ANALYTICAL SERIES

To Stick or Not To Stick: Guide to Adhesion Measurement for the Layman

By **Dr. Robert H. Lacombe**,
Materials Science and Technology, Conferences

INTRODUCTION AND OVERVIEW

This two-part article is a condensation of a much larger work[1] that deals with the full range of adhesion measurement, including details of continuum theory, fracture mechanics, measurement of intrinsic stress, and several detailed applications. It is assumed that most readers are not conversant with the technical concepts of fracture mechanics or continuum theory, so, to establish a baseline of understanding, Part I will provide a brief tutorial on the most relevant aspects of these topics before wading into the main discussion. Part II of the tutorial, to be published in the next issue of *CoatingsTech*, gives a *Consumer Reports*-style evaluation of several adhesion measurement methods that are of relevance to the coatings industry.

Applying a coating to a surface is a sticky subject and at many times a very slippery one too. The sticky aspect is obvious and needs no further comment. The intent of this tutorial is to give an overview of adhesion measurement as a tool for dealing with the slippery aspects of applying a coating and ensuring that it stays adhered. The essential problem arises from the fact that adhesion is a basic property of surfaces, to quote a famous physicist: “God created matter; surfaces were invented by the devil.”*

Surfaces are indeed devilish entities, especially for those who seek a quantitative understanding of their behavior. This arises from the fact that for nearly all macroscopic objects, the surface area forms but a very small portion of the total volume compared to the bulk and is further subject to highly asymmetric forces and strongly prone to contamination and a large variety of defects.

This tutorial will deal with the science and technology of adhesion measurement with the intent of bringing the technical aspects of the subject down to a level comprehensible to the non-specialist while in no way sacrificing the essential scientific content of the topic.

WHAT IS ADHESION AND CAN IT BE MEASURED?

There has been considerable debate in the technical literature concerning the above question and it is certainly not our intent here to further expound upon what has been plowed over many times before. However, in order to provide a certain measure of perspective and to establish a defensible position on this matter, it is worthwhile to at least briefly discuss this problem. One of the earliest overviews of this issue was given by Mittal[2] and we will take his discussion as a starting point. The basic argument comes down to what one takes as the definition of “adhesion.” Now, from a common sense point of view, one would like to think that adhesion is a simple matter of how well two different

---

*Attributed to Wolfgang Pauli, German physicist, best known for his famous quantum mechanical exclusion principle which is the basis for the compressive stability of all matter.

materials tend to stick together and that adhesion measurement is some indication of the force required to separate them. Although this approach may suffice for the "man in the street," it runs into serious difficulty when one tries to arrive at a more scientific definition of adhesion that can be useful for engineering purposes. A truly useful definition of the term adhesion needs to have the following properties:

DEFINITION A—Criteria for a Truly Useful Definition of the Term Adhesion:

If we say that "X" is the adhesion of material A to material B, then it should have the following characteristics:

1. "X" has the same meaning for all practitioners who would stick A to B;
2. "X" is unambiguously measurable by one or more commonly understood methods; and
3. Knowing "X" allows the practitioner to predict the loading conditions which will cause material A to delaminate from material B

Many would agree that the above is certainly a worthy definition of the term adhesion, but it unfortunately runs into a number of difficulties in practice due to the slippery aspects of the science of adhesion discussed previously. For instance, consider proposition 1, where two investigators are attempting to adhere coating A to substrate B assuming all conditions are identical, except that the first investigator is interested in very thin coatings, less than a micrometer, whereas the second investigator is interested in thick coatings on the order of several hundred micrometers. It can easily happen that investigator 1 will observe excellent adhesion, whereas investigator 2 will experience severe delamination problems. The important issue to be aware of in this example is that the driving force for delamination due to residual stress in the coating increases in direct proportion to the coating thickness and, thus, investigator 2 is at least 100 times more likely to experience delamination problems than investigator 1.

A second difficulty arises with the second proposition requiring that the definition enable the use of simple and unambiguous measurement procedures. From the point of view of the practical practitioner, this is quite likely the most important property one would desire in any truly usable definition of the term "adhesion." However, the two qualifications of being both simple and unambiguous tend to be mutually contradictory in that a truly simple test is not likely to be unambiguous since, in the service of simplicity, a number of important details will be either omitted or glossed over. The truly unambiguous test will specify in great detail the conditions of sample preparation, including cleaning procedures and control of material properties, as well as a precise specification of loading conditions and control of the ambient environment. Observing all of these caveats will tend to undermine the goal of achieving simplicity. Clearly, any truly usable definition of adhesion will have to seek an appropriate balance between these two criteria.

