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Optical Fiber**

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EFFECT OF pH ON THE STRENGTH AND FATIGUE OF FUSED SILICA OPTICAL FIBER

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ABSTRACT

The fatigue behavior of both bare and polymer coated silica optical fiber has been determined in various buffered pH solutions. Bare and polymer coated fibers were studied to distinguish any coating effects. Numerical integration techniques were utilized to fit the data to three kinetics models, and the fatigue parameters were calculated together with their corresponding confidence ellipses.

The apparent reaction order for the reaction between the OH⁻ ion and SiO₂ between pH 4 and pH 10 was determined to be ~ 0.3 and this value is independent of the kinetics model used to fit to the data. The relationship between fatigue and pH is nonlinear; indicating different mechanisms at high, low, and intermediate pH.

INTRODUCTION

The current industry accepted model for strength and reliability calculations is a combination of an empirically derived rate law for crack extension:^{1,2}

$$\dot{c} = \frac{dc}{dt} = v = AK_I^n, \quad (1)$$

and the well-known Griffith equation:

$$\sigma_a = \frac{K_I}{Y\sqrt{c}}, \quad (2)$$

where v is the slow crack growth velocity, A is a constant depending on the environment, σ_a is the applied stress, K_I is the stress intensity factor, and n is the stress corrosion susceptibility parameter, which is often treated as a constant. Eq. 1 is mathematically simple to manipulate

and was useful in providing the initial basis for the theory of subcritical crack growth but "has outlived its usefulness and now represents an obstacle to further progress."³ Koa⁴ determined that A followed an Arrhenius temperature dependence and that the activation energy depended on the applied stress.

For convenience, the power law, designated model 1 here, may be rewritten as:⁵

$$\text{Model 1: } \frac{dc}{dt} = A_1 \left(\frac{K_I}{K_{IC}} \right)^{n_1}, \quad (3)$$

where K_{IC} is the critical stress intensity factor. If, as is commonly assumed, n_1 is a material constant, then all the environmental dependence of fatigue must be in A_1 . Under these conditions A_1 is expected to depend on both an Arrhenius term and the concentration of the chemical species causing the crack growth. While this species is normally assumed to be water, here we will examine only the dependence on the hydroxyl ion concentration. It is well known that silica is weaker and fatigues faster in high pH.^{4,6,7}

We can rewrite A_1 as:

$$A_1 = \nu [OH^-]^x \exp \frac{-Q}{RT} \quad (4)$$

where ν is a frequency factor, x is the apparent reaction order, Q is the activation energy, and R and T have their usual meanings. One can predict the time to failure, t_f , under a constant applied stress, σ_a , by combining Eqs. 2 and 3 and integrating:

$$t_f \sigma_a^2 = \frac{2K_{IC}^2}{Y^2 A_1 (n_1 - 2)} \left(\frac{\sigma_a}{\sigma_i} \right)^{2-n_1}, \quad (5)$$

where σ_i is the inert strength. In this model, the activation energy is stress independent. Eq. 5 may be rewritten in a simplified form:

$$t_f \sigma_a^2 = B_1 \left(\frac{\sigma_a}{\sigma_i} \right)^{2-n_1}, \quad (6)$$

where the so-called “B parameter” is:

$$B_1 = \frac{2K_{IC}^2}{Y^2 A_1 (n_1 - 2)}. \quad (7)$$

B_1 is considered a constant for any material and environment. In this form evaluation of K_{IC} and Y is avoided. One problem with this simplification is that the value of B_1 is highly sensitive to the value assumed for the inert strength.

