Measurement of the receding contact angle at the interface between a viscoelastic material and a rigid surface

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We present the first quantitative measurement of the receding contact angle between a soft viscoelastic material and a solid surface during the debonding of the material. We developed a new method of observation, based on the technique pioneered by Yamaguchi et al. (T. Yamaguchi, K. Koike, and M. Doi, Euro. Phys. Lett., 2007, 77, 64002). In a probe-tack geometry, we obtained a 3D-like view of the debonding pattern as seen through the adhesive/probe interface, providing thus an excellent view of the details of the contact geometry near the interface. Combining visual and force-displacement information in a probe tack test, we identified three different categories of mechanisms and contact geometries as a function of the material parameters. For very weakly crosslinked viscoelastic materials around the gel point, air fingers form in the bulk of the layer. For higher degrees of crosslinking, the air fingers form and propagate at the interface, with a large deformation of the bulk of the layer. A well defined and reproducible receding contact angle \( \varphi < 90^\circ \) depending on the viscoelastic properties of the layer was observed at the leading edge of the moving finger. Finally for well crosslinked samples the failure occurs by interfacial crack propagation with little deformation of the layer; the contact angle at the leading edge then was close to \( 90^\circ \) as expected from elastic fracture mechanics.

1 Introduction

The debonding of thin layers of viscoelastic materials occurs in a large number of situations, such as food processing or applications involving pressure sensitive adhesives. When debonding such a thin layer from a substrate, different debonding mechanisms are observed as a function of the viscoelastic properties.

Many researchers have highlighted the importance of viscoelastic properties on the adhesive behavior in general, and more specifically on the frequency dependence of sharp transitions in mechanisms from cohesive to interfacial failure or from fibrillar deformation to failure by crack propagation. Most of the results obtained in these studies have been reviewed both from the mechanistic point of view or from the point of view of relating the rheology with adhesive behavior.

One of the outstanding problems in the full description of the debonding mechanism is the treatment of the boundary condition at the interface between the viscoelastic materials and a hard surface. In particular the geometry of the triple line formed when a crack propagates at a hard/soft interface is of great interest.

The early work in solid mechanics on crack propagation in viscoelastic materials has been followed by the insights of de Gennes and coworkers on the modeling of a propagating viscoelastic crack in the bulk or at the interface and by more sophisticated models of interfacial crack propagation. All these models use small strain linear theories which do not consider a deviation from the contact angle \( \varphi = 90^\circ \) and thus no changes in the geometry of the contact line.

However, some experimental observations of the debonding of soft adhesives strongly suggest that the contact line (in peel and in probe tack experiments) can depart from 90° if the adhesion is strong. Several groups led by Chaudhury showed that the molecular mobility of the surface, and in particular its resistance to slip, are extremely important in controlling the energy dissipated in the adhesive layer during debonding. Rather than using the classical thermodynamic description of interfacial interactions based on the Young–Dupré equation, they defined the interface as slippery or sticky depending on whether it can or cannot sustain shear stresses. The reasoning proposed initially by Newby et al. goes as follows: if the interface is slippery the soft adhesive layer is much less sheared and the overall debonding process is less dissipative. On the other hand, if the interface can sustain shear stresses, the adhesive layer can be deformed significantly before the interfacial stresses are high enough for the contact line to move.

The coupling between the level of adhesion and the shape of the contact line has been also investigated recently by Krishnan and Hui. Using a non-linear elastic large strain formalism they demonstrated that a change from a full slip (non adhesion) to a full friction (perfect adhesion) boundary condition at the interface can change completely the contact angle and hence the elastic stress fields which in turn modify the driving force for crack advancement. These examples illustrate clearly the crucial role of the contact angle for problems in adhesion and...
debonding. Because of technical difficulties however, it has never been directly measured in a well controlled way. In contrary, contact angles of simple liquids can be measured relatively easy in wetting experiments from a drop. The interesting contact angle in viscoelastic solids depends on the stress field more than on surface energetics and it is therefore of the utmost importance to control the geometry at the boundaries. Furthermore it is the receding contact angle which is of practical importance and this imposes a confined geometry where a side view (as in a sessile drop) is not easy to achieve.

