The macroscopic delamination of thin films from elastic substrates

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The macroscopic delamination of thin films from elastic substrates

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The wrinkling and delamination of stiff thin films adhered to a polymer substrate have important applications in “flexible electronics.” The resulting periodic structures, when used for circuitry, have remarkable mechanical properties because stretching or twisting of the substrate is mostly accommodated through bending of the film, which minimizes fatigue or fracture. To date, applications in this context have used substrate patterning to create an anisotropic substrate-film adhesion energy, thereby producing a controlled array of delamination “blisters.” However, even in the absence of such patterning, blisters appear spontaneously, with a characteristic size. Here, we perform well-controlled experiments at macroscopic scales to study what sets the dimensions of these blisters in terms of the material properties and explain our results by using a combination of scaling and analytical methods. Besides pointing to a method for determining the interfacial toughness, our analysis suggests a number of design guidelines for the thin films used in flexible electronic applications. Crucially, we show that, to avoid the possibility that delamination may cause fatigue damage, the thin film thickness must be greater than a critical value, which we determine.

adhesion | elasticity | stretchable electronics | blistering | buckling

Thin films are adhered to substrates in a range of technological applications either to enhance the mechanical properties of bulk materials or to give the surface novel properties (1). Traditionally, the buckling and delamination of these thin coatings have been viewed as an inconvenience with research focusing on how they might be avoided. More recently, however, both the wrinkling and delamination of such films under compression have been exploited in the development of “flexible electronic” devices (2–7). The goal for these systems is to develop electronic circuits on flexible circuit boards ultimately leading to the manufacture of, among other things, flexible displays and electronic paper (8–10). A major technological challenge limiting the development of such devices is the requirement that the substrate be able to flex without stretching and damaging the wires that make up the circuit. One way to overcome this challenge is to use a polymer substrate that is first stretched and then coated with wires according to the required pattern. On releasing the strain in the substrate, the wires are relatively stiff in compression and so buckle out of the plane to accommodate the imposed deformation. This leads first to a well-studied wrinkling instability (7, 11) and subsequently to the formation of delamination “blisters” (12): localized regions where the film and substrate are no longer bonded. Once formed, these blisters facilitate the flexion of the substrate because the wires can accommodate deformation by bending rather than stretching.

Here, we focus on the features of delamination by characterizing the relationship between the blisters’ size and the material properties and their evolution. This complements the many earlier studies, which only considered the wavelength of the wrinkling instability observed prior to delamination (11, 13, 14) and the appearance of localized structures without delamination (15). Practical applications of delamination are typically found at a microscopic scale, as for circuitry in flexible electronics (3) mentioned above. However, one unique aspect of our work is that we perform well-controlled experiments at a larger (macroscopic) scale. This enables us to readily vary and control the material properties of the system over a wider range than would have been possible at a microscopic scale. The underlying physics may nevertheless be equally applied at microscopic scales. In our experiments, a thin Bi-oriented Polypolyene film (with thicknesses \( h \) in the range 15 \( \leq h \leq 90 \mu m \)) is adhered by van der Waal’s forces to a soft polymeric substrate (Vinylpolysiloxane). We use both thin substrates (which are stretched prior to adhesion) and deep substrates (which are unstretched). Relative to this initial state, the substrate is then uniaxially compressed in a linear stage. For the adhered thin film, however, compression is energetically expensive compared with bending. Therefore, above a critical value of substrate compression the thin film wrinkles with a well-defined wavelength (7, 11). Under further compression wrinkling becomes unstable: the thin film locally debonds and buckles further out of plane.

Results

We observe that delamination occurs first with the appearance of a single blister. On further compression, a series of approximately identical blisters appear sequentially. The size of these blisters is typically much larger than the wavelength of the wrinkling instability that precedes it. A representative photograph of such an array of delamination blisters generated in our apparatus is shown in Fig. 1A. More details of the experimental procedure are given in Materials and Methods.