Other crack growth velocity models based on chemical kinetics have been proposed and are designated model 2:⁸

$$\text{Model 2: } \frac{dc}{dt} = A_2 \exp n_2 \left(\frac{K_I}{K_{IC}} \right), \quad (8)$$

and model 3:⁹

$$\text{Model 3: } \frac{dc}{dt} = A_3 \exp \left[n_3 \left(\frac{K_I}{K_{IC}} \right)^2 \right]. \quad (9)$$

These three models have been compared by Jakus, *et al.*⁵ and Bubel and Matthewson.¹⁰

In model 1 above, the activation energy is independent of the applied stress, despite experimental evidence to the contrary.^{4,11} In model 2, the stress affects the activation energy of the chemical reaction via an activation volume and is linear with stress intensity.⁸ In model 3, the activation energy of the chemical reaction is by the strain energy density at the crack tip as a chemical potential and is quadratic with stress intensity.⁹

Predicted lifetimes are highly sensitive to the form of the stress dependence of the kinetics and model 1 yields the most optimistic lifetime predictions.^{5,12} Models 2 and 3 cannot be explicitly integrated for dynamic fatigue and therefore numerical techniques are necessary. Similar to model 1, the B -parameters can be defined for models 2 and 3 as:

$$B_2 = \frac{2K_{IC}^2}{Y^2 A_2 (n_2)}, \quad (10)$$

$$B_3 = \frac{K_{IC}^2}{Y^2 A_3 (n_3)}. \quad (11)$$

In general, fatigue data appear to give the best fit to model 1.^{12,13} However, in all three models the stress dependence is determined by the n_i ($i = 1, 2, 3$) while the environmental dependence is contained within the A_i . An alternative means of testing the appropriateness of the kinetics model is to determine the trends in the fatigue parameters with changing environmental conditions, such as humidity,^{14,15} or pH.

In this research, we have determined the fatigue behavior of both bare and polymer coated silica optical fiber in various buffered pH solutions. For purposes of describing the data it was assumed that fatigue of silica involves the chemical reaction with OH^- ions only, as described by Eq. 4. Therefore, the slope of a $\log A_i$ vs. pH plot gives the *apparent* reaction order x with respect to OH^- ions.

EXPERIMENTAL PROCEDURE

Dynamic fatigue experiments were performed using a two-point bending technique on bare and coated fused silica optical fiber in temperature controlled $25 \pm 0.2^\circ\text{C}$ standard pH buffer solutions (Fisher Scientific, Fair Lawn, NJ) in the range pH 1 to 12 from Fisher Scientific. In two-point bending,^{16,17} the fiber is held between two faceplates which are brought together at a controlled rate by a computer-controlled stepper motor until the fiber breaks, as shown in figure 1. When the fiber breaks the event is detected acoustically by a transducer. The failure strain, ε_f , is calculated from the separation distance at failure, D , as:

$$\varepsilon_f = \frac{1.198 d_f}{D - d_c + 2d_g}, \quad (12)$$

where d_f is the fiber diameter, d_c is the diameter of the fiber with coating, and d_g is the depth of the groove.

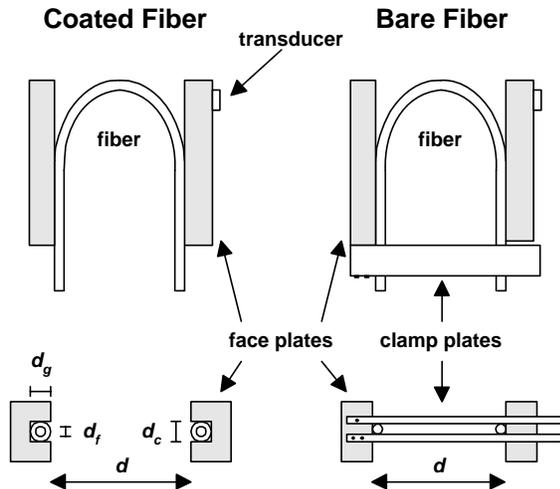


Figure 1. Two-point bending apparatus for bare and coated optical fiber.

Bare fiber specimens were prepared by stripping the polymer coating by immersing in hot sulfuric acid (~200°C) for about 30 s followed by rinsing with water and then acetone. This stripping method does not degrade the strength of the fiber.¹⁸ After stripping, the bare fiber was immersed in the pH environment for 30 s before breaking. Coated fiber was soaked for at least two weeks before breaking to fully equilibrate with the test environment. A preliminary investigation of the diffusion of ionic species through the polymer coated specimens was done to substantiate the aforementioned soaking time by monitoring strength as a function of time after immersion in the test environment. The dynamic fatigue data for bare fiber was for 12 specimens per rate, at four loading rates spanning 1.5 decades, while for the coated fiber 20 specimens per rate were used at nine loading rates spanning 5 decades.

