Environmental Effects on the Static Fatigue of Silica Optical Fiber

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The static fatigue properties of silica optical fiber are measured in 90°C aqueous environment for various pH s in the range 0 to 14 and for distilled water. The effect of a UV-curable urethane acrylate protective coating is evaluated by directly comparing coated and bare fiber. It is found that both higher pH and (at long times) the presence of the protective coating increase the fatigue rate. Enhanced fatigue is observed in which the stress corrosion parameter, n, is significantly less than the accepted value of ~20 measured from short-term experiments.

I. Introduction

STATIC fatigue, or delayed failure, of silica optical fiber, the phenomenon whereby failure can occur after being subjected for some time to a stress level too low to cause failure on a short time scale, is clearly a subject of practical interest. The fiber in an optical cable may experience an environment which contains water, and the degradation of the fiber strength by this water must be understood in order to design a cable whose fibers can survive the ambient stress and environment for the design life.

Fatigue data for brittle materials is usually represented by a fatigue diagram where the logarithm of the applied stress is plotted as a function of the logarithm of the time to failure (we will plot the axes this way around since it is used by most workers in the field, even though it is against convention). Plotted in this way, fatigue data are found to be linear for many ceramics, including bulk silica, and imply an empirical reltaionship between the time to failure, t, and the applied stress, σ, of the form

$$\log t = \log k - n \log \sigma \qquad (1)$$

where n is the stress corrosion susceptibility parameter. This relationship can be predicted from a fracture mechanics model and the empirical relationship between the subcritical crack growth velocity, $\dot{c}$, and the stress intensity factor, K_I:[1]

$$\dot{c} = AK_I^n \qquad (2)$$

This subcritical crack growth model is widely used for ceramics whose strength is determined by the presence of microcracks. Bulk silica is typical of such materials and an n value of around 40 is found by direct crack growth measurements[2] and from both static[3] and dynamic[4] fatigue experiments.

Bulk silica has a strength under ambient conditions of typically 50 MPa. In contrast, high-quality silica fiber has a strength of ~5.5 GPa, which is essentially single valued,[5] and this implies that there are no cracklike defects present. Cracks would be of atomic dimension and it is more likely that the strength-controlling defects are regions of local strain or composition fluctuation. The linear fatigue described by Eq. (1) is found to hold empirically and analysis of early data on hand-drawn fibers[6] gives $n \approx 25$ though this is rather high compared to the currently accepted value of nearer 20. This linearity led to the use of the subcritical crack growth model, using $n = 20$ now rather than the bulk value of 40, to make extrapolations from accelerated laboratory experiments to the practical situation of longer (i.e., weaker) fibers under lower loads in less aggressive environments,[7] even though neither the nature nor the behavior of the defects is known. Clearly this

extrapolation is empirical and would seem to be questionable, particularly in light of later results. The data of Wang and Zupko[8] show enhanced fatigue at lower stresses/longer times to failure for a UV-curable epoxy acrylate coated fiber in 32.6°C, 90% relative humidity air, and evaluations of n decrease from 20 at applied stresses in excess of 2 GPa to 7 at stresses less than this. Such nonlinear behavior is not predicted by simple crack growth models and, upon extrapolation of high-stress results, leads to significant overestimation of lifetimes at low stress levels. Similar behavior was independently observed by Krause for both coated[9] and bare[10] fiber in 90°C water. Later work by Chandan and Kalish[11] using a fiber coated with a UV-curable polyurethane acrylate in water in the temperature range 40° to 90°C also shows enhanced fatigue at low stress levels and, designating n_L as n in the low-stress, enhanced-fatigue regime, and n_H as n in the high-stress regime, n_L is found to range from 1.1 at 90°C to 8.4 at 40°C. Chandan and Kalish extrapolate the temperature dependence of n_L to lower temperatures of practical significance and assert that there is no enhanced fatigue (i.e., $n_L \simeq n_H \simeq 20$) within reasonable times at temperatures below 20°C. This is of considerable practical importance and it is suggested that more complete data of this type are needed to fully justify their conclusion. Specifically, more recent data of Krause and Shute[12] for bare fiber in pH 14 KOH in the temperature range 30° to 90°C, and our own results, to be described here, for bare fiber in 90°C water of pH ranging from 7 to 14, indicate that n_L for bare silica fiber is approximately 7. The data of Chandan and Kalish are entirely consistent with n_L being modified by the presence of the coating and in fact experimentally tend to the limit of approximately 7 rather than their calculated limit of $n_L \simeq n_H \simeq 20$. Figure 1 illustrates this by comparing the regression fits to the Chandan and Kalish data with fits to the data of Wang and Zupko[8] and Krause.[10] It is our belief, as well as that of Krause and Shute,[12] that the enhanced fatigue at low applied stress is a real effect, for high-strength fibers at least, that does not disappear at lower temperatures. It should not be neglected in lifetime estimates.

