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STRETCHING THE ENDURANCE BOUNDARY OF COMPOSITE MATERIALS: PUSHING THE PERFORMANCE LIMIT OF COMPOSITE STRUCTURES

A framework for predicting the service lifetime of composite polymeric coatings

Stuart Croll · Brian Hinderliter

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Abstract Relating product service lifetime to material composition by using standardized, artificial exposures, or even natural exposure, is notoriously difficult. An approach is reviewed here that has been developed to model degradation in polymeric coatings and may be applicable to other systems when they are exposed to natural or artificial weathering conditions. The approach focuses on the 'wear-out regime' not 'infant mortality' and breaks down the problem into units, which can be separately addressed. Random arrival, and action, of huge numbers of aggressive events, e.g., ultraviolet photons, grains of sand, etc., cause the accumulation of damage which may be modeled, in general, by Monte Carlo techniques or algebraically in simple cases, using the properties of large numbers of low probability events by the Central Limit Theorem. The model shows how degradation rate depends on physical and chemical materials characteristics, the initial state of the coating, and the parameters describing the environment. Well-known physical models for gloss and toughness provide a close match to experimental data and provide scientifically based, well-behaved functions for extrapolation. In addition, the effect of ultraviolet absorbers or antioxidants is modeled here in a simple way to demonstrate the flexibility of this approach.

Introduction

Devices or structures built from engineered materials, rarely combine desirable appearance and environmental stability with their ability to perform the desired function. Polymeric coatings are ubiquitous, and provide protection and appearance control for a vast array of engineered materials, equipment and infrastructure. It is crucial, economically and technologically, that they fulfill their roles for extended periods in a predictable manner. However, in common with most other engineering and structural materials, it has proved extremely difficult to predict service longevity from a priori knowledge of their composition or degradation chemistry. One of the problems is that the complexity of the composition of polymer coatings, for example, even housepaint often contains more than a dozen ingredients. These ingredients, which may include more than one polymer, more than one pigment, more than one filler, and several additives, are randomly distributed by the manufacturing process and usually dry or cure to a similarly random distribution, although some systems will display a degree of organization. They are complicated composites. In addition, there are many factors due to the environment. Degradation may be provoked or accelerated, by conventional elements of the weather such as ultraviolet light, heat, moisture, and pollution and many coatings may face particular threats, such as abrasion, chemicals, etc. It is well understood, that potentially any ingredient or environmental variable may, individually or in combination, may affect the lifetime of a coating. Thus, there are potentially more than 20 material and environmental variables that may be invoked to explain results in a particular situation.

In fact, the situation is even more complicated. Any coating property may define its utility so there are many criteria of coating failure and thus lifetime. Gloss loss and corrosion prevention are extremely important in automotive coatings, but gloss is not important for bridges, where corrosion protection determines the coating service life. The overall problem is comprised of material,

S. Croll (✉) · B. Hinderliter
North Dakota State University, Fargo 58105-5376, USA
e-mail: Stuart.Croll@ndsu.edu

environmental, and end-use variables. Definition of protective failure is related to the initiation of damage to the substrate, for example, grain-raising on wood or rust on steel. Thus service lifetime may involve failure of the coating and the deterioration of the substrate. Coating failure is not identical with the service failure in these cases. Ultimately, the scientific study of service life under these circumstances should deal with coupled and concurrent processes. A specifier or user needs to know the point at which repair or replacement is necessary with coating failure imminent and thus the substrate being threatened, so focusing on the coating failure is the conservative approach adopted here, which also serves the useful purpose of restricting the variables in the problem.

Commercial enterprise dictates that reliable and practical information are obtained as quickly as possible so that selection between material and product prototypes, benefits the company and its customers as quickly as possible. This is the arena in which reliability engineering [1] is very useful where high stress (UV, heat, concentration, rate) laboratory testing may be used to generate a failure probability distribution very quickly compared to testing coating in natural exposure. The term 'reliability engineering', depending on where it is read, may also include the mechanistic, 'physics of failure' approach [2]. Regardless, it is very difficult to correlate accelerated weathering to natural exposure because it often provokes different mechanisms of failure in either the coating or the substrate. This severely limits the interest in failure probability distributions for polymeric coatings, but accelerated testing is used extensively to eliminate candidate materials that display some weakness. Unfortunately, accelerated testing inhibits the introduction of new candidate materials because it does not indicate reliably how they behave under natural conditions.

Elsewhere in the spectrum of approaches are the many very scientific, basic studies that examine, for example, the degradation chemistry of particular polymers or other relevant materials. Modern scientific analytical instrumentation provides the understanding of any of these variables [3] and there is a wealth of literature containing specific scientific investigations, but these results are seldom in a form that can be translated into end-use properties.

There is a vast amount of data in the literature and in proprietary studies, so many correlations and so much specific scientific understanding that one might expect more concrete predictive abilities. The overall problem is formidable. The objective of the approach that is reviewed here was to provide a framework, employing only very general principles, within which many of the details of composition or environment may be inserted and a way in which the accumulated change/damage could be linked to macroscopic end-use properties. It is clear that such an organization of the chemistry and physics of degradation is needed which would aid greatly in designing robust composite coatings and introducing new materials.

Unit processes within service lifetime estimation

The basis for a useful general approach to modeling the deterioration in properties of heterogeneous and varied materials must use very general applicable ideas. The framework proposed here, focuses on the 'wear-out regime' not 'infant mortality'. Thus, failure mechanisms invoked here are due to extended, continual exposure to the environment, and not due to design or installation problems. Overall, the problem of connecting composition to service lifetime remains formidable if contemplated as a whole. However, like all problems, it can be made amenable when separated into 'unit processes'. For each of the end-use properties, the link between composition and performance can be separated into stages. Figure 1 is an example of an approach.

At this stage there is nothing proposed that is specific to polymer coatings. One should attempt to identify mechanisms as much as possible. For example, some coatings show an increase in gloss early in exposure, due to leveling of the polymer made softer at high temperature in the weathering cycle, before it falls due to roughening caused by degradation. As presented here, in separating the unit processes, this scheme has also separated the failure of the coating from any subsequent degradation of the substrate, which could also form a part of the overall study. There may well be other ways to express the linkage, but any such scheme is useful for breaking up the problem into topics on which one can focus research and make progress.

