

Anticipating Paint Cracking: The Application of Fracture Mechanics To the Study of Paint Weathering

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INTRODUCTION

Due to rapidly changing environmental regulations and ever decreasing product cycle times, the need for rapid, accurate measures of the long-term weathering performance of coatings is greater than ever. Historically, gathering long-term weathering data has been, by definition, a time consuming endeavor. Currently, the only nearly guaranteed method of predicting 10-year durability is to expose a coating on the intended substrate for 10 years. South Florida has historically been chosen as the geographic location to expose paint panels due to both its high solar load and high level of humidity.¹ However, 10-year life in Florida does not fully guarantee 10 years of performance around the world, as climates harsher than Florida exist in various parts of the world, and even nominally less harsh climates can subtly change the details of weathering mechanisms, such that one failure mechanism may be accelerated more than others. While accelerated weathering tests overcome the drawback of lengthy exposure times, they introduce a new set of uncertainties related to acceleration factors and correlation with outdoor exposure.²

Great progress has been made in the past 20 years with respect to understanding the details of the weathering process itself. Most of this work has focused on the chemical changes that take place in coatings during weathering.³⁻⁵ For many coatings these changes are primarily driven by photooxidation of the polymeric binder. This process begins when ultraviolet light is absorbed by the coating and produces free radicals.⁶ These radicals are then able to react with the polymer and can propagate many times before terminating. These reactions are, in general, deleterious to the coating and over time can lead to a degradation in performance. A variety of methods now exist to follow the details of the chemical changes that take place during weathering.³ These methods allow for the rapid evaluation of coatings and enable coatings from different chemical families to be ranked against one another. These tests can determine the rate of degradation of the polymer and the consumption rates of various additives (hindered amine light stabilizers, ultraviolet light absorbers, antioxidants, etc.) that can play an important

The relationships between the fracture energy (G_c), film thickness, stress level, and weathering time were investigated for a number of automotive clearcoats. As weathering progressed, most clearcoats embrittled due to the combined effects of photooxidation, hydrolysis, and other degradation mechanisms. This embrittlement was measured and related to the chemical composition changes that take place in the clearcoat during weathering. When the fracture energy dropped below the driving energy for cracking, G , brittle cracking occurred. The driving force for cracking was shown to depend on stress level and film thickness. The importance of fatigue loading was also qualitatively investigated. These techniques were successfully used to anticipate the long-term weathering behavior of automotive clearcoats.

role in the long-term weathering performance of the coating. Using microtomy or microscopic analysis techniques, the locus of degradation and its gradient through the coating thickness can often be determined.^{7,8}

All of the chemical changes that take place during weathering can ultimately lead to the observable phenomena that a consumer can identify as a failure: gloss loss, color changes, yellowing, and the two most catastrophic failures: cracking and peeling. Weathering-induced chemical composition changes lay at the heart of all of these failures, yet the final manner in which these changes are manifest is an optical or mechanical failure. Of these failures, by far the more severe are the catastrophic failures of cracking and peeling. Whether the coating is architectural, automotive, or industrial maintenance, cracking and peeling failures usually necessitate repainting—a costly

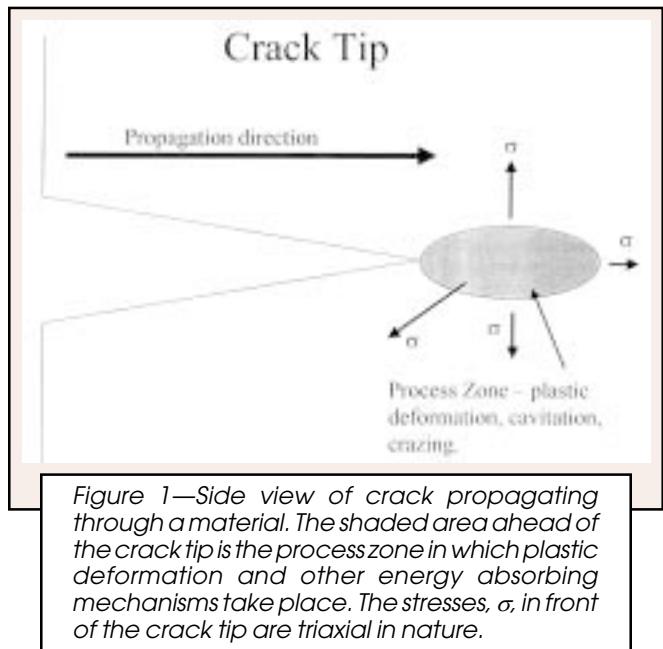
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proposition. Thus, test methods that can directly anticipate these types of long-term failures have the potential to increase the quality and value of coatings. In this paper we attempt to outline one approach to anticipating the long-term cracking behavior of coatings.

