ON STICKINESS

The behavior of tacky materials is difficult to quantify, involving as it does such dynamic phenomena as meniscus instability, cavitation and the formation of filaments.

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If you step on a used piece of chewing gum thrown away by some untidy folk, it will stick to the bottom of your shoe. It will also provide you with an apt example of undesirable stickiness. Conversely, in wrapping a package, you'll seek out stickiness in the form of adhesive tape, which is a result of long, truly interdisciplinary research that involved many physicists, chemists, and engineers, from both industry and academe.

What is stickiness and how is it measured? The American Society for Testing and Materials (ASTM) definition is that a material is sticky—"tacky" in the more professional jargon—if an appreciable force is needed to separate from it immediately after contact. When you touch something sticky, it is an everyday reflex to try every possible movement to pull your finger away. Sticky materials are designed to resist all such attempts to separate, including normal pulling off, shearing, and peeling. These requirements are often difficult to meet simultaneously, and so designing a truly sticky material is a matter of compromise. For instance, water is not considered to be sticky because, even though two wet microscope slides are difficult to pull apart, they can slide apart too easily.

Polymer melts, made of long, flexible molecules, naturally provide the desired properties of sticky materials: under stress, at long timescales, they flow like very viscous liquids, whereas at short timescales, they deform like soft, elastic solids. The characteristic timescales can be tuned by chemical composition, chain length, and molecular architecture—for example, by using branched rather than linear chains. They also depend strongly on temperature, especially near the glass transition temperature, at which the polymer transforms progressively from a viscous melt to a solid, plastic state. By incorporating different types of monomers in the same chain, one can tune the interchain friction and the dissipative processes in the material.

Controlling adhesion is important in many fields besides adhesives: the glass, tire, wood, paper, metal, ceramics, paint, and cosmetics industries often rely on it, as does even the food industry. A whole body of knowledge and understanding has been developed in each of these industries. Several contradictory descriptions, therefore, have come to coexist, each well adapted to a particular material. On the whole, the science of adhesion and adhesives has thus developed very nonlinearly. So the story we tell here is thematic rather than chronological.

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Forces too low, energies too high

The concept of stickiness is full of paradoxes. One of the most striking is that a substance is not sticky by itself: Its thickness and the mechanical and surface properties of the probe used to test its stickiness are important. If you put your finger into a honey pot, you don't need to pull strongly to remove it, even though you may draw a large honey filament over a great distance. In terms of the ASTM criterion then, honey is nontacky. But this is hard to admit: After the kids' breakfast, when the honey is spread as a thin layer on the table, you definitely need to use your muscles to pull off a stuck glass.

The rigidity of the probe counts too. If you get stuck when walking on low-quality asphalt that has softened on a horribly hot summer afternoon, you'll have a better chance of getting away if your shoes have flexible soles than if you have rigid military boots. The most common normalized test is the loop tack test: Make a loop of adhesive tape and set it down on the table; you'll need some force to pull it away. However, if you first glue the back of the tape to a block of wood, you'll need a much stronger force to remove the tape from the table, even if you make sure that the initial contact length is the same. The physics of peeling (in a flexible-loop-tack test) and of pulling off (in a rigid-probe-tack test) are thus definitely very different, and both have attracted much attention over the past 50 years as new, efficient adhesives have been developed.

Whatever the kind of stickiness experiment, the surface is often the weak link: If you wet your finger first, the adhesive tape does not stick to it any more. Alan Gent at the University of Akron and Jacques Schultz at Mulhouse University (France) quantified this observation by measuring the effect of various liquids on resistance to peeling.[1] In this and many other studies, adhesion was shown to be proportional to the difference in surface energies. Again, polymers are very handy for adjusting surface properties, as one can make very fine modifications by carefully altering the chemistry. Our understanding of surface interactions has provided a useful guide for designing surface treatments that enhance or reduce stickiness. For instance, the adhesive flap of an envelope does not stick to the treated, protective strip of paper. It can stick, howev-

FIGURE 1. STICKY LATEX particles, 80 nm in diameter. This transmission electron micrograph shows acrylic latex particles deformed under the influence of surface forces. The softer the particles, the larger the deformation and contact area, and therefore the greater the adhesion. Controlling the stickiness of latex particles is important for film formation in many applications, including paints, varnishes, and adhesives. (Photograph courtesy of Patrick Coupard, Elf Atochem Co.)

er, to the untreated paper of the back of the envelope.