Very early work on the effect of various surface treatments and coatings on the strength and fatigue of E-glass fibers was carried
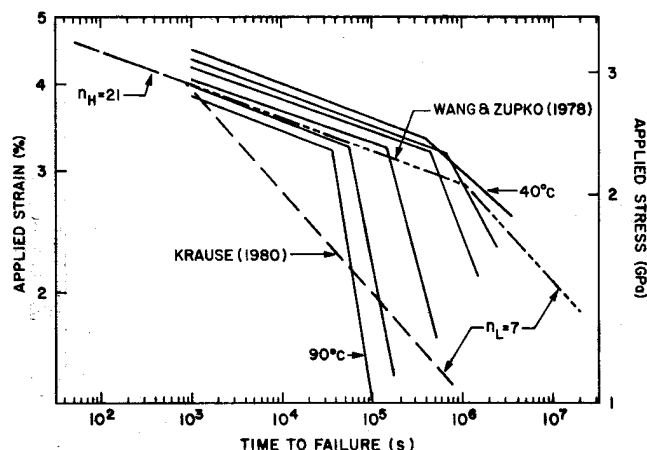

Fig. 1. Comparison of the fatigue data of Wang and Zupko (1978) (with an epoxy acrylate coating) and Krause (1980) (stripped of coating) with the data of Chandan and Kalish (1982) (polyurethane coating, solid lines) for temperatures in the range 40° to 90°C.

Table I. Constant pH Environments

pH		pOH at 90°C	Composition
25°C	90°C		
0	0	12.43	$0.5M$ H_2SO_4
4	4.20	8.23	Phthalate buffer
7	7.09	5.34	Phosphate buffer
10	9.58	2.85	Borate buffer
14	12.43	0	$1M$ KOH

out by Otto.[13] Ritter[14] did some preliminary work on the influence of polymeric coatings on soda-lime-silica rods. While it is clear that mechanical protection can be provided by a suitable coating, it is not clear how strongly and by what means delayed failure (fatigue) is influenced since most polymers have reasonable solubilities and diffusion coefficients for water. Most strength studies on silica optical waveguides have been carried out on coated fiber. Krause[9] showed that differences in fatigue are seen with similar fibers when different coatings are used, and Ritter[15] found rather wide variations in data from different investigators which he also attributed to the use of different coatings. More recently this has been reinforced by the work of Skutnik[16] and co-workers. Using a quite different coating (a fluorinated acrylate) they see no knee in the fatigue curve at 90°C in H_2O even after 3 months, but do see a knee at room temperature in $10M$ KOH after times of the order of 1 d. Thus the effect of the polymer coating on fatigue is complex; it is of practical importance to understand it but it complicates the view of the underlying silica behavior. For this reason we present here results for the same fiber in both bare and coated condition. The pH of the environment is known to have a significant effect on fatigue rates,[10,16–18] and fibers can encounter a wide range of pH in various applications. This paper examines the effect of pH on the fatigue of fiber in 90°C water.

II. Experimental Techniques

A two-point bend method is used for studying the fiber fatigue in which short lengths of fiber are bent double and inserted into precision-bore glass tubes.[19] Fracture of the fibers is monitored acoustically. The maximum tensile stress that occurs on the fiber surface is given by

$$\sigma = 2.396E \frac{r}{D - d} \tag{3}$$

Fig. 2. Fatigue data for coated fiber in distilled water.

where D is the internal diameter of the tube, E is Young's modulus of the silica fiber, r its radius, and d the total fiber diameter including the protective coating if present. This method is used firstly because there is no problem gripping the fiber and secondly because the large amount of data needed for this study is obtained relatively easily. The technique suffers from the disadvantage that only a small amount of fiber is stressed and does not imply the behavior of longer lengths. However, a direct comparison of bending and tension results[19] and comparison of data presented here with the tensile data of Krause and Shute[12] indicate that, while times to failure are generally longer for bending because of size effects, the essential fatigue behavior in bending and tension is the same.

Constant pH environments with nominal pH values of 0, 4, 7, 10, and 14 were used and Table I lists their compositions and actual pH and pOH at 90°C. Note that the ion product of water at 90°C is $-\log K_w = 12.43$ (calculated from the relations of Marshall and Franck[20]) and we assume that the H_2SO_4 and KOH are fully ionized at this temperature. The distilled-water environment was continually flushed to prevent buildup of decomposition products from the fiber's polymeric coating. All material tested was from one length of standard 125-μm-diameter fiber drawn from a silica† rod and coated with 60 μm of UV-curable urethane acrylate.‡

