

Using Fracture Mechanics to Characterize Organic Coatings

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The multitude of ways in which a coating can fail are well known to both users and producers of organic coatings. Many failures are gradual and are aesthetic in nature only, such as gloss loss and color fade. Others are more mechanical in nature such as cracking or peeling. These mechanical failures can lead to a loss of substrate protection or corrosion, which may compromise the structural integrity of the painted component as well as produce an unacceptable appearance. By understanding the manner in which these failures occur one can design coating systems in a more robust fashion to prevent them.

Most of the mechanical failures that occur in coatings are due to cracks propagating within the coating, at an interface between the coating and a substrate, or between two coating layers (Figure 1). To truly understand how these cracks propagate, the principals of fracture mechanics must be applied to the coating system. Fracture mechanics is the discipline that quantitatively describes how cracks propagate in materials and at interfaces. This approach has been used extensively to understand and predict the performance of aluminum aircraft alloys as well as high strength composite materials. Its application to coatings technology was only initiated in the last decade.^{1,2} However, recent advances have made it a powerful tool to understand the performance of many organic coatings. This article aims to introduce the reader to the principals of fracture mechanics and how the application of these principals to organic coating characterization can improve the durability and performance of coating systems.

BASICS OF MECHANICAL BEHAVIOR

Before diving into fracture mechanics itself, a short review of general mechanical behavior is required.

When a material (organic coating, metal, plastic, etc.) is subjected to a load it deforms in proportion to the load applied—the larger the load, the greater the deformation. The behavior can be quantified by using the concepts of stress and strain. The stress a material experiences is simply the load (force) applied divided by the cross sectional area of the material. The deformation is typically characterized by the strain, which is the change in length of the material divided by its original length. When the stress-strain behavior of a material is studied it is often plotted as shown in Figure 2, where the behavior of three typical coatings is shown. In all three cases, as the coating is deformed (in this case, stretched in tension) the load on the coating increases. The slope of the initial part of the stress-strain curve is called the modulus and is a measure of the stiffness of the material. The modulus is typically given the symbol, E , and has SI units of MPa.

For the curve labeled *a* the material ruptures at a rather low level of strain and the curve is quite linear up to the breaking point. This is typical of a highly crosslinked coating tested well below its T_g . For coatings like this, if the stress-strain test was stopped before the material broke and the load was released, much like the stretching and un-stretching of a rubber band but on a

smaller length scale. The middle curve (b) in Figure 2 shows a moderately ductile coating, which is representative of a lightly crosslinked coating tested at room temperature or a highly crosslinked coating tested at elevated temperatures. In this case, the stress-strain curve begins to deviate from linearity, indicating the onset of some non-recoverable deformation. This residual deformation is called plastic deformation and the point on the stress-strain curve at which it begins to accumulate is called the yield point (yield stress and yield strain). For organic materials (plastics and coatings), the yield point is strongly dependent on temperature as well as the rate of deformation. For this reason it is not possible to uniquely identify the yield stress or strain without specifying the temperature and rate of testing. These points are important to remember when discussing the fracture behavior of coatings. The bottom curve (c) in Figure 2 is typical of a lacquer or thermoplastic coating where significant deformation can occur before the coating ruptures. Here, the load actually goes through a maximum and then drops before significant drawing of the coating occurs. Rupture may not occur till the specimen has increased in length by over 100%.

Another important point to remember is that materials are rarely free of flaws. Extensive studies have shown that flaws (voids, scratches, etc.) in a material are typically the places where failures initiate. For example, during a simple tensile stress-strain test, the sample will typically fail due to the presence of a small imperfection on the surface or in the interior of the sample. The stress-

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strain curves shown in Figure 2 have been obtained from specimens prepared in a way to minimize the number of edge flaws, but no extraordinary measures were taken to remove small flaws from the specimens. Without the presence of the flaw the ultimate stress and strain measured would have been higher.³ In practice, the theoretical strength of materials is never achieved due to the presence of these flaws, which are often microscopic in size.

FRACTURE MECHANICS—BASICS

Because flaws are always present in materials, a method to anticipate the failure strength of materials necessarily must incorporate the effect of these flaws. Over the years, two different approaches have been developed to describe the breaking strength of materials and how flaws propagate as cracks during material service. An important point to remember is that fracture mechanics describes the *propagation* of cracks in a material and not the *initiation* of the small flaws from which the cracks propagate. We must assume or experimentally determine the size of flaws or a distribution of flaw sizes in order to use fracture mechanics to make predictions about the performance of materials in service.