More quantitative than the finger test of stickiness is the probe-tack test. A solid probe is moved toward the adhesive layer at a controlled velocity; it is kept in contact for a chosen time; it is then removed at a constant velocity, and the maximum force is measured. In a more instrumented test, the force is monitored throughout the separation, and the corresponding work is calculated. Typically, to pull off a steel probe with a diameter of 5 mm from a good adhesive requires a force of about 20 newtons and work on the order of 10^{-2} joules. Here we face a paradox that has been stimulating intensive research for decades: If adhesion were a matter of thermodynamics, the work needed for separation would be close to the surface energies, which are typically 10^{-2} to 10^{-1} J/m^2, and thus should be on the order of only 10^{-6} J in the probe-tack test. On the other hand, separation has often been viewed as involving processes at the molecular level. The force needed should then be as large as 10^{-6} J/10^{-10} m, or 10^4 N, where 10^{-10} m is a typical atomic size. This disparity demonstrates that surface phenomena alone cannot account for stickiness. Many other, macroscopic phenomena come into play, as do surface roughness and bulk molecular structure and dynamics.

Roughness is tough on stickiness

We know from common experience that sticky materials are soft. To understand why, we must take a closer look at the surface. Mica is atomically smooth, and so two mica surfaces can be in very close contact. Hence, the forces and adhesion energies between them are comparable to those of Van der Waals interactions, as measured in 1972 by Jacob Israelachvili, now at the University of California, Santa Barbara, and David Tabor at the University of Cambridge (England).[2] In real life, however, material surfaces are rough, and hence are never in intimate contact from the macroscopic scale down to atomic dimensions. If the real area of contact is small, adhesion is weak. That is why most solid objects, which are rough on the micrometer scale, are not sticky. A wetting liquid achieves an excellent contact, but, as we have seen, it does not cause the objects to stick, because it does not resist shear deformations, which are present on the microscopic level when rough solid surfaces are pulled apart.

Soft solids are sticky because they resist shear, present some viscous dissipation, and deform to provide a good contact, even with rough objects. How soft is soft? That question has been the subject of various empirical rules in the field of adhesives. The most famous, attributed to Carl Dahlquist of the 3M Corp,[3] defines a viscoelastic window in which materials are sticky: The elastic modulus should be lower than 10^5 pascals. This criterion is famous for its use in predicting the stickiness of wheat flour/water dough: at 40% moisture, the dough is a perfect adhesive for processing equipment in bakeries, a very unfortunate feature indeed.[4]

How can the Dahlquist criterion for stickiness be rationalized? Under the influence of attractive surface forces, smooth, nonconforming elastic bodies deform: the softer the material, the better the contact. The contact surface area is a very nonlinear function of the elastic modulus.[5] On a much smaller scale, rough surfaces display a whole landscape of micrometer-sized, spherical bumps, which have been shown to be well described by a Gaussian height distribution.[6] Tabor and his collaborators conducted a beautiful series of measurements of the adhesion between optically smooth rubber spheres and flat hard surfaces that had been roughened to various degrees, and showed how surface roughness reduces adhesion.[7] They quantitatively explained their observations by modeling how the soft surface is indented by the asperities of the hard material. Figure 1 illustrates how, on a micrometer scale, the molecular forces can appreciably deform the bodies, leading to intimate contact. Costantino Creton at the Ecole Supérieure de Physique et Chimie Industrielle in Paris and Ludwik Leibler have shown that, for typical rough surfaces, the Dahlquist criterion corresponds to the saturation of the area of intimate contact under the influence of Van der Waals forces.[8]

It is tempting to say that all this knowledge leads to a qualitative understanding of the variation of adhesion with surface energies and roughness and with bulk deformability. In fact, the amount of contact surface area is not the only important parameter. Heterogeneities of various kinds are most important, as we shall now see.