Tubes of specimens take ~10 s to thermally equilibrate with the 90°C environment and so times to failure of this order cannot be accurately determined. For this reason stresses greater than ~3 GPa are not useful at this temperature. Bare fibers were obtained by stripping coated fiber with 200°C sulfuric acid after insertion in the tubes. Times to failure are an average for at least 30 specimens. Errors in the logarithm of the mean time to failure are variable but are typically less than ±0.03 and error bars will not be shown on diagrams as they are of approximately the same size as the plotted points. The dispersion in the time to failure (defined as the ratio of the standard deviation to the mean) is variable but is found to be everywhere consistent, within experimental certainty, with both equations

$$\nu_t = n\nu_\sigma \tag{4}$$

$$\nu_t = (n - 2)\nu_\sigma \tag{5}$$

where ν_t and ν_σ are the dispersions in the time to failure and *apparent* strength and the fatigue parameter, n, is derived from the local slope of the fatigue curve. Equation (4) is derived assuming the apparent strength dispersion is derived from dispersion in the fiber diameter, while Eq. (5) assumes it is derived from *real* strength dispersion.[19] A temperature of 90°C was chosen to accelerate fatigue so that failure times were acceptably short. While a discussion of extrapolation to lower temperatures is given both here and in more detail by Krause and Shute,[12] the primary objective of this work is to identify the mechanisms and processes of fatigue. Also, the differences between bare- and coated-fiber behavior are exaggerated at higher temperatures so that coating effects can be more readily examined.

III. Experimental Results

Figure 2 shows the results for coated fiber in distilled water. The fatigue behavior shows a curved region for times to failure less than 100 s since the time taken for the specimens to reach thermal equilibrium is ~10 s. Between times to failure of 10^2 and 10^5 s fatigue is linear with an unusually high value of $n_H = 43$. Apart from this high value of n_H the data are in fairly good agreement with the 90°C data of Chandan and Kalish[11] for fiber coated with a nominally identical polymer. This discrepancy may simply be due to the fact that the Chandan and Kalish data explore a much narrower range of stress. At 2×10^5 s the fatigue rate increases dramatically and $n_L \approx 1.4$ but at 3×10^5 s fatigue again slows. This complex behavior is not an artifact of the bending technique; it is also observed in tensile experiments.[19]

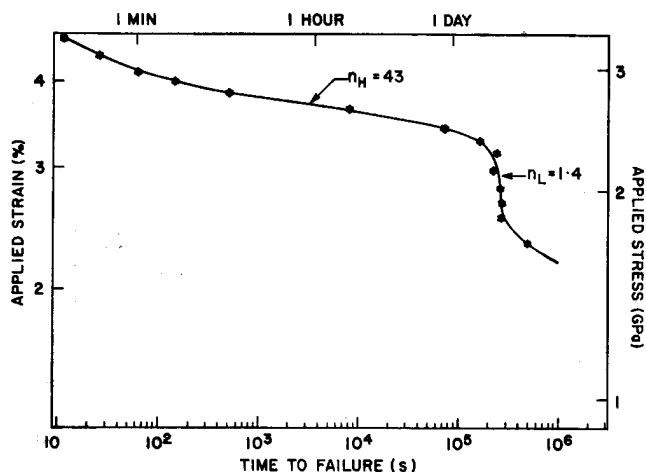The fatigue behavior of coated fiber at times to failure of less

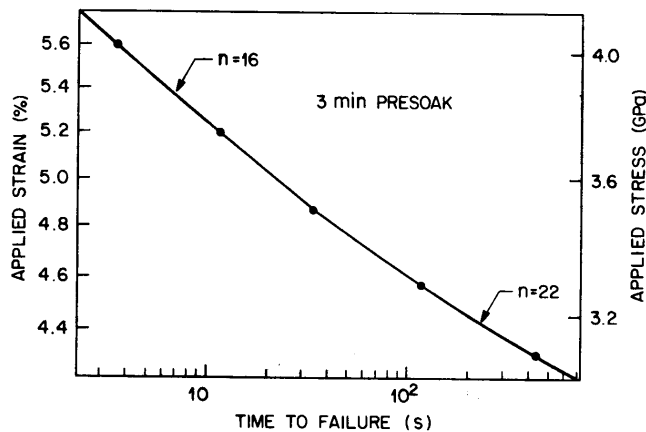**Fig. 3.** Fatigue data for coated fiber in distilled water after a 3-min presoak.
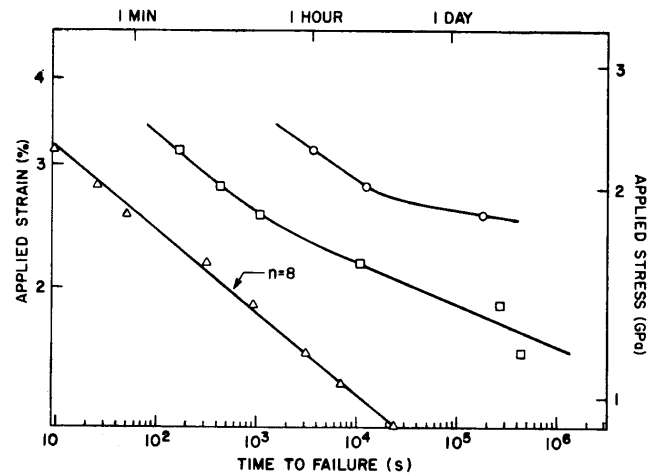
than 1000 s has been examined in more detail using a slightly modified technique in which fibers are loaded into the jaws of the dynamic bending apparatus[21] under a very small strain ($\sim$0.5%). The apparatus is then presoaked in the 90°C water for 3 min before the jaws are closed to their final separation. In this way thermal equilibration is reached long before the fiber is placed under a large stress, though the technique is not to be generally recommended since it requires testing fibers individually, which is very much less convenient than the tube method. Figure 3 shows the results and it is seen that between 10 and 1000 s a region with $n_H \approx 20$ is resolved, though at shorter times some curvature is still observed. Presoak times of 2 and 10 min gave similar results but a systematic decrease in the time to failure with increasing presoak time was observed, indicating significant strength loss on zero-stress aging over quite short periods of time.

