ACTIVATION ENERGY FOR STRENGTH DEGRADATION
OF FUSED SILICA OPTICAL FIBERS

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ABSTRACT

   The strength degradation behavior of fused silica optical fiber is well known to be sensitive to the temperature and an apparent activation energy can be determined. In addition, it has been observed that the activation energy also depends on the applied stress and the nature of the environment. However, no consistent model for this behavior has emerged. We propose a chemical kinetics model which accounts for the temperature dependence of the dissociation of water which predicts that degradation should be faster in pH 7 buffer than in pure water. Static fatigue of fused silica fibers in both water and pH 7 buffer solution has been carefully studied as a function of temperature to test the model. The apparent activation energies are stress dependent, and, while the dependency is not clear, different environments give different dependencies. These observations support the proposed model.

INTRODUCTION

   The strength degradation of silica optical fiber is controlled by the crack growth rate, $\dot{c}$, which can be treated as a chemical kinetics problem, $\dot{c}$ then has some functional dependence on the concentration of the reactants:

$$\dot{c} = c_0 k \cdot F([\text{reactants}]) \qquad (1)$$

where c_o is the bond length, and k is the rate constant which is assumed to be thermally activated with a stress dependent activation energy:

$$E = E_0 - f(K_I) \qquad (2)$$

where K_I is the stress intensity factor, and E_0 is the zero stress activation energy, which was found to be from about 75 to 100 kJ/mol for polymer coated fiber in water by several authors.[1,2,3,4] If the crack growth of the fiber is caused by water alone, the function $F([\text{reactants}])$ is almost constant with temperature. However, if the strength degradation is dominated by OH^- rather than molecular water, $F([\text{reactants}]) = F([OH^-])$. The importance of the hydroxyl ion is suggested by the pH sensitivity of fatigue.[5] Since $[OH^-]$ is temperature dependent with an activation energy E_w (the dissociation energy for water), the apparent activation energy for fatigue, E_a, would contain E_w:

$$E_a = E_0 - f(K_I) + const \cdot E_w \qquad (3)$$

This dependence on E_w has not been recognized before. We proposed a theory concerning the E_w effect on the apparent activation energy.[6] The crack growth rate is related to pOH by:

$$\dot{c} = \dot{c}_0 [OH^-]^m \exp\left(\frac{-E}{RT}\right) \propto \exp\left(-2.3m \ pOH - \frac{E}{RT}\right) \qquad (4)$$

where m is the reaction order. In pH 7 buffer, the pOH is related to the dissociation constant of water, K_w, and the free energy of the activated complex for dissociation, ΔG_w, by:

$$pOH = -\log K_w - 7 = \Delta G_w/2.3RT - 7 \qquad (5)$$

However, in distilled water, pOH = pH, *i.e.*,

$$pOH = pH = (-\log K_w)/2 = \Delta G_w/(2.3RT \cdot 2) \qquad (6)$$

The impact of this is that at high temperature where the neutral pH is less than 7, the buffer is more basic than water and is expected to be more aggressive. This behavior has been observed elsewhere[7], though the cause was not identified and was thought to perhaps be due to the complex ionic composition of the buffer rather than a simple pH effect.

The apparent activation energy in pH 7 buffer can be derived from Eq. (4) and (5), since

$$E_w = \Delta H_w = \frac{\partial(\Delta G_w/T)}{1/T} \qquad (7)$$

where ΔH_w is the enthalpy of the activated complex. Therefore, E_a is

$$E_a = E_0 - f(K_I) + mE_w \qquad \underline{\text{in pH 7 buffer solution}} \qquad (8)$$

However, the apparent activation energy in distilled water derived from Eq. (4) and (6) is:

$$E_a = E_0 - f(K_I) + mE_w/2 \qquad \underline{\text{in distilled water}} \qquad (9)$$

Comparing Eq. (8) and Eq. (9), E_a should be $mE_w/2$ higher in pH 7 buffer than in distilled water. However, this full difference might not be measured since if the reaction with molecular water also occurs it will mask some pOH of the dependence. Also, CO_2 dissolved in distilled water could perturb the results but we have calculated this to be a small effect. While the solubility of CO_2 decreases with temperature, the ionic dissociation increases so that the net effect in the temperature dependence of pOH is small.

The stress dependence of E_a for strength degradation of silica optical fiber in aqueous environment should yield some information on the form of the function $f(K_I)$. Various models have been proposed in the literature. The first model (Model 1) is the widely used empirical power law:[8,9,10] $\dot{c} = A_1 K_I^{n_1}$; the second model (Model 2) is based on simple chemical kinetics:[11,12] $\dot{c} = A_2 \exp(n_2 K_I)$; and the third model (Model 3) is derived from an atomistic model for crack propagation:[13] $\dot{c} = A_3 \exp(n_3 K_I^2)$. From these kinetics models, model 1 suggests that E_a is independent of stress, model 2 suggests that E_a varies linearly with stress, and model 3 suggests that E_a varies quadratically with stress. The three models can be integrated for a constant applied stress to find the time to failure, t_f, which then inherits the temperature dependence of $\dot{c}$ and is found to be inverse Arrhenius:[14]

$$t_f = t_0 \exp\frac{E_a}{RT} \qquad (10)$$

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where t_0 depends on the applied stress and several materials parameters, E_a is the apparent activation energy (Eq. (3)).

In this work, the static fatigue of silica fiber in pH 7 buffer and distilled water was tested at different temperatures over a range of applied stresses. The proposed model concerning the stress and E_w effects on E_a is examined by comparing the apparent activation energies in pH 7 buffer and distilled water. The results are obtained for both polymer coated and bare (*i.e.* stripped) fibers to understand any influence of the coating.