Finally, proposition 3, requiring that our definition have true predictive power, again comes into conflict with proposition 2, since in order to obtain a truly predictive measure of adhesion one must clearly give the utmost attention to all the details which will ensure an unambiguous result. Doing this will clearly sacrifice the goal of achieving simplicity. In addition, to be truly predictive, the measurements have to be fully quantitative and consistent with detailed calculations. This implies at a minimum the use of fracture mechanics methods and the continuum theory of materials. Rather than belabor this point any further, we frame the following definition:

DEFINITION B: ADHESION—We say the adhesion of material A to material B is such and such based on the following criteria:

1. The adhesion of A to B is a relative figure of merit indicating the tendency of A to stick or bind to B derived from an observation or measurement that can be entirely qualitative, semiquantitative, or fully quantitative.
2. The precise meaning of the term is entirely dependent on the details of the measurement technique employed and the experimental and environmental conditions under which the measurement was made. This leads to a hierarchy of definitions. Thus, qualitatively we might say A has good adhesion to B based on the observation that A was never observed to separate from B under a variety of common loading conditions. A semiquantitative statement of the adhesion of a coating of material A onto a substrate of material B might indicate that 2% of the coating was removed during a "scotch tape" test. Finally, a fully quantitative statement might conclude that the adhesion strength of A to B is 10 Joules/meter^2 based on a double cantilever beam experiment carried out at 50°C under 40% relative humidity.

A SHORT TUTORIAL ON TERMS AND DEFINITIONS FROM ELEMENTARY FRACTURE MECHANICS AND CONTINUUM THEORY

Guide to Elastic Behavior of Materials: Continuum Theory 101

Before beginning the review of adhesion measurement methods, it will be helpful to examine a few of the concepts and definitions from continuum theory and fracture mechanics which underlie all adhesion measurement techniques and are important for a proper understanding. Much unnecessary confusion arises from a proliferation of units used to quantify adhesion measurements, such as psi, dynes/cm^2, gm/mm, etc. To establish a common framework for discussion, the internationally accepted and commonly used SI units* will be adopted as follows:

Force should be given in Newtons (N). One Newton is approximately the force exerted by a 100 gm weight in Earth's gravitational field, which is close to the weight of a standard-sized apple. Thus, if you are holding a normal-sized apple, it is weighing down on your hand with a force load of close to one Newton.

Stress is a force distributed uniformly over a surface area which is measured in square meters (m^2). Our unit of stress is thus a Newton per square meter, or N/m^2, commonly called a Pascal (Pa), named after the famous French philosopher Blaise Pascal (1623–62), mathematician, physicist, and religious philosopher. He was the founder of the theory of probabilities, but is best known for his work elucidating the theory of hydrostatic pressure.

A typical apple does not weigh much and if you spread that weight over a square meter, it exerts an almost negligible pressure. In fact, 1 Pa is a very small stress indeed, being roughly 100,000 times smaller than the atmospheric pressure squeezing on all of us who are sitting not too much above sea level. Thus, stresses exerted in adhesion tests are typically given in kilo Pascals (10^3 Pa) (abbr. KPa) and the residual stresses in solid bodies are normally quoted in mega Pascals (10^6 Pa) (abbr. MPa).

We will also need the concept of **energy**, which is useful in describing the work needed to remove a coating from a surface. In SI units, the unit of energy is the Joule, named after James Prescott Joule (1818–89), the British physicist who established that all forms of energy were basically the same and interchangeable—the first law of thermodynamics. A Joule is the SI unit of energy, equal to the work done by a force of one Newton when its point of application moves one meter in the direction of action of the force, thus 1 Joule equals 1 Newton-meter.

It is useful to note that a stress can also be thought of as an **energy density** since N/m^2=N–m/m^3=Joules/m^3. This is a very useful notion when dealing with problems of fracture and delamination, as we will see later.

Finally, we will have to deal with the **elastic properties** of coatings and their substrates since nearly all adhesion measurement methods are affected by these properties. The following definitions will be used henceforth.

