Failure of polymeric adhesive-coated substrates: Why stickers and labels suck sometimes

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High-Level Summary

When you peel stickers or labels off of the surfaces that they're adhered to, they either come of cleanly, leave behind adhesive residue, leave behind paper residue, or some combination of the three. Whether or not this happens is dependent on how fast you peel it, the angle you peel it at, how hard you peel it, and the temperature (as well as a few other things that you can't control). The best thing you can do to get a clean removal is to heat up the sticker with a hot air gun to increase the viscoelasticity of the adhesive before slowly and gently peeling it off.

Introduction

You've probably experienced it – the dreaded frustration of peeling off a sticker or label only to have remaining paper and residue left behind. For years material scientists have researched and designed new adhesives for aerospace [1], construction [2], and biomedical joint repair [3] to name a few. Packaging labels and stickers use a special type of adhesives that are designed to fail under relatively small loads, i.e. when a user peels them from the surface of what they are adhered on to. Whether it is holding together the wings of a plane or decorating a notebook with the familiar face of Hello Kitty, the mechanics of adhesive failure is a complex topic.

For the case of adhesive-coated substrates, we can summarize the failure when being peeled from another surface with three possible failure modes. The first is that the failure occurs at the adhesive/surface interface (adhesive failure). The second failure mode occurs through the middle of the adhesive (cohesive failure). In cohesive failure, all of the substrate is removed, but leaves adhesive residue on the bulk material's surface. Finally, the third failure mode occurs when the substrate tears before the adhesive fails in either the adhesive or cohesive failure modes (substrate failure). In reality, a peel is often a mixed-mode failure that is some combination of these three failure modes.

In this paper, we use an energy model to define the conditions under which a polymeric adhesive-coated substrate fails. We assume that the adhesives are viscoelastic crosslinked amorphous polymer adhesives that have not undergone strain hardening or environmental effects. We then describe why a polymeric adhesive-coated substrate would fail in any one of the three failure modes described prior in context of this model. Finally, we briefly explain how these failure modes interact with each other and how failure can be predicted.

Energy Model & Failure Criteria

We define failure of our adhesive-coated polymer substrate as the onset of fracture in either the adhesive/bulk material interface, the adhesive, or the substrate by adopting an energy model [4, 5]. In simple terms, energy models suppose that a material fractures when enough work (i.e., pulling) and elastic potential (i.e., stretching) is applied to the material, causing it to increase its surface energy. The only way that an adhesive-coated substrate could do this would be to increase its surface area, either by 1) separating at the adhesive/bulk material interface, 2) propagating a crack within the adhesive, or 3) propagating a crack through the substrate. These three options define the three failure modes described previously: adhesive failure, cohesive failure, and substrate failure. In our system, the fracture criterion becomes:

$$G_c \leq W - U \tag{1}$$

Where W is the work done, U is the stored elastic energy, and G_c represents all energy losses incurred around the failure surface - ruptured bonds, local viscoelasticity, and plastic deformations to name a few - and is therefore representative of the total energy required to increase the crack in a material.

More conveniently, G_c can be rewritten as:

$$G_c = G_o + \psi \tag{2}$$

where G_o is energy required solely for rupturing intrinsic bonding forces, and ψ is the energy dissipated in viscoelastic and plastic deformations.

Because we've defined failure to occur as a crack propagating along a plane through either the adhesive/bulk material interface, within the adhesive, or through the substrate itself, the true energy required to break bonding forces is described by a weighted mean of the various failure paths [5,6]:

$$G_o = iG_{o,a} + jG_{o,c} + kG_{o,s} \tag{3}$$

where i, j, and k are the area fractions of the failure path and the a, c, and s subscripts of G_o are the intrinsic fracture energies for adhesive, cohesive, and substrate failure, respectively.

Likewise, the second term of Equation 2, ψ, can be described by a sum of its parts:

$$\psi = j\psi_c + k\psi_s \tag{4}$$

where the c and s subscript refer to the adhesive and substrate, respectively. By definition, there is no viscoelasticity or plasticity that can occur at the interface – all energy losses incurred at the interface are entirely made up of bonding forces between the cured adhesive and the bulk material surface. ψ has been shown by researchers to depend on the temperature [7], humidity [8], the rate that the peeling force is applied [9, 10], the strain level [11-14], and the thickness of the layer [15-19]. ψ is usually the major contribution to the value in G_c, which means that the failure mode of an adhesive-coated substrate is highly dependent on these factors [5, 20, 21].