EXPERIMENT

Static fatigue experiments have been performed on a UV-curable polyurethane acrylate coated fused silica optical fiber using a two-point bending technique[15] in the applied stress range of 2.5 to 4.5 GPa. The fiber diameter and the overall coating diameter are 125 μm and 215 μm respectively. The time to failure was measured for each stress at temperatures ranging from 30°C to 90°C. All specimens were pre-equilibrated overnight under zero stress in the testing solution at room temperature. The specimens used for the bare fiber study were prepared by stripping the coating in hot acid which does not degrade the strength of the fiber.[16] The bare fiber were tested in the temperature range from 30°C to 80°C, using a dynamic 2-point bending apparatus run in static mode. 15 specimens were used for each measurement. The apparent activation energy, E_a, is determined from the static fatigue data by using Eq. (10).

RESULTS

The apparent activation energies for coated fiber are shown in figure 1 as a function of applied stress. The error bars represent a 95% confidence interval. The error bars are big at low stress because of the onset of the fatigue "knee". In the high stress region, E_a for coated fiber does not show much difference between pH 7 and water. However, E_a diverges at lower applied stresses (figure 1). While water diffuses through the polymer coating rapidly,[17] other species, such as the buffering ions, diffuse through much more slowly.[18] Therefore, at high applied stress for which the time to failure is short, there is insufficient time for full equilibration of the buffer; the local environment at the fiber surface is similar in both water and the buffer, giving similar failure times and apparent activation energies. However, at lower stress, longer time, a difference is observed, as anticipated.

As shown in figure 1, the apparent activation energies were found to be stress dependent, although the dependencies are different in different environments. The activation energy in pH 7 buffer solution increases with the decreasing applied stress. However, in distilled water, the activation energy is
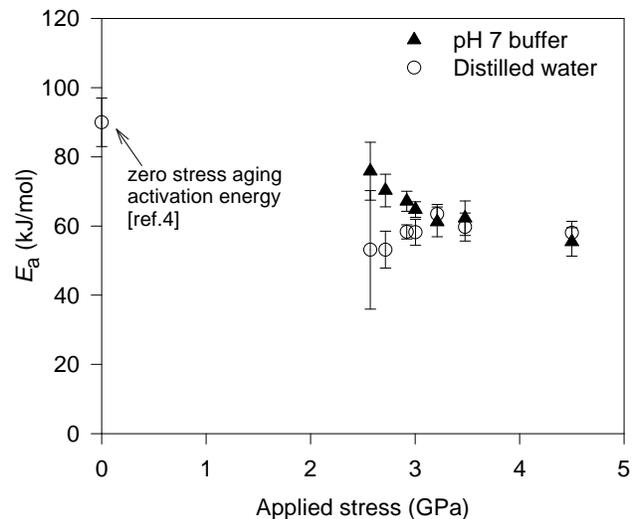

Figure 1 The apparent activation energies for coated fiber measured in pH 7 buffer solution and distilled water.

roughly constant but is slightly low at the lower applied stresses. These data are not adequate to determine whether the apparent activation energy varies linearly or quadratically with stress. It would be difficult to obtain better data because of the problems of adequately equilibrating with the environment while simultaneously avoiding strength loss due to zero stress aging effects. We are currently using dynamic fatigue to avoid these problems. However, what is clear from these data is that the activation energy is indeed higher in pH 7 than in water as predicted.

The apparent activation energies for bare fiber are shown in figure 2. The data are not extensive because of the experimental inconvenience of testing bare fibers which must be tested one specimen at a time. For two of stresses, E_a is significantly lower in water, *i.e.*, in the direction predicted by the proposed model. The apparent activation energy data for bare fiber indicate that the E_w effect can be observed even at high applied stress, if the coating influence is eliminated.

Figure 2 The apparent activation energies for bare fiber measured in pH 7 buffer and distilled water.

CONCLUSIONS

The apparent activation energies (E_a) for static fatigue of both polymer coated and bare silica optical fibers in pH 7 buffer and distilled water have been determined over the applied stress range of 2.5–4.5 GPa. E_a was found to decrease with the increasing stress in pH 7 buffer solution although this is probably a result of poor equilibration with the pH 7 environment due to the low diffusion of ionic species. The apparent activation energy for distilled water is roughly constant with stress. E_a is higher in pH 7 than in water both for coated fiber at low applied stress and bare fiber. We propose a model that simply explains the effect by how pOH varies with temperature in these two environments. Since the dependence on the activation energy for the dissociation of water is different in two environments, the pOH effect increases the apparent activation energy for fatigue in the buffer. This work shows that the apparent activation energy for fatigue depends on several processes and a unique value is not to be expected for all test environments. This might explain the considerable variability in the values of E_a in literature.

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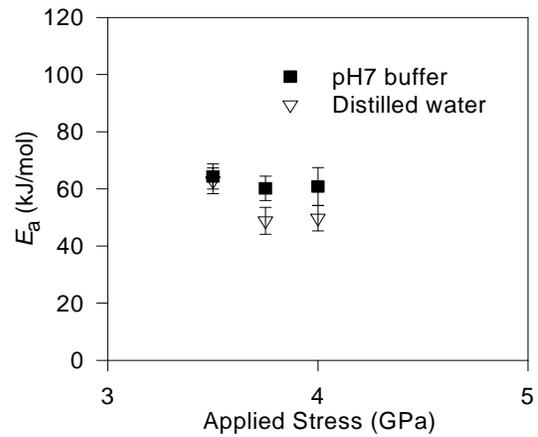4. C. R. Kurkjian and M. J. Matthewson, "Strength degradation of lightguide fibers in room

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