Fracture Mechanics

To devise tests that are quantitatively related to cracking-type failures of materials, the concepts of fracture mechanics must be introduced. For structural materials, fracture mechanics has been applied out of necessity as many technological breakthroughs have been dependent on higher strength materials, whose typical failure modes can be dominated by brittle cracking instead of ductile yielding.⁹ For most materials this brittleness is characterized using linear elastic fracture mechanics (LEFM). LEFM can be applied when the stresses and strains around cracks are governed by the elastic behavior of the material and the effects of plastic deformation are minor and confined to a small zone around any crack tip (see *Figure 1*). The equations governing crack growth in materials and structures obeying LEFM were originally derived by Griffith in the 1920s for the fracture of glass.¹⁰ His derivation was based on surface energy considerations and the energy required to create two new air-glass interfaces when a crack propagated through glass. The energy required to unstably propagate (not initiate) the crack is termed the fracture energy, G_c . Higher fracture energies represent tougher or less brittle materials. G_c is a material property, not unlike strength or heat capacity. Its value will depend, like other material properties, on processing conditions and microstructure. Thus, for coatings, bake conditions, additive types and amounts, and outdoor exposure time should have a dramatic impact on the fracture energy of a coating.

For very brittle materials, the additional surface energy of the cracked member is a substantial fraction of the fracture energy. However, for most materials, it is a small and often insignificant fraction of the total fracture en-



ergy. In these cases, the energy needed to propagate a crack originates from both the anelastic and plastic deformation processes in the zone ahead of the propagating crack. As more energy is dissipated in the zone, more energy is required for crack propagation. In testing and in service, higher crack driving forces are supplied as the mechanical stresses on the material are increased. For viscoelastic materials, such as polymeric coatings, G_c can be highly dependent on both the temperature and rate of testing.¹¹

To measure the fracture energy on structural materials, either metals, ceramics, or polymers, test specimens are fabricated and cracks of a known size are introduced into the specimen. The shape and size of the specimen and the manner in which the cracks are introduced is not an insignificant body of work.¹¹ After the specimens have been prepared, mechanical loads are applied to the specimens to cause the cracks to propagate. During testing, the load and strain at which the cracks propagate is recorded. Because of the difficulty in accurately determining initial crack size, along with other test ambiguities, many specimens are often run to improve the statistical significance of the results. However, most fracture data carries with it an uncertainty on the order of 25%.

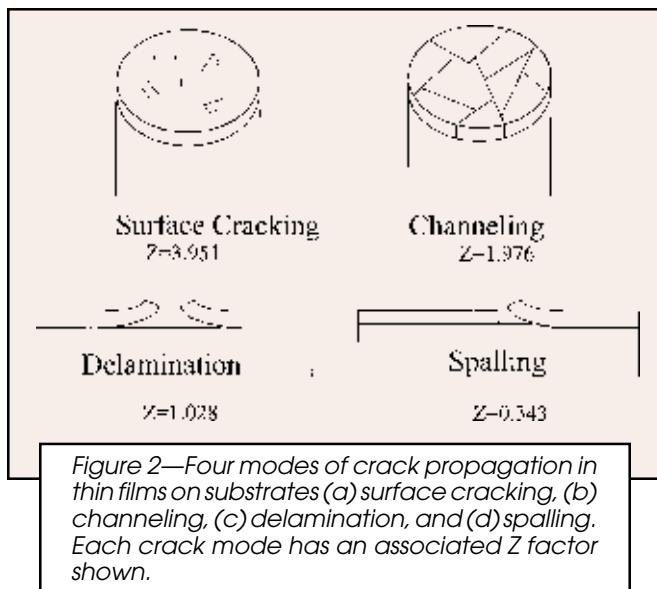
While the fundamental principles governing crack propagation in coatings and in bulk materials are the same, some differences exist. These differences also exist for inorganic thin films used in the microelectronics industry, in that the thin films are subjected to high stresses due to thermal cycling and lattice constant mismatches. Cracking or delamination of the film can lead to loss of dielectric strength and component failure. For these reasons, the fracture mechanics specific to thin films on substrates were extensively investigated from the mid 1980s onward.¹²⁻¹⁴ For organic coatings, one of the most appealing conclusions to arise from this work was the possibility of measuring meaningful fracture energies on complete paint systems adhering to substrates without having to resort to free films. Thus, paint panels that have been exposed in Florida or in accelerated testing machines are viable sources of test specimens. This allows for the incorporation of the effects of different substrates or underlying layers on the behavior of topcoats. A second advantage is that the details of the fracture mechanics eliminate the crack length as a variable.

