Int. J. Solids Structures Vol. 20, No. 8, pp. 791-804, 1984
Printed in the U.S.A.

0020-7683/84 $3.00 + .00
Pergamon Press Ltd.

INTERACTIVE MECHANICAL AND CHEMICAL DEGRADATION IN ORGANIC MATERIALS

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(*Received* 29 *March* 1983; *in revised form* 23 *August* 1983)

Abstract—A theory of interactive mechanical and chemical degradation is derived for organic materials. In the uncoupled form, the mechanical degradation is taken to be that derived from flaw growth theory for polymers. The uncoupled chemical degradation is described by first-order reaction rate theory as applied to static strength. In combined effect, the two mechanisms of degradation are coupled through the concept and characterization of intrinsic strength. Theoretical predictions are made for the lifetime of polymeric materials simultaneously acted upon by a constant load and a chemically active environment. Our results are compared with experimental data upon the lifetime of composite aramid strands.

INTRODUCTION

There is complete agreement that materials age and degrade with time, but there is no consensus on the underlying physical mechanisms, nor on how to characterize the changes mathematically. Organic materials in general, and polymers in particular, are very susceptible to environmental aging. It is now understood that materials undergo mechanical damage as the result of loading conditions. The classic example of this type of degradation is fatigue behavior. However, most of these types of behavior have only been characterized on an empirical basis. Design procedures are needed by which materials can be specified to fulfill a certain lifetime function for various load and environmental histories.

Our attention will be restricted to the behavior of polymers. Consider first the circumstance of aging as caused by irreversible chemical effects. We will refer to this as chemical degradation. Perhaps the best known example of this is the molecular-scale chain scission caused by exposure to ultraviolet light radiation. Other examples include the diffusion of a chemical specie into the polymer that attacks and destroys various bonds, including cross-linking sites. The oxidative degradation of elastomers is an example. There is a related field known as chemical stress relaxation. Aklonis, MacKnight and Shen show data of time-dependent moduli wherein the moduli decay in a time-dependent manner, with a time constant directly related to the time constant of the chemical reaction [1]. In the simplest form, the modulus degrades in a manner consistent with first-order reaction kinetics. That is to say, a single exponential function serves to describe the time-dependent change in the modulus. More complex behaviors result from higher-order or multiple-reaction kinetics. See Schnabel for a treatment of such effects [2].

There is a different type of irreversible effect in polymers that is best understood on a molecular scale. One widely employed model of molecular mobility relates to the concept of free volume. As the free volume collapses, the molecular mobility decreases, and the corresponding relaxation spectrum changes. This point of view has been fully explored by Struik [3]. The behavior of this type admits characterization through the shifting of relaxation and creep functions on logarithmic time scales. Although there may be special cases in which this type of behavior may be considered to be reversible, it is generally considered to be an irreversible aging effect, whether one considers it to be due to mechanical or chemical means.

Now, we turn to what has been called mechanical degradation, or aging. This terminology typically refers to flaw growth under load. In the most general sense, this behavior includes void nucleation and growth, crack growth and crack coalescence.

Formulations are made mostly from a continuum mechanical point of view, and have been mostly focused on determining the kinetics of crack growth as a function of load in polymers. Different, but related points of view, have been given by McCartney *et al.* [4–6]. Although the fundamental bases of these approaches are quite different, the end results share striking similarities. Namely, the crack kinetics formulations represent generalization of elastic fracture mechanics whereby the elastic compliance is replaced by the viscoelastic creep function with its argument involving the crack velocity. Certainly, the controlled growth of cracks in polymers degrades their ability to bear a sustained load; a state of damage is being accumulated. Christensen has proposed a methodology for predicting the lifetime of polymers from a mechanical degradation point of view [7].

Thus far, we have discussed separate areas of the chemical and mechanical degradation of polymers. We have already cited oxidative attack as a chemical degradation example. The straightforward static strength testing of polymers is the obvious and ultimate example of a mechanical- or load-induced degradation. It is possible to account for both types of damage through the insertion of additional parameters into constitutive relations. For example, in reversible viscoelastic constitutive relations, the relaxation function appears in the form $E(t-\tau)$ where t is current time and τ is the past time variable. This renders the constitutive relation to a convolution form. However, aging effects can be included by modifying the relaxation function to also depend upon the past history of strain, $\epsilon(\tau)$ through $E(t-\tau, t)$. Thus, the convolution form of the constitutive equation is violated and irreversible effects can be accommodated. An example of this point of view is given by Stouffer and Strauss [8]. The approach to be followed here, however, is different for the following reasons.

Thus far, uncoupled effects of mechanical and chemical degradation have been considered. There are conditions, however, under which both types of degradation could be operative. The simplest manner in which to combine these effects would be through a linearly additive form. For example, let D be some measure of material damage. Then we could write

$$D = \overset{\infty}{\underset{s=0}{F}} [\epsilon(t-s)] + f(\chi_i), \tag{1}$$

where the first term is the mechanical damage, expressed as a functional of the strain history, $\epsilon(\tau)$, and the second term is the chemical damage as a function or possibly a functional of the chemical environmental agents, χ_i. While this form accommodates the separate effects of chemical and mechanical damage, it is simple to reason that this linearly additive form could not possibly be correct. It is well understood that mechanical damage cannot be given mathematical characterization in a simple superposition form. Thus, the vastly more complicated state of combined chemical and mechanical degradation could not admit a simple superposition form. Obviously, there would be iterative effects between mechanical and chemical degradation. In order to understand the interactive chemical and mechanical degradation of materials, we consider it necessary to proceed from a well-based physical model of the effects. Without a physical model (or set of hypotheses), one could simply postulate any number of mathematical formats which would relate to one set of data but be totally useless in attempting to predict behavior under other conditions.

