Effects of Water and Moisture on Strengths of Optical Glass (Silica) Fibers Coated with a UV-Cured Epoxy Acrylate

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Synopsis

Furnace-drawn optical silica fibers coated with a uv-curable epoxy acrylate (V1F) were subjected to long-term tests in water and in humid environments. Results of stress-free aging tests showed a progressive reduction of strength both in water and in the atmosphere of 90% r.h. at 32.6°C. Stressing the fibers up to 517 MN/m^2 (75 kpsi) during aging did not result in additional loss of strength. Static fatigue tests in 90% r.h., 32.6°C, showed that the fatigue strength decreased monotonically with time of exposure in accordance with the power law of Charles. However, there were indications that Charles' theory might not be obeyed over an extended test period.

INTRODUCTION

In a previous publication,[1] it was shown that by a proper choice of the coating technique,[2] as well as of the coating resin,[3] it is possible to prepare coated silica fibers that are uniformly strong (>5 GN/m^2 or 725 kpsi) in long lengths (~1 km).[1,4] The coating used in that study was a uv-curable epoxy acrylate[3] that was specifically formulated to meet a variety of requirements for application to communications systems (e.g., adequate protection from physical damage, low microbending losses,[5] and ease of stripping by suitable chemical means).

An important consideration besides those just described is the long-term retention of fiber strength in hostile environments, particularly in water or humid air. Since silica may be extremely susceptible to corrosion by water,[6] one way of maintaining its strength would be to passivate the reactive sites on the surface by applying a resin that can effectively wet and react with silica.[7] Although the epoxy acrylate resin adheres extremely well to silica upon curing, we have added to the formulation a styryl functional silane (Dow Corning, Z6032) in the expectation that it would further promote chemical bonding to the surface of the glass, thereby providing additional protection of the fibers against attack by moisture.

The objective of this paper is to report results of long-term strength tests performed on the optical fibers coated with the uv-curable epoxy acrylate containing Dow Corning Z6032. Although the short-term (initial) strengths of coated optical fibers have been characterized extensively,[4,8–10] very little is known of their long-term strength performance in human environments.

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TABLE I
Physical Properties of Cured Epoxy Acrylate Film

Tensile strength: 12.4 MN/m^2 (1800 psi)[a]
Young's modulus: 110 ± 28 MN/m^2 (16,000 ± 4000 psi)[a]
Elongation at break: 20 ~ 28%[a]
Glass-transition temperature, T_g: ~−20°C

[a] Measured at room temperature at the strain rate of 100%/min.

EXPERIMENTAL

The optical fibers were drawn from 8-mm diameter preforms (having graded refractive index profiles) to a diameter of 110 μm using a graphite resistance furnace. Each fiber consisted of a 55-μm diameter core of germania-doped borosilicate, clad with Amersil TO-8 fused quartz. A uv-curable epoxy acrylate[1,3] containing 0.5 wt % of a styryl-functional silane (Dow Corning Z6032) was used as the coating liquid. Fibers were drawn vertically and coated in line with an applicator having a flexible exit port.[2] Curing of resin was performed between the applicator and the take-up drum using uv lamps.

Fibers were drawn at a speed of 0.4 m/sec, and the viscosity of the coating resin was maintained at about 50 P (5 Pa·S) by regulating the resin temperature at about 40°C. The organic coating was approximately 60 μm thick and the silica fiber was reasonably well centered within it.

Prior to the long-term tests, all coated fibers (each about 1.1 km long) were proof tested at 345 MN/m^2 (50 kpsi). Thus if it is assumed that the fiber did not incur additional damage in proof testing, all fibers used in this experiment must have had a minimum strength of 345 MN/m^2.