In this paper we studied the detailed geometry of the debonding mechanisms of a simple model system in a probe tack geometry. Our model system is Dow Corning’s Sylgard 184, a two component curing PDMS elastomer available commercially and widely used in its fully crosslinked state for microfluidic applications. By modifying the respective ratios of the components, it was possible to work with thin films ranging from a purely viscous Newtonian fluid to a soft elastic solid. Contrary to most of the previous work in this area we do not simply describe the global aspect of the complex mechanisms but focus more specifically on the boundary condition at the adhesive/substrate interface.

Experiments were carried out with a custom designed setup based on the contact of a rigid cylindrical probe with a soft thin viscoelastic film attached solidly to a rigid substrate. In this geometry the adhesive film is essentially confined between two stiff parallel plates moving apart from each other at a constant velocity. Because of the method of sample preparation, one of the interfaces (the probe) is weaker than the other and becomes the locus of the debonding. For each test, the force-displacement curves were acquired simultaneously with images of the debonding mechanisms. The originality of our approach lies in the simultaneous use of two cameras, a classical top view and a novel 3D visualization technique inspired by the method developed by Yamaguchi et al. Using a prism, they obtained striking images of the cavity growth in acrylic adhesives at a 45° angle giving a 3D impression. Their setup looked through the substrate/adhesive interface, so that the probe/adhesive interface was not directly visible. In the setup described in this paper however, we look through a glass probe and observe directly the probe/adhesive interface. In such a way, we observe for the first time the exact shape and contact angle of advancing air fingers during debonding.

This article is organized as follows: In section 2, we describe our model system, the sample characterization, and the experimental set up. In section 3, we first present qualitative observations using 3D images. We then combine the visual observations with the measured force displacement curves to gain precise information on the different debonding mechanisms. We then present quantitative measurements of the receding contact angle as a function of the viscoelastic properties. Section 4 concludes our results.

2 Materials and methods

2.1 Sample preparation

To prepare the viscoelastic adhesive layers, we used a commercially available poly(dimethylsiloxane) (PDMS) based product, the “Sylgard® 184 Silicone Elastomer Kit” purchased from Dow Corning. It is composed of a viscous silicone oil (shear viscosity \( \eta = 5.1 \text{ Pa s} \)) and of a curing agent. This type of two component system is typically composed of a polydisperse low molecular weight PDMS oil, functionalized with vinyl groups, and a crosslinking agent containing Si–H functions. The reaction requires temperature and the presence of a platinum catalyst. Using an under stoichiometric ratio of crosslinker we obtained chemically stable networks with different degrees of crosslinking.

The ratio of added curing agent is calculated with respect to the total mass as

\[
r = \frac{m[\text{curing agent}]}{m[\text{curing agent}] + m[\text{silicone oil}]}.
\]

A mixing ratio of one part crosslinker to ten parts base corresponds to the fully cured material as defined by the manufacturer. It should be noted that this amount does probably not correspond to a true stoichiometric ratio since this type of silicone systems typically requires an excess of crosslinker. The glass transition temperature of PDMS lies well below room temperature, \( T_g \approx -120 \degree \text{C} \).

PDMS with different \( r \) were prepared as described in detail elsewhere. Polymeric films were then deposited on standard microscopic glass slides using quadruple film applicators by Erichsen with gaps of different thicknesses. The resulting samples are rectangular films (\( w \times l \approx 1.5 \times 7 \text{ cm}^2 \)). The samples were cured in a desiccator at 80 \degree \text{C} for five hours under vacuum. The cured PDMS film was thus strongly adsorbed to the glass slides. We calculated the mean thickness of the PDMS layers from their weight and size. This method was validated by comparing the results with an optical technique using interference fringes. The samples we use here had a thickness of \( b \approx 370–540 \mu \text{m} \).