All elastic objects, when stressed by some external load, will deform by compressing or extending depending on the loading details. The simplest case is where a slender rod is pulled along its lengthwise axis. If the unstressed length of the rod is L and the load lengthens it by some small amount ΔL, then we define the strain to be $\varepsilon=\Delta L/L$. The strain is clearly dimensionless and in nearly all cases involving coatings also quite small, being on the order of about 0.01 or less. In the case of our simple rod, there is a very handy relationship between the applied axial stress and the resulting strain, called Hooke's law. This is named after Robert Hooke (1635–1703), the English scientist who formulated not only the law named after him, but remarkably, also proposed an undulating theory of light, introduced the term "cell" to biology, postulated elliptical orbits for the earth and moon, and proposed the inverse square law of gravitational attraction. Simply stated, Hooke's law is given as:

$$\begin{aligned} &a)\quad \sigma_x = E\,\epsilon_x \\ &b)\quad \epsilon_y = -\nu\,\epsilon_x \end{aligned} \tag{1}$$

Equation (1a) is the standard version of Hooke's law, simply stating that the applied stress is proportional to the imposed strain. The constant of proportionality is the Young's modulus E, named after Thomas Young (1773–1829), English physicist, physician, and Egyptologist. Apart from his work in elasticity, he contributed to the wave theory of light and also played a major part in the deciphering of the Rosetta Stone—yet another polymath from the 18th and 19th centuries. Since the strain is dimensionless, the Young's modulus must have the same dimensions as the stress and is in fact commonly measured in Giga Pascals (GPa=10^9 Pa). Typical values of the Young's modulus for common materials are:

- Rubber E=10–4 GPa
- Engineering thermoplastics E=1–3 GPa
- Window glass E=70 GPa
- Aluminum E=70 GPa

---

*A system of physical units, based on the meter, kilogram, second, ampere, kelvin, candela, and more.

- Steel E=200 GPa
- Ceramic E=350 GPa
- Diamond single crystal E=1000 GPa

Equation (1b) completes the description of one-dimensional elasticity by defining Poisson's ratio "ν," named after Siméon-Denis Poisson (1781–1840), the French mathematical physicist. His major contributions were in probability theory and electrostatics, where he developed the well-known Poisson equation governing the electrostatic potential arising from an arbitrary charge distribution. Poisson's ratio tends to lie in the range of 0.2 to 0.4 for most materials and describes the fact that when a strip of material is stretched in the axial direction, it must also contract in the perpendicular direction by an amount given by equation (1b). This is a small and largely ignored effect in one dimension but starts to play a significant role in two dimensions, which is the case of most interest for coatings. For coatings in two dimensions, equations (1a and 1b) generalize to:

$$\begin{aligned} &\sigma_x = \sigma_y = \frac{E\,\epsilon}{1-\nu} \\ &\sigma_z = 0 \\ &\epsilon_z = -\frac{\epsilon}{1-\nu} \\ &\epsilon = Planar\ shrinkage\ strain \end{aligned} \tag{2}$$

σ_x and σ_y measure the in-plane biaxial stress and the perpendicular component σ_z is zero everywhere except near edges and other discontinuities. The planar shrinkage commonly arises from the thermal expansion mismatch between the coating and the substrate but can also arise from solvent loss and various chemical reactions. We see from equation (2) that the Poisson ratio now plays a more significant role in governing the stress in coatings and can increase the stress by a factor of 1.5 to 1.7 for most materials.

Guide to Cracking and Delamination of Coatings: Fracture Mechanics 101

With the rudiments of elasticity theory behind us, we move on to the modern theory of material failure: Fracture Mechanics. Fracture mechanics theory comes about to address one of the fundamental conundrums of elasticity theory, which is the fact that it is riddled with singularities. In essence, when modeling the stress and deformation behavior of a structure such as a multilevel laminate, classical elasticity theory unequivocally predicts that the stress can be infinite near any kind of sharp discontinuities such as cracks and sharp edges.