Our approach will be restricted to the case of polymeric materials under the action of constant load while in a chemical environment. Thus, we are not attempting to produce a comprehensive damage theory. Rather, we are seeking to develop a special theory of mechanical and chemical degradation applicable to the conditions of stress rupture. First, we consider the case of mechanical degradation due to flaw growth. The basic kinetic theory is re-examined for application to our purpose. Then, the result is generalized to include the interactive effect with a degrading chemical environment.

MECHANICAL DEGRADATION

We begin by recalling the low-speed and high-speed asymptotic results derived by Christensen by the energy balance method [6]. Under high-speed conditions, it was found that the crack velocity is given by

$$c = \frac{[2\alpha h/(1-\nu^2)] \displaystyle\int_0^\infty \frac{L(\tau)}{\tau}\,\mathrm{d}\tau}{\dfrac{2\Gamma}{h(1-\nu^2)\sigma_y^2} - J(0)}, \tag{2}$$

where the problem solved was that of an infinite strip subjected to fixed transverse normal strain and steady-state growth of a semi-infinite crack. The notation in (2) is that Poisson's ratio, ν is a fixed constant, h is the strip half-width, Γ is the surface energy content, $L(\tau)$ is the uniaxial creep spectrum, $J(0)$ is the initial value of the creep function and σ_y is the transverse stress far ahead of the crack. The corresponding low-speed result was found to be

$$c = \frac{[\gamma h(1-\nu^2)/2]\left[J(\infty) - \dfrac{2\Gamma}{h(1-\nu^2)\sigma_y^2}\right]}{\displaystyle\int_0^\infty \tau L(\tau)\,\mathrm{d}\tau}, \tag{3}$$

where $J(\infty)$ is the long-time asymptotic value of the uniaxial creep function. In Christensen [6] these formulae were stated in terms of the creep spectrum of the shear function rather than as the uniaxial creep function used here. The difference involves a trivial modification of the parameters α and γ by factors involving Poisson's ratio. The factors α and γ are nondimensional parameters that are independent of the load level and the mechanical creep function. These asymptotic high- and low-speed formulae were derived by representing the stress field in the problem by doubly infinite series. The representation did not admit the inclusion of a stress singularity, thus a proper physical interpretation of these results is that they are appropriate to a crack tip condition whereby damage or surface conditions preclude the occurrence of a stress singularity. The equations noted above from Christensen [here written as (2) and (3)] were obtained by expressing the energy balance as a power expansion in $(1/c)$ for (2) and in (c) for (3) and by neglecting higher order terms [6].

While eqns (2) and (3) served to validate the application of the energy balance method to viscoelastic crack kinetics problems, the results were very limited due to their asymptotic nature. It is necessary to have a general form for crack kinetics in order to approach mechanical damage problems. For this purpose, we wish to show that the obvious generalization of elastic fracture mechanics to the viscoelastic case produces results in accordance with eqns (2) and (3). For the infinite strip problem containing a semi-infinite crack, the elastic fracture mechanics result is

$$\sigma_y^2 = \frac{2\Gamma/h}{(1-\nu^2)J}, \tag{4}$$

where J is the elastic uniaxial compliance. The obvious generalization of (4) to viscoelastic conditions is given by

$$\sigma_y^2 = \frac{2\Gamma/h}{(1-\nu^2)J(\rho/c)}, \tag{5}$$

where $J(\rho/c)$ is the uniaxial creep function: its argument involves crack velocity, c, and a parameter, ρ. In the most elementary approach, ρ should be taken to be a characteristic dimension associated with the blunted crack tip region, such as the radius of curvature at the crack tip. More sophisticated theories could seek to determine ρ as a function of the variables of the problem, rather than treating it as a fixed parameter, as is done here. We now show that the general form of (5) is consistent with the asymptotic results of (2) and (3).

Recall the forms characterizing the creep spectrum either through

$$J(t)=\int_0^\infty L(\tau)[1-\mathrm{e}^{-t/\tau}]\,\mathrm{d}\tau+J(0) \tag{6}$$

or

$$J(t)=-\int_0^\infty L(\tau)[\mathrm{e}^{-t/\tau}]\,\mathrm{d}\tau+J(\infty). \tag{7}$$

Consider first the high-speed case. Using (6), write the creep function in (5) as

$$J(\rho/c)=\int_0^\infty L(\tau)[1-\mathrm{e}^{-\rho/c\tau}]\,\mathrm{d}\tau+J(0). \tag{8}$$

Expand the exponential in (8) as a power series, to obtain (8) as

$$J(\rho/c)=\int_0^\infty L(\tau)(\rho/c\tau)\,\mathrm{d}\tau+O(1/c^2)+J(0). \tag{9}$$

Neglecting the terms of order $1/c^2$ in (9) gives (5) as

$$\sigma_y{}^2\cong\frac{2\Gamma/h}{(1-\nu^2)\left[\rho/c\int_0^\infty\frac{L(\tau)\,\mathrm{d}\tau}{\tau}+J(0)\right]}. \tag{10}$$

Solving (10) explicitly for the crack velocity, c, gives us

$$c\cong\frac{\rho\int_0^\infty\frac{L(\tau)}{\tau}\,\mathrm{d}\tau}{\left[\frac{2\Gamma}{h(1-\nu^2)\sigma_y{}^2}\right]-J(0)}. \tag{11}$$

This form is identical with the high-speed asymptotic result in (2), with $2\alpha h/(1-\nu^2)$ replaced by ρ. Other kinetic crack growth theories which have arguments of the creep function different from that in (5) would not give a result consistent with the asymptotic form of (2).

