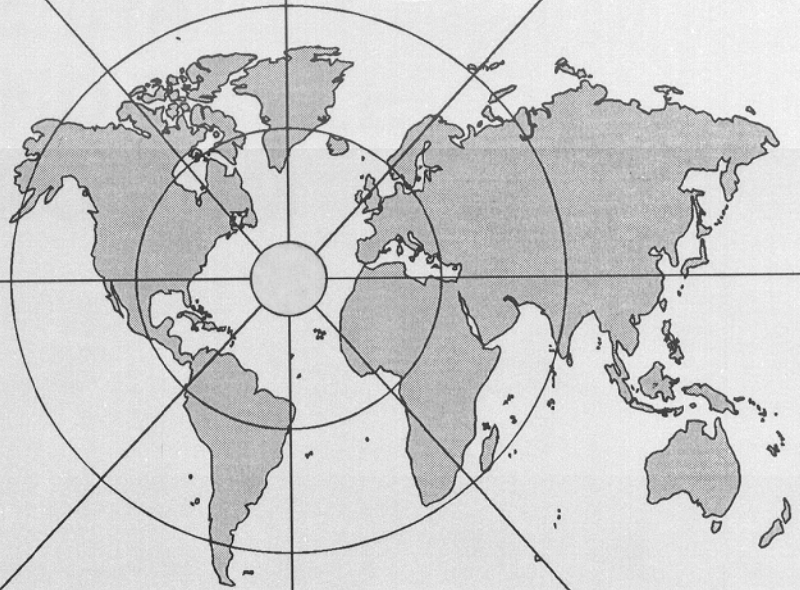


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Kinetics Models for Fatigue of High-Strength Fused Silica Optical Fiber

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ABSTRACT

The strength and dynamic fatigue behavior of fused silica fiber has been measured as a function of the ambient humidity, both when the fiber is bare and polymer coated. The use of bare fiber is important since it makes it possible to separate the effects of fatigue and mass transport through the coating. The results for coated fiber verify earlier work that suggests that the degradation reaction is approximately second order with respect to humidity in the range of 20-95% RH; the bare fiber shows similar trends. A purpose-designed computer program is used to simultaneously analyze the effects of loading rate and humidity in a self-consistent manner. The results are consistent with a simple chemical kinetics model in which the degradation rate shows an exponential dependence on stress. In contrast, careful dynamic fatigue experiments have been found to empirically show better agreement with a power law kinetics model.

INTRODUCTION

Even though there have been many studies of the strength and fatigue behavior of fused silica fiber, no self-consistent detailed model has emerged for the degradation kinetics, which relates the crack growth rate to the applied stress intensity. A power-law model has been widely used for making reliability predictions even though it is not based on any physical model and even though it predicts longer lifetimes than other, more physically reasonable models.^{1,2} Additionally, the effect of such

environmental parameters as temperature, humidity, or pH, are usually either ignored (by assuming that the proof testing, strength testing and service environments are all the same) or are incorporated in an empirical fashion.

The commonly used power law model for lifetime predictions is mathematically simple to manipulate, but is empirical and has no physical basis. Environmental effects, such as temperature, cannot be incorporated in a self consistent manner.³ The power law, designated model 1 here, may be expressed in the form:

$$\frac{dc}{dt} = A_1 \left(\frac{K_I}{K_{IC}} \right)^{n_1}, \quad \text{Model 1 (1)}$$

where n_1 is the stress corrosion parameter, K_I is the stress intensity factor, K_{IC} is the critical stress intensity factor, and A_1 is a scaling parameter. n_1 is usually assumed to be a material constant which represents the sensitivity of fatigue to stress and A_1 depends on the environment. If we assume a simple chemical kinetics model for fatigue where the reaction rate between water and silica determines the crack growth rate, A_1 may be expressed as

