

PROBE TACK TESTS OF PRESSURE-SENSITIVE-ADHESIVES ON LOW ENERGY SURFACES

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We are interested in the debonding mechanisms of a soft adhesive from low energy surfaces. We show that we can control the adhesion by modifying the composition of the surface. During the debonding on non adhesive surfaces we observed large interfacial cracks which propagate quickly from the border, whereas on more adherent surfaces we observed multiple cavities in the bulk of the adhesive layer which grow slowly and lead to a fibrillar structure.

This study shows that adhesion can be controlled by the debonding mechanism and particularly by the crack velocity. In this case, adhesion is controlled by a dynamic process rather than by a thermodynamic quantity.

INTRODUCTION

Pressure Sensitive Adhesives (PSA) are polymer melts with large molecular weight distributions. They are soft and highly visco-elastic materials (elastic bulk modulus of the order of 0,01MPa). The low energy surfaces studied are silicone elastomers. They have a much higher elastic modulus than adhesives. Experiments were performed with the same adhesive and with silicone surfaces of different compositions. Whereas surface energy measurements show very small variations with the composition of the silicone surfaces, the adhesion energy measured in a tack test is highly sensitive to it. The goal of this study is to investigate the details of the dynamic process controlling adhesion of PSA on silicone low energy surfaces.

EXPERIMENTAL METHODS

During the probe tack tests described in this paper, a flat-ended probe of 1 cm in diameter came into contact at 30 μ m/s with an adhesive film previously deposited on a glass slide. The probe stayed in contact with a pressure of 1Mpa and for 1s contact time. The probe was subsequently withdrawn at a constant velocity of 30 μ m/s. During the test the force and the displacement were recorded as a function of time. A video camera observed from underneath the glass slide the deformation mechanisms of the polymer layer. This custom designed probe tack system was described in more detail elsewhere[1].

The polished steel probe was previously coated (by spin-coating) with a film of end-functionalized PDMS to obtain a film of the order of a few microns. The probe was then put in an oven to activate the crosslinking reaction and to obtain a silicone elastomer film.

The adhesive properties of the silicone release coating were controlled by incorporating into the initial preparation a specific amount of a siloxane based resin which was rather rigid and was able to incorporate itself in the elastomer network.

The adhesive was an acrylic latex. The latex was spread with a doctor blade on a glass slide and after an air-drying step, was dried under vacuum to eventually obtain a 100 μ m thick film.

The raw materials were all provided by the Rhodia corporation.

RESULTS

As shown on figure 1, the adhesion energy of the acrylic adhesive on a silicone release coating without any resin (pure elastomer) was ten times smaller than that on steel. Moreover the stress-strain curves had different shapes for the two cases.

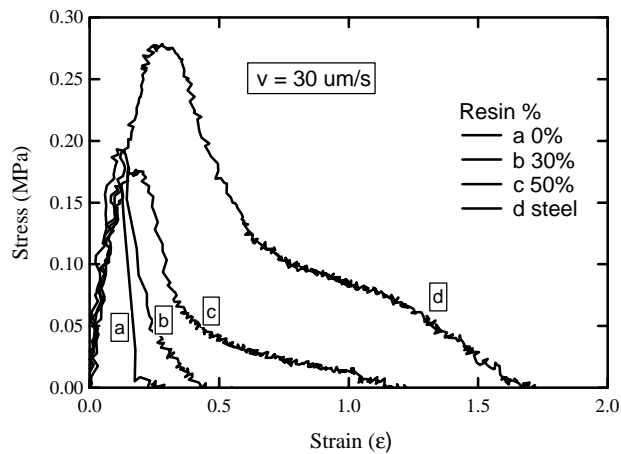


Figure 1 : Stress-strain curves for different silicone coatings.

For the experiments on resin free release coatings the stress dropped sharply to zero after its maximum value and the maximum deformation was very small.

For the experiments on steel the stress became constant forming a plateau after its maximum value. For intermediate compositions the stress decreased less sharply to zero and showed a distinctive shoulder shape which was more pronounced as the resin content increased.

The measured maximum stress was almost constant with resin content, but the maximum deformation increased markedly with % resin.

The final debonding of the acrylic adhesive we used always occurred at the probe/film interface, regardless of the composition of the surface of the probe. As the probe withdraws, the film must sustain a negative hydrostatic pressure and there is a strong driving force to reduce the degree of confinement of the film. In experiments on silicone release coatings (figure 2a), this reduction of confinement occurred through the formation of Saffman-Taylor air fingers coming from the outside of the probe.