Fracture of Coatings

The brittle fracture of coatings strongly adhering to substrates is governed by the equation

$$G = \frac{Z\sigma^2 h}{E_f} \quad (1)$$

where E_f is the modulus divided by $(1-v^2)$, v is Poisson's ratio, and Z is a geometry constant.¹⁵ Like bulk materials, a coating's fracture resistance is characterized by its critical driving force (fracture energy, G_c). When the driving force on a material exceeds the fracture energy ($G \geq G_c$), crack propagation will ensue. Equation (1) reveals a number of hallmarks about the cracking process in coatings. First, there is a linear dependence on the coating thickness. Second, the driving force depends on the stress squared, which necessitates a good understanding of the



magnitude of these stresses. Third, the pattern of cracking, discernible through the Z term, can be anticipated. Fourth, the cracking has a threshold quality, that is, there will be little warning before catastrophic crack propagation. Each of these qualities will be examined.

Perhaps the most important feature predicted by equation (1) is the catastrophic nature of cracking in coatings. Assuming the coating's mechanical properties are homogeneous, the coating will perform well with no signs of failure, until the critical driving force, G_c , is overcome. After that brittle crack propagation will occur. This is perhaps most evident in the weathering of coatings, where a coating can look very good (high gloss, little color shift) for long periods of time until cracks appear in only a very short time span. Thus, test panels can literally look good one day and cracked the next. This is owing to the embrittlement of coatings that usually takes place during weathering. Even if the stress is constant, when G_c drops below the driving force, G , crack propagation will ensue.

The Z term in equation (1) is a term that describes the pattern of cracking. For linear elastic materials, which likely applies to most highly crosslinked coatings, the term ranges from 3.951 for surface cracking to 0.343 for spalling. Each of the types of cracking and their associated Z factor are shown in Figure 2.¹⁵ What can be simply deduced, however, is that the simplest form of cracking, and the form likely to be first manifest, is that of surface cracking, where a pattern of fine unconnected cracks appear. For automotive coatings these cracks may be referred to as stress cracks. These cracks will require the lowest stress to satisfy the critical condition for cracking ($G > G_c$) for the coating. As some stress is relieved by their propagation, only when additional stress is applied (or when the coating further embrittles) will the cracks propagate and form a network of cracks, such as in channeling. Again, an automotive example may be that of microchecking, where the clearcoat whitens due to a very fine pattern of cracks in the clearcoat. The same ideas apply to the delamination modes of failure shown in Figure 2.

The effect of thickness is empirically known by many. In fact, the testing standards for mandrel bend tests (crude

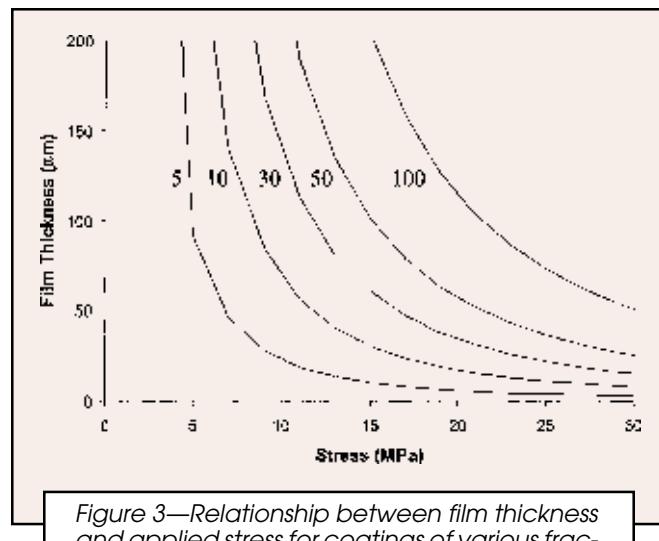


Figure 3—Relationship between film thickness and applied stress for coatings of various fracture energies, G_c . Each curve represents a material of a different indicated fracture energy. G_c values are in J/m^2 .

measures of coating brittleness) acknowledge this reality.¹⁶ However, equation (1) allows one to account for this variable. Coating thickness is plotted against stress in Figure 3. The curves shown are for coatings of different G_c values. Below and to the left of any given curve the coating will not crack; for example, in Figure 3 the coating with a $G_c=15 \text{ J/m}^2$ and a film build of 50 μm , can sustain a stress of 12 MPa without cracking, but will crack when the applied stress is over 12 MPa. Thus, if the coating thickness is known, and the stress to which a coating is subjected is known or can be estimated, the allowable brittleness of the coating can be calculated. Conversely, if a coating has already been formulated and chosen and its fracture energy is known, then a maximum safe film build can be calculated given the applied stress.