Next, we turn to the slow-speed case. This situation is much more complicated than the high-speed case just considered. The reason for this being that the exponential term in (7) or the corresponding form for (6) admits a power series expansion for a large c and thus a small argument, but it does not have an expansion for a small c and thus a large argument. We will not be able to reduce (5) to slow-speed conditions by standard asymptotic expansion means. Rather, we merely demonstrate that, through the use of some reasonable approximate forms, (5) can be brought to the form of the slow-speed result in (3). This equivalence of (5) and (3) must be approached by heuristic means. First, develop an approximate form for (7). Replace the exponential term by the step function

$$\mathrm{e}^{-t/\tau}\rightarrow h(\lambda\tau-t). \tag{12}$$

Determine parameter, λ, by minimizing the total square error over the semi-infinite interval of the difference between these two forms. We found that

$$\lambda=\ln 2. \tag{13}$$

Now, using (12) as a replacement in (7), we find

$$J(t) \cong -\int_{t/\lambda}^{\infty} L(\tau)\,\mathrm{d}\tau + J(\infty). \tag{14}$$

Using (12) is not as drastic as it might seem to be at first. Typically, spectra are spread over many decades of times. Accordingly, when viewed on a log scale, the difference of the two forms in (12) is not great.

Still, (14) is not convenient to use. It does show that for large time arguments, only the long time part of the spectrum is involved. However, for later purposes, a form is needed which involves the time variable outside of the integral. This is required so that we can solve for velocity explicitly when we replace time by the velocity-dependent argument shown in (5). We wish to show that the integral in (14) is close to the integral shown below:

$$\frac{1}{t}\int_0^{\infty} \tau L(\tau)\,\mathrm{d}\tau. \tag{15}$$

Decompose this integral into the two parts:

$$\frac{1}{t}\int_0^{\infty} \tau L(\tau)\,\mathrm{d}\tau = \frac{1}{t}\int_0^{t} \tau L(\tau)\,\mathrm{d}\tau + \frac{1}{t}\int_t^{\infty} \tau L(\tau)\,\mathrm{d}\tau. \tag{16}$$

Consider first a discrete spectrum of the form

$$L(\tau) = \sum_{i=1}^{N} L_i\delta(\tau_i), \tag{17}$$

where $\delta(\tau_i)$ are delta functions spaced at one-decade intervals. Take the time variable to be between the last two retardation times as

$$\tau_{N-1} < t < \tau_N. \tag{18}$$

Assume that the amplitudes L_i change at a rate less rapid than as $1/\tau$. With these conditions, the first integral on the right hand side of (16) can be neglected, leaving

$$\frac{1}{t}\int_0^{\infty} \tau L(\tau)\mathrm{d}\tau \cong \frac{1}{t}\int_t^{\infty} \tau L(\tau)\,\mathrm{d}\tau. \tag{19}$$

Now, with the condition in (18), t and τ are of the same order of magnitude, thus

$$\frac{1}{t}\int_0^{\infty} \tau L(\tau)\,\mathrm{d}\tau \cong \int_t^{\infty} L(\tau)\,\mathrm{d}\tau. \tag{20}$$

Similar conditions are assumed to apply for a continuous spectrum, as just described for the discrete spectrum. Using (20), then (14) can be written as

$$J(t) \cong -\frac{1}{t}\int_0^{\infty} \tau L(\tau)\,\mathrm{d}\tau + J(\infty), \quad t \cong \tau_N, \tag{21}$$

where the parameter λ is so close to one that it can be neglected and τ_N is the highest retardation time in the spectrum. The form in (21) is what is needed to obtain a slow-speed result. We must emphasize that it is not valid in an asymptotic sense of long times. Rather, it has been derived as being valid in the range of times near the longest retardation time of the material. However, such times are so large that the end result of this derivation will correspond to a very small velocity value.

Replace (5) with (21), with the appropriate change of argument to obtain

$$\sigma_y^2 \cong \frac{2\Gamma/h}{(1-\nu^2)\left[-\dfrac{c}{\rho}\displaystyle\int_0^\infty \tau L(\tau)\,\mathrm{d}\tau + J(\infty)\right]} \tag{22}$$

Solving (22) for crack velocity, gives

$$c \cong \rho\left[\frac{J(\infty) - \dfrac{2\Gamma}{h(1-\nu^2)\sigma_y^2}}{\displaystyle\int_0^\infty \tau L(\tau)\,\mathrm{d}\tau}\right]. \tag{23}$$

This expression is identical with the low-speed asymptotic result in (3), with $\gamma h(1-\nu^2)/2$ replaced by parameter ρ. We emphasize that (23) has been derived subject to the restriction shown in (21), which, when expressed in terms of velocity, gives $\rho/c = \tau_N$ where τ_N is the largest retardation time of the material.