The aging studies included the evaluation of tensile strengths upon exposure to three environments—(1) water, 22°C; (2) 90% r.h., 32.6°C; and (3) 50% r.h., 22°C—and static fatigue tests in 90% r.h., 32.6°C. Variations in humidity and

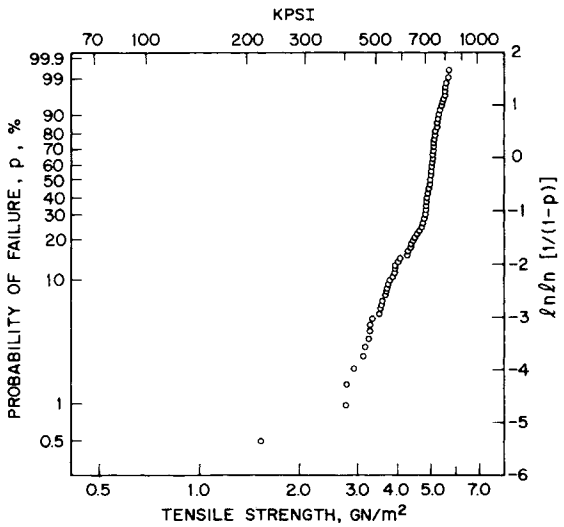

Fig. 1. Weibull plots of initial strengths of the fiber prior to aging. (For clarity, some data points have been omitted at the upper end of the curve.)

temperature were maintained at ±3% r.h. and ±1.5°C, respectively, of the specified values throughout the aging period.

Tensile tests were performed with an Instron at a strain rate of 21%/min and a gage length of 0.61 m. Except for the specimens aged in water, all specimens were conditioned in the test environment of 50% RH and 22°C for about 15 min prior to tensile tests. Water-soaked specimens were tested immediately upon removal from water. Static fatigue tests were performed on 0.61-m gage-length specimens using standard dead-weight loading units individually equipped with electric timers.

Specimens for each test were taken at random intervals along the fiber length. To achieve a close representation of the strength distribution, a minimum of 60 samples was used in each test, except in the water-immersion and the static-fatigue tests, where the smallest number of specimens used was 30. To prevent ingress of bulk water from fiber ends, specimens used in the water-immersion test were sealed at both ends with a water-resistant epoxy prior to immersion.

Tensile properties of the coating material were determined from free films of epoxy acrylate prepared under comparable curing conditions, and the results are given in Table I. Since the coating was very soft compared to glass, its contribution to the measured strength was negligible.

RESULTS AND DISCUSSION

The strength distribution of the fiber prior to aging is shown in Figure 1, where the cumulative probability of failure (based on 210 measurements at a gage length of 0.61 m) is plotted against the failure stress on a Weibull scale.[11] Although the distribution is rather broad, it is interesting to note that the majority of the specimens (>70%) failed in the narrow range between 4.8 and 5.7 GN/m^2 (700 and 820 kpsi). In addition, the plot reveals two linear regions (or two distribution modes), suggesting that the strengths of the coated fibers may be associated with two different failure mechanisms.

Details of flaws have not been determined; however, failures at low stresses (less than 1.03 GN/m^2 or 150 kpsi) have been found to be caused primarily by particulate contaminants generated from the hot furnace components. An example is shown in Figure 2, where the fracture source was identified as a microscopic particle containing iron and platinum. At higher strengths, the specimens invariably shattered on fracture, and the fracture faces were not available for microscopic examination.

The changes of median strengths with aging time in the three different environments are shown in Figure 3. Since fibers drawn and coated in different runs had slightly different initial strengths, the results have been normalized against the initial median strengths to facilitate comparison. Although aging in water and in 90% r.h. resulted in a substantial weakening of the fiber, it is significant that exposure to the atmosphere of 50% r.h. did not bring about any change in the strength over an extended period (ca. 36 months). Thus, if it is assumed that the weakening phenomenon resulted from some sort of reaction between silica and water during aging, it is hard to understand why the fiber did not degrade in the atmosphere of 50% r.h.