Figure 4 shows the fatigue behavior of bare fiber. The pH has a strong effect on the fatigue — an order-of-magnitude increase in the lifetime caused by decreasing the pH by approximately 3. At around 2.5 GPa the fatigue appears to give a value of $n \approx 8$ for all fibers though at pH 4 and 7 n increases at lower stresses. Similar nonlinearities were observed at similar times for pH 12 and 14 according to the data of Krause and Shute[12] though at lower stresses.

Figure 5 shows the data for coated fibers for different values of pH. At times to failure less than approximately 100 s all environments follow the same fatigue curve, as exemplified by the distilled-water data of Fig. 2. On this time scale there is no possibility of transporting ions through the polymer coating and, as far as the silica surface is concerned, all environments are equivalent. At failure times greater than 100 s the environments can influence the chemistry at the silica surface and their behaviors diverge. pH 14 produces an initial n of 20 but at 1000 s n falls to 0.5. This time corresponds to that at which the coating becomes completely hydrolyzed and dissolved in the $1M$ KOH and fatigue for the bare fiber is very much more rapid (Fig. 4). The time to failure is the sum of the coating dissolution time and the much shorter subsequent fatigue time. The logarithmic plot then produces an artificially small value for n. A more reasonable value for n would be obtained if the coating dissolution time were subtracted from the time to failure. At longer times the coated behavior approaches the bare-fiber behavior. Both pH 10 and 7 environments show an n of 20 but at stresses below 3 GPa n falls to values ranging between 3 and 7. At high stresses pH 4 and 0 show abnormally high n values (35 and 85, respectively) but at longer times n decreases to 4.5 for pH 4 and 30 for pH 0. Thus in very low pH ($\sim$0) in agreement with Krause,[9] the n value does not decrease to $\sim$5 within the time scale of our experiments.

IV. Discussion

The fatigue behavior of high-strength silica is clearly complex

Fig. 4. Fatigue data for bare fiber in various environments: (O) pH 7, ($\square$) pH 10, ($\triangle$) pH 14.

and is sensitive to environmental effects such as pH and the presence of a protective coating. All these effects must be understood in order to design reliable systems, and we will discuss here certain aspects of the observed behavior and propose possible mechanisms.

(1) Bare-Fiber Fatigue

Kurkjian, Krause, and Paek[22] suggest that, in the absence of cracks, the strength of "perfect" silica fibers will be controlled by surface roughness and that during degradation, such as fatigue, rounded ellipsoidal pits form by dissolution. These pits will behave quite differently from cracks, explaining the difference in the values of n observed for pristine fibers and bulk silica. The evolution of pits explains the aging behavior of the fibers whose strength falls by a factor of 2 or 3 on soaking in water under zero stress.[10] Once the pits reach their equilibrium shape, further aging changes only their size and so, since the strength depends only on the eccentricity of the pit profile, it remains constant after the initial degradation and this is observed. As will be seen for coated fiber, changes in the aging behavior correspond to the change in the fatigue behavior as it passes into the enhanced-fatigue regime. Clearly, using the pit model, aging and fatigue will be initimately linked processes.

The pit model necessarily includes dissolution of silica, or more correctly, the preferential dissolution of silica at high-energy surface sites. While the solubility and etch rates of silica in water are
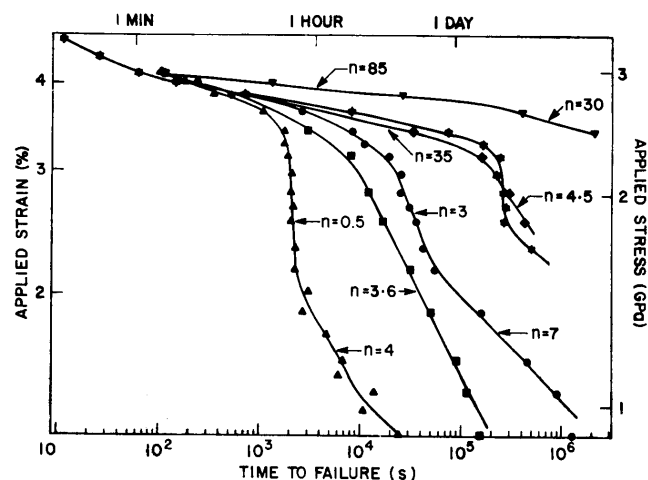