Our investigation is twofold because we focus on understanding both the characteristic dimensions of the first blister at the onset of delamination and the evolution of multiple blisters between delamination events. Consequently, we performed two different types of experiments. First, we measured the width of the first blister at onset \( \lambda \), as a function of the material properties of the system. Second, we measured (using an inclined laser sheet) the evolution of the height profile of the blisters as the compression is increased beyond onset. A schematic diagram of this arrangement is presented in Fig. 1B. Representative (plan view) photographs before and after the onset of delamination for a 90-\( \mu \)m-thick strip are shown in Fig. 1C. From these images, we extract the height profile of the strip, a typical example of which is shown in Fig. 1D. This profile is well approximated by a cosine form,

\[
y = d(x) \equiv \frac{\delta}{2} \left[ 1 + \cos \frac{2\pi x}{\lambda} \right],
\]

where \( \delta \) and \( \lambda \) are the height and width of the blister, respectively. The form in Eq. 1 is expected for the buckling of an Euler column for small deformations (16, 17). This allows for \( \delta \) and \( \lambda \) to be readily determined by fitting of the experimental profiles.
Our analysis is presented in terms of the end-to-end displacement $\Delta L = L_o - L_i$, where $L_o$ is the total uncompressed length of the flat strip and $L_i$ is the distance from the left to the right edge of the strip once compression is applied (see Fig. 1C). In our experiment, the total end-to-end displacement of the substrate is controlled, not $\Delta L$ itself. However, we treat $\Delta L$ as an imposed control parameter, which is measurable directly in experiments. To illustrate the evolution of blister dimensions as $\Delta L$ increases, Fig. 1E shows the dependence of the height of the blister $\delta$ on $\Delta L$. Under compression of the substrate, the sheet initially remains approximately flat up to a point where both $\delta$ and $\Delta L$ change sharply. This discontinuous jump corresponds to the delamination of the strip from the substrate; a blister forms. On increasing the compression $\Delta L$ further, the height of the blister also increases. When the compression $\Delta L$ is subsequently decreased, $\delta$ decreases smoothly following the previous path. However, the blister persists beyond the compression at which it first appeared, disappearing only once $\Delta L \approx 0$. In what follows we do not discuss this hysteretic behavior but believe that it would be of interest to study this further in future work. Henceforth, we will focus on the onset and evolution of blisters under compression only.

An alternative way to represent the evolution of the blister profile is to construct a space-compression diagram in which the strip height profiles $d(x)$ of the center line of the strip are stacked as a function of $\Delta L$. Two representative examples of such diagrams are given in Fig. 2A and B for sheets of thickness $h = 90 \mu m$ and $h = 30 \mu m$, respectively. In these diagrams, the color represents the height at each point $x$ along the center line of the strip for a given value of $\Delta L$. In Fig. 2A the value of $\Delta L$ at
two relevant limiting regimes: (a) large blisters (appearance and evolution of multiple blisters with stiffness developed a scaling law for the size of the thin film and substrate deformation occurs (schematic presented in Figures 3A and B, respectively) scales as the area \( \lambda^2 \), multiplied either by (a) the thickness of the substrate \( t \) or (b) the width of the strip, \( w \). The substrate energy density in each case is \( U_e = \frac{E_e}{2} \epsilon^2 \) so that the energy is \( U_e = \alpha E_e \epsilon^2 \lambda^2 \) with \( \alpha \sim t \) for large blisters and \( \alpha \sim w \) for small blisters. The total elastic energy for \( n \) identical blisters is therefore given by

\[
U = n \left( \frac{\pi^4 B^3}{\lambda^3} + \alpha E_e \epsilon^2 \lambda^2 \right),
\]

where the unknown parameters are the number of blisters \( n \), their width \( \lambda \), height \( \delta \), and the strain \( \epsilon \) accommodated by each of them. Using the blister profile given in Eq. 1, we obtain the geometrical relationship

\[
\frac{\Delta L}{n} = \frac{\pi^2 \delta^2}{4 \lambda},
\]

which may be used to eliminate \( \delta \) from Eq. 2 in favor of \( \Delta L \). Also, the strain accommodated by each blister is \( \epsilon = \Delta L / n \lambda \). Because \( \Delta L \) is treated as a control parameter, the two unknowns are then the blister width \( \lambda \) and the number of blisters \( n \). If we require that the energy release rate \( \Delta L \) is increasing in our (displacement-controlled) experiments, blistering first manifests itself with \( n = 1 \). Furthermore, this finite value of \( \Delta L \) at onset explains the jump in \( \Delta L \) observed at delamination (see Figs. 1E and 2A). The threshold blister size, \( \lambda_c \), is now found by substituting the critical value of \( \Delta L / n \) into Eq. 4. For large blisters \( (\lambda_c \gg w, t) \) we find

\[
\lambda_c \sim \left( \frac{B \gamma w}{E \epsilon^2} \right)^{1/5},
\]

whereas for small blisters \( (\lambda_c \ll w, t) \) we find

\[
\lambda_c \sim \left( \frac{B^2}{E \epsilon \Delta \gamma} \right)^{1/5}.
\]