In a similar study on pristine fused silica fibers by Proctor et al.,[12] it has been reported that the strength of the fiber is not affected by water in the aging environment, but is dependent only on the humidity level in the atmosphere in

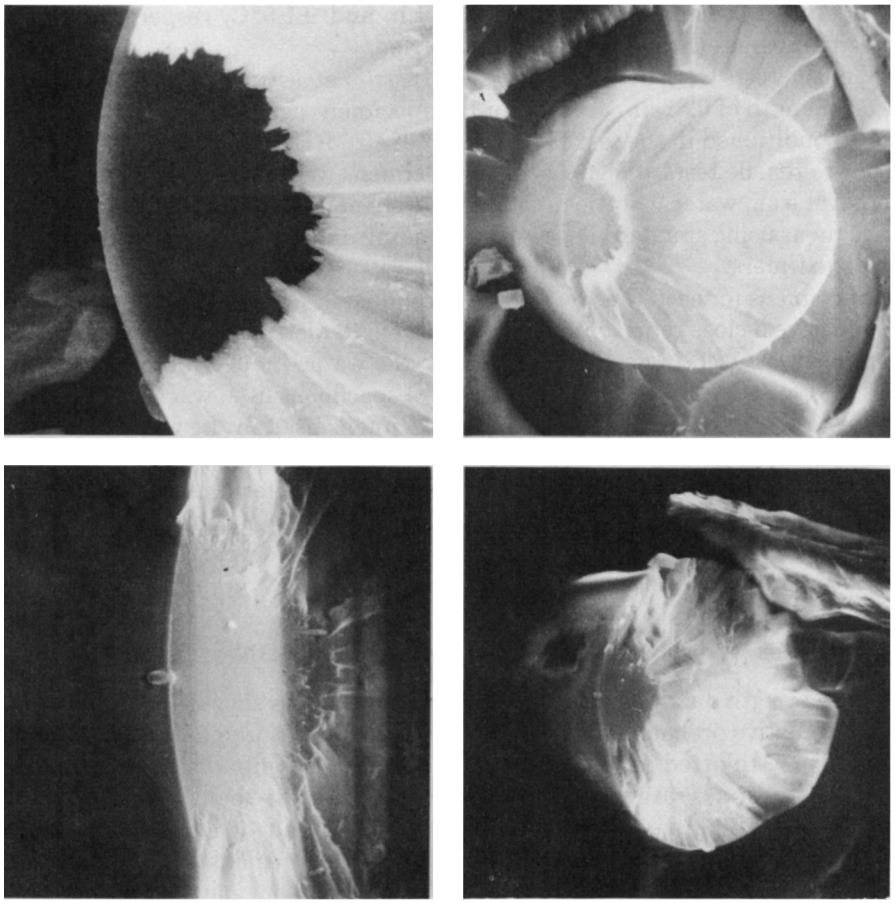

Fig. 2. Photomicrographs of fracture surfaces of a specimen failed at 345 MN/m^2 (50 kpsi). Contaminants, Fe and Pt.

which the fiber strength has been measured. Since in the case of coated fibers the glass is not directly exposed to the tensile test atmosphere, their strengths should be more sensitive to the moisture level in the organic coating layer than to the test atmosphere. Therefore, the strength reduction observed in the coated fiber is probably brought about by water absorbed by the polymer in the aging treatment that subsequently interacts with silica under the influence of applied stress during tensile testing (dynamic fatigue[13]). This would explain why the coated fiber did not display any change in strength even after prolonged exposure to the tensile test environment (50% r.h., 22°C).

After 202 days of storage in water, several specimens were removed from the container (glass tube) and dried for 10 days in a vacuum oven maintained at about $\frac{1}{3}$ atm and 22°C. Tensile tests performed after 1 hr of conditioning in the test environment showed a recovery of strength to about 77% of the initial strength (Fig. 3). This partial recovery of strength again suggests that the strength losses observed in the aged fibers arise from dynamic fatigue during tensile testing. However, the fact that the drying treatment did not result in full recovery of strength indicates that some water molecules in excess of the equilibrium value (in 50% r.h. and 22°C) may still be trapped at the interface.