For coatings, measuring the stress at any given time is a difficult task. Perera and coworkers have made the most comprehensive studies of stresses in coatings.¹⁷⁻¹⁹ In summary, the stresses come from three main sources: thermal expansion mismatch, humidity stresses due to mismatches in swelling between the coating and the substrate, and densification due to physical aging. Depending on the system, one or another of these stress sources may dominate.²⁰ For all of these sources, the stresses arise due to the constrained nature of coatings. A coating strongly adhering to a substrate will undergo a stress if an environmental condition is changed that effects the coating and substrate differently. For example, the biaxial stress, σ , in a flat coating due to a change in temperature can be calculated by

$$\sigma = \frac{E_c \cdot \Delta T (\alpha_c - \alpha_s)}{(1 - \nu)} \quad (2)$$

where E_c is the modulus of the coating, ΔT is the change in temperature, and α_c and α_s are the thermal expansion coefficients of the coating and substrate, respectively, and ν is Poisson's ratio of the coating. An equation of the same form will predict the response to a change in moisture content of a coating-substrate system and the stresses due to a change in the density of the coating. For certain coat-

ing systems, the deformations the coatings are subjected to can be quite large. For example, architectural coatings for wood must be able to withstand large strains without cracking as the wood can expand significantly due to moisture uptake. Upon drying the paint must not wrinkle or crack due to buckling stresses.²¹ These coatings have very low moduli (and yield strength) and are capable of large elastic recoverable strains without cracking. For all coatings, the viscoelastic nature of the polymer will result in the stresses being time and temperature dependent. The stresses will often be highest right after a change in temperature or humidity and then relax away to a much smaller level. For noncrosslinked coatings these stresses may relax away to zero given enough time, but for crosslinked coatings below T_g some stress will always remain.

A number of other factors differentiate the fracture of thin coatings from that of bulk materials. In bulk materials, care is taken to ensure that the specimen thickness is much greater than the plastic zone size, such that the vast majority of the test specimen is in the "plane strain" state. This ensures that the lower bound on the fracture energy is measured. For coatings, the size of the plastic zone can approach the coating thickness. This can be calculated from the modulus and yield strength of the coating.⁹ For coatings with fracture energies on the order of 100 J/m², the size of the plastic zone is on the order of a 50 μm . Thus, coatings thinner than this would seem tougher due to increased plasticity occurring throughout the coating thickness. In principle this could be experimentally tested by measuring the fracture energy of the same coating applied at different film builds. However, because cure behavior varies with thickness, the results are not always unambiguous. For very brittle coatings ($G_c \sim 15 \text{ J/m}^2$), coatings as thin as a few microns thick can be reliably tested.

For very tough coatings, measured G_c values will be greater than 1000 J/m². However, these high values indicate a large degree of plasticity occurring ahead of the crack tip. Other methods for measuring the toughness of these films are likely to be more quantitatively correct, such as the method of essential work or J-integral methods.^{22,23} Both of these methods suffer from the same drawbacks: only free films can be used as test specimens and the initial crack length must be known for each specimen.

EXPERIMENTAL TECHNIQUE

For a coating strongly adhering to a substrate the fracture energy of the coating can be measured in a straightforward manner. Thin strips of the coating/metal composite are cut using a hand shear. Typical strips are 10 \times 1 cm. The strips are then pulled in tension in a mechanical testing machine at 20 mm/min. The strain at which cracks propagate across the coating is recorded. Typically 8-10 samples are tested for each material at a given amount of weathering time. This reduces the uncertainty on any fracture energy value to $\pm 25\%$. The fracture energy is then calculated as

$$G_c = \frac{\varepsilon^2 h E_f \pi g(\alpha, \beta)}{2} \quad (3)$$

where h is the film thickness, ε is the strain at cracking, $E_f = E/(1-v^2)$ (E is the modulus of the coating, v is Poisson's