2.2 Sample characterization

The linear rheological properties of the different materials were determined as follows. Each material was directly crosslinked in a TA ARES rheometer for four hours at 80 \degree \text{C}. After cooling down to 25 \degree \text{C}, oscillatory frequency sweep tests were carried out in a plate–plate geometry with a plate diameter of 25 mm at a deformation of 10%. The storage modulus \( G' \), the loss modulus \( G'' \), and their ratio \( \tan \delta = \frac{G''}{G'} \) were obtained as a function of the oscillation frequency \( \omega \). Results are shown for some selected materials with different degrees of crosslinking in Fig. 1 and 2.

![Fig. 1](image-url) Storage and loss moduli \( G' \) (full symbols) and \( G'' \) (open symbols) as a function of frequency \( \omega \). From ref. 30.
respectively. At \( r = 0.11 \), the material is at the gel point, and \( G' \) and \( G'' \) are parallel over a wide range of frequencies. At \( r = 0.16 \), \( G' \) and \( G'' \) are of the same order of magnitude, but the storage modulus dominates at low frequencies. Adding more crosslinker, both moduli increase, and the storage modulus dominates in a larger range of frequencies. At \( r = 0.3 \), the elastic modulus is virtually independent of the frequency. In general, the material properties depend on the frequency and thus on the shear rate for all materials. To summarize, the PDMS precursor behaves as a Newtonian oil in its non crosslinked state. Adding more and more curing agent increases the number density of crosslink points and introduces viscoelasticity. With increasing crosslinker content, the viscoelastic fluid stops flowing since the network percolates. Further addition of crosslinker leads then to an increase in the elastic modulus and at the same time to a decrease in the relative importance of the dissipation.

2.3 Set up

The debonding tests were carried out with a modified probe tester fitted on a tensile machine (MTS 810) described in detail elsewhere. The basic principles of the probe test have been developed by Zosel et al., the interpretation of the force-displacement curves has been reviewed by Shull and Creton. Our setup mainly consists of a glass disk that can be brought into contact and debonded from a tacky adhesive sample with thickness \( b \) at a controlled speed \( v \). During the test, the probe displacement and the normal force on the probe are measured. Each experiment can thus be characterized by a typical force-displacement curve. Typical debonding speeds in our experiments lay between 10 \( \mu m \) s\(^{-1} \) and 100 \( \mu m \) s\(^{-1} \). Top view observation with a camera via a mirror in a 45\(^{\circ}\) configuration provides the contact area and qualitative information on the in-plane projected image.

During debonding, different kinds of patterns can emerge. Unlike other studies, we observed cavity growth nucleating inside the contact area only occasionally due to the combination of a low adhesion, low applied debonding rates, and the small elastic moduli of our materials. However, we observed a strong fingering instability from the edge of the contact in all our experiments. The wavelength dependence of the fingering patterns on the material parameters was the focus of a previous study and will not be discussed in the present paper.

Top-view images can of course only provide in-plane projections of the deformation patterns occurring during the debonding process. To obtain information from the \( z \)-direction, along the thickness of the layer, we modified the setup of the tensile machine following Yamaguchi’s guidelines. We developed a new prototype specifically designed to acquire 3D-like images of the debonding mechanisms. Fig. 3 gives a schematic view of the setup and of the optical observation path. A glass disk with diameter \( D = 10 \) mm and thickness \( h = 1 \) mm is glued onto a glass prism with dimensions 10 mm \( \times \) 15 mm \( \times \) 74.7 mm. The prism is tapered at an angle of 25\(^{\circ}\). The small glass disc replaces the usual steel probe and comes in contact with the viscoelastic layer. The illumination is realized via an optical fibre that is placed in such way that the light is directed into the prism. The probe surface is observed through the prism and the disk itself. As the contact is established and the probe is lifted away from the interface, the camera shows a view of the patterns as if the plane of view was rotated by an angle \( \theta \) from the normal, giving the impression of a 3D view. Knowing the exact geometry it is then possible to make measurements in the \( z \)-direction.