To sum up, we have shown that the general kinetic crack growth formula, (5), gives high- and low-speed results, (11) and (23), which are in agreement with the asymptotic high- and low-speed forms in (2) and (3) derived earlier by Christensen [6]. Equation (11) was found to be the asymptotic high-speed form of the general form in (5), whereas (23) is a low-speed form; but in accordance with its manner of derivation, it does not have asymptotic validity. Nevertheless, these results suffice to show that the general form in (5) for kinetic crack growth corresponds to the previously found asymptotic results. Other crack theories have an argument of the creep function which is different from the velocity argument shown in (5). With this justification for the kinetic form in (5), we proceed to utilize it in a life prediction methodology. Before proceeding explicitly to the lifetime prediction matters, we first will seek to determine under what conditions the crack velocity form (5) can be approximated by a power law form, as is commonly employed on an empirical basis.

Following the derivation in Christensen [7], the creep function can be taken as a "double" power law form:

$$J(t) = \frac{J_0(1+\gamma_1 t^n)}{(1+\gamma_2 t^n)}, \quad (0 \le n \le 1), \tag{24}$$

where $J(0) = J_0$ is the initial value and the asymptotic long time value of the creep function is $J(\infty) = (\gamma_1/\gamma_2)J_0$. Parameters n, γ_1 and γ_2 would be adjusted to fit data, typically over many decades. Using (24) in (5) then gives

$$c^n = \frac{2\Gamma\gamma_2\rho^n - \sigma_y^2 J_0\gamma_1\rho^n h}{\sigma_y^2 J_0 h - 2\Gamma}. \tag{25}$$

Under the following restrictions:

$$2\Gamma\gamma_2 \ll \sigma_y^2 J_0\gamma_1 h \text{ and } \sigma_y^2 J_0 h \ll 2\Gamma, \tag{26}$$

the first terms in the numerator and denominator of (25) can be neglected to give

$$c = \left(\frac{J_0\gamma_1 h}{2\Gamma}\right)^{1/n} \rho\sigma_y^{2/n}. \tag{27}$$

Thus, the crack velocity has a power law dependence upon stress. The conditions under which this approximation is true are derived from (26);

$$\frac{2\Gamma\gamma_2}{hJ_0\gamma_1} \ll \sigma_y \ll \frac{2\Gamma}{J_0 h}. \tag{28}$$

It is physically plausible there would be an accessible intermediate stress range in which (28) could be satisfied. With success in developing an approximate power law form for crack growth, we will turn next to life prediction, to understand the possible limitations implied by a power law form there.

Christensen derived the following expression (eqn 12 in Ref. [7]) for lifetime of a polymeric material system under constant stress:

$$\tau = \int_1^{1/\tilde{\sigma}^2} \left(\frac{1 - \tilde{\sigma}^2\zeta}{\tilde{\sigma}^2\zeta - \tilde{\gamma}}\right)^{1/n} \mathrm{d}\zeta, \tag{29}$$

where τ is nondimensional time to failure, and $\tilde{\sigma}$ is nondimensional stress as defined by

$$\tilde{\sigma} = \frac{\sigma}{\sigma_i}, \text{ with } \tilde{\gamma} = \frac{\gamma_2}{\gamma_1}, \tag{30}$$

and where the intrinsic strength, σ_i, is defined by

$$\sigma_i = \sqrt{\frac{2\Gamma}{h_0 J_0}}. \tag{31}$$

The method of derivation in (29) proceeds by associating dimension $h(t)$ with that of the half crack length, with h_0 being the initial flaw size. Then (25) is integrated to determine the time until a single, isolated crack, subjected to constant stress, σ, will grow to unstable size. The intrinsic strength, σ_i, relates to what is typically called the static strength or instantaneous strength as opposed to the reduced strength behavior that occurs under long-time, stress-rupture conditions. The concept and formalization of intrinsic strength will be of great importance in the later formulation of interactive chemical and mechanical degradation. The power law forms to be derived here also will be of later use. As it stands, the relation in (29) has a much more complicated form than that of a simple power law relation.

Having succeeded in deriving a power law form for crack velocity in (27) and (28), it is reasonable to see if the life expression in (29) admits a power law form. Begin by assuming

$$\tilde{\sigma}^2 \ll \tilde{\gamma} \text{ and } \tilde{\gamma} \ll 1. \tag{32}$$

These conditions are sufficient to neglect the last term in the denominator of the integral in (29), leaving

$$\tau = \int_1^{1/\tilde{\sigma}^2} \left(\frac{1}{\tilde{\sigma}^2\zeta} - 1\right)^{1/n} \mathrm{d}\zeta. \tag{33}$$

To proceed further, expand the integral in (33) to obtain

$$\left(\frac{1}{\tilde{\sigma}^2\zeta} - 1\right)^{1/n} = \left(\frac{1}{\tilde{\sigma}^2\zeta}\right)^{1/n} - \frac{1}{n}\left(\frac{1}{\tilde{\sigma}^2\zeta}\right)^{1/n-1} + \cdots. \tag{34}$$

Substitute (34) into (33) and integrate to obtain

$$\tau = \frac{1}{\tilde{\sigma}^2}\left[\frac{1}{-\frac{1}{n}+1} - \frac{1}{n\left(-\frac{1}{n}+2\right)} + \cdots\right] + \frac{1}{\tilde{\sigma}^{2/n}}\left[\frac{1}{\frac{1}{n}-1} - \frac{\tilde{\sigma}^2}{n\left(\frac{1}{n}-2\right)} + \cdots\right], \tag{35}$$

where the first terms come from the upper limit, and the second terms come from the lower limit. For $\sigma \ll 1$ and $n < 1$, the second and succeeding terms in the second bracket in (35) can be neglected compared with the first term. Further, the first grouping of terms in (35), of order $\tilde{\sigma}^{-2}$, can be neglected compared with the term of order $\tilde{\sigma}^{-2/n}$. This leaves (35) as

$$\tau \cong \frac{1}{\left(\frac{1}{n}-1\right)\tilde{\sigma}^{2/n}}. \tag{36}$$