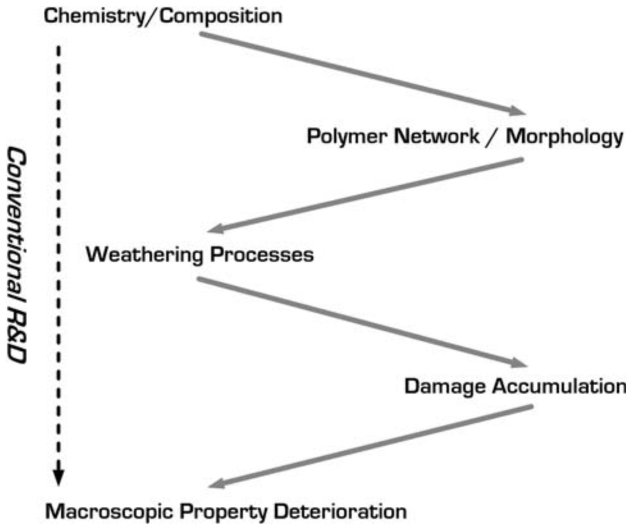

Fig. 1 A scheme for partitioning the overall task of predicting service lifetime into 'unit processes'

Commercial materials development needs results very quickly and goes directly to the last stage from the first, usually by employing accelerated testing of some kind. As mentioned above, this is the conventional representative of reliability engineering in the coatings (and other) industries. This can eliminate coatings with an intrinsic weakness but has proved incapable of predicting real-life performances. Extrapolation to a service lifetime is much more secure and conservative, if it is based on fundamental knowledge of the degradation processes.

The first three steps could be referred to as the "bottom-up" approach. If one understands the chemical and physical structure, one can determine through analytical means what the degradation mechanisms are. These steps are essential to understanding how to change materials so that they perform better and can be achieved by a variety of well-known traditional and modern spectroscopy and microscopy techniques, and this type of investigation forms the bulk of the literature. However, they are not always predictive about which factors are the most crucial nor how the lifetime will be affected.

Quantitative estimation of service lifetime requires understanding of how damage accumulates and how to apply that in calculating how macroscopic properties deteriorate. These last steps in the scheme are the main focus of this work.

Damage accumulation

Any aggressive environment produces a vast number of individual molecular or nanoscale degradation events, that occur at random locations and times across the area or volume of the material. For example, normal weathering exposure includes huge numbers of ultraviolet photons, water molecules or acid molecules. Photon flux is approximately 1 $\mathrm{kW/m^2}$ at midday in Florida which corresponds to approximately 10^{18} $\mathrm{photons/m^2/s}$ or 1 $\mathrm{photon/nm^2/s}$. Other environments may include huge numbers of sand grains, pebbles, space debris, or ionizing radiation. Random arrival and action, of huge numbers of these aggressive events causes the accumulation of damage which may be modeled, in general cases, by Monte Carlo techniques. Occam's Razor suggests that modeling the effects of random damage is the simplest explanation that might apply to all materials. Many coatings or other composites have a degree of organization imposed by the application or manufacturing process, for example, coatings tend to have a polymer rich layer at the interface with air or there may be some surface texture imparted by brushing, rolling, or spray application. One can easily see how analogous organization may occur in engineered plastic parts or other construction materials. Nevertheless, sooner or later, repeated random assaults produce a surface topography (or bulk damage) that becomes randomly distributed after many events. At any stage, the prevailing topography or morphology may be used in physical models that relate macroscopic, end-use properties to the changes caused by the damage.

In general situations, especially for modeling the progress and effect of the damage in composites that are organized, or have several phases that degrade differently, it is easy to see how to use Monte Carlo simulations. Initially, one would have a computer-stored matrix that represents the position and properties of each element of the composite. Then, depending on the environment to be modeled one would use a suitable random number generator to determine where the aggressive event occurs, and another random number to determine what happens at that location. Then the prevailing topography or morphology can be used together with the material properties at each location to calculate properties such as reflectance, colour, toughness, etc. This has been done for variations in polymeric coatings [4] and is a very versatile and potentially complete method for modeling the degradation of many systems. Unfortunately, while being a very graphic and thus easily appreciated method it does not produce any algebraic output that can be manipulated easily.

For the remainder of this article, we will apply further simplifications to show, more algebraically, how this approach produces useful models and demonstrates general aspects of attempts at service lifetime prediction. As an example, we will focus on the outer surface of a coating since it is the well-known, dominant location for coating failure, and degradation. Assuming that the surface (or bulk morphology) has been randomized by aggressive species from the exterior environment, for a material that is being degraded over an exposure period, t,

$$\begin{aligned} \mathrm{d}N(t)/\mathrm{d}t &= \text{Average rate of fragments being removed at points across the coating} \\ &= \text{Flux of photons} \times \text{Absorption probability} \times \text{Efficiency of removing a length of polymer} \\ &= \text{constant}(K) \end{aligned} \tag{1}$$

If the concentration of labile moieties is high enough, then the rate will not be controlled by their concentration, and the rate will be unchanged with exposure time (essentially zero order chemical kinetics). This is more easily imagined here than in typical chemical reactions, because the failure point for a coating or any material occurs well before all the material disappears (and one can also argue that, in some cases, fresh material is continually exposed).

If the exposure conditions (i.e., flux in Eq. 1 above) remain constant or fluctuations are very short compared to the length of exposure and material is eroded but the remaining material is unchanged (i.e., absorption coefficient, quantum efficiency do not change), then the number of successful aggressive events is given by

$$N(t) = K \times t \tag{2}$$

The degradation process is simple and linear under these circumstances so that mass loss, thickness decrease, or overall photo-oxidation will be a linear function of exposure time. In practice, this is often a very good approximation [5] to the actual experience. In fact, measuring weight loss or thickness are simple measurements that would provide very direct evidence of whether this simple approach is correct or whether additional factors should be considered (see below).

