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Adhesion: Molecules and Mechanics

Kevin Kendall

There is a difference between adhesion at the molecular level and adhesion in engineering. There is no doubt that molecules of solid materials stick together and can be separated mechanically. The problem is explaining the connection between molecular attractions and mechanical measurements. False ideas such as keying and gluing require critical assessment because they confuse molecules and mechanics. Mechanisms such as adhesive hysteresis, stringing, and clustering deserve evaluation. A rational theory of these phenomena should be based on the theoretical concept of reversible work of adhesion and on the measured quantity of adhesive energy, which includes the extra energy required to restructure the interface as surfaces move.

A critical observation can define a concept in a spectacular way. Brownian motion is one such observation: It defines kinetic theory by showing that micrometer-sized particles in a fluid are in eternal haphazard motion as if bombarded by invisible moving atoms (*1*). This behavior contrasts strongly with the static behavior of engineered objects.

In the study of adhesion, the equivalent observation is the spontaneous jumping of smooth surfaces into contact (*2*, *3*). Two ultrasmooth pieces of mica, gold, polymer, or solid gelatin solution cannot be held apart when their separation becomes small enough, typically 1 to 10 nm. Such attraction is impossible to explain by electrostatic, magnetic, or gravitational forces, which act from the center of bodies and obey the inverse square law. These forces can be detected at much greater separations. The attractive force that pulls the surfaces into contact is more akin to surface tension, a short-range surface force that can be changed by a single layer of molecules laid at an interface. Engineered objects are not usually much affected by these short-range surface forces.

After the surfaces have abruptly pulled

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themselves together, an opposite force can be applied to separate them. This mechanical force cannot generally be set directly at the interface molecules but is positioned some distance away, wedging, pulling, or peeling the materials apart. So the force is separated from the molecules by a mechanical mechanism that may be quite complex. As the force is raised, a point is reached at which a crack runs between the molecules at the interface and the bodies separate. The maximum force is the adhesion force. This adhesion force can be explained in terms of the molecular adhesion evidenced by the jumping into contact and the mechanical mechanism linking adhesion force and molecules in the cracking test (*4*).

Anyone who has observed these phenomena, of smooth solid surfaces leaping spontaneously into contact and of cracks running through adhesive interfaces, must rearrange their ideas about the behavior of engineered objects. One's previous experience is that bodies do not stick together without some assistance: Wood is joined with mortise and tenon joints (Fig. 1A), which key the surfaces in position, and bricks are held by cement, an adhesive glue that links the surfaces in contact (Fig. 1B).

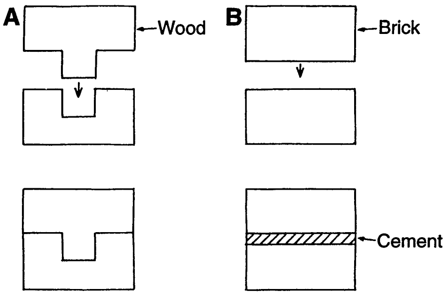

Fig. 1. Two engineering devices producing adhesion. (**A**) A mortise and tenon joint for wood works by keying. (**B**) A cemented joint between bricks demonstrates gluing.

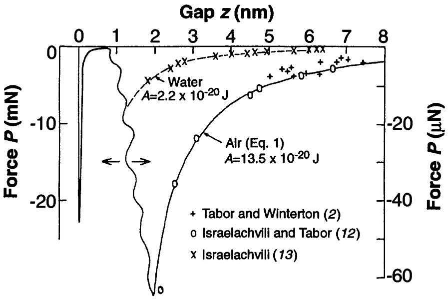

Fig. 2. Comparison of theory and results for the attractive force between crossed-cylinder mica surfaces in air (solid line) and in water (dashed line). The results fit Eq. 1 for gaps between 2 and 10 nm. Above 10 nm, the weaker retarded van der Waals forces apply. Note the change of scale below 2 nm. The results have been scaled to account for the different radii of the mica cylinders in different tests.

Both these ideas, keying and gluing, which apply to the macroscopic engineering world, must be discarded when we approach small sizes where molecular adhesion operates. Nanometer machines cannot work because their parts spontaneously jump together.