$$A_1 = \nu f(a_{H_2O}) \exp\left(-\frac{Q}{RT}\right), \quad (2)$$

i.e. the reaction kinetics are thermally activated with an activation energy, Q , and has some functional dependence on the water activity, $f(a_{H_2O})$; and ν is a frequency factor. In this model the activation energy, Q , is assumed to be stress independent even though there is evidence to the contrary.⁴ a_{H_2O} is the

thermodynamic activity of the water. For water vapor at moderate pressure, $a_{\text{H}_2\text{O}}$ is equal to the partial pressure of water vapor, $p_{\text{H}_2\text{O}}$. At a given temperature, $p_{\text{H}_2\text{O}}$ is proportional to the relative humidity

$$RH = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^{\text{sat}}} \quad (3)$$

The reaction between water and silica is not in the vapor phase, but assuming that the water at the crack tip is in equilibrium with the vapor (a good approximation since the fibers are strong meaning that very little water is consumed by the growth of such small cracks), Eq. (2) then reduces to the form:

$$A_1 = v_1 f_1(RH) \exp\left(-\frac{Q}{RT}\right) \quad (4)$$

The more physically reasonable chemical kinetics model proposed by Wiederhorn,⁵ assumes that the stress at the crack tip modifies the activation energy of the chemical reaction via an activation volume. This leads to a kinetics model (designated model 2) of the form:

$$\frac{dc}{dt} = A_2 \exp\left(n_2 \frac{K_I}{K_{IC}}\right), \quad \text{Model 2} \quad (5)$$

where $A_2 = v_2 f_2(RH) \exp\left(-\frac{Q_0}{RT}\right)$, (6)

and where Q_0 is the activation energy under zero applied stress. In this model the activation energy is linearly dependent on K_I (i.e. it treats stress as if it were a negative hydrostatic pressure).

A third model (designated model 3), based on an analysis due to Lawn⁶, assumes that the strain energy density at the crack tip modifies the activation energy as a contribution to the chemical potential. After some simplification, this leads to a quadratic dependence of the activation energy on the stress and hence

$$\frac{dc}{dt} = A_3 \exp\left(n_3 \left(\frac{K_I}{K_{IC}}\right)^2\right), \quad \text{Model 3} \quad (7)$$

where $A_3 = v_3 f_3(RH) \exp\left(-\frac{Q_0}{RT}\right)$. (8)

Lifetime extrapolations are sensitive to the assumed form of the kinetics model.^{3,2} Determination of the kinetics model by measurement of both static and dynamic fatigue over a broad range of failure times tends to favor the power law, model 1.³ An alternative way of assessing models is to examine the environmental dependencies. The above three models all assume that the stress dependence is contained in the n_i , ($i=1..3$), while the environmental dependence is contained in the A_i , and explicitly depends on the humidity by the functions $f_i(RH)$. In this paper we examine the kinetics models by measuring the strength and dynamic fatigue at various humidities to determine which model is most consistent with the data; i.e. shows the least dependence of n_i on humidity. Further, we will use the results to determine the reaction order, m , defined by

$$f_i(RH) = RH^m \quad (9)$$

While the humidity dependence of strength of fiber has been studied elsewhere,^{4,7,8} none of these studies interpreted their results in terms of kinetics models. The data are generally sparse and only consider polymer coated fiber. Since the presence of the coating may perturb the kinetics, we will present results not only for coated but also for bare fiber.

The derivation of fatigue equations combines with the crack growth kinetics equation (1), the concept of sharp, well-defined cracks, as embodied by the Griffith equation:

$$K_I = \sigma_a Y_c^{1/2} \quad (10)$$

However, pristine fiber does not contain such cracks.⁹ The fatigue equations are very much more dependent on the kinetics equation (1) because of its stronger dependence on stress. Therefore, even though the micromechanical details of the weakening process described by equation (10) are probably not accurate, use of the standard fatigue equations gives a good description of the degradation kinetics