Here we have postulated that the damage is done, and accumulated, at random so we can use a well-known result (from the Central Limit Theorem) for the standard deviation in the distribution of a large number of identical random events,

$$\text{Standard deviation} = (\text{number of events})^{1/2} \tag{3}$$

Surface roughness can be expressed as the root mean square of the surface height distribution, σ_{RMS}, which would be given by the standard deviation in the average number of polymer fragments removed at a location and thus by the square root of $N(t)$.

$$\text{Roughness} = \sigma_{\text{RMS}} = \varepsilon\sqrt{N} = \varepsilon\sqrt{Kt} = \sqrt{kt} \tag{4}$$

where ε = characteristic fragment size (linear dimension).

It would be possible to incorporate another trend, for surface change from a process that produced a fractal or a different power spectrum. One can imagine how blisters [6] produced during degradation or other processes, e.g., phase coarsening, might do this but surfaces in real circumstances seem to be modeled well by Gaussian height distributions [7] and roughness has been found to increase with the square root of exposure time [8] so that is the path continued here.

The result here, is derived from assuming random erosion producing a randomized surface without anything specific about the chemical or physical processes, but it does provide a place to input information specific to a material and the environment. Degradation chemistry of the coating, and environmental conditions, can be input because the degradation rate parameter, k, includes the effect of absorption, bond scission chemistry, size of the erosion event and radiation intensity. The value of k would be unique to the material and the environment that it was experiencing. An Arrhenius or Williams–Landel–Ferry temperature dependence for these parameters can be inserted to accommodate temperature as a variable. All can be determined from scientific research done in the “bottom-up” stages. Additionally, one might be able to compare differing environments and how they affect service lifetime through their different irradiation spectra and temperatures.

As an example of a sub-process, one can easily see how to incorporate the growth of a absorbing chromophore in an otherwise UV transparent coating by including an expression for its growth. Alternatively, one could similarly model the damaging effect of loss of an UV absorber, or the loss of a light stabilizer. Such factors could be readily introduced and examined by Monte Carlo simulations. However, one can include simple changes and still obtain algebraic results. If a polymer has been protected by the inclusion of light stabilizers, such as ultraviolet absorbers, UVA, which limit absorption by the polymer binder or antioxidants (which limit the quantum yield) then the degradation will be slowed. However, the stabilizers degrade themselves. The change brought about by these processes can be idealized by (analogous to first order chemical kinetics),

$$\text{Change} = A\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{5}$$

Here the time constant represents the decay of the UVA, etc. so the absorption probability and/or quantum yield in Eq. 1 will change and will increase the beginning of the exposure and will reach the value characteristic of the unprotected material. If the polymer is protected by one of these means, Eq. 2 becomes (ignoring variation through the coating depth),

$$N(t) = K' \cdot t - K'\tau\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{6}$$

where $K' = K \cdot A$

Thus, initially the protection afforded by the stabilizer is complete but dies away depending on its own lifetime. In reality, not all the polymer bonds will be protected, so a linear combination of Eqs. 2 and 6 would be more reasonable (but more cumbersome).

It is not uncommon to observe that weight loss increases after an initial period. One explanation for this in pigmented coatings is that, the initial slower rate of weight loss is from the outer polymer layer that engulfs the pigment particles in a system, where the pigment is wetted

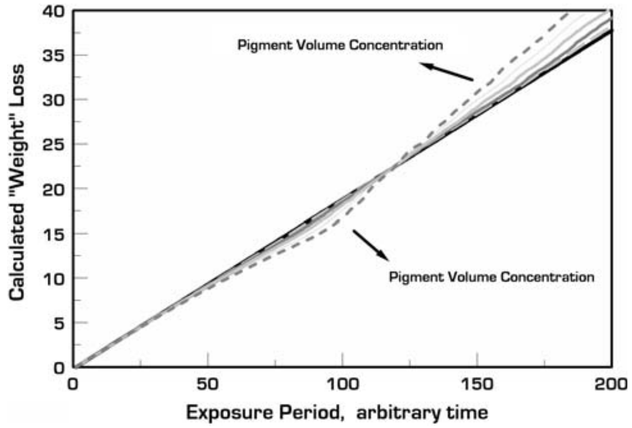

Fig. 2 Monte Carlo simulation of weight loss in pigmented coating, showing how the rate of weight loss changes as the nature of the material lost changes. The pigment volume concentrations used are 0, 5, 15, 25, 35, and 45%. The weight loss of unpigmented polymer was chosen to follow the most simple, linear case

well by the polymer. When the polymer has been eroded enough, that pigment particles fall out ("chalking"), the weight loss rate increases due to the larger size of the fragments, and their density increases. An intermediate stage, with a temporarily reduced rate due to the diminishing projected surface area containing polymer can occur. These processes can be readily simulated by the Monte Carlo approach, see Fig. 2, where the axes are in simulation units and not the result of measurements. For the example in Fig. 2, the weight loss of unpigmented polymer was chosen to follow the most simple, linear case and the polymer was assumed to have a density of 1.1 and the pigment 4.0. The element/pixel size was 15 voxels/pigment diameters (i.e., 20 nm size) since this simulation was targeting titanium dioxide pigment that typically has a diameter of 300 nm. Each degradation step was set to 100,000 photons over an area of 726 × 726 voxels. Pigment particles were assumed to be purely protective (absorptive), so photons that hit pigment cause no damage to the surface until the polymer is eroded beyond the equator of the pigment particle, which then falls out.

Some polymers are stable, but the concentration of chromophores or other labile moieties produced by an impurity or additive builds up as exposure progresses, so the chance of degradation accelerates. The form of Eq. 6 would also represent a simple version of this case when damaging absorption or quantum yield is produced by a finite concentration of an impurity, for example. In this case, the constants would be such that the rate of degradation would be increased in a combination of the rate for the polymer only and an expression like Eq. 6 for the effect of the damaging chromophore. Alternatively, it may be possible to have an exponentially increasing effect of the damaging chromophore if it is not limited by a finite concentration of precursor.

It is also possible to obtain algebraic expressions if one includes an expression for changes that follow second order (or higher integer order) chemical kinetics in Eq. 1, but it is not clear at present whether that would represent any realistic situation, so it is not pursued here. In the example pursued, later only the simple form of Eq. 6 will be used to illustrate the effect of stabilization. Other choices can be explored depending on the circumstances.