As an illustration, consider a simple engineering device that passes objects through a hole. Such a sieve operates readily at ordinary dimensions, but it does not work below the micrometer size range because the sieve clogs by adhesion. Similarly, a lock and key receptor could not slide together at the nanometer scale. The key would stick before it got into the lock. Consider a mechanism connecting two rotating shafts. Such a clutch must be forced into contact or joined by adhesive in a macroscopic machine. At the nanometer level, however, the parts naturally jump into contact, and the problem is keeping the shafts separate. A dispersing agent must be applied to push the components apart chemically by reducing the molecular attractions. Thus, adhesives are not necessary at the molecular level, where solids always stick together. Indeed, adhesives wetting the surfaces must reduce molecular adhesion, and therefore act as dispersing agents.

The conclusion from these arguments is radical. Just as Perrin (*1*) concluded that a fluid's "apparent repose is merely an illusion" because the fluid molecules are in a state of "eternal and spontaneous" motion, so must we believe that molecules of solids always adhere strongly, and that the lack of adhesion we see in engineering situations is an aberration resulting from mechanical mechanisms. At the molecular level, we see true adhesion, so lock and key devices cannot operate, and adhesives do not stick surfaces together but separate them. These apparently paradoxical points can be addressed by defining adhesion through the jumping phenomenon, considering the transition between adhesive and nonadhesive states, noting the influence of chemistry, and pointing out interesting mechanisms such as hysteresis, stringing, and clustering.

Definition of Adhesion Through Jumping

Early experiments on the spontaneous jumping into contact of polished silica lens surfaces were reported by Derjaguin and Abrikossova (*5*). Previous studies by Tomlinson (*6*) and Bradley (*7*) had shown that smooth silica spheres and fibers adhered strongly. The Russian workers studied this effect in more detail, recognizing the instability in the attractive movement and devising an electronic feedback loop to hold the gap constant while the attractive force was measured. Results indicated a rapid increase in adhesive attraction as the gap narrowed, but the surfaces were too rough to achieve good contact, the minimum gap being around 100 nm, measured by optical interference (*8*).

Tabor and Winterton (*2*) improved on these experiments..First, they used crossed cylinders of mica, which were cleaved atomically smooth to obtain perfect molecular contact. Then they used multiple beam interferometry to measure gaps to 0.1 nm. Finally, they made ingenious use of the jump distance to determine the attractive force from the instability criterion, which depended on the stiffness of the mica supports. Their results (Fig. 2) revealed true van der Waals forces. Previous workers (*5*) had only seen the weaker, retarded forces that act at large gaps, above 30 nm.

These results could be explained by the London (*9*) theory of van der Waals forces (solid line, Fig. 2). This curve had been predicted by de Boer (*10*) and Hamaker (*11*) in the 1930s and is described by the equation

$$P = -AD/12z^2 \qquad (1)$$

for crossed cylinders, where P is the force (negative for attraction), D is the diameter, z measures the gap between surfaces, and A is the Hamaker constant, 13.5×10^{-20} J for mica in air. Other geometries of rigid bodies approaching contact have their own equations (Table 1).

Table 1. Equations for surface force attractions P between rigid solids approaching contact and cracking forces F for elastic bodies being pulled from contact, assuming reversibility (A is Hamaker constant, D is diameter, z is gap, W is work of adhesion, b is crack width, θ is angle, E is Young's modulus, and d is thickness).

Geometry	Equation
Attraction	
Crossed cylinders or sphere on flat	$P = -AD/12z^2$
Sphere on sphere	$P = -AD_1D_2/12z^2(D_1 + D_2)$
Flat on flat	$P/\text{area} = -A/24\pi z^3$
Fracture	
Equal spheres	$F = 3\pi WD/8$
Sphere on sphere	$F = 3\pi WD_1D_2/4(D_1 + D_2)$
Peel at $\pi/2$	$F = Wb$
Peel at θ	$F = Wb/(1 - \cos\theta)$
Lap shear	$F = b\,(4WEd)^{1/2}$