Fracture, cavities, and fibrils

Here is yet another paradox. Heterogeneities often appear in the adhesive material in the course of separation and can have two major effects on the mechanisms involved in

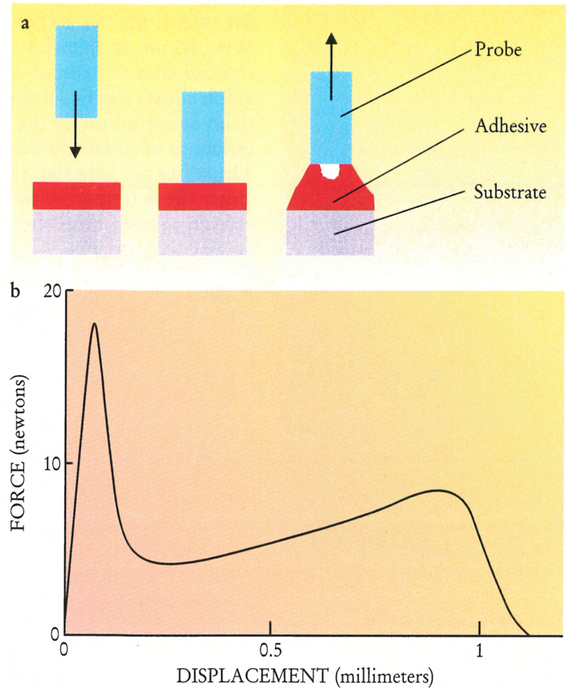

FIGURE 2: PROBE-TACK TEST. (a) A flat, solid probe is moved into an adhesive film at a constant velocity and is kept in contact for a chosen time. The traction force is monitored as the probe is removed at constant velocity. (b) A typical force–displacement curve (courtesy of François Court and Vincent Royackkers, Elf Atochem Co). The plateau corresponds to the appearance of fibrils. Cavitation and fibrils allow for very large deformations: The adhesive film is only 0.1 mm thick, whereas the displacement at the breaking point is about 1 mm.

stickiness. On the one hand, because some regions of the adhesive material are less deformed when the stress is heterogeneous, the adhesive's overall performance can be weakened. On the other hand, new dissipative mechanisms may give extra adhesive energy to the bulk or the interface. Heterogeneities are also one reason for the very nonlinear traction curves that are well documented. Very often, as the probe is pulled away from the sticky material, the force first increases and then falls sharply. But the probe still sticks, as the force remains at a nonzero value (figure 2).

In 1958, Gent and his coworkers discovered that, when the adhesive joint is being pulled, cavities may suddenly appear in the bulk of the adhesive material at a well-defined load.[9] They observed that the appearance of such bubbles, known collectively as cavitation, is often marked by an "accident" in the load–displacement relation and "sometimes by an audible popping." Although, the bubbles impair the strength of the joint, they reinforce the adhesion energy. Their presence enables the joint to deform appreciably while still requiring a nonnegligible load to further separate the probe from the substrate.

Why do the bulk cavities form? For thin films, the imposed displacement cannot be accommodated by the expansion of the adhesive or by some displacement of the adhesive material initiated at the edge of the sample (figure 3). Except with porous substrates, air cannot migrate from the outside into the adhesive material. Diffusion is far too slow—typically 10^{-6} cm^2/s, meaning that it takes air ten days to reach the center of a contact region 1 cm in diameter. When the pressure in the adhesive is sufficiently lower than the outside pressure, the cavities burst into existence. This phenomenon is favored when the thickness of the adhesive is much smaller than the dimension of the contact region. In any case, the surface must be able to sustain the stress so as not to debond.

For a purely elastic material under sufficient applied stress, a fracture at the interface with the solid propagates at the velocity of sound, because there is no dissipation. Such separation, in which no adhesive material is left on the probe after complete separation, is said to be adhesive. In the absence of dissipation, the adhesion energy is small. Fortunately, other cavities come to help, and hold the probe and the sticky material together. In fact, bubbles may be present even before a pulling-out load is applied. Indeed, they can be located at the interface, where they are trapped inside the surface roughness during contact formation.

Our own research has shown that such bubbles act like microscopic suction cups and strongly reinforce the surface adhesion.[10] The bubbles are forced to expand progressively when the solid surface is pulled, and the corresponding deformation of the elastic material around them requires some extra work. The presence of interfacial bubbles may also be responsible for nonlinear force–displacement curves. In particular, the stress peak occurs just before air rushes into the breaking suction cups. But more important is that the bubbles may delay the propagation of the fracture from the edges of the adhesive joint and allow the bulk cavitation to occur, and that in turn produces an even more complex, discontinuous behavior.