EXPERIMENTAL PROCEDURE

The specimens used in this study were 125 μm diameter fused silica coated fiber with a UV-curable polyurethane-acrylate, giving an overall diameter of 250 μm . The fiber strength was measured at five different faceplate velocities (1, 10, 100, 1000, 5000 $\mu\text{m/s}$) using a two-point bending apparatus.¹⁰ The strength was measured in different humidities by allowing the coated fiber to equilibrate overnight in the appropriate environment, which ranged from 20 to 95% RH at $25 \pm 0.1^\circ\text{C}$. Bare specimens were prepared by stripping the coating in $\sim 200^\circ\text{C}$ concentrated sulfuric acid. Stripping in this way does not degrade the strength of the fiber provided sufficient care is taken.¹¹ Bare fibers were tested immediately after immersion in the humid environment since it was found that no equilibration time was necessary. Since only one bare specimen can be broken at a time, ten samples were measured at each speed. Twenty samples were measured at each speed for the coated specimens.

The strength data were fitted to each of the kinetics models and the fatigue parameters, A_i and n_i , were determined by utilizing a computer program. Probably the main reason the power law (Eq. 1) is used so widely is that it is comparatively simple to extract analytic expressions for fatigue behavior under simple loading conditions. In contrast, the exponential forms (Eq. 5 and 7) are not analytically integrable for dynamic fatigue (constant rate of loading). Fitting to experimental data was therefore achieved using a purpose-written computer program to perform the integration and parameter fitting. A key feature of the program that distinguishes it from earlier work¹ is that it performs careful statistical analysis in order to estimate the confidence limits on the fit parameters together with their cross correlations. Throughout this work, reasonable

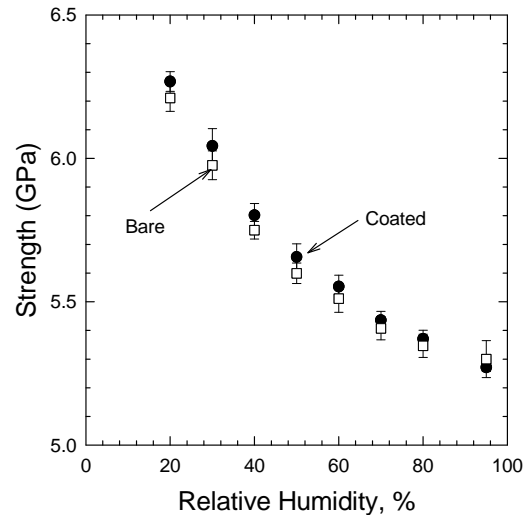


Figure 1: The strength of both the bare and coated fibers as a function of relative humidity, calculated for a faceplate velocity of 75 $\mu\text{m/s}$.

values for key parameters were assumed: $K_{IC} = 0.75 \text{ MPa}\cdot\text{m}^{1/2}$, $Y = 2.06$, and $\sigma_i = 14 \text{ GPa}$.* The n_i values are sensibly independent of these parameters; the A_i values are not independent but, while their magnitudes do depend on the values chosen, the trends observed with humidity do not change. Therefore all of the conclusions drawn from this work are independent of these values. All error bars presented here represent a 95% confidence interval.

RESULTS AND DISCUSSION

Figure 1 shows the strength of coated and bare fibers as a function of relative humidity. These data were interpolated from all five faceplate speeds to a speed of 75 $\mu\text{m/s}$. This effectively considers all of the data to give a smaller error bar than would be obtained from the data at a single speed.¹² The coated and bare fibers show similar trends. The relationship between the strength and humidity is nonlinear, both on this graph and on a semi-log plot.