This simple, algebraic approach assumes that the surface or bulk morphology is random throughout its service life. In cases, where the degradation has not proceeded yet to a random defect structure or more than one process occurs, or the phase-structure of the coating is complicated, or the incident radiation is highly collimated then the degradation can be followed using Monte Carlo computational techniques [8]. Nevertheless, the structure of the degraded material will eventually be determined by the dominant process and obey the relationships above, governed by Gaussian statistics.

Calculation of macroscopic properties

Service lifetime is determined by the user's appreciation or fears about a macroscopic property. There are well-known and robust theories that connect molecular- or microstructure to macroscopic properties. These can be used to employ the equations or numerical results for the accumulation of damage. The models used here, are the simplest choice possible from an engineering or scientific field, but they demonstrate how much of this seeming formidable problem, of lifetime prediction, can be modeled with the most general assumptions.

Reflectance

Appearance of coatings is crucial for many users. "Gloss" is an expression of the specular reflectance relative to the reflectance of a standardized black (absorbing) glass, see for example ASTM method D523, so it is controlled by reflection from the first surface. It is also a very easy, non-destructive, quantitative, physical measurement wherein service life is decided either by decrease of the gloss itself or loss relative to the initial value for the pristine coating. Since it is easy and non-destructive, gloss is often used to track the degradation of coatings in the field or in accelerated laboratory testing, even if appearance control is not the primary function of the coating. It is also very useful because, materials inevitably are degraded first, or most, at the outermost surface.

As conventionally measured, reflectance (gloss) is usually measured over an area that is approximately 1 cm in diameter, so the area average surface reflectance is determined. Other properties are also determined conventionally by an average over a significant area, e.g., yellowing.

As degradation proceeds, the coating surface becomes increasingly rough. The simplest model that connects surface roughness to specular reflectance is given below [9–11]

$$\frac{R_s}{R_0} = \exp\left[-\left(\frac{4\pi\sigma\cos\varphi}{\lambda}\right)^2\right] \tag{7}$$

where R_s = specular reflection of the rough surface, R_0 = reflection of a perfectly smooth surface of the same material, σ = R. M. S. deviation of the surface from its mean, assuming a Gaussian distribution, and assuming that its value is smaller than the wavelength of incident light, φ = "specular" angle, λ = wavelength of the illumination (note that most determinations of gloss use a standard illumination spectrum, not a single wavelength).

Specular reflection of the smooth surface, R_0, can be obtained from Fresnel's equations if one knows the optical constants. Equation 7 above gives very good results at high gloss angles of 20° and 60° [12] but not when diffuse reflectance and shadowing become important near grazing incidence. More exact and inclusive models of the reflectance from rough surfaces already exist [13, 14] and permit closer representation of the changes with weathering, but they do not provide convenient algebra for this discussion.

Roughness of a surface at any exposure time will combine its initial value, σ_{initial}, due to application procedures and composition, and the subsequent increase due to degradation, Eq. 4. Thus the gloss diminishes according to,

$$\begin{aligned} R_s(t) &= R_0 \exp\left[-\left(\frac{4\pi\cos\varphi}{\lambda}\right)^2\left(\sigma^2_{\text{initial}} + kt\right)\right] \\ &= R_0 \exp\left[-\left(\frac{4\pi\sigma_{\text{initial}}\cos\varphi}{\lambda}\right)^2\right] \\ &\quad \cdot \exp\left[-\left(\frac{4\pi\cos\varphi}{\lambda}\right)^2 kt\right] \end{aligned} \tag{8}$$

If we examine only the gloss relative to its initial value, $R_s(0)$, the need to measure σ_{initial} is avoided,

$$R_s(t)/R_s(0) = \exp\left[-\left(\frac{4\pi\cos\varphi}{\lambda}\right)^2 kt\right] \tag{9}$$

Relative gloss is predicted to decay in a simple exponential fashion. As explained before, material parameters are contained in the degradation rate parameter, k, and now the initial state of the surface roughness and the optical constants for the coating material are contained in $R_S(0)$. Equation 9 indicates that reflectance will eventually decay to zero, which is often essentially true, but for coatings that scatter light significantly, e.g., white pigmented films, there is always some diffuse reflectance [15], regardless which could be included in a more complete expression.

Surface wetting

Whilst it is seldom a crucial property that determines service lifetime, wetting of a surface is sensitive to degradation through changes in its chemical and physical nature. However, the ability to clean a surface may be important in some cases. Measuring contact angle is also a non-destructive test that is also a property that is averaged over an area, that of the liquid drop. As surface roughness increases, we may use the Wenzel equation [16, 17] to calculate changes in surface roughness

$$r\left(\frac{\gamma_{\text{solid-vapor}} - \gamma_{\text{solid-liquid}}}{\gamma_{\text{liquid-vapor}}}\right) = \cos\theta \tag{10}$$

where r = ratio of the actual (rough) vs. projected areas of contact, γ = surface free energy between subscripted phases, θ = wetting contact angle.

This equation does not include chemical change but there are ways to incorporate changes in surface energy when chemical changes occur [18].

Here roughness, r, depends on the surface slope, m_i. This is calculated by using the formula, $m_i^2 = 2\sigma^2/a^2$ [9, 19], where a is the autocovariance length which describes the horizontal correlation of the height features, which is also assumed to be Gaussian. If the surface gradients across the surface are the same in both directions, then,

$$r = \sqrt{1 + m_x^2 + m_y^2} = \sqrt{1 + 2\left(\frac{2\sigma^2}{a^2}\right)} \tag{11}$$

As before, roughness is due to both the initial state of the coating and the subsequent degradation. If the unexposed coating surface profile is reasonably smooth then a starting assumption is that it becomes dominated by the degradations but does not change the horizontal autocovariance length [12]. The expressions for how contact angle changes with degradation via surface roughness, have been published before [12] and are not continued here, because the algebra becomes ponderous and less illustrative. However, one can see how two surface properties are related via their relationships to the surface roughness that is generated by degradation. In principle, one could predict one property from the other, if one knew about the material properties that were involved.

Toughness

Many protective properties, and some aspects of appearance, are related to the development of cracks in a coating. For example, abrasion resistance, corrosion protection, chemical resistance, and brittleness of coatings all depend on the presence of cracks. Automotive coatings gradually suffer from abrasion either from hard particles in the environment or from certain types of washing operations and the damage can become visible and thus objectionable and thus determine the lifetime.