Experimental tests of the predictions Eqs. 6 and 7 are shown in Fig. 3A and B, respectively. The raw data (for \( \lambda_c \) vs. \( w \)) are provided in Fig. 3A and B Insets. The experimental results are in excellent agreement with the above scalings (dashed lines in Fig. 3). In particular, we note that large blisters, \( \lambda_c \gg w, t \), follow the \( \lambda_c \sim w^{1/5} \) scaling expected, whereas for small blisters, \( \lambda_c \ll w, t \), \( \lambda_c \) is approximately independent of \( w \). Furthermore, we observe that the rescalings suggested by our analysis yield a good collapse of our data onto a master curve over a wide range of material parameters. Note that our analysis is only valid if the thin film

\[1\] We assume here that \( n \) is chosen to minimize the elastic energy, although the final result may also be obtained by assuming that it is the strain accommodated by each blister, \( \delta \), that is chosen to minimize the elastic energy.
is incompressible compared with the substrate. For large blisters, this requires that \( Eh \gg E_t \), but for small blisters the condition is \( Eh \gg E_t \lambda \). In our experiments these inequalities were satisfied by \( \lambda \gg \delta \). We also note that the geometrical relationship of Eq. 3 is well satisfied for an arbitrary number of blisters (Fig. 4 Inset). However, the experimental values of \( \delta \) are slightly above our predictions. We speculate that this slight discrepancy may be ascribed to the softness of the substrate: the film induces a dip in the surface of the substrate in the region of the contact between film and substrate (25).

**Discussion and Conclusions.** Having validated our theoretical formalism with macroscopic experiments, we conclude by considering its application to the microscopic situations relevant for a wide range of technological applications.

**Measuring the Interfacial Toughness.** We note that the interfacial toughness \( \Delta \gamma \) can be simply expressed in terms of the height and width of the blister by eliminating \( AL \) between Eqs. 8 and 4:

\[
\Delta \gamma = \frac{2\pi^2 B\delta^2}{\lambda^2}.
\]  

Fig. 4. The evolution of the mean blister height \( \langle \delta \rangle \) as the end-to-end displacement \( \Delta L \) is increased. Experimental results (points) are shown for a variety of different film thicknesses and widths and for different values of the substrate properties. The solid line shows the theoretical prediction Eq. 8, which has no adjustable parameters. (Inset) Experimental measurements of the blister geometry (points) compare well with the theoretical prediction Eq. 3 (line). \( \langle \cdot \rangle \) denotes the average over multiple blisters (here, results are presented for up to 5 blisters) and error bars show the standard error in this average. Points with no error bars correspond to single blisters.

**Evolution of Blisters.** We have already observed that the blisters appear sequentially. In between each of these delamination events we see, e.g., Fig. 2, that the blister size \( \lambda \) and height \( \delta \) evolve as the end-to-end compression, \( \Delta L \), increases. We expect that, with \( n \) fixed, \( \lambda \) should be governed by Eq. 4, or, after using Eq. 3,

\[
\delta = \frac{2\lambda^{3/2}}{\pi^{1/2} E_t^{1/2}} \left( \frac{\Delta L}{\lambda} \right)^{3/2}.
\]  

We emphasize that Eqs. 4 and 8 depend only on the end-to-end displacement per blister, \( \Delta L/n \). Thus, these relationships are equally valid for a single blister, \( n = 1 \), and for identical multiple blisters, \( n > 1 \). Fig. 4 shows experimental measurements of the mean blister height, \( \langle \delta \rangle \), as a function of \( \Delta L/n \) for a range of different material properties and with different numbers of blisters. Plotting the results in this way allows a direct comparison of the evolution of single and multiple blisters with the theoretical prediction in Eq. 8. The agreement between Eq. 8 and the experimental results is striking because there are no adjustable parameters in our model. Hence, \( \Delta \gamma \) can be easily estimated if the value of the bending stiffness \( B \) is known along with the blister profile, in particular, the values of \( \lambda \) and \( \delta \). In the delamination of thin metal films—\( h = O(100 \text{ nm}) \)—from polymeric substrates under compression \( B \) is known and the blister dimensions—\( \lambda = O(10 \text{ \mu m}) \) and height \( \delta = O(1 \text{ \mu m}) \)—are typically measured by atomic force microscopy. However, the value of the interfacial toughness \( \Delta \gamma \) is much more difficult to determine (18, 26, 27). In Table 1 we provide a survey of the relevant parameters from several studies of straight-sided blisters in the literature (22–24). By substituting these values into Eq. 9 we are able to estimate the interfacial toughness for each of those cases (Table 1, last column). Our estimated values are in
reasonable agreement with values determined in similar systems via alternative methods (27, 28). We note, in particular, that in the experiments of Foucher (24) only the film thickness was varied and we therefore expect that the estimates of $\Delta \gamma$ should be mutually consistent, as is indeed the case.