Fig. 5. Fatigue data for coated fiber in various environments: (*) distilled water, ($\blacktriangledown$) pH 0, ($\blacklozenge$) pH 4, ($\bullet$) pH 7, ($\blacksquare$) pH 10, ($\blacktriangle$) pH 14.
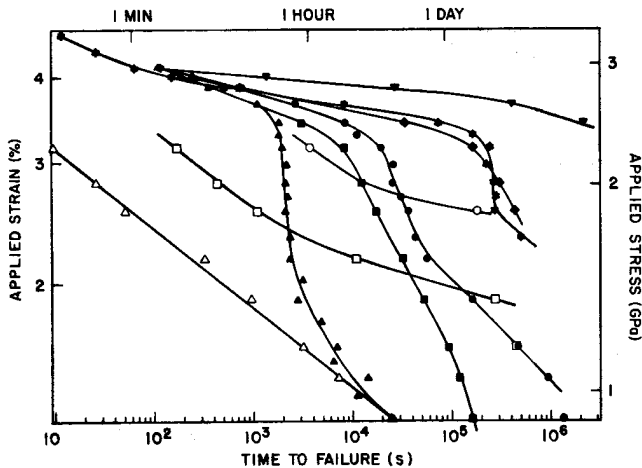
Fig. 6. Combined data from Figs. 4 and 5 (q.v. for key to symbols).

small at pH values less than 10,[23,24] only a few silicon–oxygen bonds need be broken to significantly change the strength. The sensitivity of solubility to pH is reflected in the sensitivity of the fatigue behavior.

The accepted value for n in the high-stress regime is around 20 for fiber in pH 7. Krause and Shute,[12] however, observe that this value falls to ~10 at pH 12 to 14. Interestingly, calculations of n from the data of Weiderhorn and Johnson[25] show a similar fall in n by a factor of 2 for macroscopic cracks (from ~40 to ~20). This suggests, not surprisingly, that at least the chemistry, though not the "crack" geometry, is similar for the fatigue of pristine fiber and bulk silica.

(2) Protective Coating Effects

Figure 6 summarizes the data of Figs. 4 and 5 and directly compares data for coated and bare fibers and the differences between them can be understood in terms of the two influences that the coating has on the fatigue. Firstly, it acts as a barrier and impedes the transport of the outside environment to the silica surface and reaction products away.[26] Secondly, the coating can influence the chemical environment of the silica surface directly.[9,10]

The first effect will be particularly apparent at short times to failure. At all values of pH the fatigue behavior follows the same curve up to ~100 s and this curve corresponds to fatigue at the pH at the silica surface in the absence of external influences — our data are consistent with a pH value of 6 to 7. At longer times the environment can penetrate the coating, and behaviors for different pH values diverge. At a pH above the starting pH (7, 10, and 14) the fatigue initially proceeds at the high-stress n value of approximately 20 before turning into the enhanced-fatigue region with a lower n value. This turnover occurs at a longer time for a lower pH. For a pH lower than the initial pH, the life is prolonged as soon as the pH penetrates to the silica surface. Thus, at high stress the time to failure is initially characteristic of pH 6 to 7 but at lower stress is characteristic of some lower pH. The effect is to give an abnormally high value of n, 38 at pH 4 and 85 at pH 0, but at lower stress where the penetration time is not significant compared to the time to failure, n decreases to more reasonable values, a low-stress-regime value of 4.5 for pH 4 and a high-stress-regime value of 20 for pH 0, though this latter value is not observed on the time scale of our experiments.

The coating can affect the chemistry at the silica surface in other ways apart from determining the initial pH. The coating material hydrolyzes at all pH's at 90°C. It has been found that degradation is more rapid in both dilute acids and bases than in pure water.[27] As mentioned above, the coating entirely dissolves in ~1000 s at pH 14, it swells and becomes gelatinous at pH 10, and at pH 7 or less it turns from a pale yellow to brown and thins on the time scale of days and then becomes a thin black layer on the time scale of

weeks. The chemical interpretation of fatigue as being the hydroxyl ion attack of strained silicon–oxygen bonds[28] is a simple chemical reaction unlikely to be strongly influenced by other species. The sensitivity of fatigue to pH, seen both here for high-strength silica and for the growth rate of macroscopic cracks,[25] indicates that OH^- concentration will be the dominating influence. Scission of the polymer chains can produce either an acid or basic environment depending on the detailed chemistry of the polymer. If this is a significant mechanism for influencing the local pH at the silica surface, it will be most noticeable in the water environment which has the weakest buffering effect. A plausible explanation for the observed behavior in water can be proposed if the degrading coating removes OH^- from the silica's environment. This lowers the pH and an abnormally high effective n is observed initially. At ~2 × 10⁵ s the apparent n falls in value but the change is very abrupt, possibly because it coincides with exhaustion of the degradation reaction leading to an increase in the local pH, perhaps to a level characteristic of the surrounding distilled water. Evidence for this is that the abrupt n change coincides with the coating color changing to dark brown. At longer times n again increases, perhaps to the low-stress value of 7 for bare fiber at pH 7, though the data do not explore long enough times to confirm this.