Thus, the power law form has been recovered. The following conditions for (36) to be valid are

$$\left.\begin{array}{l} \tilde{\gamma} \ll \tilde{\sigma} \ll 1 \\ \tilde{\gamma} \ll 1 \\ n < 1 \end{array}\right\} \tag{37}$$

These are certainly possible conditions that could be satisfied for a particular material. The revealing characteristic, however, is that the power law form for life cannot have any validity as an asymptotically correct form, neither at very high nor very low stress levels. Rather, there is merely the possibility of a power law form at an intermediate stress range in viscoelastic materials. This range of limited validity of the power law form will be sufficient for our purposes in the next section.

MECHANICAL AND CHEMICAL DEGRADATION

In the preceding section, we outlined a theory of mechanical degradation for conditions of stress rupture. The essential aspect of the development was that of the growth due to load of initial flaws to reach a critical size, at which time the material would rupture. As a totally separate matter, materials can age chemically under a stress-free state. What then must occur when a material is simultaneously subjected to load and an active chemical environment? We consider that very complicated situation next.

Our interest centers on the practical situation of polymeric materials subjected to a constant load, and simultaneously subjected to a degrading chemical environment. The theory of the preceding section accounts for mechanical degradation with no chemical degradation. Let us now consider separately the case of uncoupled chemical degradation. Then, we shall interrelate the two effects. Materials under no load but in a deleterious chemical environment are characterized by strength testing, that is, the material is allowed to chemically age for a specified period of time and then it is tested to determine its static strength. When done in a sequence of times, the strength can then be expressed as a function of time, assuming constant chemical environment. The static strength would be written as

$$\sigma_s = f(t, \chi), \tag{38}$$

where χ is the chemical parameter denoting the concentration or strength of the chemical reactant or agent. In the most elementary form, if the reaction proceeds according to first-order reaction kinetics, the chain scission and/or bond rupture would be expected to occur at a corresponding rate. The static strength would then be expressed as a simple exponential of the form:

$$\sigma_s = \hat{\sigma}\, e^{-t/t_c}, \tag{39}$$

where $\hat{\sigma}$ is a stress amplitude and the time constant, t_c, would be a function of the concentration of the chemical reactant. Although much more complicated forms could be taken for the static strength degradation due to chemical environment, certainly (39) is the simplest, most realistic form, inasmuch as it comes from reaction rate theory. Also, the simple form of (39) adequately models a variety of chemical degradation data. Equation (39) represents the result of a theory of chemical degradation at exactly the same level as (29) represents a theory of mechanical degradation. One deals with the variation of static strength due to a degrading chemical environment, while the other predicts the time to failure of materials undergoing kinetic flaw growth (mechanical degradation) due to the presence of internal stress. The problem now is to interrelate these two effects. This will be done, first in a deterministic manner; thereafter, the method will be generalized to account for statistical variability.

The key to synthesizing these two different theories of material degradation is to recognize the relationship of each theory to the common characterization known as static strength. Equation (39) directly reveals the effect of chemical degradation upon static strength. The life prediction form of (29) involves the concept of intrinsic strength, (31), through the nondimensional stress form (30). From (31), the intrinsic strength is seen to be nothing more than the static strength of the material as determined by sufficiently fast rates of testing, such that the material response is governed by the glassy value of the creep function, $J_0 = J(0)$. With this identification, we shall henceforth refer to the static strength as the intrinsic strength, since the latter term herein has been given a physical meaning. Accordingly, we note that the mechanical degradation theory in (29) depends upon the intrinsic strength of the material, but the intrinsic strength of the material can be degraded through chemical means, as for example in accordance with (39). This then provides the coupling mechanism between the mechanical and chemical degradation effects.

We begin the derivation of interactive degradation by recalling the differential form for flaw growth, (25), and its subsequent restriction to the power law region, (27), through restrictions, (28). Rewrite (27) here as

$$\left(\frac{\mathrm{d}h}{\mathrm{d}t}\right)^n = \frac{J_0 \gamma_1 \rho^n}{2\Gamma} h(t)\sigma^2, \tag{40}$$

where now the characteristic dimension, $h(t)$, is taken to be the half-length of the crack, and σ is the applied stress. Writing (40) in terms of the intrinsic strength, (31), gives

$$\frac{\mathrm{d}h}{h^{1/n}} = \left(\frac{\gamma_1 \rho^n}{h_0}\right)^{1/n} \left(\frac{\sigma}{\sigma_i}\right)^{2/n} \mathrm{d}t. \tag{41}$$

Were this separation of variables form integrated with σ/σ_i being a constant, the power law life prediction form of the previous section would be obtained. However, we now introduce the effect of chemical degradation, whereby the intrinsic strength, σ_i, is taken to be a function of time according to the prescribed rate of chemical degradation. At this point, it is important to note that we are developing a theory of mechanical and chemical interaction only in the range where the mechanical degradation by itself would be of a power law form. We do not attempt the more complicated problem involving behavior outside the power law region.