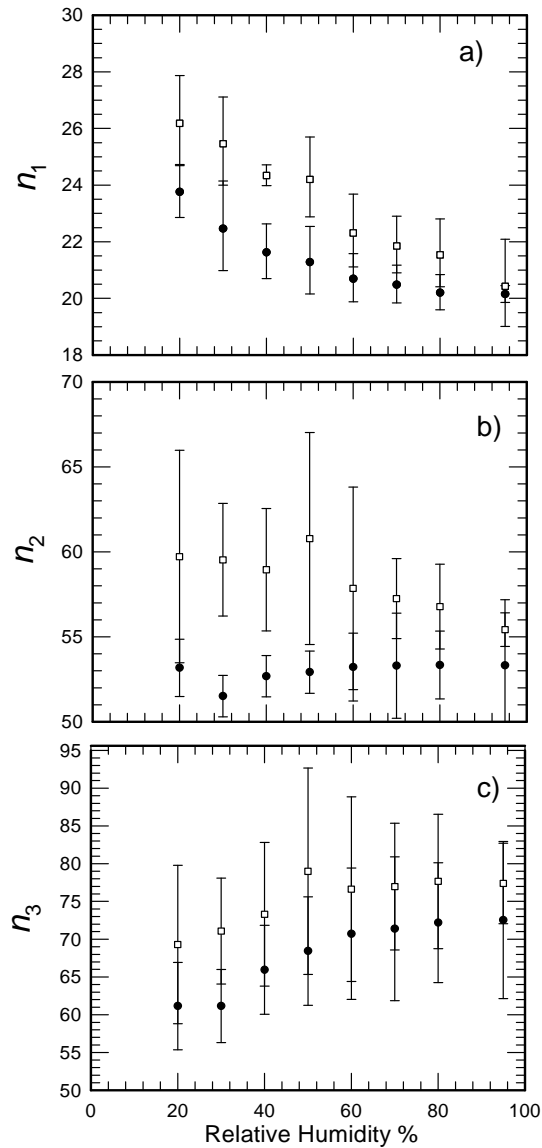


Figure 2: Fatigue parameter, n_i , for each model vs. relative humidity for (●) coated fiber and (□) bare fiber.

The fatigue parameters, n_i and $\log A_i$, found by fitting model 1 to the humidity data, are shown in Figures 2(a) and 3(a) and (d). The value of n_1 shows a systematic decrease with humidity for both bare and coated fibers, while the value of A_i is roughly constant; as described above this violates a common assumption of model 1, that the humidity should be solely contained in A_1 . This represents an internal inconsistency with the power law model if it is to be considered as anything other than purely empirical. Earlier

work also showed similar trends in n_1 . (e.g. ref.4). These trends in n_1 are modest compared with the size of the error bars. However, this is deceptive since the trends in the raw data are clear. The error bars are large because the values of A_i and n_i are strongly correlated. Since the models all assume that n_i are constant, we found values for A_i assuming fixed values for n_i which is calculated from a weighted average of the values in Figure 2. This is a weak constraint since it uses an underlying assumption of the models. The result of the constraint is that the error bars on A_i are substantially smaller and more closely represent the obvious trends in the raw data. However, Figures 3(a) and (d) show that the value of A_1 found by constraining n_1 (triangles) show different trends compared to the unconstrained values (squares). This again shows that model 1 does not give a consistent description of the data.