ratio (typically taken to be near 0.35)), and $g(\alpha, \beta)$ is a constant relating to the modulus mismatch between the coating and the underlying layer.²⁴ For a coating on steel or aluminum $g(\alpha, \beta) = 0.78$, while for a clearcoat on top of a basecoat in a complete automotive paint system $g(\alpha, \beta) = 1.26$. This calculation assumes linear elasticity, that is $\sigma = E\varepsilon$, which is unlikely to be true for the ductile or moderately ductile materials. To be rigorously correct the corresponding stress at cracking would be determined from the actual stress strain curve of the coating and then substituted into equation (3) in place of the strain and modulus. We have previously termed the fracture energy based on that more rigorous method to be the true, or actual fracture energy, while that calculated assuming linear elasticity we have termed the apparent fracture energy.²⁵ We choose to concentrate on the apparent fracture energy for two reasons. First, it is simpler to calculate requiring only a knowledge of the modulus of the coating, which can be measured using dynamic mechanical testing or high speed tensile testing. Second, the true fracture energy discriminates against coatings with low yield stresses as the stress during cracking is quite low, while the strain can be quite high. These low yield stress coatings perform well in the field, with regards to cracking, but would possess low true fracture energies. Additionally, as weathering progresses, the amount of anelastic deformation a coating undergoes before fracture decreases. Thus, the difference between the true and apparent fracture energy becomes negligible at long weathering times. For the remainder of this paper the fracture energy will refer to the apparent fracture energy. Additional details on the measurement technique can be found in other publications.²⁵⁻²⁷ Equation (3) is strictly true only for the case of crack channeling, that is cracks propagating across a coating and through its entire thickness. For isolated clearcoats on top of metal this has been observed to be true. It is also true in the majority of cases for clearcoats on top of basecoats in automotive paint systems, where the cracks propagate through the thickness of the clearcoat and arrest at the basecoat/clearcoat interface.²⁷

Case Study: Automotive Basecoat/Clearcoat Paint Systems

Beginning in the 1980s, most automotive manufacturers switched from monocoat paint systems to basecoat clearcoat systems. This switch was motivated by the desire for coatings with superior initial appearance (gloss, DOI) and potentially longer term appearance retention. Basecoat/clearcoat (BC/CC) systems provided such properties. However, in transitioning to BC/CC systems, the main mechanism of discerning the long-term weathering behavior of a paint system, gloss retention, was lost. BC/CC systems can remain very glossy for long periods of time up to and after they have cracked. Most of these systems have sufficient mechanical properties such that they will not crack early in their lifetime. However, because of their long potential exposures and their long-term appearance retention, other means have been devised to monitor the long-term weathering behavior of BC/CC paint systems. The most successful techniques augment appearance measurements with chemical composition change rate measurements. These techniques in-

clude: FTIR spectroscopy of the coating as a function of weathering time,²⁸ UV light absorber longevity measurements,⁷ and hindered amine light stabilizer longevity measurements.⁸ Thus, if the degradation rate of the coating can be measured, and the longevity and effectiveness of the two main weathering-active additives can be measured, much of the risk of using BC/CC systems can be minimized.

However, the underlying assumption in all chemical change rate measurements is that all coatings can tolerate the same amount of chemical composition changes during weathering before failing mechanically. This is unlikely to be true. Because of the catastrophic nature of cracking, the amount of chemical change necessary to "push a clearcoat over the edge," that is, to decrease a clearcoat's fracture energy sufficiently such that the driving force for cracking now exceeds the clearcoat's fracture energy, is likely to be different for each clearcoat. Additionally, the rate of change of the fracture energy does not have to be in direct proportion to the rate of change of the chemical composition.

We have made fracture energy measurements on a number of automotive BC/CC systems.²⁷ As stated earlier, for most of the systems the cracks propagate only in the clearcoat and arrest at the BC/CC interface. For some systems with very high measured fracture energies (as calculated using equation (3)), the cracks propagate all the way to the e-coat/phosphate interface. The values of the fracture energy calculated for such coating systems is not rigorously correct and should only be used in a qualitative manner. While of interest from a fundamental standpoint, these coatings systems are sufficiently tough that the cracking of the clearcoat is unexpected in the field. Many of the coatings that display this tough cracking behavior initially will display brittle cracking in the clearcoat after some degree of weathering due to gradual embrittlement of the clearcoat.²⁹ After this embrittlement, their fracture energy can be measured quantitatively.