In practice, the material is viscoelastic rather than purely elastic. This property brings new phenomena into play. For instance, the fracture that would propagate from the edge at the interface with the solid is slowed down not only by interfacial bubbles, but also by viscous losses. Such viscous losses are of the same order of magnitude whether the fracture is cohesive (within the adhesive material) or adhesive (at the interface between the adhesive and the probe).[11] The slowed fracture propagation allows high tensile stresses to develop and facilitates bulk cavitation at the center of the contact region.

The stress distribution near the fracture head, and hence the shape of the fracture, reflect the complex viscoelasticity of the polymeric material. Regions near the fracture head are deformed at higher rates than regions farther away, and thus respond in a different manner (figure 3). Pierre-Gilles De Gennes at the College of France in Paris has predicted that the fracture in weakly crosslinked elastomers containing many dangling chains should have a spectacular trumpet shape, which indeed was observed in beautiful experiments by Thierry Ondarçuhu on silicone melts.[12] At the fracture head, the volume of adhesive material within which energy is dissipated as the fracture propagates, is enhanced enormously in these materials, which are thus particularly sticky. That's why weakly crosslinked rubbers are used to make race car tires. Strangely enough, the drivers wish to truly stick to the road.

If the material is even more viscous, it flows from the edges toward the central region of the joint between the probe and the rigid substrate surface. The viscous material causes a pressure drop that may lead to bulk cavitation. It also causes "dewetting," which is the word for interfacial fracture used in the literature on liquids.

More spectacularly, the edge meniscus may become unstable (the classic Taylor instability), allowing air fingers to penetrate the adhesive from the outside.[13] As the

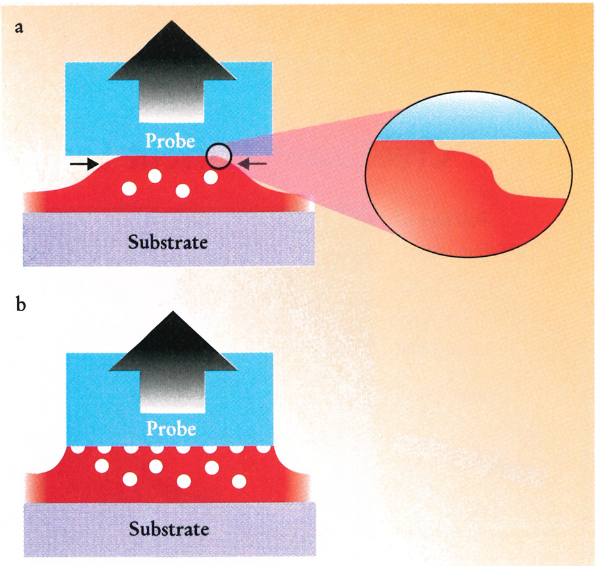

FIGURE 3: CAVITATION IN THIN FILMS. When thin films are subjected to normal pulling off, they may be unable to accommodate the imposed displacement, because it would require a large volume increase. Instead, bubbles appear in the volume of the film and relieve the stress—a phenomenon known as cavitation. If the film is viscoelastic, it progressively debonds from the probe under traction. But the propagation of this fracture from the edge is slowed down by viscoelastic losses. At high pulling velocities, the tensile stress is still very high in the center, and bubbles can appear (**a**). Because the response of viscoelastic polymers depends strongly on deformation rates, the shape of the fracture opening is a complex function of the distance from the fracture head. If the film is purely elastic, the fracture propagation is immediate, and no cavitation occurs unless interfacial bubbles are present (**b**). Such bubbles act as tiny suction cups and stop the propagation of the fracture.

fingers propagate, filaments known as fibrils may develop by deformation of the polymer webs between the air fingers (figure 4). Nice fibrils can be easily observed when opening the flap of a self-adhesive envelope. Fibrillation was first studied in peeling geometries.[14]

Fibrils are not the only curiosity of peeling experiments. When you unroll adhesive tape under certain conditions, the peeling motion proceeds in discrete jumps and is accompanied by a characteristic acoustic emission, a phenomenon known as stick–slip. What happens very often is that two different fracture mechanisms exist—for example, adhesive fracture at large velocities (with little energy dissipation) and cohesive fracture at lower velocities (with greater dissipation). If the average pulling velocity is within some definite range, the elasticity of the whole system (the pulling apparatus and the adhesive backing) allows for oscillation between the two fracture mechanisms.[15] The noise results from the corresponding velocity jumps. Peeling is thus quite complex, on the whole.