This method, which led to the surface force apparatus, was redesigned by Israelachvili and Tabor (*12*). It was then used by a number of researchers to study the behavior of mica surfaces in water (which reduces the attraction) (broken line, Fig. 2), in solutions, at various pH, with polymers and surfactants, in various organic liquids and so forth, over a whole range of conditions (*13, 14*). The problem with this method is that it can only be used for weak attractions, when the mica behaves almost as a rigid material. As the attractions become larger on closer approach of the surfaces, the surfaces deform and Eq. 1 no longer holds. This is especially true when the surfaces nearly touch: The attractions reach a peak, and repulsive forces come into play to offset the attractions (shown schematically on the left side of Fig. 2). The surface force apparatus can only measure about 0.1% of the maximum adhesion force in air.

A further development of this kind of experiment was the atomic force microscope (AFM) (*15–17*), which relied on a profilometer-type stylus, originally developed from phonograph principles to measure surface roughness electromagnetically. Typically, such an AFM stylus would have a tip diameter around 1 μm and could detect roughnesses of 1 nm. By measuring the stylus movement with a scanning tunneling microscope, the resolution could be improved to 0.001 nm, although laser methods were normally used to measure displacement to around 0.5-nm resolution. Capacitor methods have also been used to locate and control stylus tips in these microscopes (*18, 19*). The jumping together of surfaces can now be readily studied in such instruments, as well as the influence of contamination. For example, it is interesting that jumping can be prevented by putting water on the cleavage face of calcite (*16*).

Jumping of rubber surfaces into contact was first seen by Roberts and co-workers (*20–22*), who built a surface force apparatus for polymers. The rubber was molded in glass lenses and was found to make molecular contact with glass and other polymers. Although the rubber was not as smooth as mica, it was much more compliant, so that it could spread around roughnesses or dust grains, which were therefore less of a problem than in mica or silica experiments. Rubber jumped onto glass and other surfaces, giving a flat contact region by elastic deformation, like the spreading of a liquid over a surface resisted by the elasticity of the rubber. The edge of the intimate contact region was a sharply defined circle that could be easily measured with a microscope. Inside this circle, there was molecular contact, whereas outside, there was no contact, the circle itself being a line of mathematically infinite stress, like a crack. This complex situation could be described with an energy balance argument, in which equilibrium occurs when the change in adhesion energy equals the change in elastic energy.

Work of Adhesion

The work done by the surface attractions is the work of adhesion W (energy per unit area) multiplied by the area of contact. This work can be thought of as the area under the force separation curve (Fig. 2); that is, the reversible work required to pull apart a unit area of the interface. After separation, each equal surface has a free surface energy γ, half of W, which can pull the surfaces back into contact. For unequal surfaces, the Dupré equation ($W = \gamma_1 + \gamma_2 - \gamma_{12}$) applies.

Work of adhesion is a useful quantity because it distinguishes the two states, contact and separation. This work is done over a very small distance. For van der Waals forces, 99% of the work is achieved when the surfaces are pulled 1 nm apart. For other types of bonding, such as ionic or covalent, even smaller distances are involved. Thus, the precise shape of the force separation curve need not be known to understand many phenomena. Indeed, the precise shape may not be measurable because of the instability of jumping.

Bradley (*7*) used this work of adhesion concept to calculate the mechanical force F needed to separate from molecular contact two identical spherical particles of diameter D and work of adhesion W (Fig. 3A). The resulting equation

$$F = kWD \qquad (2)$$

where k is a constant near unity, is a wonderfully simple connection between mechanics and chemistry, reminiscent of the equation for surface tension measurement by the drop weight method. Johnson *et al.* (*21*) found k to be $3\pi/8$ for elastic spheres.