Retaining the time dependence of σ_i, integrate (41) to obtain

$$\frac{\left(\dfrac{h}{h_0}\right)^{-(1/n)+1} - 1}{\left(-\dfrac{1}{n} + 1\right)} = \int \left(\frac{\sigma}{\sigma_i}\right)^{2/n} \mathrm{d}\tau, \tag{42}$$

where h_0 is the initial crack size and τ is nondimensional time, written as the following:

$$\tau = \frac{\gamma_1^{1/n}\rho}{h_0}t. \tag{43}$$

Taking $h(t)$ to be large, representing a state of failure, we neglect the first term in the numerator of (42) to obtain

$$\int\left(\frac{\sigma}{\sigma_i}\right)^{2/n} \mathrm{d}\tau = \frac{1}{\frac{1}{n}-1}. \tag{44}$$

This is the basic form we have been seeking. With specified $\sigma_i = \sigma_i(\tau)$ due to chemical degradation, then (44) can be integrated to determine the lifetime. We can rewrite the chemical degradation form (39) in terms of nondimensionalized time as

$$\sigma_i = \hat{\sigma}\,\mathrm{e}^{-\tau/\tau_c}, \tag{45}$$

where τ_c is the time constant of chemical degradation. The combined forms of (44) and (45) thus comprise the interactive theory of mechanical and chemical degradation. The key to the present approach is the identification of the static strength degradation due to chemical means with the intrinsic strength of flaw growth theory.

We take the applied stress, σ, as being constant, insert (45) in (44) and integrate to give the basic result:

$$\tau = \frac{n\tau_c}{2\log e}\log\left[\frac{2/n\tau_c}{\left(\frac{1}{n}-1\right)\tilde{\sigma}^{2/n}}+1\right], \tag{46}$$

where $\log = \log_{10}$ is conventionally used. Equation (46) then provides a deterministic prediction of the nondimensional time to failure, τ, under constant stress and constant chemical environment, with $\tilde{\sigma}$ being the nondimensional stress according to

$$\tilde{\sigma} = \frac{\sigma}{\hat{\sigma}}, \tag{47}$$

which is normalized with respect to the amplitude in (39), rather than as in (30) where there was no chemical degradation. Thus, $\hat{\sigma}$ is the intrinsic strength of the material before the onset of chemical degradation. Although n relates to the exponent in the creep function characterization, (24), as a practical matter it would be evaluated to fit lifetime experimental data.

It should be noted that a procedure similar to that just given could be followed, but rather than starting with the differential form in (40), we could have started with the lifetime form in (36) and then let σ_i in $\tilde{\sigma}$ be chemically degraded. If the latter procedure were followed, a completely different result would have been obtained. The approach followed here, however, is preferable since it allows the degrading intrinsic strength, σ_i, to alter the crack growth kinetics which is a physically realistic circumstance.

Before evaluating (46) numerically, it is appropriate to outline the generalization of the deterministic procedure just given to account for statistical variability.

To generalize the procedure to a statistical form, consider first the case of the initial intrinsic strength, loosely called the static strength. According to (39), the variable $\hat{\sigma}$ is the initial intrinsic strength in the deterministic theory. Now take the initial intrinsic strength to be a random variable specified through its relation to a cumulative distribution function, as

$$C_{DF} = F\left(\frac{\hat{\sigma}}{\hat{\sigma}_s}\right), \tag{48}$$

where $C_{DF} = F(\ )$ is the cumulative distribution function of unspecified form and $\hat{\sigma}_s$ is a statistical parameter of nondimensionalization, as for example the scale parameter in the Weibull distribution. We solve (48), whatever its form, for $\hat{\sigma}$ in terms of C_{DF} and $\hat{\sigma}_s$ and write the solution as

$$\hat{\sigma} = \frac{\hat{\sigma}_s}{f(C_{DF})}, \tag{49}$$

where the function form $f(\ )$ depends upon $F(\ )$. We substitute (47) with (49) to obtain

$$\tilde{\sigma} = \frac{\sigma}{\hat{\sigma}_s} f(C_{DF}). \tag{50}$$

With the statistical form of (50), the deterministic result in (46) can be generalized to this statistical form:

$$\tau = \frac{n\tau_c}{2\log e}\log\left\{\frac{2/n\tau_c}{\left(\frac{1}{n} - 1\right)\left[\frac{\sigma}{\hat{\sigma}_s} f(C_{DF})\right]^{2/n}} + 1\right\}, \tag{51}$$

giving the statistical distribution of lifetimes parameterized with respect to the variable of the cumulative distribution function. The procedure used to deduce (51) applies to any distribution function; however, there is an inherent assumption in this statistical generalization. All of the statistical variability has been accounted for by letting $\hat{\sigma}$ in (45) be a random variable. A consequence of this assumption is that the distribution of intrinsic strength is independent of time as the chemical aging progresses. This is a rather strong assumption, of course, but it is probably one of the simplest means of incorporating statistical variability into an interactive theory of mechanical and chemical degradation. More complicated forms could be taken whereby τ in (45) is also allowed to be a random variable. The advantage of the present approach is that the statistical formula for lifetime in (51) has exactly the same form as the deterministic formula in (46). This relationship will be usefully employed in the next section.