The details of the embrittling mechanism are understood in a general way for most clearcoats, but are poorly understood for specific formulations. As weathering progresses, UV light initiates photooxidation in the clearcoat. Much of the UV light is screened by UVAs in the clearcoat, but the surface cannot be well protected, and as weathering progresses, the UVA can be depleted from the bulk of the clearcoat. As photooxidation progresses, free radicals will attack the clearcoat polymer causing crosslink scission, chain breakage, and crosslink formation. The balance of these three reactions has much to do with the rate of embrittlement of the coating.³⁰ Additives, in particular HALS, play an important role in the balance of these reactions as well as the overall rate of weathering-induced chemical change.³¹ Intuitively, if the crosslink density of a clearcoat increases dramatically during weathering, the fracture energy would be expected to decrease due to an increase in the yield strength and decrease in the mobility of the network. However, crosslink/chain scission can also embrittle a clearcoat due to the introduction of network defects into the clearcoat. These defects can ease crack propagation through the network. Thus, many clearcoats are probably at or near their maximum in toughness before weathering. The exception may be those

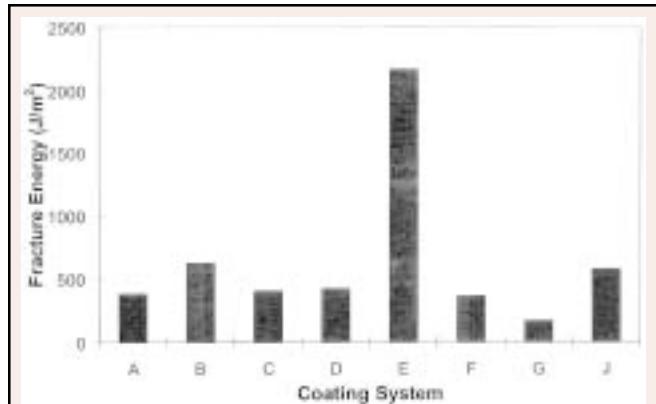


Figure 4—Initial fracture energy of eight automotive clearcoats measured in complete paint systems. Extension rate was 20 mm/min.

clearcoats that undergo significant ambient post-cure such as two-component polyurethanes or hybrid crosslinking systems.

In Figure 4 the initial fracture energy of a number of clearcoats in BC/CC systems is shown. A wide spectrum of fracture energy values is evident, with some so tough as to be only qualitative in nature (CC E) and others approaching the fracture energy of glass (CC G). That such a wide range of fracture energies is displayed is surprising, as all of these coatings have been formulated to provide the same attributes: high gloss, good long-term weathering behavior, good scratch resistance, and good chip resistance. The fracture energy undoubtedly plays a role in all but the first of these properties. Thus, it is likely that optimizing the mechanical performance of these coating systems is not well understood nor is it of the highest importance. These mechanical properties must, of course, be counterweighed against other equally important properties such as application ease, appearance, and cost where the sensitivity to formulation variables is historically more easily understood.

As weathering progresses all the clearcoats embrittle. The change in the fracture energy of three of the clearcoats

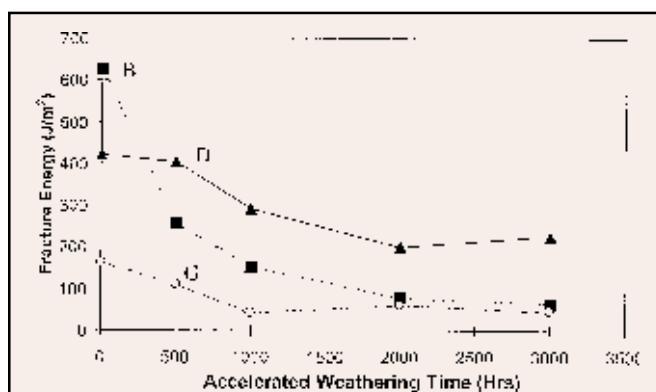


Figure 5—Fracture energy of three automotive clearcoats as a function of accelerated weathering time. Weathering was conducted using SAE J1960 Jun 89 with borosilicate inner and outer filters at 0.55 W/m² irradiance.

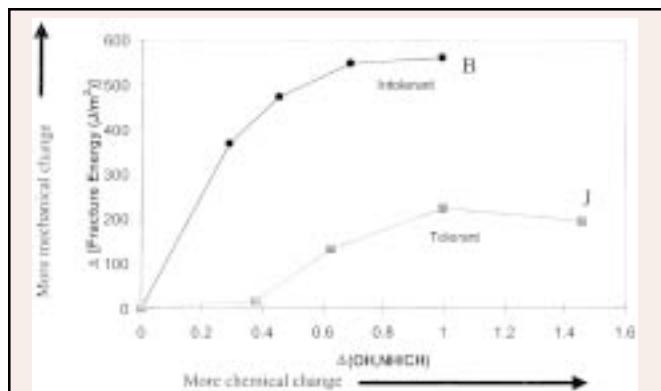


Figure 6—Relationship between the change in the fracture energy of two clearcoats and the change in the $-\text{OH}, -\text{NH}/\text{CH}$ ratio. The vertical axis represents the changing mechanical properties and the horizontal axis the changing chemical composition.