Figure 1 illustrates this problem for a uniform coating on a rigid disk. The normal stress component σ_z is zero in the interior of the disk as predicted by equation (2), but this equation holds only for an infinite coating with no edges. For a finite disk, the edge represents a sharp discontinuity, and in consequence, elasticity theory predicts an unbounded or infinite stress level at this point. This comes about because continuum theory assumes all matter is homogeneous and continuous down to the smallest dimensions imaginable, which clearly breaks down at the atomic and molecular level. Nevertheless, even at dimensions as small as 10 nanometers (1 nanometer=10^{-9} meters), continuum theory gives an excellent approximation to reality since even at this small dimension, atomic and molecular matter are so densely packed as to behave as a uniform continuum. However, the question still remains as to how to deal with the singularity problem and the answer lies in dealing with the elastic strain energy as opposed to focusing on the stress level.

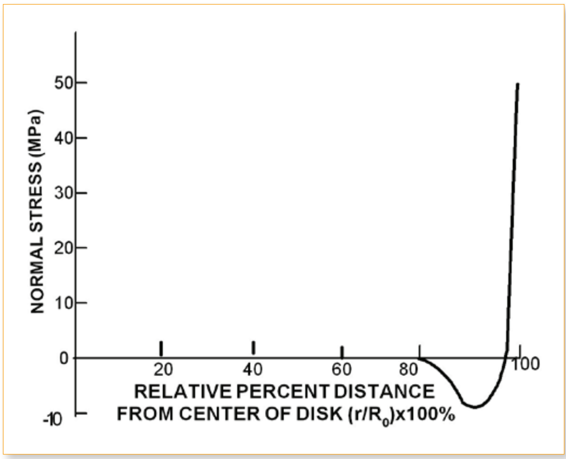

Figure 1—Normal stress distribution in a uniform coating on a rigid disk substrate of radius R_0. The stress increases without bound at the edge of the disk.

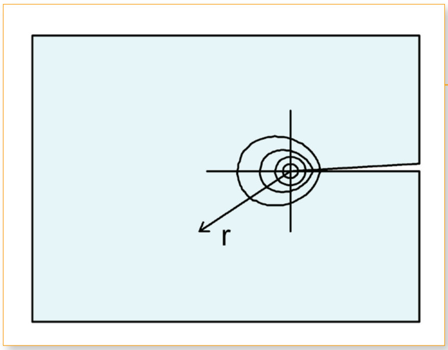

Figure 2—Singular stress field at the tip of a sharp crack.

Figure 2 illustrates the problem for a sharp crack. The figure illustrates a sharp crack and we have positioned a coordinate system at the crack tip showing the radius vector r giving the direction and distance from the crack tip to any point in the material. The basic finding of elasticity theory is that the magnitude of the stress σ varies as the inverse square root of the distance to the crack tip as follows:

$$\sigma = \frac{K}{\sqrt{r}} \tag{3}$$

The singular behavior is captured in the inverse square root dependence on the magnitude of the radius vector r, which clearly becomes unbounded as r tends to zero. The factor K hides all the geometric and material complexities of the problem and will depend on the detailed geometry and elastic properties of the material. K is nonetheless a finite number called the **stress intensity factor** and is used to differentiate one type of singularity from another, since the inverse square root dependence on the radius vector is a universal property for all singularities whether they arise from sharp edges, cracks, or whatever. Remembering now that the stress can also be thought of as an energy density, we can ask, What is the contribution of the singular stress field near the crack to the total elastic strain energy in the solid? To answer this question, we need to integrate the stress field in equation (3) over some volume encompassing the crack, which works out as follows:

$$U = \int_V \frac{K\,dV}{\sqrt{r}} =$$

$$4\pi K \int_0^R \frac{r^2\,dr}{\sqrt{r}} = \qquad (4)$$

$$4\pi K \int_0^R r^{3/2}\,\mathrm{dr} = 4\pi \mathrm{K} R^{5/2}$$

The main point of equation (4) is that the elastic strain energy contributed by the stress singularity at the crack tip is a finite number depending on the stress intensity factor K and the size of the volume element surrounding the crack tip, i.e., the singularity disappears when working with strain energy as opposed to stress. This result suggests that one convenient way to circumvent the stress singularity problem is to work with strain energies as opposed to stresses, which leads directly to the concept of the **strain energy release rate**. *Figure* 3 illustrates this concept in the case of a highly stressed coating on a rigid substrate. The coating has a high level of stored elastic energy due to a high stress level. This could arise from either a thermal expansion mismatch with the substrate or other shrinkage process such as solvent loss or chemical reaction which causes the coating to try to contract, which it cannot do because it is adhered to the immovable substrate.