DATA EVALUATION

First, we consider the set of test data reported by Chiao for the stress rupture of strands of an aramid fiber embedded in epoxy resin (Fig. 1) [9]. These results have been obtained from an extensive and comprehensive test program at Lawrence Livermore National Laboratory, with contributions from many people over many years. The testing method involved hanging dead weights on the strands and recording the time of failure. The volume fraction of the fiber phase was about 70%. The applied stress was normalized with respect to the static strength, or the initial intrinsic strength in the terminology of the present work. The various percentages in Fig. 1 are the percentages of strand failure. It is seen from the data that at the higher stress levels the data seem to follow approximately straight lines, but at the lower stress levels, the curves turn downward. It is our hypothesis that the upper stress level behavior in Fig. 1 is controlled by mechanical degradation, whereas the downturn represents the increasingly important effect of chemical degradation. In view of the fact that the statistical life result in (51) and the deterministic result in (46) have the same form, we will use the latter form to test the hypothesis on the 9% failure envelope in Fig. 1. Only the 9% curve in Fig. 1 is used since it contains the most test data.

Before evaluating specific data cases, it is appropriate to discuss the idealization involved in applying the present flaw growth theory to model the failure of the aligned fiber strands. Certainly on a miscroscale, immensely complicated failure events must occur. However, in our present idealization, the strand is taken to be totally fiber-dominated. Under this idealization, neighboring fiber failures are viewed on a macroscale as an advancing crack. Thus, the crack is taken to run transverse to fiber direction. Also, the

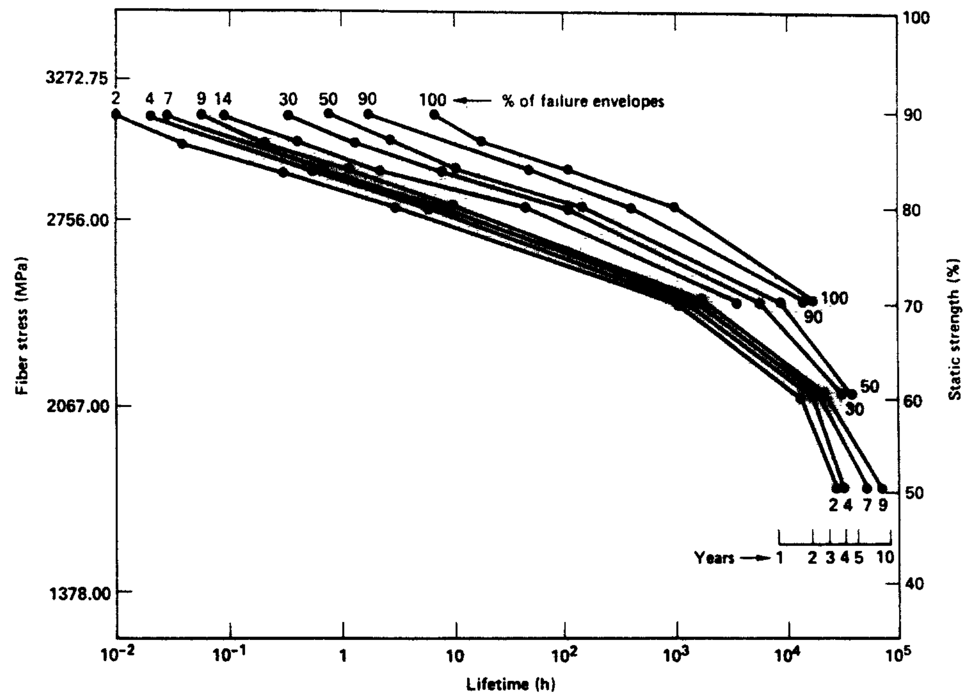

Fig. 1. Stress-rupture of aramid epoxy strands at 20–28°C and 40% max. R. H.

chemical degradation is taken to relate to fiber deterioration. These idealizations are probably quite reasonable for organic material fibers, as we consider here. For inorganic fibers, a totally different type of model might be called for, one which would give more emphasis to the matrix phase.

It is convenient to recast the result in (46) into real time variables. Let

$$\tau = \frac{t}{t_0} \quad \text{and} \quad \tau_c = \frac{t_c}{t_0}, \tag{52}$$

where t_0 is the time parameter of the mechanical degradation theory and t_c is the time constant of the chemical degradation, according to first-order reaction rate theory. Using (52), (46) becomes

$$\frac{t}{t_c} = \frac{n}{2\log e}\log\left[\frac{2t_0/nt_c}{\left(\frac{1}{n}-1\right)\tilde{\sigma}^{2/n}}\right]+1 . \tag{53}$$

Letting $t_c \to \infty$ in (53), we recover the power law form:

$$\frac{t}{t_0} = \frac{1}{\left(\frac{1}{n}-1\right)\tilde{\sigma}^{2/n}} . \tag{54}$$

Letting $t_c \to 0$ gives $t \to 0$, meaning that the material degrades instantly. Equations (53) and (54) are sufficient to accomplish our data reduction purposes.

The 9% failure envelope (or the 91% survival envelope) from Fig. 1 is replotted in Fig. 2 on a log–log scale. The upper portion of the data does indeed appear to be a straight line, as would be predicted by a lifetime power law form. Accordingly, the parameter n and the time constant t_0 in (53) and (54) are evaluated such that (54) fits the straight line portion of the data in Fig. 2. We found that $n = 0.0533$ and $t_0 = 0.0561$ h.