as a function of accelerated weathering time is shown in Figure 5. Clearcoats B and D start with reasonably high fracture energies; however, clearcoat B's fracture energy quickly decreases. Test panels with these coatings failed by microchecking after only three years in Florida while test panels with clearcoat D remain uncracked after more than eight years in Florida. Clearcoat G is quite brittle to begin with and embrittles more quickly. Test panels with these clearcoats failed by cracking in Florida in less than two years. Thus, at long exposure times, a clearcoat whose fracture energy decreases to a very low value poses a substantial risk for cracking during extended exposure. Those clearcoats whose fracture energy has plateaued or is decreasing slowly pose a much lower risk of cracking failures.

As previously mentioned, changes in the fracture energy cannot always be inferred by weathering-induced changes in the chemical composition of the clearcoats. This is demonstrated in Figure 6, where the change in the fracture energy of two clearcoats is plotted against the

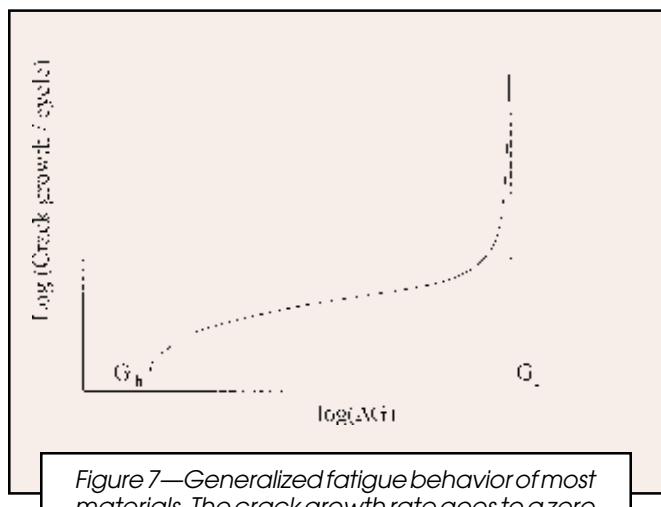


Figure 7—Generalized fatigue behavior of most materials. The crack growth rate goes to a zero value at low driving forces (threshold) and increases asymptotically at high driving forces (static G_c).

change in the chemical composition. The chemical composition change is quantified by a photoacoustic infrared (PAS-IR) spectroscopy measurement of the accumulation of photooxidation products. This metric has been termed the $-\text{OH}, -\text{NH}$ over $-\text{CH}$ method and appears to be a generic measure of the progress of photooxidation in a clearcoat.^{32,33} Both of the clearcoats in Figure 6 started with approximately the same fracture energy before weathering. The test panels were then weathered and their fracture energy values recorded as a function of weathering time as were their PAS-IR spectra. The changes in each are then plotted against one another to show the mechanical tolerance of the clearcoats to chemical change. Clearcoat J photooxidizes readily, as demonstrated by the length of the curve along the x-axis. However, its fracture energy changes only by 200 J/m^2 . Clearcoat B undergoes a large change in its fracture energy with only 65% of the chemical composition change of clearcoat J. Clearcoat J is tolerant of chemical composition changes, clearcoat B is not.

Knowledge of the changes in the fracture energy alone allows for a ranking of coatings based on an intrinsic material property. However, the construction of failure envelopes based on equation (1) requires a knowledge of the film thickness and the stresses the clearcoat will encounter during service. For automotive paint systems, clearcoats are typically applied at approximately $50 \mu\text{m}$ thickness. However, repairs, either in-plant or in the field, can add to the total film thickness above the metal and increase the driving force substantially.

The stresses an automotive paint system sustains during its lifetime are difficult to measure, due to the ever-changing environment an automobile experiences and due to the long lifetime of vehicles. One approach is to make short-term measurements of the stresses and build in a margin of safety. Another approach is to measure the fundamental coefficients and constants that govern the hygrothermal and physical aging characteristics of the clearcoat as a function of time and then model the long-term behavior of the system. We have previously reported on these measurements and modeling.²⁰ In summary, the