These air fingers covered rapidly the entire contact surface, coalesced and no adhesive remained attached to the probe.

The observed instability led to fingers with a shape similar to that of a Saffman-Taylor instability. However, in the Saffman-Taylor instability a less viscous fluid is pouched against a more viscous fluid in a confined geometry. The observed fingers are the result of an instability due to viscosity and surface tension. Here the driving force for the formation of these fingers is essentially elastic: the adhesive can relieve the negative hydrostatic pressure by forming fingers, and the fingers are formed at the interface between the silicone film and the adhesive and not in the bulk of the adhesive layer as previously described by Crosby et al. in a similar adhesive adhering on glass [2].

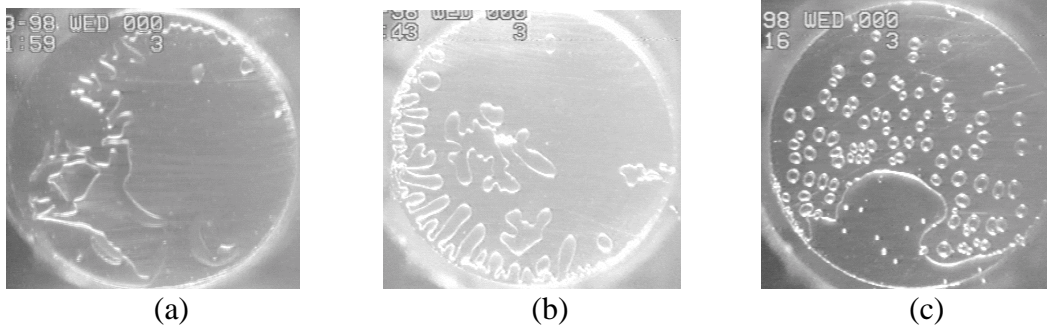


Figure 2 : Video observation (a) silicon resin free coating, (b) 50% resin coating, (c) steel

As the proportion of resin increased the fingers grew less rapidly and some adhesive remained attached to the probe longer before the final debonding occurred. This last stage corresponded to the shoulder in the stress-strain curve.

For experiments carried out on a steel probe (figure 2c), we observed the nucleation of numerous small round cavities (stage A) at the adhesive-probe interface. The cavities grew first mainly in the plane of the film (stage B) until they nearly touched each other but did not coalesce and formed a honeycomb structure. This structure was then elongated vertically (stage C) as observed in a previous study[1]. The walls of the cavities progressively broke and the honeycomb structure evolved progressively towards a fibrillar one. These stages corresponded to the maximum in stress, the decrease after the maximum and the plateau in the stress-strain curve respectively. The formation of stable fibrils led to a large maximum deformation and the energy dissipated in the fibril elongation was a major contribution to the adhesion energy. For coatings with 50% incorporated resin (figure 2b), we observed an intermediate mechanism with cavities and Saffman-Taylor fingers.

Measurements have been performed on the video sequences to classify the various debonding mechanisms and to characterize the dynamics of the debonding. On each picture the total number (N) of cavities and Saffman-Taylor fingers was measured and the total area (A) debonded by the cavities and the Saffman-Taylor fingers was measured during stages A and B of the debonding. We defined the average surface of a structure (finger or cavity) by $A_m=A/N$. On Figure 3 it appears that when the acrylic adhesive debonds from a release coating made of a pure elastomer, there were few large structures growing quickly whereas on coatings made with elastomer + resin there were many smaller structures growing slowly.

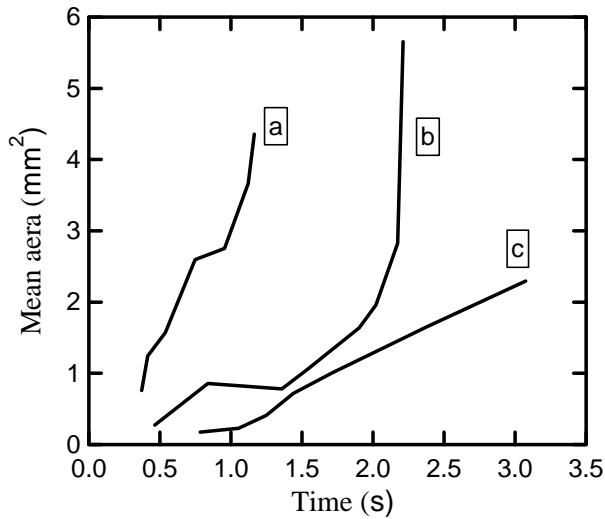


Figure 3 : Mean surface of the structures (cavity or finger) versus time
(a) 0% resin, (b) 50% resin, (c) 100 %resin

If one considers that these debonded structures are interfacial cracks, the average lateral velocity of advance of the edge of one of these cracks can be roughly estimated in the following way: we defined an average length (L) by $L = \sqrt{A_c}/N$ where A_c is the initial contact surface. We measured the time (t_d) for the cavities or Saffman-Taylor fingers to grow and come in close contact with each other (end of stage B). Then the average crack velocity could be defined as $V_m = L/t_d$.