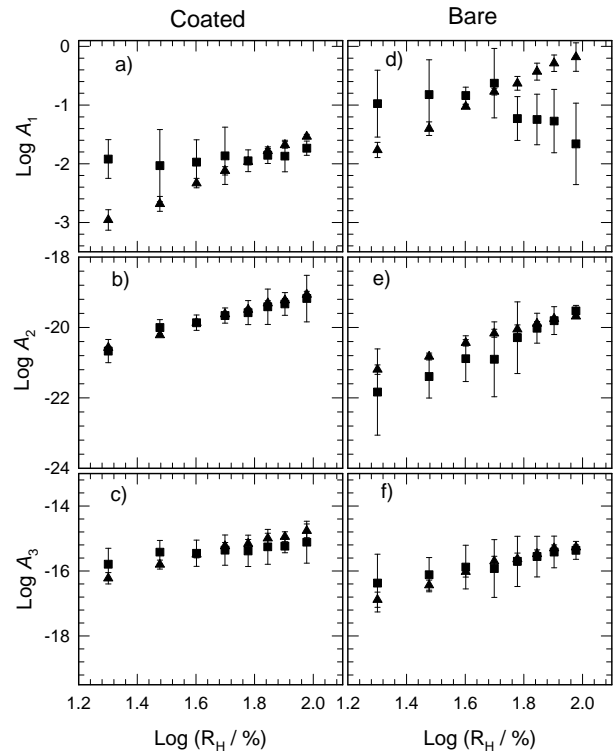


Figure 3: $\log A_i$ vs. \log (Relative Humidity) using (■) unconstrained and (▲) constrained values of n_i . (a) to (c) are for coated fibers, and (d) to (f) are for bare fibers

Table I: Reaction orders calculated for each model using (u) unconstrained and (c) constrained values for the n_i 's

	Coated		Bare	
	u	c	u	c
Model 1	0.40 ± 0.28	2.16 ± 0.12	-1.17 ± 0.87	2.48 ± 0.15
Model 2	1.98 ± 0.40	2.31 ± 0.14	3.68 ± 0.27	2.18 ± 0.26
Model 3	0.75 ± 0.29	2.12 ± 0.22	1.51 ± 0.17	2.29 ± 0.34

Figures 2 and 3 also show the fit parameters for models 2 and 3. Model 2 shows the least dependence of n_i on humidity. The constrained and unconstrained values of A_2 show essentially identical behavior. Model 3 shows some discrepancy between constrained and unconstrained A_3 values, though not as severe as for model 1.

The reaction order, m , in Eq. 9, can be determined by the slopes of the data in Figure 3, and results are shown in Table I. Values are given for fits to A_i for both the constrained and unconstrained values of n_i . Clearly the values for model 2 are more reliable since the constrained and unconstrained values are the same. Here all models give similar values for the constrained data, but substantially different values for the unconstrained data. These clearly show that calculations of a reaction order from strength data must be performed with care. The results may be dependent upon which kinetics model is assumed. We show here that the reaction order is roughly independent of the kinetics model assumed only if a constant value of n_i is assumed, even if it is observed to vary with the environment.

From Table I, the reaction order for coated fiber is around two. This value is in agreement with Duncan *et al.*⁴ who analyzed their data assuming a power law. An approximate second order was also found for E-glass fibers.¹³ A 2.5 order was obtained from direct measurements of slow crack growth rates.¹⁴ The simplest interpretation of a second order reaction is that two water molecules take part in the rate

determining step. The actual reaction mechanism, while not known, is likely to be much more complex.

Up until this point, each model has been discussed in terms of how well it incorporates the dependence on the test environment. It is also important to examine how well each model fits the dynamic fatigue data, irrespective of the environmental conditions. Figure 4 shows the residual sum of squares for each model as a function of relative humidity; the model that fits the best will have the smallest residual sum of squares. From Figure 4, it is clear that model 3 gives by far the worst fit. The residual sum of squares for models 1 and 2 give similar degrees

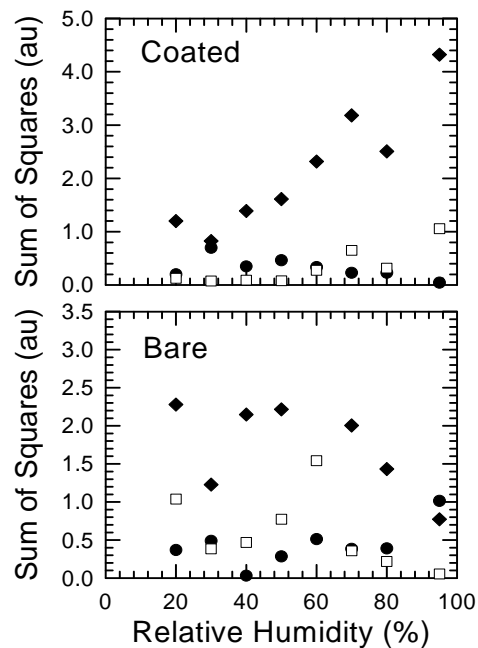


Figure 4: Residual sum of squares vs. relative humidity • Model 1 □ Model 2 ♦ Model 3

of fit. These results are consistent with earlier, more extensive experiments³, which also showed a poor fit for model 3 but a considerably better fit for model 1.