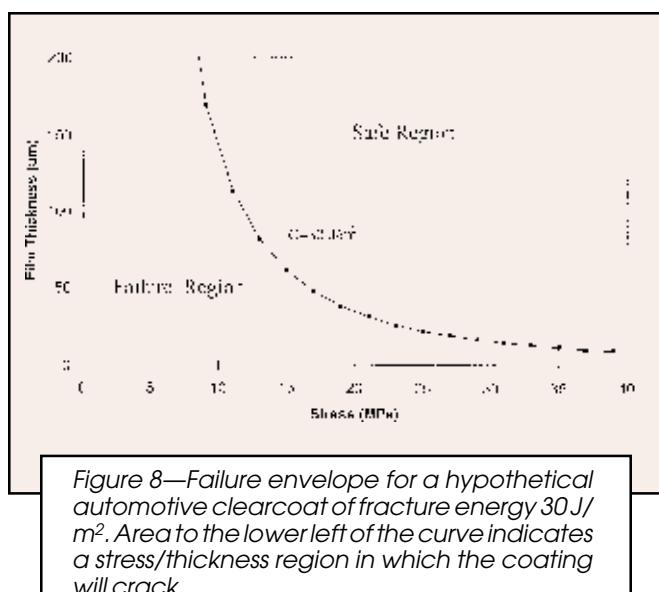


Figure 8—Failure envelope for a hypothetical automotive clearcoat of fracture energy 30 J/m^2 . Area to the lower left of the curve indicates a stress/thickness region in which the coating will crack.

stresses after weathering are highest in the clearcoat and primer layers due to weathering and high levels of filler respectively. Stresses in the clearcoat are mostly due to densification and thermal expansion mismatch. Peak stresses approaching 15 MPa are likely to occur in the clearcoat after long weathering times.

An important characteristic of the stresses in these paint systems is their cyclic (fatigue) nature. The thermal and humidity stresses will track the environmental conditions. Thus, in a sunny climate (Florida) the thermal stresses will be in phase with the diurnal cycle and will undergo one loading and unloading cycle each day. The same is true with humidity-induced stresses, which should track the dew point closely. The response of these clearcoats to cyclic stresses should be no different than the response of other materials to cyclic stresses; that is, most materials will fail at lower stress levels under fatigue loading than under monotonic loading.⁹ Highly crosslinked structural adhesives, whose crosslink density is similar to most clearcoats, display this type of behavior.³⁴

The cyclic nature of the stresses imposed upon a material during fatigue can be represented by the difference between the minimum and maximum stress during each cycle ($\Delta\sigma$). Because stresses can be related to driving energies for cracking, these cyclic stresses can easily be reformulated in terms of ΔG . The general fatigue behavior of most materials is shown in *Figure 7*, where the change in the driving energy (ΔG) is plotted against the crack growth rate. The crack growth rate is the length a crack will advance during one loading and unloading cycle. At low ΔG levels, the crack growth rate is small and goes to zero at some non-zero value of the ΔG . This is termed the threshold level. Thus, an infinite number of cycles could be imposed on a material without a crack propagating. At the other extreme, as driving energy increases, the rate of crack growth increases dramatically and asymptotically approaches an infinite value. This behavior at high driving energies is akin to a single cycle of stress applied when measuring the static fracture energy, G_c . Thus, predicting coating performance under fatigue loading by measuring the fracture energy under monotonic loading is a simplification of real world performance. In the absence of true fatigue crack growth data on coatings of interest, this oversimplification must be accepted in the short term.

Once the stress levels, material properties, and processing parameters are known, reasonable failure envelopes and design criteria can be established. The material properties and stress levels must, however, be known as a function of time, as initial properties and stresses are usually the most favorable. For automotive BC/CC systems with a typical clearcoat thickness of 50 μm , and a long-term stress maximum near 15 MPa the fracture energy of the clearcoat must stay above $\sim 30 \text{ J/m}^2$ for the anticipated lifetime of the coating (*Figure 8*). Clearcoats whose fracture energy stays above this level have performed well on panels exposed for many years in South Florida. Safety factors of course must be built in to account for rare thermal shock events, high film builds, fatigue, and 99th percentile customers who may take their vehicles to extreme climates where weathering and environmental changes may be more severe.

CONCLUSIONS

The application of fracture mechanics to coatings strongly adhering to substrates can be successfully used to anticipate the long-term weathering behavior of coatings. In particular, by measuring the fracture energy of the clearcoat in a complete paint system as a function of weathering time and estimating the maximum stresses produced, one can construct failure envelopes and formulate design guidelines to minimize the risk of long-term cracking in coatings. These techniques, along with detailed measurements of chemical composition changes, additive longevity and effectiveness, and the use of rational weathering conditions can dramatically reduce the risk of long-term in-service cracking failures. Advances in nonlinear fracture mechanics may allow similar types of analysis for more ductile coatings in the future.

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