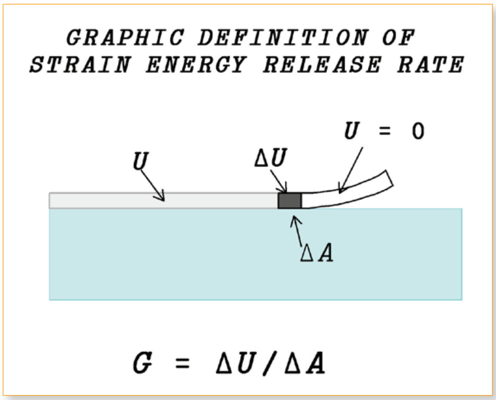

Figure 3—Strain energy release rate, defined as ratio of the increment of energy ΔU required to separate an increment of area ΔA of a coating from a substrate.

Thermodynamically, the coating would like to lower its internal energy as much as possible, which it can do through a delamination process. The driving force for this process is measured by the amount of internal energy ΔU which can be released per increment in newly created surface area ΔA. This ratio defines the so-called strain energy release rate $G=\Delta U/\Delta A$. Confusion arises many times because G is not a rate in time but a rate of incremental change in internal elastic energy per unit increase in surface area. A companion to G is what is called the **surface fracture energy** γ. Since the coating is bonded to the substrate through intermolecular forces, delaminating an increment of the coating requires a certain amount of energy to overcome these forces and γ measures the amount of energy required for a unit increment of delaminated area to be created. Thus, G has to be at least as large as γ for delamination to occur. If G is less than γ then there is not enough elastic energy available to advance delamination and the process is arrested.

Similar kinds of arguments can be invoked for those who prefer to work with stresses instead of energies. In the stress formulation, the stress intensity factor K is the prime quantity of interest. K is said to measure the strength of the stress singularity with large values of K corresponding to dangerous cracks that are likely to propagate and small values corresponding to relatively benign flaws that are likely to remain arrested. Analogous to the energy formulation, one can speak of the **critical fracture toughness** K_c as a measure of the strength of a material in resisting crack propagation. Thus, if the stress intensity factor K at a crack tip is less than the fracture toughness of the material K_c, the driving force propagating the crack is too weak and the crack is said to be arrested. Interestingly enough, through some miracle of mathematical prestidigitation, the concepts of strain energy release rate and stress intensity factor are fully equivalent, and, in fact:

$$G_I = (1 - \nu^2)\frac{K_I^2}{E} \qquad (5)$$

Thus, one can work in either the stress formulation or the energy formulation and use equation (5) to convert between the two, if necessary. Equation (5) also brings us to one final technical point which requires elucidation. Note that equation (5) involves the quantities G_I and K_I, which are referred to as the mode I strain energy release rate and stress intensity factor. There are also mode II and mode III versions of these quantities and all are required to cover the allowable loading configurations which are possible. Thus, mode I behavior occurs when the material is being separated in pure tension, as when one pulls on the ends of a string. Mode II refers to the case when the loading is in pure shear, as when trying to slide an object over a sticky surface. Mode III is a rather more arcane situation of a shearing type of motion perpendicular to the direction of crack propagation and is observed in rather rare situations. The Velcro® fastener material gives a ready illustration of the difference between mode I and mode II loading situations. A Velcro joint is highly resistant to mode II or shear loading but separates readily when loaded in mode I, explaining why your ski jacket remains tightly closed when in use but opens quite easily when pulled apart in pure tension.

Part II of this article, to be published in the September issue of CoatingsTech, provides an overview of the most common adhesion measurement methods.

References

1. Lacombe, R., *Adhesion Measurement Methods: Theory and Practice,* CRC Press: Boca Raton, FL, 2006.
2. Mittal, K.L., “Adhesion Measurements: Recent Progress, Unsolved Problems, and Prospects,” in *Adhesion Measurement of Thin Films, Thick Films, and Bulk Coatings, ASTM STP-640,* Mittal, K.L. (Ed.), American Society for Testing and Materials: Conshohocken, PA, pp 5-17, 1978.

AUTHOR

Robert H. Lacombe, Ph.D., Materials Science and Technology, Conferences; 3 Hammer Dr., Hopewell Junction, NY 12533; rhlacombe@compuserve.com.