**Implications for Stretchable Electronics.** We conclude by highlighting some of the implications of our work for stretchable electronics, the technological application that motivated our study. First, we note that the film-substrate system produces blisters with an intrinsic size. This is important for experiments using predefined adhesion patterns (3) because the presence of an intrinsic length scale may lead to the appearance of defects in imposed patterns with different length scales. Indeed, Sun et al. (3) found empirically that the highly adhesive patch of their substrate patterning should be narrower than some critical width to avoid the formation of unwanted delamination blisters (see ref. 3, figure S1).

Our formalism can be used to predict this critical size in terms of the mechanical properties of the system. Moreover, the microfabrication process could be simplified significantly by tuning the material properties to produce blisters of a given size, removing the need to selectively alter the substrate adhesion.

In applications of flexible electronics, it is vital that the device retains its mechanical and electrical integrity during repeated use (29). In particular, the buckled wires in these devices should not deform plastically or fracture because this would compromise their conducting characteristics. There are two possible routes to minimize such effects. One is to appropriately choose the material properties of the mechanical system so that buckling does not cause damage. Alternatively, more complex design strategies, for example, multilayer neutral mechanical plane designs (4), can be employed. We consider the former possibility here and show that a simple design criterion could be used in delamination-based devices (3) to avoid irreversible deformation. For this, we assume that irreversible deformations occur when the stress reaches a critical value, $\sigma_c$, the yield stress. In linear elasticity theory the maximum stress in a deformed sheet is proportional to both the thickness of the sheet and its curvature (30).

Requiring this maximum stress to be smaller than $\sigma_c$, we find that

$$\sigma_c > \pi^2 \frac{E h \Delta \gamma}{1 - \nu^2} \frac{1}{\lambda^2} \equiv \Delta \gamma \frac{h}{E \lambda^2},$$

where $E$ is the Young's modulus of the film and $\nu$ is its Poisson ratio. For a given material, this requires that the thickness be greater than a critical value

$$h > h_c \equiv \frac{6 E \Delta \gamma}{\sigma_c^2 (1 - \nu^2)} \frac{1}{\lambda^2} \equiv \frac{\Delta \gamma}{E \lambda^2},$$

where $\sigma_c = \sigma_{i\infty}/E$ is the yield strain of the film. This safety requirement is independent of the degree of compression and it applies equally well to multiple blisters far beyond onset as it does to a single blister just beyond the blistering threshold. For the films used in our experiments, we measured $\sigma_{i\infty} = 14 \pm 3$ MPa giving $h_c = 27 \pm 12$ $\mu$m. This estimate is consistent with our observations that only the thinnest films ($h = 15$ $\mu$m) used in our experiments undergo irreversible deformations.

For thin metal films, the critical thickness in Eq. 11 is at least 100 $\mu$m and, more typically, 10 $\mu$m. These relatively large critical values explain why cracking has been observed in some microscopic experimental realisations (24, 31), while also suggesting that plastic deformation may have occurred in others. With films made from other materials, however, it may be possible to make use of significantly thinner sheets without risking irreversible deformations. For example, using typical values for silicon we find $h_c \approx 10$ $\mu$m. Assuming that the strength of ultrathin graphite films is comparable with the extremely high strength of monolayer graphene sheets (32), our analysis yields $h_c \approx 0.5$ nm, which corresponds to one or two atomic thicknesses [Recent experiments have shown that the deformation of ultrathin graphite films down to thicknesses of as few as 8 atomic layers are well described by continuum elasticity theory (34).] Recently, there has been significant progress in developing techniques for uniform film deposition (33) and transfer onto arbitrary substrates (35). From a mechanical point of view, these advances along with a small critical thickness $h_c$ suggest that ultrathin and high-strength films, such as graphene sheets, may be the ideal material for applications of bendable circuitry at small scales using delamination structures. Moreover, there is potential for further improvement on the robustness of devices by combining the criterion for material properties that we have proposed with more advanced multilayer designs (4).