An observation of practical importance is that at pH 7 and 10 the fatigue curves for coated and bare fiber cross; times to failure are shorter for coated fiber at lower stresses. This phenomenon may be explained in terms of dissolution processes which are discussed in the next section.

(3) Aging and Fatigue

The development of surface pits, as described by Kurkjian, Krause, and Paek,[22] explains the aging behavior observed by Krause,[10] who found that the fiber strength decreases upon soaking under zero stress in 90°C water. France, Duncan, Smith, and Beales[29] found a similar phenomenon in sodium borosilicate fiber and proposed a simple model for combining aging and fatigue in which both processes are assumed to occur independently at the same time. They assumed that linear fatigue occurred by subcritical "crack" growth and that superimposed upon this was additional "crack" growth dependent on time and not stress at a rate inferred empirically from aging data. They found that the predicted combined aging/fatigue behavior agreed well with experimental data, showing a decreasing n value at lower stress/longer times to failure.

Figure 7(A) shows aging data for a UV-curable epoxy acrylate coated silica fiber immersed in 100°C distilled water under zero stress. The strength, measured under laboratory conditions of temperature and humidity, is normalized to the strength of unsoaked fiber and shows a rapid strength degradation from 10⁴ s. A small but statistically significant loss of strength, similar to that observed from the fatigue experiments after presoaking, is seen over quite a short time scale; however, this initial loss is not significant compared to the much more dramatic loss of strength observed at ~10⁴ s. The fatigue data taken under the same experimental conditions are shown in Fig. 7(B) and are identical in form to the 90°C data of Fig. 2. The solid line is the predicted combined aging/fatigue behavior using the France et al.[29] model (except assuming the room-temperature-aged strength is approximately equivalent to the liquid-nitrogen strength after normalizing to the zero-soak-time strength) and while the fit to the experimental data is not good, the model does predict a change in the apparent n value at approximately the right time. The model can be criticized for assuming the presence of cracks and for assuming that aging is a separate process from fatigue when really it probably should be considered continuous with fatigue and identical to it in the limit of zero applied stress. On the other hand, the aging behavior does give us the insight that silica dissolution is an important mechanism in fatigue, particularly at low stress/long time to failure. However, the link between the two phenomena is not clear; silica solubility[23] and solution rate[24] are approximately independent of pH for pH <7 and rise rapidly for pH >7, while fatigue times show approximately equal sensitivity to pH over the entire pH range.

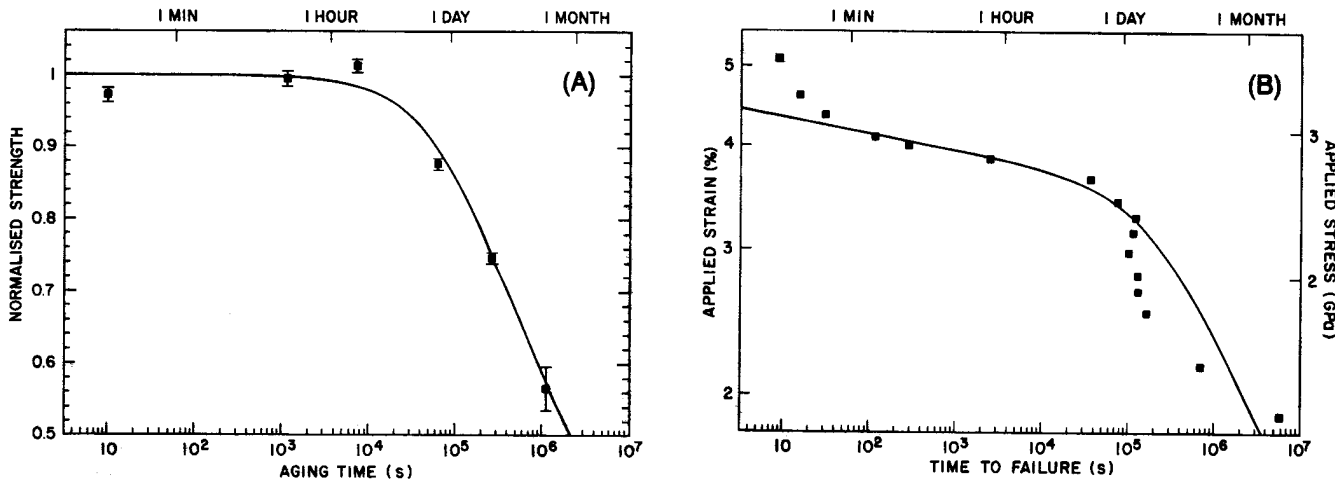A possible explanation for the crossover of the coated- and

Fig. 7.   (A) Zero-stress aging and (B) fatigue data for UV-curable epoxy acrylate coated fiber in 100°C distilled water.