In this work, strain was converted to stress, σ , using the following expression:¹⁹

$$\sigma = \epsilon_f E_0 (1 + 2.125 \epsilon_f), \quad (13)$$

where the Young's modulus, E_0 , is 72.2 GPa. This equation will not be valid at high strains

because the modulus will eventually decrease with strain since the tangent modulus ($d\sigma/d\epsilon$) must approach zero at the theoretical strength of the material.

RESULTS AND DISCUSSION

The effect of loading rate and pH is seen in figure 2 for bare fiber. These results loosely correlate with published data for the pH dependence of the dissolution rate in aqueous solutions, as seen in figure 3.²⁰ We also tested coated fused silica fiber and found results similar to the bare fiber data, as seen in figure 4. The error bars in figures 2 and 4 represent 95% confidence intervals. Typical Weibull moduli were in the range of 70 to 90 for both bare and coated fiber.

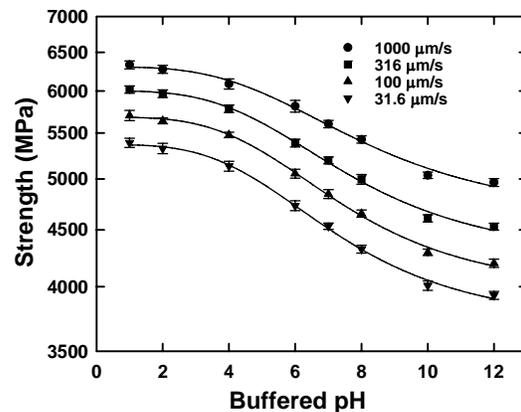


Figure 2. Strength of bare fiber in two-point bending at 4 loading rates in various 25°C pH buffer solutions.

Numerical methods were utilized to find the fatigue parameters from the dynamic fatigue data. The observed trends in the calculated parameters and the size of the error bars make it difficult to interpret the fatigue behavior. The error bars for the fatigue parameters are large because these parameters are correlated with one another. For example, figure 5 shows the ellipses for the bare fiber in pH 7. The ellipses are all narrow and the area of the normalized ellipses are a measure of the uncertainty, *i.e.*, the smaller the ellipses, the better the fit. In figure 5, model 1 had the best fit while model 3 clearly had the worst fit. Although model 1 fits

best here, model 2 also had a good fit. At low pH, model 2 had the smallest ellipses while at high to moderate pH, model 1 had the smallest ellipses.

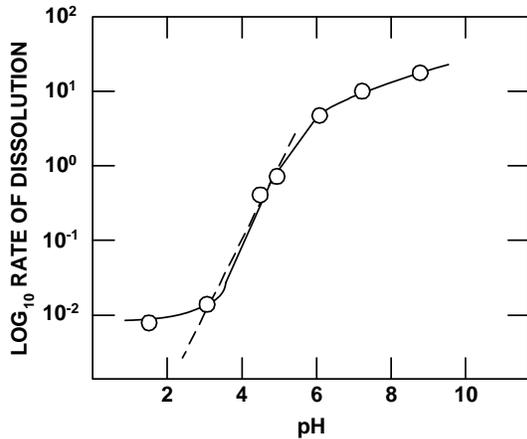


Figure 3. Dissolution rate vs. pH for fused silica.²⁰

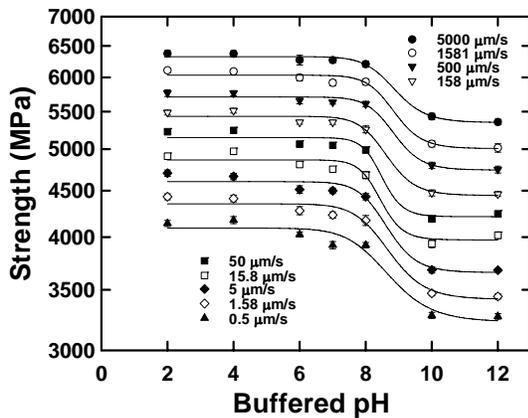


Figure 4. Strength of coated fiber in two-point bending at 9 loading rates in various 25°C pH buffers.

