

PROBE TACK TESTS OF PSA'S ON SILICONE RELEASE COATINGS

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INTRODUCTION

The first stage of the manufacturing of adhesive labels is normally the coating of the adhesive on a silicone-based release coating which also acts as a protective film for the sticky PSA surface. In the final application, the label must be easily removed from the protective film while maintaining its adhesive properties: i.e. sticking to a surface upon application of a light pressure during a short contact time. The goal of this study is to understand the mechanisms controlling PSA adhesion on release coatings.

The silicon release coating is very thin relative to the adhesive layer and as it is more elastic than the adhesive, the energy dissipation during the debonding mainly takes place in the adhesive. The dissipation is of two kinds : a surface dissipation in the vicinity of the interface due to the separation and a second type of dissipation due to the bulk deformation of the visco-elastic adhesive. It is expected that the surface dissipation is mainly controlled by the nature of the interface, i.e. the composition of the release coating, while the bulk dissipation would be mainly controlled by the visco-elastic response of the adhesive. Given these premises there are three main questions arising :

- How to separate and estimate these two contributions ?
- The entire debonding mechanism, and so also the bulk deformation, is controlled by the interface. How does then the release coating control the debonding mechanism ?
- On a more practical level the properties of the silicone release coating are tuned by introducing a resin siloxane-based resin which is incorporated. Adhesion increases with the amount of resin present in the elastomer. How does the resin act at the molecular level ?

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 The probe was subsequently withdrawn at a constant velocity of 30 μ m/s. During the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 is 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 is then put in a oven to activate the crosslinking reaction and to obtain a silicone elastomer film.

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

The adhesive is an acrylic latex. The latex is spread with a doctor blade on a glass slide and after an air-drying step, is 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) is ten times smaller than that on steel. Moreover the stress-strain curves have different shapes for the two cases.

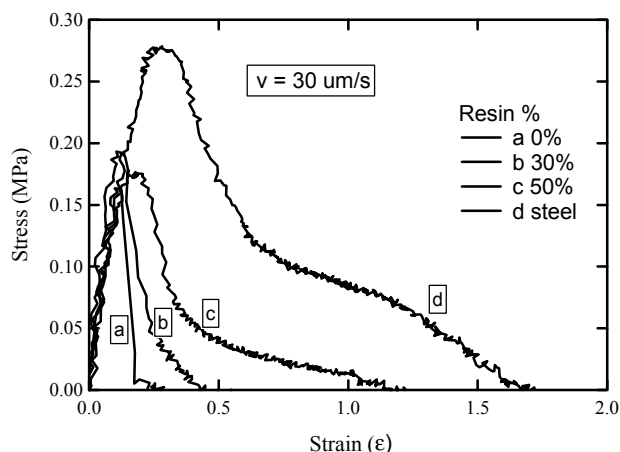


Figure 1 Stress-strain curves for different silicone coatings.

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

For the experiments on steel the stress becomes constant forming a plateau after its maximum value. For intermediate compositions the stress decreases less sharply to zero and shows a distinctive shoulder shape which is more pronounced as the resin content increases.

The measured maximum stress is almost constant with resin content, but the maximum deformation increases 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 coating (figure 2a), this reduction of confinement occurs through the formation of Saffman-Taylor air fingers coming from the outside of the probe. These air fingers cover rapidly the entire contact surface, coalesce and no adhesive remains attached to the probe. The observed instability leading to the fingers shape is similar to a Saffman-Taylor instability. In the Saffman-Taylor instability a less viscous fluid is pushed against a more viscous fluid in a confined geometry. Here the more viscous fluid, the adhesive, is submitted to a negative hydrostatic pressure.

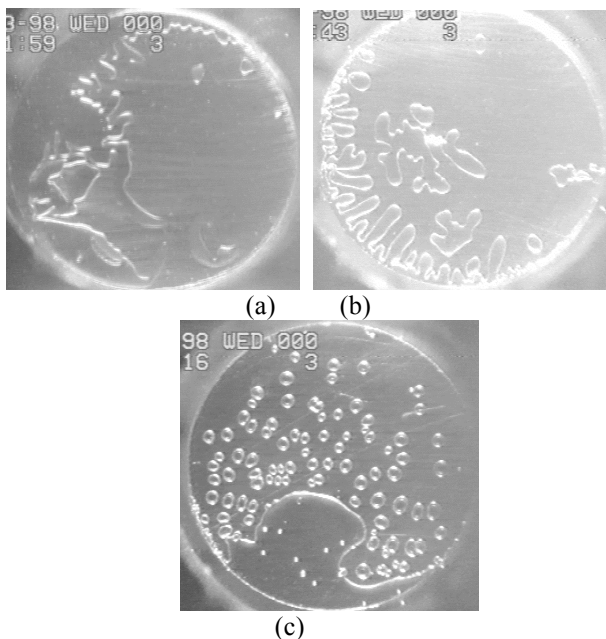


Figure 2 : Video observation (a) silicon resin free coating, (b) 50% resin coating, (c) pure resin coating