Energy Approach

The first method developed to examine the propagation of cracks in materials was proposed by Griffith, who was studying the breaking behavior of inorganic glass.⁴ He suggested that the mechanical energy required to cleave a piece of glass was equal to the surface energy penalty for creating two new surfaces when a crack propagated through the glass (see Figure 3). Thus, the breaking strength, σ , could be related to the surface energy, γ_s ; the flaw size, a ; and the elastic modulus, E ; by the equation

$$\sigma = \left(\frac{2E\gamma_s}{\pi a} \right)^{\frac{1}{2}} \quad (1)$$

For the brittle, inorganic glasses Griffith was studying, experiments showed that the theoretical prediction underestimated the measured value by approximately a factor of two. However, the discrepancy between the measured breaking strength and the strength cal-

culated from the surface energy contribution alone is much larger for more ductile materials. This discrepancy is largely due to other energy-absorbing mechanisms that occur near the tip of a propagating crack. These energy-absorbing mechanisms are numerous, and include crack deflection, crack pinning, cavitation, and others (Figure 4); but the most important of them is the plastic deformation of material around the

crack tip. This occurs due to the locally high triaxial stresses that occur near the tip of a propagating crack. For a brittle material, such as glass, the amount of plastic deformation possible is quite small. For more ductile materials, the amount of plastic deformation can be quite large and the contribution to the fracture energy will dwarf the surface energy contribution. This is most easily understood by going back to the stress-

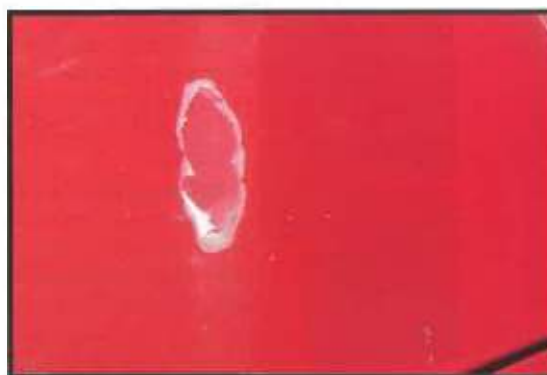
Figure 1—Common cracking failures in coatings: (a) cracking of automotive topcoat, (b) cracking of architectural paint on wood, and (c) delamination on automotive clearcoat.



(a)

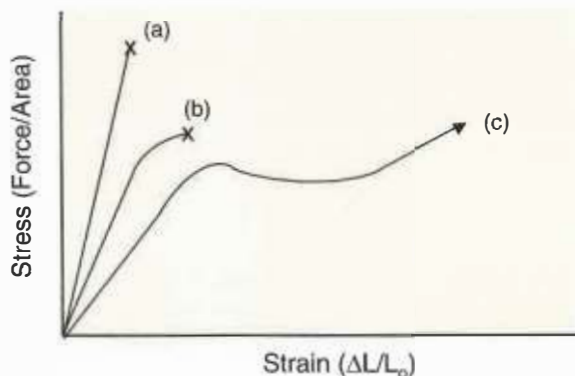


(b)



(c)

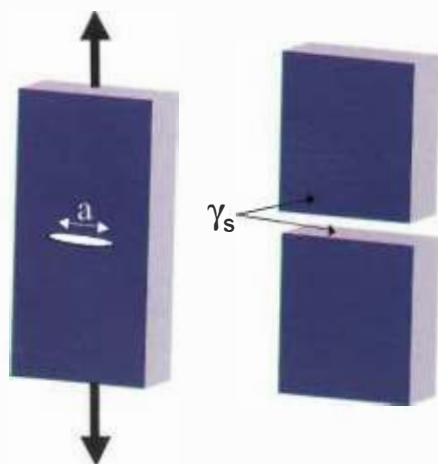
Figure 2—Stress-strain curves of various coating types: (a) rigid, elastic coating showing little strain before break, (b) semi-ductile coating showing some plastic deformation before break, and (c) ductile coating showing extensive plastic deformation and flow before rupture.