bare-fiber fatigue behaviors is that degradation of the coating increases the pH at the silica surface. However, the distilled-water data imply that the pH decreases. Also, at pH 10 the coating would need to generate an environment at pH 14 and it is unlikely that such a large change in OH⁻ concentration can be achieved. An alternative explanation is that a transport mechanism is more likely. If one imagines a surface flaw as a hemispherical pit (Fig. 8), then dissolution will occur preferentially at the bottom of the pit where the highest stress occurs (we ignore here that enhanced dissolution at the edge of the pit due to the convex curvature of the surface — this effect is the same for both coated and bare fiber and can be ignored for our purposes here). The differential dissolution rate between the bottom and top of the pit brings about a sharpening of the pit profile and an increase in the stress amplification factor when compared to the behavior under zero stress (Figs. 8(a) and (b)). At a later stage, when the growth of the depth of the pit becomes sufficiently fast, the slow dissolution is replaced by bond rupture as the major mechanism for increasing the pit depth and the shape of the pit evolves toward that of the sharp crack that subsequently leads to failure of the specimen. The early stages of this process could be affected by the polymer coating which impedes the transport of dissolved silica away from the pit. As the concentration of dissolved silica rises, the dissolution rates at the top and bottom of the pits fall but the rate at the bottom of the pit, compared to the top, increases — in the limit of a saturated silica solution, material will still be dissolved from the bottom of the pit. Thus, while the size of the pit increases more slowly for coated than bare fiber, the sharpness increases more rapidly (Fig. 8(c)) and this could explain why at low stresses, where dissolution has more time to occur, times to failure are shorter for coated fiber.

(4)   Temperature Effects

The results presented here were obtained under an accelerated condition of high temperature. Although only one temperature has been used, there is information in the literature which indicates how these reactions may be interpreted for the more common practical situation of much lower temperatures.

A great deal of experimental and theoretical work has been done on the fatigue of soda-lime glasses, and it is clear that atmospheric moisture is responsible for strength degradation in this case (see Mould[30]). The general model that is used is that proposed by Charles[28] in which flaw growth (or rather, crack tip sharpening) is due to a stress-enhanced corrosion reaction of water with the glass

$$— \overset{|}{\underset{|}{Si}} — O — Na + H_2O \rightarrow — \overset{|}{\underset{|}{Si}} OH + Na^+ + OH^-$$
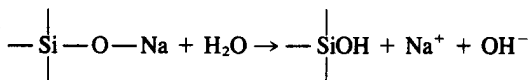
The rate of degradation is controlled by the bulk diffusion of sodium in the glass which has been shown to be enhanced by a

tensile stress.[31] In fused silica the reaction causing degradation is certainly one involving H_2O:

$$— \overset{|}{\underset{|}{Si}} — O — \overset{|}{\underset{|}{Si}} — + OH^- \rightarrow — \overset{|}{\underset{|}{Si}} — O^- HO — \overset{|}{\underset{|}{Si}}$$
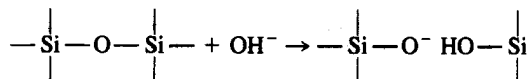
Kao[32] found that the time to failure is a thermally activated process with an activation energy that varies with applied stress from 45 kJ/mol at 3.4 GPa to 75 kJ/mol at zero stress for polymer-coated fiber in water. Duncan, France, and Craig[33] found that the activation energy for silicone-coated fiber in water varies from 57.5 kJ/mol at 0°C to 45 kJ/mol at 100°C. Krause and Shute[12] found values close to 63 kJ/mol for both the low- and high-stress regimes for bare fiber in 1M KOH. While these values agree quite well within experimental accuracy, the activation energy has not been accurately determined as a function of stress, temperature, and environment and any extrapolations should reflect this uncertainty. In addition, the activation energy is not really very useful in trying to understand the details of the mechanism, since all SiO_2–H_2O reactions (e.g., hydrolysis, solution, and diffusion) exhibit similar values (Bershtein,[34] Moulson, and Roberts[35]). Interestingly, recent work by Tomozawa[36] has verified that the diffusion of water in silica is enhanced by a tensile stress, in agreement with the work described above by Charles for sodium in soda-lime silicate.

The coating, which has a strong effect at least at 90°C, further complicates the picture. Degradation of the coating material and diffusion through it are processes that need to be characterized. However, activation energies associated with the coating can be
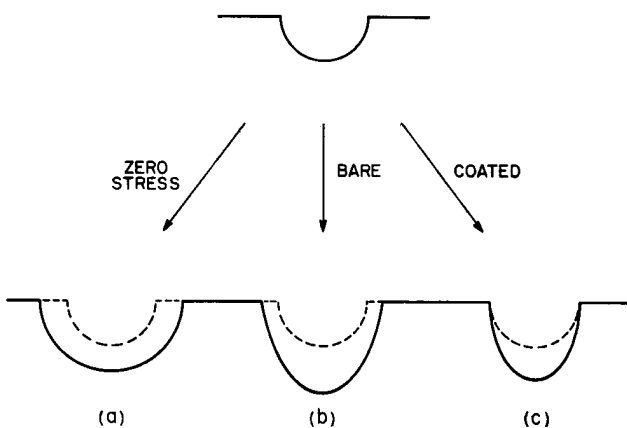

