the silicone liner). On the other hand the adhesive with a higher value of  $G''/(G')^2$ , shows much higher values of the work of adhesion and shows even a transition in failure mechanism from interfacial fracture to cavitation and fibrillar failure.

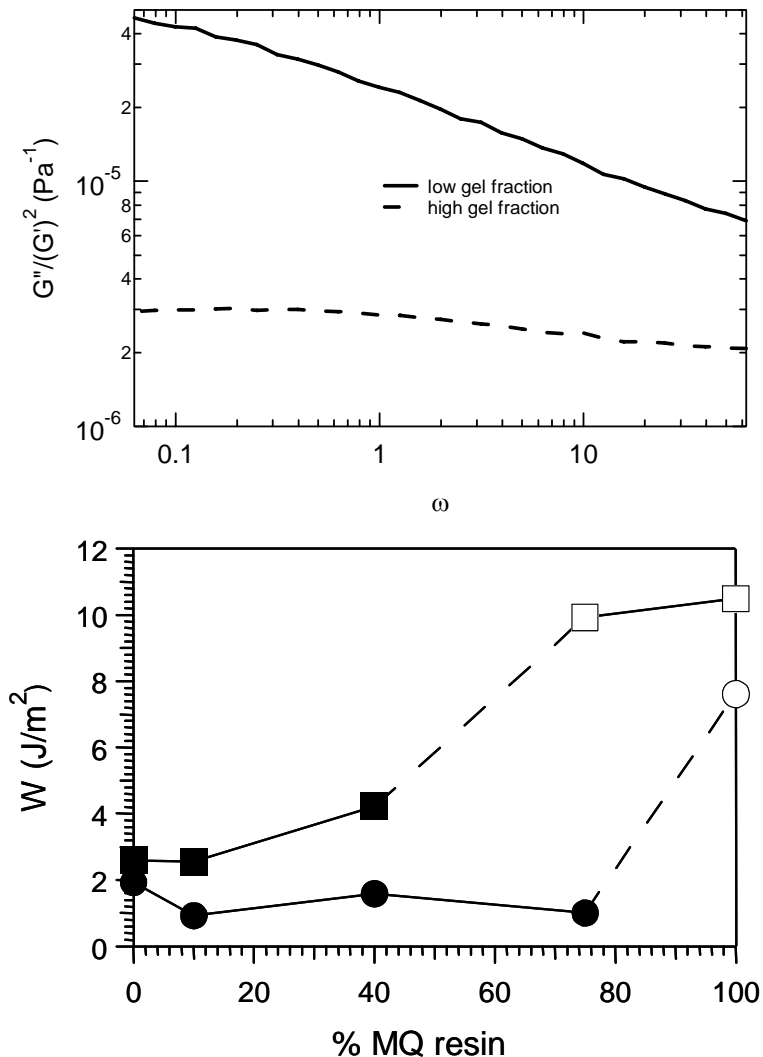


Figure 1: Adhesion energy of two acrylate adhesives on various silicone surfaces as a function of the amount of MQ resin in the silicone. Increasing amounts of MQ resin causes  $G_0$  to increase. Measurements performed by probe tack with a 1  $\mu\text{m/s}$  debonding rate. Square symbols: low gel fraction – Round symbols: high gel fraction; Full symbols :interfacial fracture – empty symbols : cavitation and fibrillation

The implication of these results, which have been found also for other adhesive systems is that a necessary condition for a soft material to be adhesive is the existence of dissipative mechanisms at the molecular level (molecular friction) and a low elastic modulus so that the material can easily be deformed.

### Fracture of hydrogels

How can these concepts be transferred to the fracture of a different type of soft material, i.e. a hydrogel ? Hydrogels are typically much softer in terms of elastic modulus than the soft adhesives ( $E \sim \text{kPa}$  vs. 50-100 kPa) and molecular friction mechanisms are difficult to obtain since most of the material is water with a negligible viscosity. However one expects even for these materials that an increase in dissipative mechanisms should improve adhesive properties and fracture resistance.

Coming back to the results obtained for adhesives, there seem to be two strategies to increase fracture resistance of hydrogels: increase the energy dissipated very close to the crack tip

where the strain levels are very high, or increase the overall viscoelastic dissipation of the material by introducing dissipative mechanisms at the molecular level.

We have investigated both paths and will present data obtained with two different types of hydrogels: an IPN of poly-AMPS/PAA developed by Gong and coworkers[7] initially for low friction purposes, and a hydrophobically modified hydrogel of PAA synthesized in our own laboratory.

For the first system, Gong et al. attribute the extremely high toughness of their gel to the presence of heterogeneities in the primary network or PAMPS, which are filled with a second much softer and dissipative network of PAA[7]. Our rheological experiments on the gel show a very elastic material at all strain rates for low strains but a significant increase in dissipation when the deformation goes beyond 10%. Although more systematic experiments are in progress, this suggests that the gel would have strong nonlinear viscoelasticity similar to what is typically encountered for carbon-black filled rubbers.

For the second system, the structure of the hydrophobically modified hydrogels is the following: a base polymer of polyacrylic acid (PAA) is functionalized in water with 3-5% of C<sub>12</sub> side groups and 10% of double bonds side groups. These double bonds become then reactive sites to chemically crosslink the solution into a gel using dithioerythritol. The dynamic moduli G' and G'' were measured during the gelling process and while the presence of hydrophobic groups changed dramatically the rheological properties of the final gels, it did not perturb the kinetics of reaction and the gels remained fully transparent.

The introduction of 5 mol% of C<sub>12</sub> groups caused G'' to increase by two orders of magnitude while G' remained constant. According to the argument set forth above this introduction of dissipative mechanisms should toughen the material. Indeed preliminary results with compression tests in large strain show unambiguously that the hydrophobically modified polymer is significantly tougher than the fully elastic gel, even at low strain rate, for an equivalent modulus.

## Conclusion

Our results show that adhesion and fracture of soft materials is strongly dependent on having the right balance between the elasticity of the network provided by the chemical or physical strong bonds, and a significant degree of viscoelasticity due to mechanisms providing molecular friction. In soft polymers these mechanisms are usually provided either by an imperfect network with many pendant chains, or by the addition of a high T<sub>g</sub> molecule which increases the molecular friction. In the case of hydrogels, more sophisticated methods to introduce dissipation must be used and we will discuss here two such methods in detail.

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