strain behavior shown in Figure 2. For a brittle material, such as represented by curve *a* in Figure 2, the material ahead of the crack tip can only deform a small amount before its breaking strength is reached. Little to no plastic deformation is possible. However, for more ductile materials, such as represented by curve *c* in Figure 2, the material can plastically deform ahead of the crack tip, much like it can in the simple stress-strain test. In doing so, much energy is absorbed and propagation of the crack is hindered. Thus, taking these extra mechanisms into account, Griffith's original equation can be modified to⁵

$$\sigma = \left(\frac{EG_c}{\pi a} \right)^{\frac{1}{2}} \quad (2)$$

Figure 3—Cleavage process in materials whereby two new surfaces (air/material interfaces) are produced. Surface energy penalty of each new surface is γ_s .



where, G_c is termed the fracture energy and is a material property. Thus, if the size of the flaw is known, and the fracture energy is measured, the breaking strength of the material can be calculated. Methods to measure the fracture energy will be discussed shortly.

The energy approach is a general one, in that it can be applied to all materials regardless of ductility or stiffness. For more brittle materials, a number of simplifications can make the measurement and calculation of a material's

brittleness much more straightforward. For one specialized case, the bulk of the material away from the crack tip is assumed to deform in a linear elastic manner, and plastic deformation is confined to a small area adjacent to the crack tip. When these conditions are satisfied the mechanics are simplified into what is termed linear elastic fracture mechanics (LEFM).

Stress Intensity Factor Approach

Because the stresses at a crack tip become infinitely large, using the stresses themselves as a metric for crack propagation is not possible. Irwin proposed using the stress intensity factor as a way of circumventing this problem for the special case when LEFM applies.⁶ The stress intensity is a mathematical way of describing the stress field around a crack and is typically given the symbol, K . When the stress intensity reaches a critical value, a crack will propagate. Thus, the criticality condition for crack propagation is $K > K_c$. K_c is termed the critical stress intensity factor, or fracture toughness, and has units of $\text{Pa}\cdot\text{m}^{0.5}$. A variety of geometries and test set-ups can be used to measure K_c for materials.⁷

Because LEFM is a specialized case of general fracture mechanics, K_c and G_c can be related to each other. For the case of thin specimens (plane stress), such as paint films

$$K_c = (EG_c)^{\frac{1}{2}} \quad (3)$$

For thicker specimens (plane strain)

$$K_c = \left(\frac{EG_c}{1-\nu^2} \right)^{\frac{1}{2}} \quad (4)$$

where E is the modulus (stiffness of the material) and ν is Poisson's ratio. Measuring G_c and converting to K_c is only possible when the material behaves in accordance with LEFM. One must also remember that because of the viscoelastic nature of polymers, the values of K_c and G_c will vary with testing rate and temperature. [Note: Fracture nomenclature can be confusing. In many instances critical properties such as K_c and G_c are often denoted with an extra subscript, K_{Ic} or G_{Ic} . These extra subscripts refer to the mode of fracture, but are beyond the scope of this article. Interested readers can examine appropriate texts.⁷]

FRACTURE MECHANICS TEST METHODS IN COATINGS

For coatings, fracture mechanics can be used to answer the most basic of questions: Will a coating crack or delaminate? If so, when? How thick can I apply a coating before it will crack upon drying or in service? These are straightforward questions that have proven difficult to answer in the past. Fracture mechanics allows the paint formulator or user to answer these questions in a quantitative way. The only knowledge required is an estimate of the stresses the coating will experience, the fracture energy (or related quantity), and the flaw size.

In order to choose the most appropriate method to characterize a material's propensity to crack, a qualitative assessment of the materials ductility must first be made. For ductile coatings, where the coating can elongate more than a few percent in a standard tensile test at room temperature, the method of essential work is the preferred approach to testing. For more brittle coatings, G_c or K_c can be measured directly on free films or, in certain cases, on coatings that are strongly adhering to substrates. Each of these methods will be discussed. The advantage of using fracture mechanics-based tests to evaluate the mechanical properties of coatings instead of standard tensile testing, is that the presence of flaws is expressly accounted for. Thus, the link between real-world performance and laboratory measured properties can be made with confidence.

Ductile Coatings—Method of Essential Work

Ductile coatings, which includes many architectural coatings, coatings for plastics, and coil coatings, will elongate significantly before rupturing in a tensile test. For these coatings, the yield strength is low enough that significant plastic deformation will occur before rupture. Because of this low yield strength, the process zone ahead of an advancing crack will be large and the energy required to advance that crack will be substantial. These coatings are generally considered quite tough and LEFM does not apply due to the large size of the plastic zone. However, techniques have been developed that do allow for the quantification of the brittleness of the coating.