Fig. 8.   Pit model for the fatigue.

expected to be less than that of the reaction of water with silica and therefore coating effects will be less important at lower temperatures; the silica/water reaction rate falls faster as the temperature decreases and tends to become the rate-controlling step. This implies that, in the absence of knowledge of the details of coating behavior, extrapolation of coated-fiber data to lower temperatures will be incorrect. Extrapolation of bare-fiber data, though also quantitatively incorrect, will also be a reasonable qualitative indicator of coated-fiber behavior since both behaviors tend to the same limit at low temperatures. For example, in Fig. 1, the 40°C Chandan and Kalish[11] data are very similar to the 32.5°C Wang and Zupko[8] data and clearly the bare-fiber 90°C data of Krause[10] are a better predictor of this behavior than the 90°C coated data.

(5) Initial Fiber Strength

The experiments described here and elsewhere in the literature are concerned with specimens of length typically less than 1 m whose strengths are greater than 5 GPa. Multikilometer lengths of fiber contain a small population of relatively weak defects and the strength of long lengths can be ensured by proof testing for critical applications at stresses as high as 1.4 GPa. These defects can usually be attributed to contamination of the silica, often by particles which adhere to the surface during the drawing process. The behavior of such defects cannot be assumed to be the same as those controlling the strength of pristine fiber and extrapolation of the fatigue behavior of the latter, but using a lower initial strength, is fraught with danger. In practice a fiber cable will often not be subjected to a uniform stress along its entire length, but rather, short sections will be stressed where, for example, the cable turns a corner. The probability of a severe flaw occurring in these sections may be reduced to an acceptably low risk. Under such circumstances the fatigue of pristine fiber will be relevant.

Recent work by Dabbs and Lawn[37] shows an abrupt change in the indentation behavior of silica fiber at low indentation loads. The "subthreshold" flaws produced at low loads do not contain cracks and are assumed to model the low-strength defects encountered in multikilometer lengths. Interestingly, they measure an apparent fatigue parameter, $n \simeq 19$, which is close to the value of ~20 for pristine fiber. This leads one to suggest that defects in the fiber that are not associated with cracking may show the same fatigue behavior, whatever their origin. The strengths of long lengths of fiber are intermediate between those encountered in indentation experiments and investigations on pristine fiber. It may well be that interpolation between the two types of flaws does apply to the region of interest.

Dabbs and Lawn warn of the possibility that subthreshold flaws can spontaneously "pop in," producing very low strength postthreshold flaws, and that prior proof testing does not therefore guarantee the strength. They suggest that abrupt changes in fatigue behavior observed by Chandan and Kalish[11] could be evidence for this. However, we have here attributed these abrupt changes to a coating effect which is not observed for bare fiber. Further, the same abrupt changes are shown by our bending data and since the bend specimens are equivalent to tensile specimens only a few tens of micrometers long, it is not possible that subthreshold flaws are sufficiently numerous to explain this observation.

The indentation work does raise the possibility that the less abrupt enhanced-fatigue behavior of bare fiber could also be due to delayed pop-in. However, extrapolation of the Dabbs and Lawn[37] data for strength would give an equivalent indentation load of 1.4 mN for a 5.5-GPa pristine fiber. Extrapolation of pop-in data for different indentation loads[38] gives a pop-in time of $\sim 10^{12}$ s at 25°C. While this value is not very reliable, since it lies well outside the range of the experiments, it cannot account for the enhanced fatigue which is observed at times less than $\sim 10^6$ s.

V. Conclusions

The fatigue of high-strength silica fiber has been studied in 90°C water as a function of pH in both its coated and uncoated states. Fatigue is very sensitive to pH, being more rapid for higher pH's. Enhanced fatigue (n significantly less than 20), similar to that

reported by a few previous workers, has been observed at all but the lowest pH. It must therefore be considered a reality and should not be ignored when extrapolating to deduce lifetime under practical conditions.

The coating has a strong effect on fatigue at this temperature. It can either impede or enhance fatigue depending on the stress level and ambient pH. Possible mechanisms for these effects are given which depend on degradation of and diffusion through the coating material. These mechanisms suggest that coating effects are less important at lower temperatures. Therefore, the results of high-temperature accelerated tests on coated fiber are not reliable predictors of lifetime at lower temperature. Bare-fiber results can be expected to give more realistic predictions.

Experiments on coated fiber in distilled water give an apparent value of the stress corrosion parameter, n, which is unusually high, but this effect disappears at low applied stress. We may thus conclude that short-term experiments in an "uncontrolled" water environment with coated fiber are particularly poor indicators of long-term behavior. A controlled-pH aqueous environment would be more useful.

A crossover in fatigue behavior between coated and bare fiber is observed. At low applied stress coated fiber has the shorter lifetime while the converse is true at higher stresses.

Aging experiments suggest that the enhanced fatigue is due to the evolution of surface pits by dissolution. The transformation of regions of residual stress into macroscopic cracks, namely, "pop-in," does not account for this behavior.

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