Finally, the geometry of the peel must be considered. We use a generic peeling model where a force F_c is applied to the adhesive-coated substrate at an angle α from the bulk material surface [5], as shown in Figure 1.
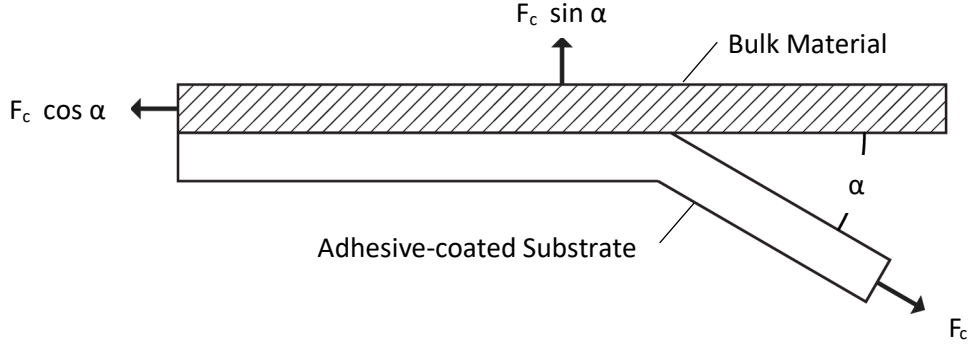
Figure 1: Schematic of the application of peel force on an adhesive-coated substrate

In this geometry, the state of stress at the peel front is independent of the amount of peeling that has taken place. Thus, we can rewrite Equation 1 as:

$$\sum(G_c x b)_{a,c,s} = F_c x (1 - \cos \alpha) - \sum(U x b h)_{c,s} \tag{5}$$

Where x is the distance the adhesive-coated substrate is pulled, α is the peel angle, U is the volumetric strain energy, and h is the thickness. The $\sum(G_c x b)_{a,c,s}$ term represents the total fracture energy of the bonds, and can be further simplified by Equations 2-4. The $F_c x (1 - \cos \alpha)$ term is equivalent to the amount of work applied, or W from Equation 1. The $\sum(U x b h)_{c,s}$ term, on the other hand, represents the stored strain energy U from Equation 1.

In the next part of this paper, we will apply our assumptions to Equation 5 and show the relationship between the peel force, fracture energy, and strain energy for unimodal adhesive, cohesive, and substrate failures.

Adhesive Failure

Adhesive failure is representative of a clean sticker or label removal. In adhesive failure, the failure occurs along the interface between the adhesive and the bulk material leaving no residue behind. Ideally, all stickers and labels would fall under this category.

Figure 2: Depiction of an adhesive failure [24]. 100% of the substrate and 100% of the adhesive is removed from the bulk material surface.

So how would we be able to predict if an adhesive-coated substrate fails in the adhesive failure mode? Substituting Equations 2 and 4 into Equation 5, we can neglect the small strain energy of the adhesive/bulk material interface and the substrate to have:

$$G_{o,a} = \frac{F_c}{b}(1 - \cos \alpha) \tag{6}$$

Thus, we have a simple equation that relates the fracture energy for adhesive failure, $G_{o,a}$, to the applied force of peel, the width of the adhesive layer, and the peel angle.

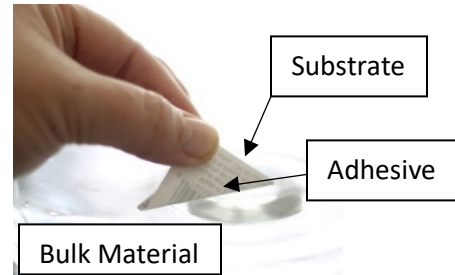## Cohesive Failure

Cohesive failure is categorized of a complete removal of the substrate, but with residue of the adhesive layer remaining behind. Commercial products such as goo-gone advertise solvent-based removal of this residue, but what conditions cause this type of failure to begin with?