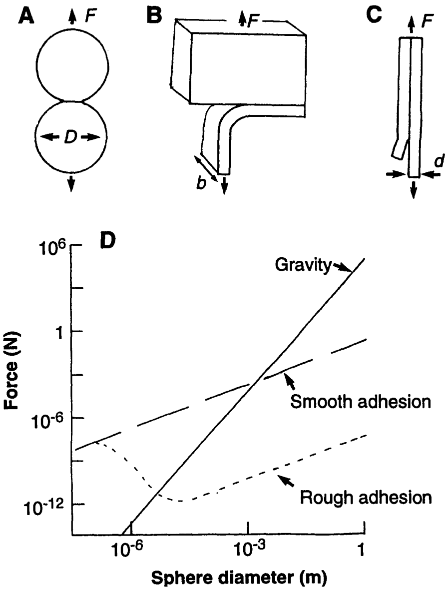

Fig. 3. (**A**) Two identical spheres in contact under the van der Waals attractions with a force F applied to separate them. (**B**) Peeling of an elastic film from a rigid surface. (**C**) Cracking of a lap joint. (**D**) Comparison of the adhesion force and gravity for very smooth and rough spheres of different diameters.

With the application of this methodology to different geometries, a range of adhesion equations could be derived to describe the mechanics of adhesive joints (Table 1). For example, Rivlin (*23*) showed that a polymer film peeling from a rigid substrate is also described by Eq. 2, but with D replaced by the film width b (Fig. 3B). His adhesion experiment is easily demonstrated by peeling "cling film" from a glass oven dish. Frictionless cleavage of an adhesive joint follows the same equation (*24*). In more complex situations, where the joint is stretched significantly during breakage as in the lap joint of Fig. 3C, the elastic modulus E and thickness d of the materials become important and the adhesion criterion for fracture becomes (*25*)

$$F = b(4WEd)^{1/2} \qquad (3)$$

which has the same form as Griffith's cracking equation for glass (*26*).

These equations are instructive because they show that adhesion force can vary substantially with geometry and material stiffness, as well as with the molecular surface forces quantified by W. In other words, mechanism is as important as molecules when fracturing adhesive joints. Moreover, the mechanism and the molecular forces interact, by changing the contact geometry, for example, as demonstrated by many results on polymer interfaces (*21*). Also, the adhesion force does not usually depend on contact area, so adhesion strength does not often enter the equations. This result is at first surprising to engineers but follows from the cracking failure of adhesive joints, in which stress is not uniform but is concentrated at the crack tip. The main benefit of Eq. 2 is that it explains why adhesion is not normally seen in engineering situations yet dominates at the nanometer scale.

Transition from the Engineering to the Adhesive Regime

Inspection of Eq. 2 shows that a ball bearing 10 mm in diameter with a dirty surface of $W = 0.1$ J m^{-2} should experience an adhesion force of 1.2 mN. By contrast, gravity gives a force about 41 mN (Fig. 3D). Because a ball bearing is much rougher than the 1-nm range of the surface forces, only the asperities make real contact, thus reducing the adhesion by several orders of magnitude (dotted line, Fig. 3D). The measured adhesion force is therefore rather small compared with gravity for objects of engineering dimensions.

By contrast with such engineering behavior, a small ball bearing 1 μm in diameter experiences an adhesion force more than a million times greater than the force of gravity, because adhesion force falls linearly with size whereas gravitational force falls with the cube of size (Fig. 3D). This means that virus-size particles stick to their neighbors or to surrounding surfaces, unless the adhesion is reduced by some interposing material that diminishes the work of adhesion.

The transition from the normal engineering regime to the adhesive regime occurs at the crossover point in Fig. 3D, between 1 μm and 1 mm diameter, depending on the smoothness and compliance of the surfaces. Below 1 μm, everything in air sticks, and we must discard our ordinary conceptions of engineering.

Fortunately, chemistry allows the work of adhesion to be reduced to low levels, so that small particles can move freely, displaying Brownian motion in certain environments. The adhesion of mica, for example, is reduced by a factor of 5 in water (Fig. 2). Again, in the surface force apparatus, hydrocarbon rubber spheres give a work of adhesion of 71 mJ m^{-2} in air, but this fell to 6.8 mJ m^{-2} in water, as expected from Young's equation for a contact angle of 64° (*21*). When sodium dodecyl sulfate was added to the water, to make the liquid wet the surface, the work of adhesion became negative; in other words, the surfaces were pushed apart by the intervening fluid. Such repulsive surface forces caused by the adsorption of ions on the surfaces were first measured by Perrin and Constantin in 1914 using Brownian motion (*1*). Theoretical explanation of this effect in terms of the combination of van der Waals attractions and ionic repulsions to provide colloidal stability of particles in aqueous suspensions was put forward by Derjaguin and Landau and by Verwey and Overbeek (*27*).