Coatings become brittle as they degrade, thus the Griffith equation for fracture strength can be used to incorporate the results of damage accumulation. If, in this examples we assume that the cracks that determine the fracture strength are initiated by surface degradation, we can use the results gained above. The simple Griffith equation (for coin-shaped cracks) is,

$$\text{Stress}_{\text{G}} = \sqrt{\frac{2E\gamma_{\text{s}}}{\pi a}} \tag{12}$$

where $E =$ Young's modulus, $\gamma_s =$ fracture energy per unit area, $a =$ half length of the initiating crack, $\text{Stress}_{\text{G}} =$ Griffith stress, the critical stress above which the crack propagates.

Instead of a property being determined by the average over a significant area, here we are seeking the deepest surface roughness feature as the initiating crack. As before, the initial surface roughness of the unexposed coating and that due to degradation are added together, and inserted in the equation above,

$$\text{Stress}_{\text{G}} = \sqrt{\frac{2E\gamma_{\text{s}}}{\pi n\sqrt{\sigma^2_{\text{initial}} + kt}}} \tag{13}$$

where $n =$ number of standard deviations defining the probability of the crack size.

Here the property depends on the largest defect present at any stage of the exposure. The numerical factor, n, multiplies the standard deviation in the surface topography (within the region sampled), so that the equation uses the largest (infrequent) value of height deviation, and not the average. It is expected that toughness is determined at the surface, but if it were determined in the bulk, the same formula would be used, but with a different source of initial defects, e.g., pigment agglomeration. This equation shows that coatings that are applied badly, or have an inconsistent structure, i.e., a high value of σ_{initial}, will never be very tough and any coating that degrades quickly (a high value of k) will fail rapidly even if it was applied well.

Fracture strength can expressed as a function of exposure time relative to the initial fracture toughness (before weathering) following the same approach used in the equations for gloss:

$$\frac{\text{Stress}_{\text{G}}(t)}{\text{Stress}_{\text{G}}(0)} = \left(1 + \frac{kt}{\sigma^2_{\text{initial}}}\right)^{-1/4} \tag{14}$$

The parameter describing the initial value of fracture strength contains much of the information about the material. Unfortunately, fracture strength of thin films is difficult to measure due to local variations in film thickness, initial defects, and results containing considerable scattering.

An essentially identical equation, but with different k and $\sigma_{initial}$ can be generated to describe, how adhesion diminishes with exposure, if the adhesion failure can be thought of as a crack that propagates between the coating and the substrate. Adhesion performance would be diminished by polymer degradation, or corrosion progression, at the interface with the substrate. There is no quantitative data published that allows this to be checked, but that is the subject of current research.

Comparison with data

Gloss

It is very common to see a monotonic decrease in gloss with exposure to polymer coatings that have no light stabilization [12, 20, 21]. The gloss data in Fig. 3 is taken at a specular angle of 20 degrees for a polyurethane topcoat in accelerated laboratory exposure involving cycles of 4 h of ultraviolet irradiation from fluorescent tubes followed by 4 h of cool, moist conditions according to ASTM method G53. There is some scatter that is typical of data acquired under practical conditions but the exponential relationship in Eq. 9 is a good representation, as can be seen.

There are a number of approaches in which such data can be technologically useful. If one fits an exponential to a data from the first 25 weeks, it is very close to the curve fitted for the whole data, which indicates that this relationship is useful for extrapolation. Alternatively, one could use this data to make a conservative estimation by fitting an exponential to the lower gloss values from the

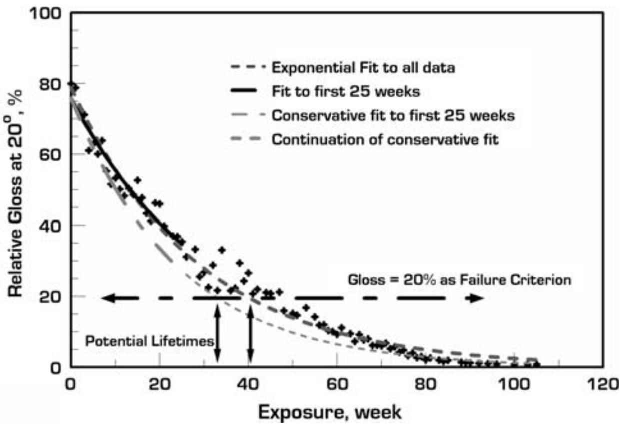

Fig. 3 Approaches to choosing a service lifetime using gloss data. The arrows show how the fitted curves for all the data and a conservative use of the lower produce a value for lifetime

initial 25 weeks (see Fig. 3). Clearly this will result in a lower estimate of service life. If we choose a reduction in gloss to 20% of the initial value as the criterion of failure we can quantify the consequences. The overall fit indicates that the lifetime would be 41 weeks in the accelerated exposure, and the continuation of the safer estimate indicates that it would fail after 33 weeks. One could choose variations on this approach and vary the degree of conservatism. This approach allows confidence in use because the extrapolation is based on a scientifically derived function, and not on an empirical curve fitting.

The equation used here indicates that the gloss diminishes to zero after sufficient exposure. In other situations properties fall but remain finite, however, this approach will still be useful for conservative estimation, particularly since no user of a coating would wait for the properties to vanish completely. Calculations using more complete descriptions of the physics, including diffuse reflection and the effects of masking and shadowing [22] can model real data, including gloss that never falls to zero (due to diffuse scattering), but there is no algebraic representation suitable for this review. As an example, Fig. 4 shows the effect of diffuse, subsurface reflection added to the specular component, above, calculated from a physical theory that has been used extensively in computer rendering [23]. This additional source of reflection would be typical of light coloured coatings. Clearly, the gloss does not decay as fast, nor as completely, if the additional details were added. The overall framework is very simple as presented here, but it also provides clear avenues for including more exact physics as well as the "bottom-up" data on individual materials, if required.