Mechanisms other than the Taylor meniscus instability may also produce fibrils. And fibril formation is not characteristic solely of peeling geometries. Albrecht Zosel at the BASF Co has shown that in the probe-tack geometry, fibrils may appear even in the central region of the sample.[16] The force is then basically constant over the whole deformation, and this stage in the separation process corresponds to the plateau in the force–displacement curve. In some cases, fibrils reach about 1 mm in length, which is ten times the initial film thickness.

Fibrils display a variety of behaviors at the late stages of deformation. If they eventually break apart, then there will remain some adhesive material on both sides, and the separation is said to be cohesive. If, on the other hand, the fibrils detach from the solid, then the separation is purely adhesive. Cohesive versus adhesive failure is a very complex, open problem: It is governed not only by the early stages of deformation, but also by the large deformations in the fibrils. The mode of failure is thus expected to be one of the major areas of study in the years to come, because of its great industrial interest. Here we face yet another paradox: At first, fibrils are the manufacturer's nightmare, when the adhesive is being deposited on the backing to make tape; later on, fibrils are often looked for, as they bring a large dissipation.

The state of the art

For years, researchers have been fascinated by all these phenomena accompanying stickiness—meniscus instability and air fingering, interface and bulk cavitation, filament formation and rupture. They have used their skills

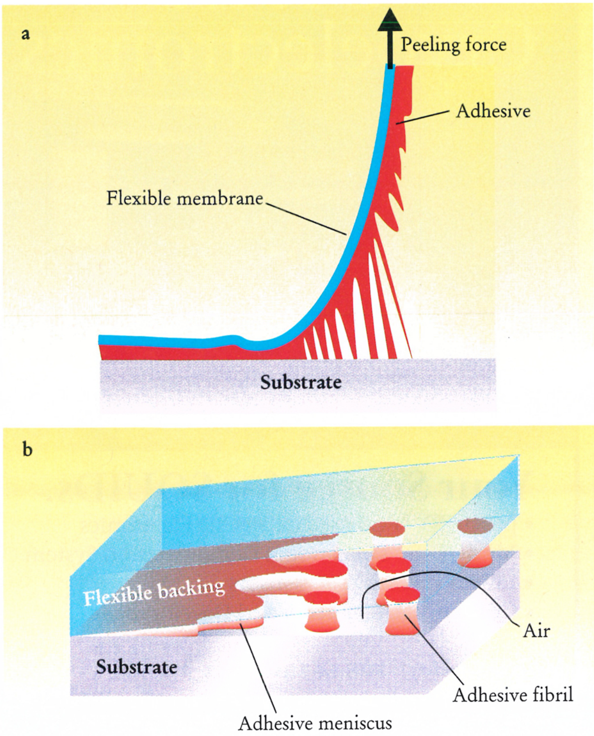

FIGURE 4: PEELING AND MENISCUS INSTABILITY. Fibrils often appear when adhesive tape is peeled (**a**). They are the result of the complex response of the adhesive film and the flexible backing. (Drawing after D. H. Kaelble in ref. 14.) One mechanism for fibril formation is the following: The meniscus of adhesive material between the flexible backing and the solid undergoes a Taylor instability, and the resulting long webs of adhesive material in turn destabilize into separate columns (**b**).

to measure forces and displacements simultaneously, while monitoring damage in the samples. More recently, they have made a considerable effort to control precisely the roughness of both the probe and the adhesive, and to study systems with a well-characterized rheology. In this context the tack studies of Zosel[16] and of Creton and his coworkers[17] are particularly important. They provide tools for a deeper understanding of the relation between stickiness and molecular architecture.

Very instructive also is the recent progress in molecular dynamics simulation. At Johns Hopkins University, Arlette Baljon and Mark Robbins simulated a tack experiment with 128 short (16-monomer) polymer chains. Promisingly enough, even with such small samples, they identified cavitation, plastic yield, and microfibril rupture.[18]

Polymers are marvelous not only because they are viscoelastic, but also because they can be easily structured on mesoscopic scales and can respond finely or abruptly to variations in external conditions such as temperature, pressure, or humidity. Small changes in polymer molecular architecture or formulation sometimes induce dramatic changes in adhesive properties. What the detailed mechanisms are seems to be an open question not treated in much detail in the scientific literature. We therefore dedicate this text to all the anonymous researchers who have made very efficient adhesives and who have understood a lot more than is presented here, but who were never allowed to or did not care to tell their secrets.

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