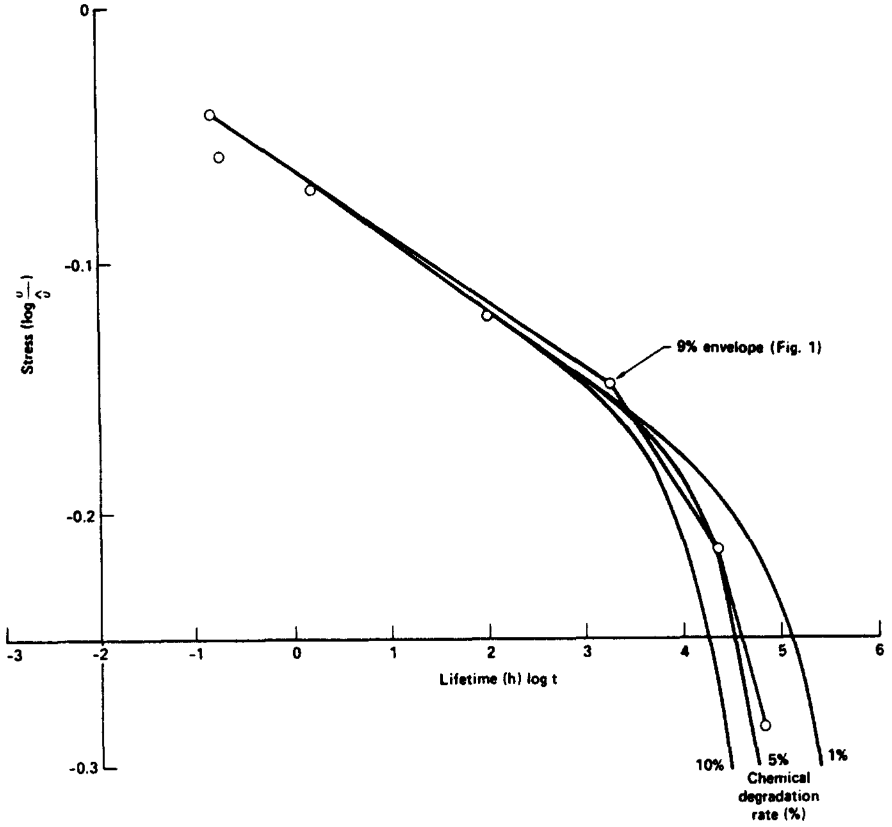

Fig. 2. Theoretical predictions of interactive degradation (eqn 53).

Next, we must evaluate the time constant, t_c, of chemical degradation. First, however, we must have a reasonable indication that there was, in fact, a harmful chemical environment. There is, in fact, independent evidence of such an effect. Chiao has reported results on tests of strands that were stored in the same environment as the mechanically loaded strands, but were not loaded [10]. That is, strands were stored without load, but otherwise in the same environment as the loaded strands. These environmentally exposed strands were then tested for static strength. It was reported that about a 5% degradation occurred in static strength due to environmental effects in one year. Furthermore, it was argued that the specific environmental agent in this case, and time range, was ultraviolet light radiation. The UV radiation induced chemical damage. For our purposes, we simply treat the chemical degradation as being at an initial level of 5% of static strength per year. Noting that 8.76×10^3 hours equals one year, we evaluate t_c from

$$e^{-(8.76 \times 10^3/t_c)} = 0.95,$$

which gives $t_c = 1.71 \times 10^5$ h.

For purposes of comparison, the levels of chemical degradation of 1 and 10% per year also give 1%/y, $t_c = 8.72 \times 10^5$ h and 10%/y, $t_c = 8.31 \times 10^4$ h.

The complete calculations predicted by (53) are shown in Fig. 2. The independently specified value of 5% per year chemical degradation does indeed come closest to matching the experimental data in Fig. 2.

The procedure derived here does show that it is possible to interrelate mechanical degradation and chemical degradation in a rational manner. Certaintly more elaborate theories could be derived if necessary. In that event, the present approach may provide guidelines for relating theoretical forms to experimental data even with multiple and fundamentally different mechanisms of aging and degradation. We believe that the physical concept of intrinsic strength and its mathematical formulation, as utilized here, are central to the means of characterizing damage growth and strenth degradation in polymeric materials.

Acknowledgement—Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

REFERENCES

1. J. J. Aklonis, W. J. MacKnight and M. Shen, *Introduction to Polymer Viscoelasticity*. Wiley, New York (1972).
2. W. Schnabel, *Polymer Degradation: Principles and Practical Applications*. Macmillan, New York (1982).
3. L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials*. Elsevier, Amsterdam (1978).
4. L. N. McCartney, Derivation of crack growth laws for linear viscoelastic solids based upon the concept of a fracture process zone. *Int. J. Fracture* **16**, 375 (1980).
5. R. A. Schapery, A theory of crack-initiation and growth in viscoelastic media III. Analysis of continuous growth. *Int. J. Fracture* **11**, 549 (1975).
6. R. M. Christensen, A rate-dependent criterion for crack growth. *Int. J. Fracture* **15**, 3 (1979).
7. R. M. Christensen, Restrictions on life-prediction methodology in polymers. *Mech. Res. Commun.* **9**, 241 (1982).
8. D. C. Stouffer and A. M. Strauss, Theory of material divagation. *Int. J. Engng Sci.* **16**, 1019 (1978).
9. T. T. Chiao, Private communication, Lawrence Livermore National Laboratory, Livermore, CA (1982).
10. T. T. Chiao, Internal memorandum, Lawrence Livermore National Laboratory, Livermore, CA (1982).