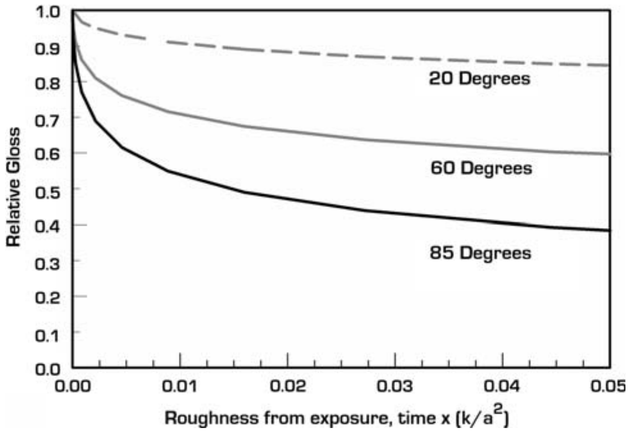

Fig. 4 The combined effect of specular reflection and diffuse scattering from within the coating according to a model by Oren and Nayar. Shadowing and multiple reflections are most important in gloss at 85°

Fracture strength

Equation 14 may be compared successfully [8] with some published data, on toughness of coatings during exposure [24] (see Fig. 5). Here the fit for the unstabilized data was decided by raising the relative fracture strength to the fourth power and fitting a straight line to find the value of $k/\sigma^2_{\text{initial}}$. Apart from one point, the curve is a good representation of the data with a value of 0.15 for $k/\sigma^2_{\text{initial}}$ and seems to be a reasonable continuation for the data.

Explicit calculation of lifetimes

Returning to the expression for how reflectance falls with exposure, the initial rate of reduction in reflectance is,

$$\left.\frac{\mathrm{d}R_{\mathrm{s}}(t)}{\mathrm{d}t}\right|_{t\to 0} = -k \times R_{\mathrm{s}}(0)\left[\frac{4\pi\cos\varphi}{\lambda}\right]^2 \qquad (15)$$

The initial deterioration rate is proportional to the chemical and physical changes contained in k, for any coating, as one should expect, as well as depending on the initial state of the coating contained in $R(0)$. If one was constrained to obtain results only from very short exposure periods then the early rate of gloss loss is sensitive to composition through k. Thus different candidate compositions could be compared provided that the candidates had been prepared so that their initial structure ($R(0)$) was the same or could be measured and included in Eq. 15. Such a comparative approach to choosing between compositions is probably more practical and conservative rather than trying to estimate a lifetime. It is clear why there is no acceleration factor between accelerated (laboratory) testing and natural weathering that is universally applicable, because there is too much that is composition dependent in the factors that make-up the degradation rate constant, k.

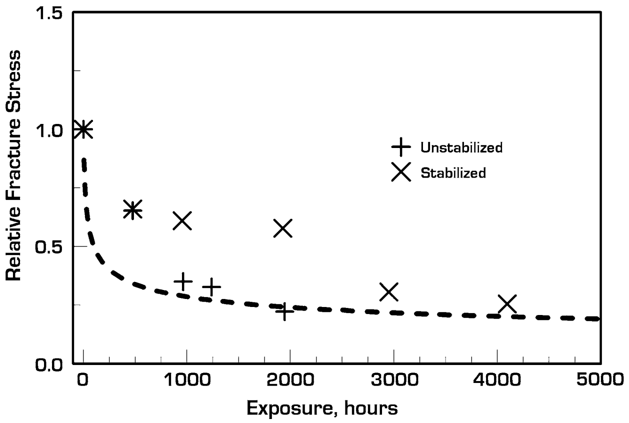

Fig. 5 Relative loss in fracture strength of a clearcoat with exposure. Data from Mark Nichols

Lifetime estimation is very straightforward using these algebraic expressions. If one defines a value of gloss, R(T), that represents the pass/fail level as in Fig. 3, then Eq. 9 defines the service lifetime of the coating when $t = T$:

$$T = -\frac{1}{k}\left(\frac{\lambda}{4\pi\cos\varphi}\right)^2 \mathrm{Log_e}\left[\frac{R_s(T)}{R_s(0)}\right] \tag{16}$$

Lifetime is inversely proportional to the rate parameter, as readily anticipated. Lifetime also depends on the experimental conditions given by the wavelength and the gloss angle. In this, mode of failure defined by gloss, and lifetime depends on the logarithm of the criterion R(T).

Similarly, we can explore toughness. There is very little data in the literature, so Eq. 14 cannot be subjected to the same level of testing, but it is a very important aspect of coatings or any material's performance. However, Figure 5 shows that it is consistent with the data. Calculating the initial rate of change of fracture strength from Eq. 14, leads to similar conclusions as in the case of the reflectance,

$$\left.\frac{\mathrm{d\,Stress_G}(t)}{\mathrm{d}t}\right|_{t\to 0} = -k\frac{\mathrm{Stress_G}(0)}{4\sigma^2_{\mathrm{initial}}} \tag{17}$$

The initial rate of decrease is again confirmed to be proportional to the rate parameter, k, and the initial state of the material that is given in this case by $\mathrm{Stress_G}(0)$ and $\sigma_{\mathrm{initial}}$. If the criterion of failure is that the fracture strength falls to $\mathrm{Stress_G}(T)$ then it corresponds to a lifetime, T,

$$T = \frac{\sigma^2_{\mathrm{initial}}}{k}\left\{\left[\frac{\mathrm{Stress_G}(0)}{\mathrm{Stress_G}(T)}\right]^4 - 1\right\} \tag{18}$$

Lifetime is again inversely proportional to the rate parameter, k, in this simple linear approach, so that a comparative use of early results is confirmed as a very practical way to choose candidate systems.

Now, these simple equations make obvious that, the value of service lifetime is dependent on the property chosen. Clearly, a lifetime chosen with respect to the reflectance of a coating falling to a certain value will not, in general, have the same value as a lifetime defined by a given reduction in fracture toughness, or any of the properties that depend on it, e.g., flexibility, etc.