**Materials and Methods**

**General.** Biaxially oriented polypropylene sheets (Innovia Films) with thicknesses $h = 15, 30, 50$, and 90 $\mu$m were used. The rectangular strips had widths in the range $1 \text{mm} < w < 25$ mm. Experiments with strips of different length showed that the onset blister size was not significantly altered provided that the length is greater than $\lambda_c$. For all experiments reported here $\ell > 2\lambda_c$. Polymer substrates were made from Vinyloctylxylene (Zehrmack). Two different polymer melts were used: pink (8 Shore A) and green (22 Shore A). In general, the Young’s moduli of these materials were $E_i = 220$ kPa and $E_i = 800$ kPa, respectively though variations were accounted for by direct measurements (see: Measurement of material properties).

For deep substrates we compress uniaxially starting from the undeformed state. For thin substrates, this would produce buckling of the substrate and so we instead first stretch the substrate (uniaxially), adhere the strip to the substrate, and then release the strain gradually. Within the theory of linear elasticity, this is equivalent to a compression relative to the stretched state.

**Blister Profile Measurements.** The blister width at the onset of delamination $\lambda_c$ was measured from digital photographs (taken from above) by using ImageJ. To measure the evolution of $\lambda$ and $\lambda_c$ as the compression $\Delta \lambda$ is varied, the thin films were painted black. (Measurements of $\lambda_c$ using this method were consistent with those obtained using the first method confirming that painting has little effect on the material properties of the film.)

A laser sheet at an oblique angle was then used to highlight the deflection of the blister and digital photographs were taken from above. Image analysis software, based on the MATLAB image processing toolbox, was written in-house and used to extract the blister profile, $d(x)$. The maximum of this profile gives the blister height $h$. Denoting the two values of $x$, where $d(x) = \frac{1}{2}$, as $x_l$ and $x_h$, we define the blister size by $\lambda = 2(x_l - x_h)$ (i.e., double the width at half-maximum), which is consistent with the natural definition of $\lambda$ because of the sinusoidal blister profile in Eq. 1. However, this is a more robust and reproducible method of measuring $\lambda$ than measuring the point of contact of the film with the substrate from laser profiles.

**Measurement of Material Properties.** The elastocapillary length, $\ell_{\infty}$, was measured by clamping one end of the film with an imposed vertical displacement and measuring the extent of de-adhered part of the film. This experiment is the dry adhesion equivalent of the capillary-induced sticking of two hairs (20). In processing our experimental data we use the value of $\ell_{\infty}$, not $\Delta \gamma$. However, for completeness we note that typically the corresponding interfacial toughness is $\Delta \gamma \approx 0.3$ $\text{Jm}^{-2}$.

The bending rigidity of films was obtained by clamping horizontally one end of several strips of film and measuring the deflection under their own weight as a function of their length. We define bending rigidity by comparing these results with numerical integration of an elastic beam in a gravitational field with the same mass density (measured directly with a precision scale).

<table>
<thead>
<tr>
<th>Reference</th>
<th>Thin film type</th>
<th>$h$ (nm)</th>
<th>$\lambda$ (nm)</th>
<th>$\lambda_c$ (nm)</th>
<th>$\Delta \gamma$ (Jm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleymand et al. (22)</td>
<td>Stainless steel</td>
<td>58</td>
<td>250</td>
<td>2.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Parry et al. (23)</td>
<td>Nickel</td>
<td>50</td>
<td>250</td>
<td>3.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Foucher (24)</td>
<td>Nickel</td>
<td>100</td>
<td>340</td>
<td>3.4</td>
<td>3</td>
</tr>
<tr>
<td>Foucher (24)</td>
<td>Nickel</td>
<td>200</td>
<td>670</td>
<td>8.9</td>
<td>2</td>
</tr>
<tr>
<td>Foucher (24)</td>
<td>Nickel</td>
<td>300</td>
<td>1,000</td>
<td>12.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

These experiments were all performed on polycarbonate substrates.

Table 1. Typical values from the literature for the properties of blisters and the associated estimate of the interfacial toughness $\Delta \gamma$. 

The bending rigidity of films was obtained by clamping horizontally one end of several strips of film and measuring the deflection under their own weight as a function of their length. We define bending rigidity by comparing these results with numerical integration of an elastic beam in a gravitational field with the same mass density (measured directly with a precision scale).
The stretching stiffness, $E_{sl}$, of thin substrates was measured by using a dynamometer to measure the force-displacement curve for stretching strains <10%. Over this range of strains, the force-displacement curve is linear, allowing the stretching stiffness $E_{sl}$ to be determined from the gradient.


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