Nonwetting liquids increase adhesion, as shown by experiments with polydimethyl siloxane rubber, which gave a work of adhesion to itself of 43.6 mJ m^{-2} in air. In water, a nonwetting liquid, this rose to 74 mJ m^{-2}, whereas in methanol, a wetting liquid, the value fell to 6 mJ m^{-2}, again consistent with Young's equation (*28*). When certain molecules were reacted with the rubber surface to make specific organic groups stick out from the surface, the work of adhesion values were consistent with wetting measurements on the same surfaces. Such experiments demonstrate molecular control of adhesion at a fine level. These specific molecular interactions are particularly interesting in biology, where adhesion of cells is important to healing, to inflammation, and to metastasis of malignant growths (*28*).

Effects of Fluid Molecules near the Surface

Fluid molecules near surfaces have two effects that alter adhesion substantially.

The first effect is adsorption on the surface, which reduces adhesion. This was seen first by Obreimoff (*29*), who cleaved mica both in air and in vacuum and demonstrated that the cleavage energy was reduced by a factor of 13 in air. He also observed electrical discharges between the surfaces and noticed that time was required for cleavage to occur in different atmospheres, several seconds being needed at atmospheric pressure, compared with some days at low pressure. Bailey and Kay (*30*) followed up those observations by showing that the work of cleavage of mica is 616 mJ m^{-2} in dry air, dropping to 510 mJ m^{-2} in hexane, and to 215 mJ m^{-2} in water. The conclusion from such experiments is that adhesives, that is, fluids that spread on solid surfaces, reduce adhesion in a molecular sense, because the surfaces cannot jump together completely but are separated by a layer of molecular contamination. However, at the engineering level, adhesives may increase adhesion by filling gaps and altering the fracture mechanism, as in adhesive stringing.

The second effect of fluid molecules was observed by Horn and Israelachvili (*31*) as the gap between smooth mica surfaces became comparable with the size of the fluid molecules in between. The surfaces did not jump together in one step but jumped in a series of steps governed by the size of the fluid molecule. Using octamethylcyclotetrasiloxane, an inert liquid of approximately spherical molecules 0.9 nm in diameter, they showed that oscillating attractive and repulsive forces that exceed the van der Waals force come into play when the gap is less than 10 molecular diameters (Fig. 4A). The overall work of adhesion was 11 mJ m^{-2}, but there were several possible metastable equilibrium points of reduced adhesion, at the zero points in the curve shown in Fig. 4A. Subsequent measurements on other liquids, such as benzene, cyclohexane, and carbon tetrachloride, confirmed this argument and showed that the periodic jump distance was almost equal to the molecular diameter of the fluid.

In water with electrolyte, comparable behavior was observed (*32*) but now superimposed on the ionic double layer repulsions. These findings are relevant to the behavior of colloidal particles such as clays, which swell in water as hydration forces push the ceramic surfaces apart. These forces may also be used to control the dispersion of pigments, inks, paints, cosmetics, pharmaceuticals, and other products.

The oscillatory solvent forces became significant below 2-nm separation (Fig. 4B). Large repulsions were observed. Very smooth surfaces were necessary to see such fine-scale variation in these hydration forces. More often a steady increase in repulsion was observed as surfaces approached in water (*33*). In particular, when polymer molecules were dissolved in the water (*34*), repulsions were observed at large separations (40 to 80 nm), and these repulsions increased steadily as the gap became smaller (Fig. 4C). Moreover, significant kinetic effects were then observed as time was required for the surface structures to alter. Such kinetic effects are examples of the more general phenomena known as adhesive drag and hysteresis.

Adhesive Drag and Hysteresis

Because an adhesive interface can exist in several possible metastable states, separated by energy barriers (Fig. 4, A and B), it is plausible that the interface can change from one state to another as a function of time, temperature, and applied force, as postulated some years ago (*35*). Equilibrium may take some time to occur and, in some cases, may never be achieved. Energy is lost as heat during these rate processes because jumping between states is not a steady thermodynamic process; contact is not reversible, and the theories of Eqs. 2 and 3 no longer apply.