Previously published data [12] gave a suitable value of k to be 132 nm^2/day for pigmented acrylic coatings. If a value of $\sigma_{\mathrm{initial}} = 42.1$ nm is chosen so that a coating has an initial reflectance of 80% with respect to that of a perfectly smooth surface at 60° specular angle at a wavelength of 560 nm (Eq. 8), one can easily calculate, how sensitive the lifetime is to the value of the failure point chosen. If one changes the criterion of mechanical failure to a third of the initial strength, from a half, lifetime is extended by a factor of $80/15 = 5.3$. If we use a similar change in criterion for gloss, then the relative increase in lifetime is $1.1/0.69 = 1.6$. The two properties are connected through their common origin in degradation at the surface and the deterioration in both is modeled using the same material parameters, k and $\sigma_{\mathrm{initial}}$. However, it is evident that the relationship between the two properties as they decay with weathering exposure is non-linear so one cannot monitor for an apparent failure in strength or protection by monitoring a criterion for gloss failure in the absence of a physical model connecting the two properties. If these simple algebraic relationships were accurate one could use the initial value of gloss to deduce $\sigma_{\mathrm{initial}}$ and the decay rate in gloss to deduce the degradation rate parameter k then calculate the likely deterioration in strength.

There is a hierarchy of method in applying this framework of predicting service lifetime. These algebraic relationships are very simple, but they do convey much of the underlying physics and make good representations of experimental data without resorting to complicated or ad hoc explanations. It is certainly possible to include more detailed physics for those properties, where discriminating measurements can be made, e.g., gloss and surface wetting. In these cases, it may be possible to establish equations to model the property or processes, but find that they can only be solved by numerical means. For properties such as fracture strength, adhesion, and corrosion protection where data include significant scatter, there may be no advantage in applying more details because the data will not be discriminating. In these latter cases, the simple equations may fulfill the needs. In the most complete approach, if material composition is complicated and several or linked processes occur, then damage accumulation and subsequent calculation of properties can be done via Monte Carlo computer simulations.

The equations also demonstrate another, more general issue that is present in experimental data as well. All properties deteriorate as exposure progresses. The competence of the coating becomes low and diminishes further on an increasingly shallow curve. For example, a coating in one location might resist the local environment or stresses for a long period, but in another location on the same structure where the stress is a modest increment higher or the environment is slightly harsher, that same coating would be defeated much earlier. Although the difference in stresses may be small, the property-exposure curves could be so shallow that the coating exhibits a tremendous difference in the resultant service lifetime (see Fig. 6). Unless the environmental stresses are known quite exactly, service lifetime will always be difficult to predict under field conditions [25]. This will be especially true when properties depend on local defects, rather than on an averaged, macroscopic condition. It is probably more practical and conservative to seek an early part of the "wear-out" regime where the rate of failure accelerates, not the actuarially most likely lifetime.

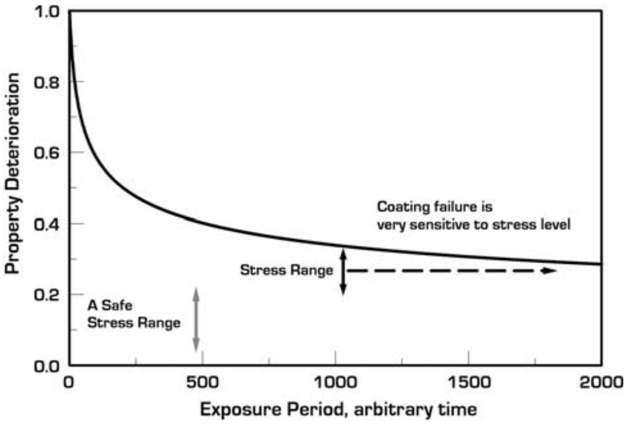

Fig. 6 General trends in property deterioration with exposure. Shows how the lifetime becomes increasingly sensitive to variations in stress as the trend becomes increasingly shallow. The property and stress are illustrations only

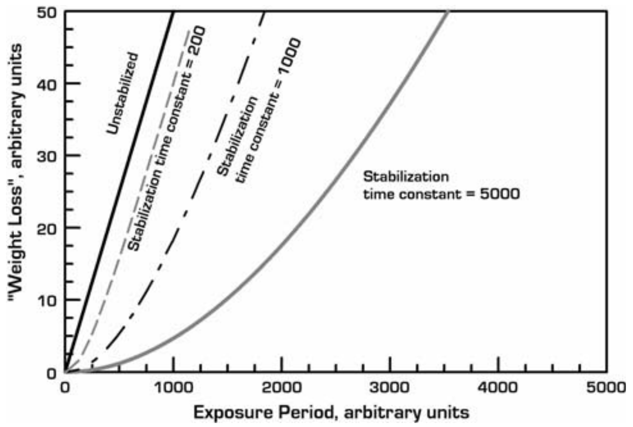

Fig. 7 The patterns in weight loss as a function of exposure (with arbitrary units); calculated using the simple algebraic approach showing how the different degrees of stabilization delay weight loss

Although the recognition that degradation occurs through a large number of random events has yielded these simple algebraic equations, an advantage of the 'unit process' aspect of this framework is the ease with which variations may be introduced. The exploration of additional processes may require usually a return to numerical Monte Carlo simulations, but an additional, simple mechanism that is algebraically tractable is used as an example below.

Polymer stabilization

High performance coatings are often formulated with additives that stabilize the polymer binder. These may be either an ultraviolet absorber, UVA, and/or an anti-oxidant such as a hindered amine light stabilizer, HALS. The purpose is to preserve appearance or to lengthen protection in other applications, e.g., marine wood finishes, corrosion protection, etc.

Equation 6 gives a simple expression for the effect of one of these stabilizers assuming that its own lifetime is finite and its concentration, and thus its protection, is governed by simple kinetics. The number of fragments lost with time is directly the weight lost without the need to use another equation to connect damage and a macroscopic property. Figure 7 shows how the shape of the weight loss function (in arbitrary units) varies according to the decay constant, τ, of the stabilizer.

Here the lifetimes were chosen arbitrarily to show an effect over an exposure period that is consistent with Fig. 5. Other graphs use the same variation in decay constant, but use abscissae chosen for clarity. The exposure period increment can be scaled easily to match requirements.

Figure 7 can be contrasted to the Monte Carlo simulation in Fig. 2. In practice, it would be straightforward to evaluate the length of a stabilizer's lifetime and its decay kinetics by a separate spectroscopic experiment. In fact, it is not uncommon to use more than one stabilizer, each of which would have a separate lifetime. It is easy to see how this would be included, but it is not demonstrated here.