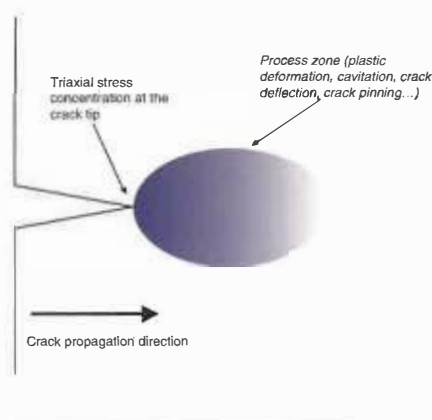
The method of essential work is the most common method used to characterize the fracture resistance of ductile polymers.⁸⁻¹⁰ The specimens used are free films of the coating that have been carefully prepared. As in all coating testing, the thickness of the film should be representative of the thickness that is used in service. While a few different specimen geometries are possible, the most common is the double edge notch (DEN) shown in Figure 5. Typically the notches are made in a rectangular coating sample with a chilled razor blade. Care must be taken in handling the free films to insure no other edge flaws of comparable size are produced.

During crack propagation in a ductile coating, the mechanical energy input into the coating can be apportioned into the essential work of fracture, w_e , and the plastic work of fracture, w_p . The essential work of fracture is that energy that is needed to drive the crack tip forward and plastically deform material in the vicinity of the crack tip. The plastic work of fracture is that energy that is used to plastically deform material away from the crack tip. These two quantities can be used to calculate the total work of fracture

$$w_f = w_e l t + \beta w_p l^2 t \quad (5)$$

where l is the ligament length (see Figure 5), t is the coating thickness, and β is a shape factor depending on the specimen geometry. The total work of fracture is taken as the area under the stress-strain curve for a given specimen. To determine the essential work of frac-

Figure 4—Process zone ahead of a crack propagating through a material.



ture, a number of specimens of varying ligament lengths are tested. The total work of fracture divided by the ligament length and thickness is then plotted as a function of ligament length. The essential work of fracture is then determined by extrapolating back to zero ligament length as shown in Figure 6.

The essential work of fracture is a material property like the modulus or T_g of a coating. Like these other properties, its value will be influenced by extrinsic conditions such as temperature and testing rate as well as composition or crosslink density. Thus, not all polyester coatings will have the same essential work of fracture, and the essential work of fracture may change with time or exposure, as most coatings become more brittle during service.

Brittle Coatings—LEFM Applications

For coatings that adhere to the restrictions of LEFM there are two possible routes to determine the resistance to crack propagation. The first method is to use free films to directly measure K_{Ic} or G_c using a number of different specimen geometries. The second approach is to use the paint and substrate together, provided the coating strongly adheres to the substrate.

When using free films to measure K_{Ic} or G_c , care must be taken to prevent damage to the specimen. As these films are usually brittle, this is not an insignificant experimental difficulty. Once free films have been obtained, a starter crack must be inserted in the specimen, usually with a chilled razor blade. Various geometry specimens may be used, the most popular being the single edge notch (SEN, Figure 5). The equation for calculating K_{Ic} in SEN testing is also shown in Figure 5. Conversion to G_c values can be made using equations (3) or (4), depending on sample thickness.

The drawbacks to using the free film method outlined above are the same as with any test method that requires free films. Preparation of films can be difficult and time consuming. If the interactions between the coating and the under layers are important (such as intermixing during cure), the free film sample may not be representative of the composition of the coating in service. Obtaining free films from weathered

Figure 5—Popular geometries for fracture mechanics testing of polymers and coatings. Equation below the SEN specimen is for calculating K_{Ic} .