Figure 3: Depiction of a cohesive failure [25]. 100% of the substrate and <100% of the adhesive is removed from the bulk material surface, with the remainder being left behind as residue on the surface.

Cohesive failure occurs when the chemical and physical interaction forces between molecules of the adhesive itself is less than the forces that adhere it to the surface of the bulk material. Once again, we can describe this failure by substituting Equations 2-4 into Equation 5. However, unlike the interface bonds in an adhesion failure, the bonds in a cohesive failure allow for plasticity and viscoelasticity:

$$G_{o,c} + \psi_c = \frac{F_c}{b}(1 - \cos \alpha) - Uh_a \qquad (7)$$

As we recall from earlier, $\psi \gg G_o$ [5, 20, 21]. Thus, cohesive failure heavily depends on factors such as temperature and strain rate to break the physical and chemical bonds within the adhesive. Because the adhesive layer can also store strain energy, patches of localized area may exhibit greater resilience to cohesive failure than other, leading to the 'stringiness' phenomenon during the peel [20].

Substrate Failure

Finally, substrate failure leaves highly visible residue of the substrate. A crack initiates in the plane of the applied force and quickly propagates through the substrate material. This failure typically occurs when the peeling load is applied too quickly for the viscoelastic adhesive to absorb the energy.

Figure 4: Depiction of a substrate failure [26]. The substrate fractures during the peel such that <100% of the substrate is removed leaving both adhesive and substrate residue behind on the surface

While the other two failure modes are most accurately described by an energy method, substrate failure can also be described by linear-elastic fracture mechanics [20, 22, 23]. However, we continue with the energy model here for consistency. Substrate failure occurs when the work that is applied to the adhesive-coated substrate is not enough to overcome the intrinsic fracture energy of either the bonding forces at the interface or the cohesive forces within the adhesive itself, but it is enough to fracture along a plane of the substrate. Once again, we solve for Equation 5 with our assumptions for the substrate layer:

$$G_{o,s} + \psi_s = \frac{F_c}{b}(1 - \cos \alpha) - Uh_s \qquad (8)$$

While this equation is similar to Equation 7, it should be noted that the value for ψ is much different here, because the substrate does not necessarily have the same viscoelasticity of an adhesive, but is subject to plasticity. In other words, the ψ_s term has a much smaller dependence on temperature and peel rate when compared to ψ_a of Equation 7. However, bending stresses at the peel-front may cause plastic deformations within the substrate in the course of peeling, which is accounted for by the ψ_S term [5]:

$$\psi_S \cong \frac{b^2 \sigma_y}{4r_c}(1 - \cos \alpha) \tag{9}$$

Where σ_y is the yield stress of the substrate and r_c is the radius of curvature. This term is a constant, so as the peel force increases, first the Uh_s term increases until it reaches the yield stress, and then increases until it reaches its plastic limit. At that point, only $G_{o,s}$ may increase, which means the bonds break and the crack propagates.

Mixed-mode Failure

The various bonding energies calculated above hold valid for unimodal failures, i.e. a failure that is occurs entirely at either the interface, within the adhesive, or within the substrate. In reality, most peel failures will be mixed-mode5. Even most 'clean peels' do not fail entirely in the adhesive failure mode, and rubbing a finger across the surface will often reveal a small amount of residue left behind, indicating some degree of cohesive failure. We can describe the mixed-mode failure by combining Equations 1-9 to write the complete energy balance as:

$$G_c = i \left(\frac{F_c}{b}(1 - \cos \alpha)\right)_a + j \left(\frac{F_c}{b}(1 - \cos \alpha) - Uh_c - \psi_c\right)_c + k \left(\frac{F_c}{b}(1 - \cos \alpha) - Uh_s - \frac{b^2 \sigma_y}{4r_c}(1 - \cos \alpha)\right)_s \tag{10}$$

Thus, as the peeling force is applied to the adhesive-coated substrate, the energy is absorbed unequally in the different layers as elastic strain energy, plastic deformation, and finally, fracture.

Conclusion

In conclusion, we have defined the constitutive equations that govern fracture in a generic peel test. We then used this model to describe unimodal adhesive, cohesive, and substrate failure in an adhesive-coated substrate and when one would expect one type of failure over another. Finally, we briefly discuss mixed-mode peeling failure.

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