In controlled laboratory exposure conditions, weight loss is a very valuable and quantitative measure of degradation. It is less practical when coatings are exposed in natural environments where accidents may occur to obscure the weight loss by degradation.

The effect on reflectance can be evaluated by using the square root of the expression for the number of fragments lost, Eq. 6, and reworking Eq. 9:

$$R_s(t)/R_s(0) = \exp\left\{-\left(\frac{4\pi\cos\varphi}{\lambda}\right)^2 k'\left[t-\tau\left(1-e^{-t/\tau}\right)\right]\right\} \tag{19}$$

Here the degradation rate parameter has been changed to k' to signify that, combining the kinetics of the stabilizer with that of underlying degradation might produce a different value of the constant. Curves in Fig. 8 are very close in form to results seen for the loss in gloss of stabilized polymers [20, 21].

Similarly, one may include this variation in Eq. 14 for relative fracture strength,

$$\frac{\mathrm{Stress_G}(T)}{\mathrm{Stress_G}(0)} = \left\{1+\frac{k'\left[t-\tau\left(1-\mathrm{e}^{-t/\tau}\right)\right]}{\sigma^2_{\mathrm{initial}}}\right\}^{-1/4} \tag{20}$$

These variations are demonstrated in Fig. 9 which uses the fitted value of $k/\sigma^2_{\mathrm{initial}}$ from the data together with the same selection of stabilizer time constants as used in other graphs. The experimental results from Fig. 5 are included and the trends seem consistent with the change seen in the stabilized coating compared to the unstabilized coating, but

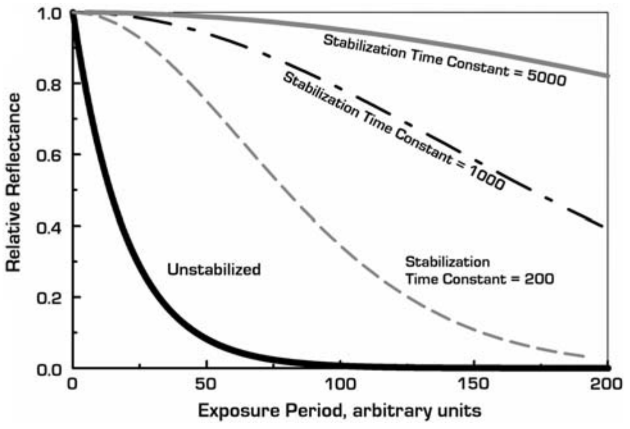

Fig. 8 The patterns in relative gloss loss as a function of exposure (with arbitrary units); calculated using the simple algebraic approach showing how the different degrees of stabilization slow the gloss loss

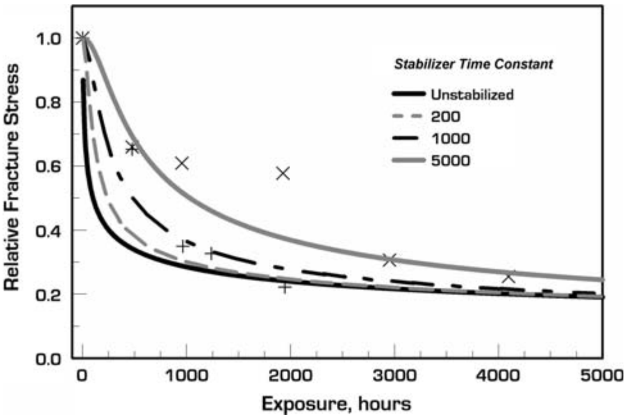

Fig. 9 The patterns in fracture strength as a function of exposure using units to correspond with the data in Fig. 5. The curve demonstrating stabilization lifetime of 5,000 ("hours") is a close match to the stabilized data, but is not the result of numerical curve fitting

there are so few data points that there was no attempt to numerically fit the curves to the data. This approach produces expected trends for both gloss and toughness when a very basic method is used to input the effect of a light stabilizer, so it gives confidence that this simple approach does permit additional sub-processes to be input in a stable fashion.

Summary

Instead of contemplating the formidable difficulty of linking composition directly to service performance lifetime, one can partition the problem into unit processes, each of which is more tractable. A possible, mechanistic framework has been presented here for which a simple approach yields algebraic expressions for change in properties with exposure period. The first steps in the scheme assemble the analytical, materials science information about the coating and its environment that may be incorporated in a degradation rate parameter. A fundamental element of the scheme is that degradation is caused by a multitude of random, repeated random events and we may employ Gaussian statistics after the material has acquired a random structure. This is basic and general but the framework does permit specific chemical or physical "bottom-up" materials knowledge to be included either in the calculation of the rate of damage accumulation, or in the consequent deterioration in properties. In fact, this approach may well be applicable to other material and composites in their various service environments.

Well-known theories are applied that connect the damage, such as roughness or flaw size, to service properties, e.g., by using Griffith's theory of fracture. More inclusive and detailed approaches fit naturally into the scheme and if they cannot be modeled algebraically they may be calculated numerically or simulated completely by computer with Monte Carlo approaches. The focus here has been on the coating failure but, given suitable knowledge, the failure of the substrate could be added as a further unit process. One cannot say that this particular scheme is the best or only possibility, but it does provide grounds for optimism that a viable scheme can be found because it represents experimental data and known trends well. In fact, this approach is useful in identifying material parameters necessary to make a particular prediction of service lifetime. It provides insights into how service lifetime depends on the initial condition, appropriate degradation processes, the environment and the service requirements so that robust product design or selection can be effected.

In the simplest case presented here, there is a simple, inverse relationship between rate of degradation (measured most usefully early in exposure) and service lifetime. More complicated, or combined, degradation processes can be followed by Monte Carlo computer techniques, but it is unlikely that practical coatings would show deterioration patterns that would counter such a relationship.

This scheme demonstrates how the deterioration rates of different properties may be connected and so technologists may use, perhaps, a non-destructive test to assess how sensitive the coating is to changes in composition, rather than being obliged use a destructive test, with all its inherent variation. In fact, gloss measurements are often used in the coatings industry although it has been done without any indication of how it may be connected to other properties.

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