Reliability predictions usually avoid considering the values of K_{IC} and Y by using the so-called B parameter:

$$B = \frac{2K_{IC}^2}{AY^2(n-2)}, \quad (11)$$

which separates fatigue effects and the inert strength. The value of B is a subject of discussion since its value is sensitive to the assumed inert strength, σ_i . However assuming $\sigma_i = 14 \text{ GPa}^*$, we found B , calculated from the unconstrained values of A_1 , is in the range of $(0.79 - 1.39) \times 10^{-6} \text{ GPa}^2 \cdot \text{s}$ for the coated data and $(0.5 - 2.55) \times 10^{-7} \text{ GPa}^2 \cdot \text{s}$ for the bare. If the value of n_1 is constrained, B ranges from 4.90×10^{-7} to $1.29 \times 10^{-5} \text{ GPa}^2 \cdot \text{s}$ for the coated data and 1.84×10^{-8} to $7.08 \times 10^{-7} \text{ GPa}^2 \cdot \text{s}$ for the bare over the humidity range 95 to 20% respectively.*

The above three models were also fitted to data for polyimide, silicone, and double buffer acrylate coated fibers and similar trends and results were found for the reaction order.

CONCLUSIONS

The results show that fatigue data must be analyzed carefully in order to extract valid values for parameters such as the apparent reaction order with humidity. In particular, the values obtained may depend as much on the kinetics model assumed as anything else. We outline a protocol for calculating the reaction order independently of the kinetics model. The strength degradation kinetics of both coated and bare fiber are approximately second order in humidity.

While in earlier work the power law was found to give the best fit to fatigue data, we show here that the power law gives a poor and inconsistent

description of the humidity dependence. The simple exponential model, $\sim \exp(K_1)$, gives the best description of the humidity data and a moderately good fit to fatigue data. The quadratic exponential, $\sim \exp(K_1^2)$, gives a poor fit to fatigue data. Based on this and earlier results, the simple exponential model gives the best description of the overall behavior. It should be noted that lifetimes predicted by extrapolating are significantly shorter when using the exponential than the commonly used power law.

In general, coated and bare fibers give similar results. The polymer coatings studied here have a negligible effect on the kinetics. This may not be the case for other coatings. Therefore, it is always useful to compare coated and bare data to distinguish if there is a coating effect.

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*The σ_i , Y , and B were incorrectly stated in the proceedings paper, but are corrected here.

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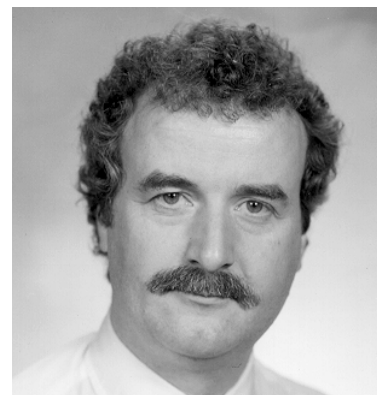
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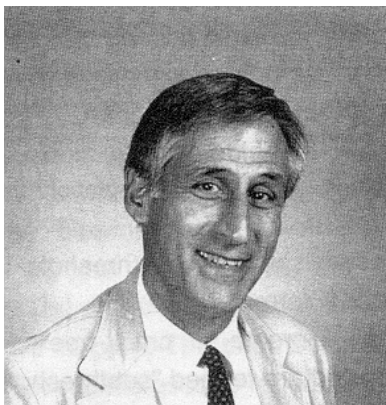
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