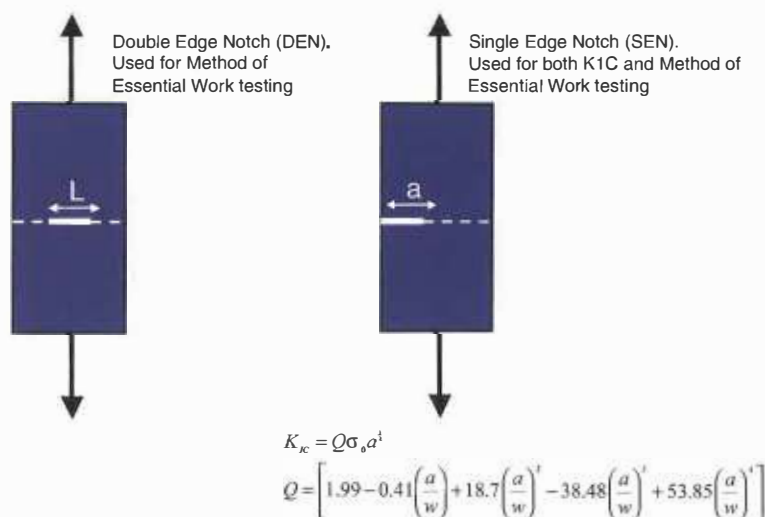
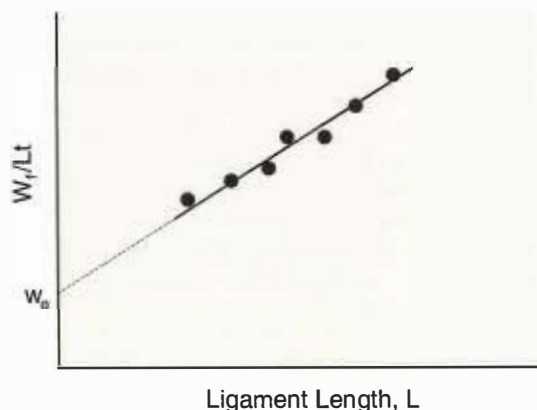


Figure 6—Typical data generated from a series of essential work of fracture tests. Extrapolation of the data back to zero ligament length gives the essential work of fracture for the coating.



samples is usually not possible, so if changes in properties during service are important, the use of free films is problematic.

For the reasons just outlined, coatings that conform to the limits of LEFM are often most easily characterized while still adhering to their substrate. This approach also allows coatings to be characterized after weathering exposure or other nondestructive testing regimens. Another significant advantage of this method is that a knowledge of the flaw size is not required to measure the fracture energy. All that is required is that a population of super-critical flaws (length on the order of the film thickness) must be present.¹¹ Specimen preparation techniques can ensure this. In addition, the strain-to-break of the coating must also be smaller than that of the substrate for meaningful testing.

The test method itself is straightforward. Small strips of the coating/substrate composite must be cut or sheared from a larger specimen. These strips are then pulled in tension until cracks are seen or heard to propagate across the specimen (Figure 7). The strain at which the cracks propagate is then used to calculate the fracture energy of the coating by using

$$G_c = 0.5\pi t \varepsilon^2 \bar{E} g(\alpha, \beta) \quad (6)$$

where t is the coating thickness, ε is the strain at cracking, E is the modulus of coating divided by $(1-\nu^2)$, and $g(\alpha, \beta)$ is a constant related to the modulus mis-

match between the coating and the substrate.¹² For organic coatings on rigid substrates, this value is approximately 0.76. This method has been successfully used to quantify the brittleness of automotive coatings and hardcoats on plastic substrates.^{1,13,14}

Unlike other types of data the coatings scientist uses, fracture data contains a significant amount of variability, regardless of its source. This is inherent in the measurement techniques and physical nature of the fracture process. Careful experimental technique can minimize the variability, but it cannot be

completely eliminated. Even good fracture mechanics data typically shows variability on the order of $\pm 25\%$.

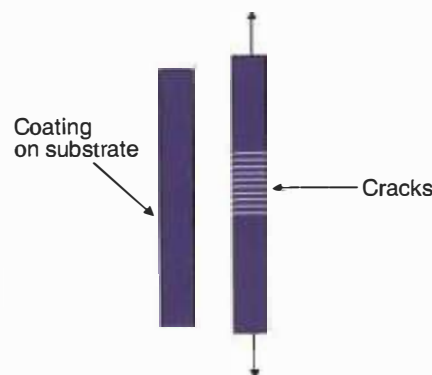
FAILURE/PROCESS ENVELOPES

The brittleness of a coating is valuable information in and of itself. However, using this information to make predictions is even more valuable. The driving force, G , for cracking in a coating attached to a substrate can be described by

$$G = \frac{Z\sigma^2 t}{E} \quad (7)$$

where σ is the stress on the coating and Z is a constant related to the particular