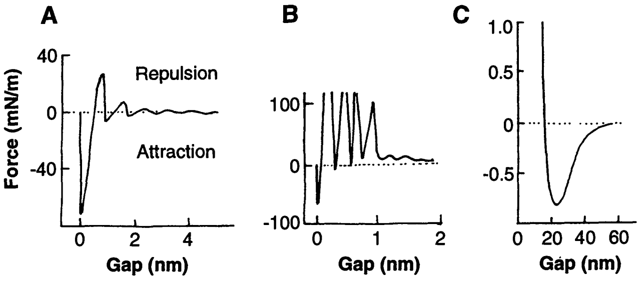

Fig. 4. (**A**) Measured surface forces between mica surfaces immersed in octamethylcyclotetrasiloxane, showing the several metastable equilibrium points where the force is zero (*31*). (**B**) Surface forces in water with added electrolyte, showing the effect of ionic forces adding to the van der Waals and solvent forces (*32*). (**C**) Surface forces in water with added polymer (*34*).

Perhaps the simplest example of this phenomenon was seen in rubber that had been cross-linked with sulfur during molding in a concave glass lens. Upon removal from the lens, the rubber was optically smooth and adhered well to glass, giving reproducible results in the sphere adhesion test. However, after being left in air for several days, the rubber became dull and sulfur particles were observed on the surface, having diffused from the interior. These sulfur particles reduced the adhesion considerably. But when the rubber was left in contact with the glass lens for several more days, the surface became smooth again, and the adhesion recovered its original value. It appeared that the sulfur particles had been pushed back into the bulk rubber, restructuring the surface. This is an example of the dwell-time effect, in which adhesion increases with contact time (*36, 37*).

Another easily measured kinetic effect is adhesion drag. When a force is applied to separate two surfaces, the separation is not instantaneous but takes some time. As the applied force is raised, the rate of separation increases. Increasing the temperature also increases the separation rate. This effect is most conveniently measured by observing the crack front in a peeling test and plotting the logarithm of crack speed against the ratio of applied force to crack width, which is equivalent to adhesion energy. This measured nonequilibrium value of adhesion energy, denoted *Æ*, is to be distinguished from the equilibrium work of adhesion *W*, which is a thermodynamic parameter.

Typical results are shown in Fig. 5 for the cracking of a rubber-glass interface (*35*). The data follow a typical Eyring curve, tending to a constant force at low speed and giving a straight line at high speed. Also shown are results for formation of the contact. Clearly, there is adhesive drag during the contacting process. The interesting thing about *Æ* is that it can be used in the equilibrium equations of Table 1, replacing *W* to give useful results for engineers (*37*). The limits of such substitution are not known.

Even at low speeds, equilibrium may not be attained. There may be a substantial difference between the adhesion energy measured during the making of the joint and that measured during the break (Fig. 5), even after a long time has been allowed to encourage equilibriation. This difference is adhesive hysteresis. The equilibrium value of adhesion energy, that is, the work of adhesion *W*, lies between the extreme values of *Æ* at long times and is generally nearer the make rather than the break value. Adhesive hysteresis can increase when the rubber is less cross-linked, that is, less elastic (dashed line, Fig. 5).

The problem with the interpretation of these results, which are reminiscent of contact angle hysteresis data, is the allocation of mechanisms to explain the energy loss. For example, some of the energy loss may not be at the interface itself but may take place in the surrounding materials, which are often not truly elastic and can therefore cause hysteresis (*37*). However, it was found by varying the parameters independently that much of the adhesive drag was interfacial in origin but that hysteresis could be amplified by viscoelastic losses away from the interface (*35–38*). An example of a near perfect elastic system, based on silastomer, has now come to light. This system gave limited adhesive drag and no hysteresis when the surface was clean or covered with certain hydrocarbon monolayers. However, significant hysteresis was found when the monolayers could reconstruct with time (*19, 39, 40*).