One should note that the crack velocity was much higher than the velocity at which the probe was being withdrawn and was clearly dependent on the type of surface of the probe. This was due to the probe tack test geometry and should be compared to the case of a peel test where the crack velocity is usually the control parameter.

Coating %resin	0	30	50	steel
$V(\mu\text{m/s})$	6200	2800	1100	70

Table 1: Average edge velocity for different coatings (probe velocity $30\mu\text{m/s}$).

It is clear from Table 1 that the crack velocity was much higher on the pure elastomer release coating than on steel. Furthermore in the case of the silicone release coating the crack propagated in a spontaneous manner once initiated, its velocity being limited only by the dissipation occurring during propagation. This was not true on steel where the crack propagated in a controlled way. This suggests a very different energetic cost for the propagation of a crack at a steel and at a silicone interface.

Large digitation patterns are the result of an easy interfacial crack propagation. In fracture mechanics terms this means that the critical energy release rate (G_c) is low. At the opposite end the cavitation of small bubbles results from a difficult crack propagation, and a higher G_c . The following qualitative analysis in terms of competition between crack propagation and cavitation explains this trend [3,4].

When a tensile stress is applied to a thin and soft confined film the elastic energy can be released by a reduction of the confinement. This reduction can occur either by crack propagation (when the energy

release rate G is equal or higher than the critical energy release rate G_c), or by cavitation in the bulk of the adhesive (when the negative hydrostatic pressure reaches the order of magnitude of the elastic modulus) [5].

When the probe is withdrawn and applies a tensile stress, G increases with \mathbf{u}^2 where \mathbf{u} is the displacement of the probe. We follow the G curve on Figure 4 from left to right. For the cases where G_c is low (silicone), the G curve reaches first the value of G_c , whereas when G_c is high (steel) the G curve reaches first the cavitation criterion.

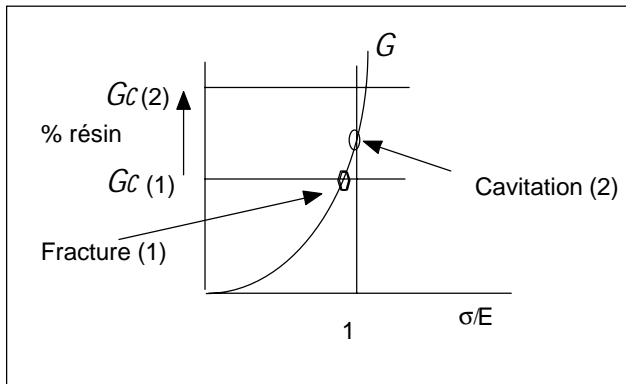


Figure 4 : Analysis of the competition between crack propagation and cavitation

It has been shown by JKR measurements that G_c , for these silicone adhesive interfaces increases with resin content [6]. The prediction is then that silicone coating made of pure elastomer will give large structures whereas coatings made with a high resin content will give cavitation. This in broad agreement with our experimental results.

CONCLUSION

It has been shown that adhesion of an acrylic adhesive on a silicone release coating is largely reduced compared to adhesion on steel. Moreover the debonding mechanisms are different : We observed a rapid propagation of interfacial cracks on silicone release coatings as opposed to small cavities growing slowly on steel. The proportion of resin in the silicone release coating controlled the propagation velocity of the cracks and therefore the maximum deformation of the adhesive before debonding.

As the adhesive film was debonded from the silicone surface deformation, and therefore energy dissipation, mainly took place in the adhesive and should, therefore, be mainly controlled by the rheological properties of the adhesive. Our results showed on the contrary that the adhesion energy was mainly controlled by the interface. This result was explained by the fact that nature of the debonding mechanism was very sensitive to the nature of the interface. On non adhesive surface the cost for crack propagation was low and the adhesive debonded before it reached a high deformation. Whereas on adherent surfaces, the cost for crack propagation was high and led to a high deformation of the polymer before failure. Although the dissipation took place in the adhesive in both cases, the debonding mechanism and then adhesion was mainly controlled by the interface properties in a very similar way to what is observed at interfaces between glassy polymers.

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