In addition to the stress-free aging, a number of specimens were stressed to

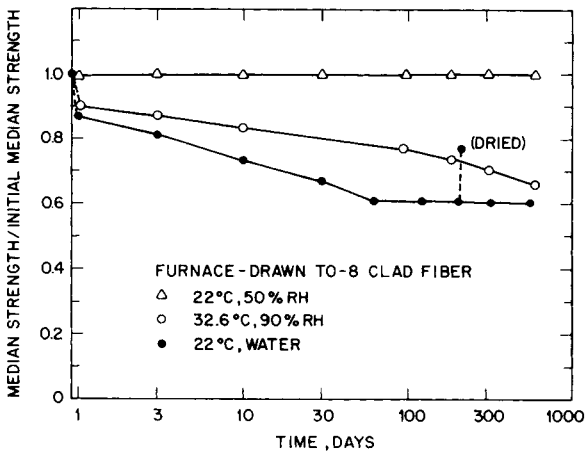

Fig. 3. Plots of median strengths (normalized with initial median strengths) vs time of aging in three different environments. Each median was determined from 30 to 60 measurements.

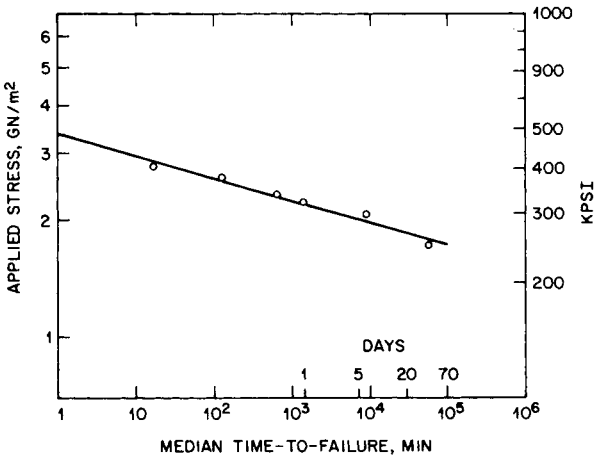

Fig. 4. Log-log plots of applied stress vs median time-to-failure in 90% r.h. and 32.6°C. Each median was determined from 30 measurements.

345 MN/m^2 (50 kpsi) and 517 MN/m^2 (75 kpsi) while being exposed to the different environments. Strength measurements of these specimens after 200 days of aging showed no additional effect due to stressing, indicating that these stresses were perhaps too low to promote corrosion of glass by water.

The results of static fatigue tests in 90% r.h. at 32.6°C are shown in Figure 4, where the applied stress is plotted against the median time-to-failure on log-log axes. According to the stress-corrosion theory of Charles,[14]

$$\sigma^n t = K \tag{1}$$

(where σ is the applied stress, t is the time-to-failure, n is the coefficient of stress corrosion susceptibility, and K is a constant), such a plot should yield a straight line with the slope equal to $(-1/n)$. A least-square fit of the data points gives an n value of 17.4, which is somewhat larger than the value obtained by Charles[14] for uncoated E-glass fibers ($n = 16$). Extrapolation of the data shows that half of the fiber specimens can sustain a load of 1.38 GN/m^2 (200 kpsi) in 90% r.h. and 32.6°C over the expected 40-year service period. However, a closer examination

of the data plots reveals a slight but noticeable bend toward the abscissa, suggesting that the power law of Charles may not be obeyed by the coated fiber over a long time span. For this reason, caution must be exercised in applying the extrapolation scheme to predict the long-term ($20 \sim 40$ years) strength. One obvious way of minimizing the error from such an extrapolation would be to extend the tests to lower stress levels until more data are obtained in the neighborhood of 10^6 or 10^7 min. These tests are currently underway, and the results will be presented in a future report.

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