Figure 7—Schematic of fracture energy test for brittle coatings adhering to a substrate. Note parallel cracks that appear in the coating after loading.



cracking geometry.¹⁵ For cracking through the thickness of a coating, $Z = 3.951$. Other values have been calculated for delamination and spalling. When $G > G_c$, crack propagation will occur, much like the criticality condition for LEFM, $K > K_c$. Note that equation (7) has the same form as equation (6) if εE is substituted in for the stress, σ . Intuitively, this equation makes much sense, as many paint professionals know that thicker coatings tend to crack more easily than thinner coatings. This is explained by the thickness dependence of the driving force. Thicker coatings have a higher driving force for cracking than thinner coatings. Thus, the criticality condition ($G > G_c$) will be reached at lower stresses for a thicker coating due to the higher driving force, G .

These principles can be used to construct failure envelopes for coatings of various fracture energies. This is shown in Figure 8 where the film build is plotted against the internal stress for coatings possessing various values of fracture energy. Plots such as these can be used to place boundaries on process variables or service lifetimes. For example, rigid coatings used for outdoor applications can typically expect to be subjected to peak stresses on the order of 20 MPa.¹⁶ These stresses are the result of thermal expansion mismatch between the coating and the substrate, densification of the coating over time, and moisture absorption by the coating. In Figure 8, the coating with a fracture energy of 90 J/m² could be applied at a thickness of up to 150 μ m and support stress of 20 MPa without cracking. However, two things must be considered. First, most coatings embrittle as exposure time increases. Thus, a coating's fracture energy will decrease as time progresses. The coating may initially have a fracture energy of 90 J/m², but after five years of outdoor exposure may only have a fracture energy of 30 J/m². At 30 J/m² the coating can only be 50 μ m thick and still support the 20 MPa stress. Thus, the true limit on the film build is 50 μ m, as coatings must be formulated and applied to last multiple years in their given service environment.

The second caveat to remember is that the stresses imposed on coatings are typically cyclic in nature. Thus, their failure is dominated by fatigue processes. These processes have not been studied in polymeric coatings, but their characteristics should be similar to those observed in other materials in-

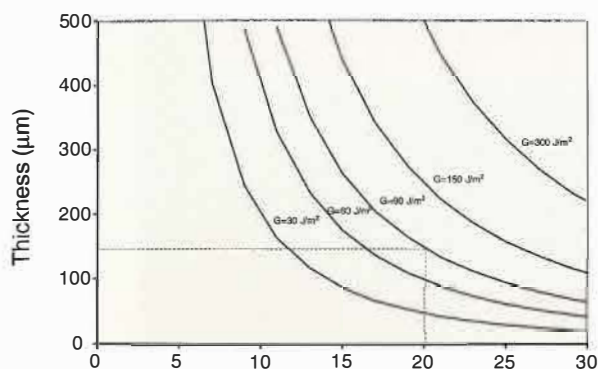


Figure 8—Cracking failure envelope for coatings with various fracture energies. Embrittlement moves coating behavior from curves with higher fracture energy to lower fracture energy. Note coating with fracture energy of 90 J/m² can support a stress of 20 MPa at a film build of 150 μm, but only 50 μm at 30 J/m².

cluding bulk polymers and composites. In the case of those materials, the failure stress during fatigue loading is always significantly lower than during static loading.⁷ Therefore, failure envelopes developed using the above technique should be taken as upper bonds on the allowable thickness, with the actual allowable thickness somewhat lower. The fatigue of coatings is worth future investigation.

ADHESION TESTS

The proceeding discussion dealt predominantly with the propagation of cracks within a material. However, fracture mechanics can be used to describe the propagation of cracks at an interface as well, where they lead to delamination. Unfortunately, the usefulness of this approach has not been sufficiently exploited yet. The attempts that have been made to characterize the toughness or fracture energy of paint interfaces have been unwieldy.¹⁷ Thus, the industry remains saddled with less than ideal tests such as tape pull adhesion.¹⁸

SUMMARY

Fracture mechanics is a powerful tool for the coatings technologist. Application of its methods allows for the prediction of failure envelopes and the optimization of formulations for mechanical integrity. Adoption of the principals involved in fracture mechanics is also useful in assessing the quality of current coatings tests and in developing new tests that are meaningful and reproducible. **CT**

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