3 Results

3.1 3D visualization

Fig. 4 and 5 show snapshots of interfacial and bulk fingering as taken in the modified 3D configuration. On Fig. 4, one sees the formation of interfacial air fingers in the case of well cured PDMS with predominantly elastic properties (here \( r = 0.2 \)). These fingers resemble cracks and cause very little out of plane deformation of the layer. The darker color corresponds to direct air–probe contact, meaning that the debonding happens really at
the interface between PDMS layer and probe. Fig. 5 shows an experiment with a very weakly crosslinked PDMS, here $r = 0.11$. No dark area, and hence no direct air–probe contact is observed. The fingers are thus formed in the bulk of the layer. The qualitative difference between the bulk and interfacial mechanism is immediately clear from these pictures shown at the same scale.

3.2 Debonding mechanisms

Although the debonding mechanisms of adhesives in a probe test in general have been described previously,12,26,30,38 it is useful to review the mechanisms here and take advantage of the additional information brought by the prism view of the patterns.

The stress–strain curves are shown in the top row of Fig. 6. The stress $\sigma$ is the force divided by the maximum contact area $A_0$, which can be easily measured from the top view images. The nominal stress with respect to $A_0$. The strain $\varepsilon$ is the probe displacement $d$ divided by the initial film thickness $b$. We study a few selected materials which are representative for each type of behavior.

Combining the shape of the stress–strain curves and the visual observation of the debonding process, it is possible to differentiate three different types of debonding mechanisms. First, the debonding can be cohesive, involving the formation of fibrils between probe and viscoelastic layer which, at the end of the process, break up in the middle. Residues of the polymeric film can be found on the probe surface after the test. This mechanism corresponds to the stress–strain curve $r = 0.11$ [Fig. 6(c)]. Second, the debonding can involve a large bulk deformation with formation of fibrils, but the fibrils will eventually detach and no residues are left on the probe surface (adhesive debonding) as for $r = 0.16$ [Fig. 6(b)]. We call this mechanism adhesive-bulk. Third, we observe adhesive debonding involving a maximum deformation smaller than 100% ($\epsilon_{\text{max}} < 1$) and interfacial fracture propagation between the adhesive and the probe as for $r \geq 0.3$ [Fig. 6(a)]. This mechanism is called adhesive interfacial.

The question of whether the mechanism is adhesive-bulk or adhesive-interfacial depends on the interplay of material parameters and surface characteristics. The initiation of the debonding has been studied in ref. 30. The two controlling factors are on the one hand the energy it costs to deform the material in the bulk and on the other hand the energy it costs to propagate an interfacial crack.5,13,41 When the probe is moved away, the volume between the probe and the glass slide is increased. As the adhesive can be considered as a nearly incompressible material, the increase in volume can be realized via a material flow (or deformation) from outside the contact patch, a debonding of the adhesive from the probe surface, or via the creation of air or vacuum pockets in the bulk of the adhesive, as cavities or lateral air fingers. If it is costly to deform the bulk, the system debonds at the interface; conversely if the resistance to crack propagation is too high, the bulk is deformed and fibrils are formed. A stretched fibril can, at the end of the debonding process, detach from the probe or break up in the middle. If the material strain-hardens in tension, then the fibrils can detach from the probe.17,22 On the other hand, if the material starts to flow, the force decreases continuously, and the fibril gets thinner until it breaks up triggered by the Rayleigh plateau-instability.34,38