As the proportion of resin increases the fingers grow less rapidly and some adhesive remains attached to the probe longer before the final debonding occur. This last stage corresponds to the shoulder in the stress-strain curve.

For experiments carried on a steel probe (figure 2c) or on a probe coated with a silicone film crosslinked with pure resin, 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 corresponds to the maximum in stress, the decrease after the maximum and the plateau in the stress-strain curve respectively. The formation of stable fibrils leads to a large maximum deformation and the energy dissipated in the fibril elongation is 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 $A_m = A/N$.

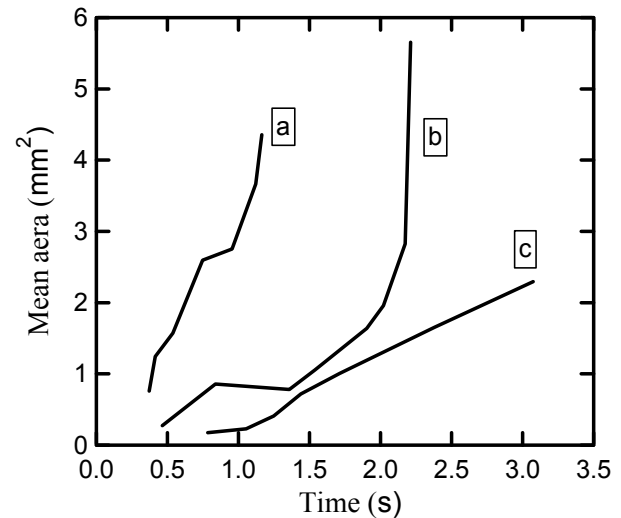


Figure 3 : Mean surface of the structures (cavity or finger) versus time (a) 0% resin, (b) 50% resin, (c) 100 %resin

On Figure 3 it appears that when the acrylic adhesive debonds from a release coating made of a pure elastomer, there are few large structures growing quickly whereas on coatings made with elastomer + resin there are many smaller structures growing slowly.

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 reach each other (end of stage B). Then the average crack velocity can be defined as $V_m = L/t_d$.

One should note that the crack velocity is much higher than the velocity at which the probe is being withdrawn and is clearly dependent on the type of surface of the probe. This is 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 is much higher on the pure elastomer release coating than on steel. Furthermore in the case of the silicone release coating the crack propagates in a spontaneous manner once it has been initiated, its velocity being limited only by the dissipation occurring during propagation. This is not true on steel where the crack propagates 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.

Digitation patterns of large size 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 [2].

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) [4].

When the probe is withdrawn and applies a tensile stress, G increases with u^2 where 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.

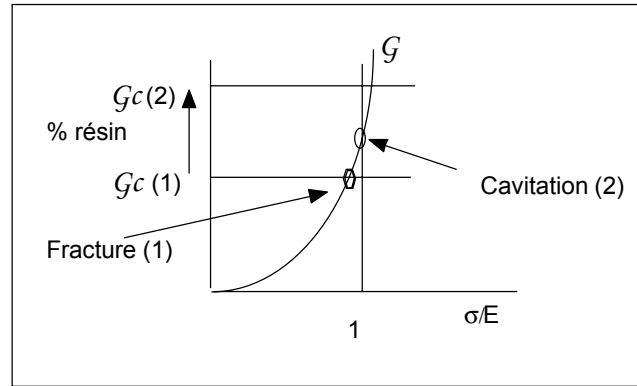


Figure 4: Analysis of the competition between crack propagation and cavitation

It has been shown by JKR measurements that G_c for these silicone adhesive interfaces increases with resin content[3]. 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 agreement with the 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 controls the propagation velocity of the cracks and therefore the maximum deformation of the adhesive before debonding.

We are grateful to Rhodia Recherches for financial support. We thank Mr M. Dorget and Mr P. Peccoux for their collaboration.

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