Interesting Adhesion Mechanisms

Adhesive drag and hysteresis are examples of mechanisms that are partly molecular and partly mechanical. Therein lies their charm. Two other such mechanisms are stringing and clustering.

Stringing is a phenomenon that is often seen on adhesive tapes and was mentioned by Rivlin (*23*). The rubbery adhesive layer does not separate by simple cracking but bridges the adherends by drawing out strands that continue to hold the surfaces together as significant separation occurs (Fig. 6). This stringing mechanism is significant because it has similarities to crazing in polymers (*41*), fiber reinforcement of composite materials (*42*), and plastic flow at the tip of a crack in a metal (*43*). In all of these examples, the dangerous crack is restrained because the bridging fibers hold the crack faces together and make the adhesive joint less brittle. Essentially, this mechanism allows extra energy dissipation and moves the fracture of the joint further from equilibrium. This is necessary for engineered joints because even the strongest chemical bonds have work of adhesion around 10 J m^{-2}, 1/10,000 of the adhesion energy required by designers to resist fracture of joints.

Consider the adhesive joint shown in Fig. 6. A force *F* is applied to the joint of cross-sectional area *bd*, opening a crack of length 2*c*. The adherend material has an elastic modulus *E*, and the adhesion energy of the adhesive is *Æ*. If the adhesive did not string out across the crack, then the Griffith fracture criterion would apply (*26*)

$$F = bd\left(\frac{E\text{Æ}}{\pi c}\right)^{1/2} \qquad (4)$$

This equation describes brittle behavior where the joint is sensitive to defects and where the crack accelerates strongly after initiation. However, when the adhesive strings out and supports a stress *S* across the crack face, the crack criterion changes to

$$F = bd\left[S + \left(\frac{E\text{Æ}}{\pi c}\right)^{1/2}\right] \qquad (5)$$

This equation describes safer behavior, less sensitive to defects and with more graceful failure. Ideally, the string stress *S* should be large for this mechanism to be effective.

Clustering is a phenomenon that is seen in the grinding of fine powders (*44*). Consider a fine zirconium oxide powder with

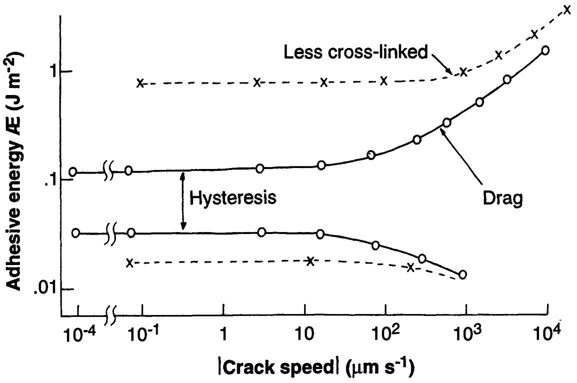

Fig. 5. Peel adhesion results for rubber on glass as a function of peel crack speed. The vertical axis is the ratio of the peel force to the width of the peeling strip—this is the adhesive energy. The lower solid curve shows the results for making contact, the upper for breaking contact. The dashed lines show the increase in hysteresis when the rubber was less cross-linked.

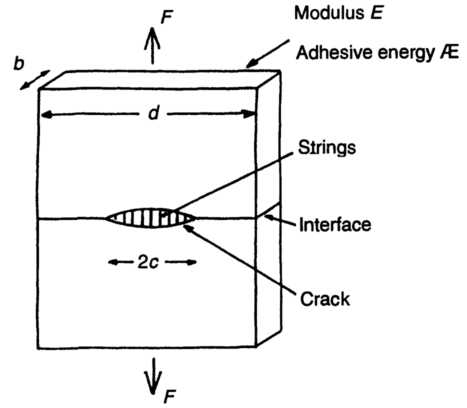

Fig. 6. Geometry of a crack traveling along an interface with stringing across the face of the crack. The stress supported by the strings is assumed to be a uniform value *S*.

roughly spherical particles 150 nm in diameter (Daichi HSY8). This is usually handled in dry powder form, and the adhesion between the particles is substantial. A particle size measurement by laser light scattering shows that most of the particles are agglomerated (Fig. 7A) and that these agglomerates resist breakdown in a 5-W ultrasonic bath.