3.3 Shape of the contact line

The most interesting information that can be extracted from the 3D-like images is the geometry of the contact line. As discussed in the introduction, this is a dynamic and not trivial measurement for a viscoelastic material in a confined geometry. In order to extract quantitative information from the 3D images, a precise synchronization between the top view, the 3D view, and the mechanical measurements is required. In the graphs presented in the first row of Fig. 6, a vertical line indicates the strain value $\varepsilon'$ for the particular moment at which the images shown below (for each respective column) were taken. The strain level determines the distance between probe and glass plate and therefore the average thickness of the stretched sample at the moment of the analysis. Having the top view images (second row, Fig. 6) as reference and finding the angle of reflection in the prism $\theta$ (see Fig. 3), it is possible to calculate the thickness and the contact angle $\phi$ of the five fingers numbered in the three 3D images (third row of Fig. 6).

The first step in the quantitative analysis is to fit a circle to the image of the probe in the top view [Fig. 7(a)]. The diameter of the probe is known to be $D = 10$ mm and serves to calibrate the length scale. The center of the circle and two diametral lines perpendicular to each other, and parallel to the borders of the 3D image, are carefully mapped into the corresponding 3D image [Fig. 7(b)]. By this mapping, the center of the probe and its radius $R$ (one half of the horizontal line in the figure) are found in the 3D image. A circle with diameter $D = 2R$ is centered at the center of the probe; a rotation of the circle around the horizontal line transforms its projection into an ellipse. For a particular angle of rotation $\theta$, the ellipse fits best the border of the probe on the 3D image. $\theta$ is defined as the angle relative to the normal to the viscoelastic layer (see Fig. 3).

The part of the polymeric sample between the probe and the glass slide can be described as a cylinder of diameter $D$ and height $h' = h(1 + \varepsilon')$. $h$ is the initial thickness of the sample. Knowing that the pictures are recorded from an angle $\theta$, it is possible to locate all the points in the system. The top view pictures offer additional references. Distances along the radius can be measured as a fraction of it and vertical distances are reduced by

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$A_0$ can be smaller than the probe surface area since the polymeric films are not perfectly flat and there could be slight misalignment. The contact is however almost 100% of the surface of the probe in our tests.
a factor sin θ. A straight line is drawn along the surface of the finger tip, from the point where the tip of the finger touches the probe surface, and following the direction of the finger tip until the point where the surface curves in the vertical direction [Fig. 7(b)]. The projections of this line in the radial direction d₁ and in the vertical direction d₂ form a rectangular triangle. d₃ measures the height of the curved zone at the finger tip. In the rectangular triangle presented in Fig. 7(b) the contact angle adjacent to the probe surface is \( \varphi = \arctan\left(\frac{C₂}{C₁}\right) \), where \( C₁ = \frac{d₁}{r} \) and \( C₂ = \frac{d₂ \sin \theta}{R} \). The thickness of the finger is given by \( H = h \sin \theta / R \), where \( h = d₂ + d₃ \). The distances are measured in
Table 1  Different measures from Fig. 6. Quantities are defined in the text

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<th>$\theta$</th>
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<td>65</td>
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<td>II</td>
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<td>563</td>
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<td>420</td>
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<td>IV</td>
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<td>V</td>
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pixels, resulting in dimensionless values of $C_1$, $C_2$ and $H$ that are fractions of the known radius of the probe $D/2$.

Table 1 summarizes each of the five numbered fingers of Fig. 6, the values of the angle at which the 3D image was recorded $\theta$ ($^\circ$), the thickness of the finger $H$ ($\mu$m), the contact angle between viscoelastic layer and probe $\varphi$ ($^\circ$), the initial thickness of the sample $b$ ($\mu$m), the strain at the moment of the measurement $\epsilon'$, and the thickness of the sample at the moment of the measurement $b'$ ($\mu$m).