Figures 6 and 7 show the fatigue parameters, n_i , for bare and coated fiber, respectively. By examining these figures we see that n_i is not constant with changing environment. The trends in the data are modest compared with the size of the error bars. It was therefore decided to use the assumption that n_i is constant and re-examine the data. This was accomplished by calculating the weighted average n_i for each model. Since an underlying assumption of the models is that all the environmental effect should be in A_i , i.e., n_i is constant, this constraint

on n_i is reasonable. The effect of constraining n_i on the A_i value is shown in figure 8. The error bars for the constrained fit are substantially smaller. Model 2 shows the least change in n_i with pH. Only model 2 showed the same trends in A_i with pH for constrained and unconstrained n_i .

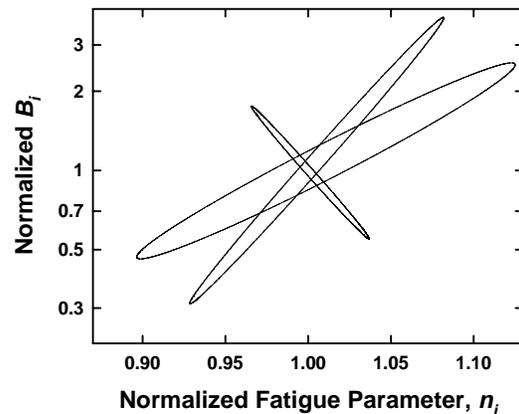


Figure 5. B_i and n_i confidence ellipses calculated for bare fiber in pH 7 at 25°C and normalized to the best fit values.

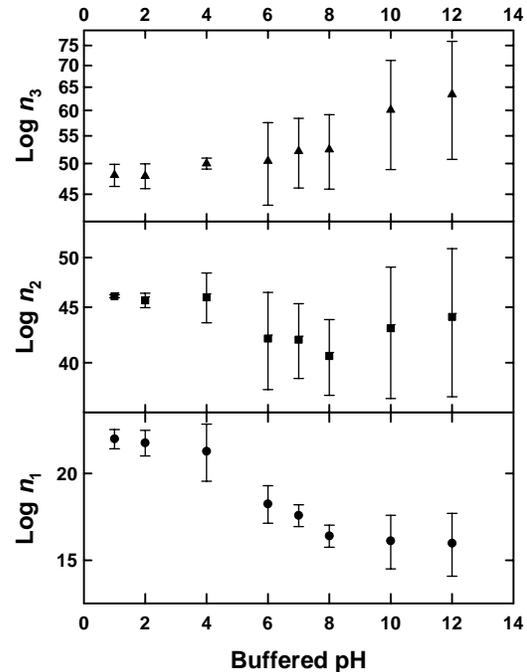


Figure 6. Fitted fatigue parameter n_i vs. pH for bare fiber.

A simple chemical kinetics model was used that assumed that the fatigue of silica involves the chemical reaction with OH^- ions, as written in Eq. 4. It is certain that a reaction with molecular water is occurring simultaneously. In the buffer solutions, the activity of water is essentially unity and constant. If the simple chemical kinetics model were correct, the slope of a $\log A_i$ vs. pH plot would give the true reaction order x with the OH^- ion. The *apparent* reaction order between pH 4 and pH 10 is ~ 0.3 , as seen in figure 8, and this value is independent of the kinetics model used to fit to the data.