The simplest way to break up such strong agglomerates is to mix the powder with water, to give a solids volume fraction of 0.2, and to shake the suspension in a polyethylene bottle with zirconia grinding media (cylindrical beads 6 mm in diameter and 6 mm long). After 2 hours of shaking, the particle size distribution reached a steady state (Fig. 7B), in which the breakdown of the existing agglomerates was balanced by the formation of new agglomerates. At this point, few individual zirconia particles could be detected at a size of 0.15 μm. Most of the particles were in agglomerates around 2 μm in diameter.

After 2 days, the particle size distribution was remeasured (Fig. 7C). The 2-μm agglomerates had grown slightly to 4.4 μm as the fine particles adhered to the agglomerates, but a distinct cluster had appeared at 34 μm. This cluster was resistant to ultrasonic breakdown and did not grow further with time, suggesting a particular stability for this cluster size.

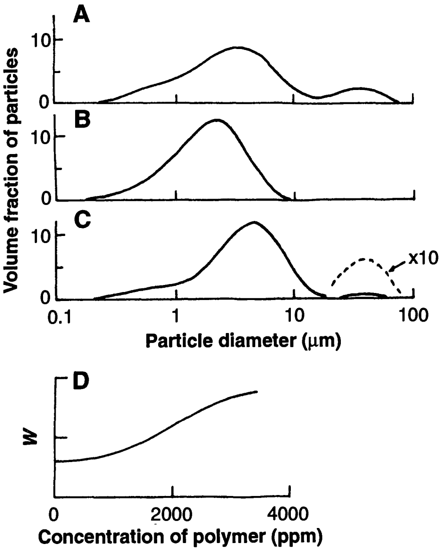

Fig. 7. Particle size distribution (Malvern Mastersizer) for (**A**) dry zirconia powder as received (Daichi HSY8, Japan), (**B**) for the same sample after shaking it in water with zirconia beads for 2 hours, (**C**) and for the same sample after letting it rest for 2 days, showing the emergence of the cluster peak at 35 μm. (**D**) Reduction in cluster diameter with addition of ammonium polyacrylate (measured in parts per million) indicates an increased work of adhesion (in arbitrary units).

A theory for the stability of particle clusters was suggested recently, on the basis of a nucleation model (*45*), in which it was assumed that the fine particles were moving with Brownian motion and were in thermal equilibrium with clusters that could grow and break up. The critical cluster size was calculated by balancing the free surface energy of the cluster with its bulk elastic energy. A stationary point occurs at a size Δ given by

$$\Delta = 0.064\left[\frac{2ED^{5/2}}{W(1-\nu)^2}\right]^{2/3} \qquad (6)$$

where ν is Poisson's ratio. Putting in values for $E = 2 \times 10^{11}$ Pa, $\nu = 0.3$, $D = 150$ nm, and $W = 0.3$ J m^{-2} gave the critical cluster size as 34 μm, which fits the experimental result.

A polymer dispersing agent, ammonium polyacrylate [Allied Colloids (Bradford, United Kingdom), Dispex], was added to the powder mix, and the experiment was repeated. The cluster size decreased systematically with polymer concentration. From Eq. 6, this suggests that the work of adhesion was increasing with polymer addition (Fig. 7D). This increase may be explained by depletion of polymer in the gaps between the particles.

Conclusions

All solid surfaces in air adhere by jumping together. The lack of adhesion that we observe in engineering circumstances is therefore an aberration (*46, 47*) that depends on the mechanisms of contact rather than on molecular adhesion. If we define the molecular forces through *W*, the work of adhesion per unit area of contact, equations for the mechanical force of adhesion in particular geometries can then be derived. Such equations define the link between adhesion mechanism and adhesion of molecules. For example, Bradley's equation giving the adhesion force between two contacting spheres can be derived to explain the transition between the engineering world in which adhesion is negligible and the nanometer-scale world in which adhesion dominates. The mechanisms of adhesion, and other fascinating phenomena like adhesive stringing and clustering, are worthy of further study and elucidation.

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