The estimated error in the measurement of $\theta$ corresponds to 2$. The errors in the measurement of the linear distances are given by the resolution of the images, but are to a major degree due to the nature of the surfaces. The interface between air and the viscoelastic material is curved in all directions, making it difficult to fit straight lines. Furthermore, reflections of the light at these interfaces make it difficult to locate them precisely. The agreement between independent radial measurements in the top view [Fig. 7(a)] and in the 3D image [Fig. 7(b)] corroborate the quality of the analysis.

In the following, we discuss each type of debonding mechanism in more detail.

$r = 0.3$. From the sharp edge of the 3D image in Fig. 6(g) we can estimate a right angle between the air finger and the probe in the case of a well cured PDMS. The symbol (*) accompanying the value of 90$^\circ$ in Table 1 indicates that this value is an estimate. A precise measurement was not possible since the air finger was too thin (40 $\mu$m) compared to the magnification of the image. Note also that the thickness of the finger is very small relative to the thickness of the layer (500 $\mu$m), in agreement with an interfacial debonding mechanism. The fact that the debonding here occurs at the interface between the probe and the PDMS layer is also clearly visible from the color difference between direct air-probe contact (dark area) and PDMS-probe contact (greyish area). The failure here was fully adhesive.

$r = 0.11$. In contrast to the previous case, we observed no contact between the air finger and the glass probe for the material at the gel point, see Fig. 6(i). The absence of the darker area (direct air-probe contact) indicates that the air fingers are completely formed in the bulk of the PDMS sample and that a thin layer of PDMS remains on the probe during the complete debonding. This can be compared to the case of complete wetting. A triple line between air, viscoelastic material, and glass probe does not exist. The failure in this case was cohesive.

$r = 0.16$. The intermediate case exhibited a more complex finger shape, see Fig. 6(h). In the very beginning, the debonding takes place in the bulk. Subsequently, the dark air–probe contact area became clearly visible at the probe’s border. At the tip however, the air fingers were still clearly in the bulk (tip blunting). Later, complete detachment from the borders of the probe led to adhesive debonding. The thickness of the fingers seems to gently increase when they penetrate further into the sample (visible for example in the fact that $H(\text{II}) > H(\text{III})$). However, the contact angle remains more or less constant around 30$^\circ$. Note that the error bars here are mainly due to the difficulties in differentiating between $d_2$ and $d_3$ in Fig. 7(b). Here the air finger occupies more than half the thickness of the layer. This result reinforces the explanation for the formation of the fingers we introduced in the previous paragraph as well as the schematics displayed in Fig. 6(k).

4 Conclusion

In conclusion, we presented in this article the first direct visualization of the contact area between a soft viscoelastic layer (PDMS) and a hard glass probe during debonding tests in confined conditions. We were thus able to measure for the first time directly the receding contact angle at the triple line between viscoelastic material, glass probe, and air. Our visualization setup yields at the same time force-displacement curves and visual information, top-view images and a 3D-like view of the contact area. Combining these complementary data sets we obtained detailed information on the debonding process, not accessible so far.

We showed that the contact angle during debonding depends strongly on the properties of the viscoelastic material. For a well crosslinked material, a purely interfacial debonding mechanism with a contact angle close to 90$^\circ$ was observed. For viscoelastic solids, we observed an interfacial crack with pronounced tip blunting and a contact angle that became distinctly smaller than 90$^\circ$. Finally, a pure bulk mechanism with cohesive debonding was observed for very weakly crosslinked networks. In this case there is no contact between the air and the glass probe and a triple line between air, viscoelastic material, and glass probe does not exist.

We confirmed thus that the contact angle during debonding of a viscoelastic material can significantly differ from 90$^\circ$ as suggested by a number of authors[25,33] but never directly visualized from the probe side so far. The knowledge of the boundary conditions between the viscoelastic material and the solid substrate is a necessary ingredient for a correct modeling of the debonding process. Our new visualization technique provides the means for measuring receding contact angles also for other classes of viscoelastic materials and adhesives. It will thus facilitate the prediction and modeling of adhesive properties, as for example the adhesion energy, for these materials.

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References