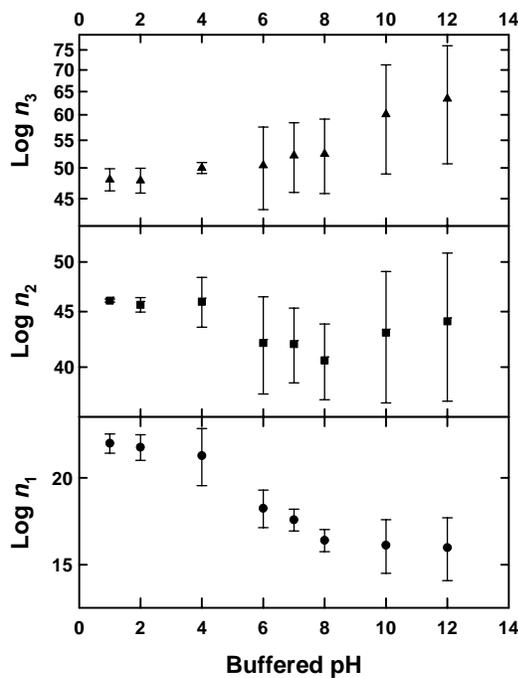


Figure 7. Fitted fatigue parameter n_i vs. pH for coated fiber.

CONCLUSIONS

The various kinetic models were fitted to fatigue data for both coated and bare fiber. It was found that both the power law, model 1, and the exponential, model 2, describe the stress dependence equally well. Trends in the fatigue parameters with pH favors model 2, which therefore gives the best overall description of

the behavior. Since predicted lifetimes are highly sensitive to the kinetic form of the stress dependence of fatigue and model 1 is the most optimistic in lifetime predictions, one should use a more conservative and logical kinetic form, such as model 2. This model is based on physical principals, rather than model 1, which is empirical in nature.

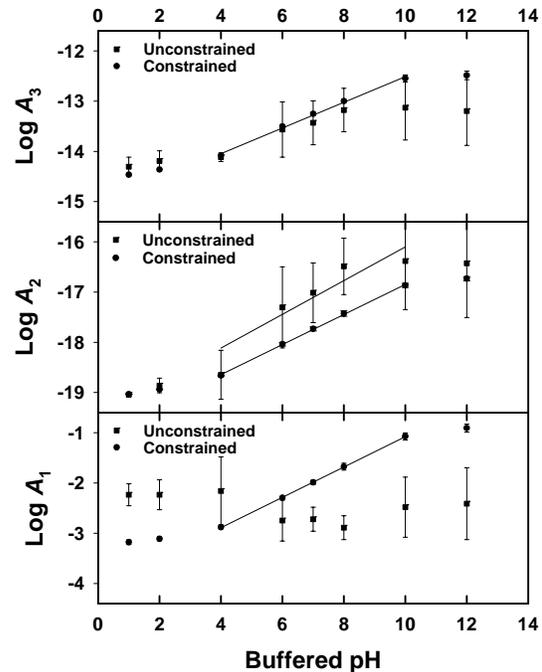


Figure 8. $\log A_i$ vs. pH for models 1, 2, and 3 for bare fiber at 25°C showing both as fitted and constrained values.

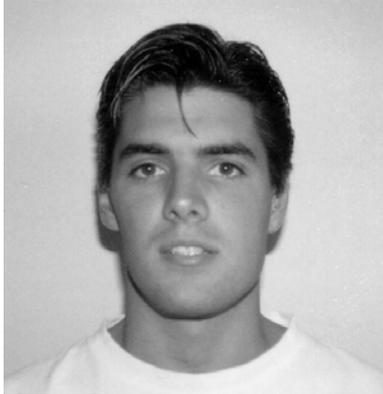
The apparent reaction order with respect to the OH^- ion between pH 4 and pH 10 was found to be ~ 0.3 and is approximately zero outside this range, i.e., fatigue is substantially independent of pH at high and low pH. It is likely that the behavior between pH 4 and 10 is more complex and might show a stronger $[\text{OH}^-]$ dependence over a more limited range.

ACKNOWLEDGEMENTS

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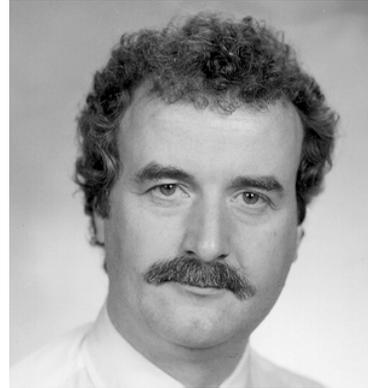
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