

Strength degradation and recovery during zero-stress aging of fused silica optical fibers

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ABSTRACT

The two-point bending technique has been used to measure the strength of both polymer coated and bare fibers in liquid nitrogen after the fibers were first aged in an aggressive environment followed by a drying process. The results show that some strength recovery occurs upon drying of polymer coated samples while continuing degradation was seen when drying bare samples. The healing process observed for coated fiber is thought to be caused by condensation of the hydrated surface layer formed during aging.

Keywords: Optical fiber, fused silica, strength, fracture, reliability, aging.

1. INTRODUCTION

In order to ensure reliability of silica fiberoptic based systems, it is necessary to avoid both defects in the surface of the glass fiber and strength loss after prolonged exposure to moist environments. While few failures have been reported due to strength loss of the fiber itself,¹ the associated economic risk is appreciable because of the high cost of fiber repair or replacement.

The fatigue exhibited by oxide glasses containing micro-cracks is now well understood and is attributed to the combined action of stress and an environmental reactant which is usually water. The reaction, proposed by Michalske and Freiman,² causes the local crack front to advance by one bond length as each siloxane bond is ruptured; the force supported by the broken bond is transferred to an adjacent bond and the process continues until the stress at the crack tip exceeds the strength of the material and catastrophic failure occurs.

Kurkjian and Paek³ showed that the strength of pristine fiber is essentially single valued, and under inert conditions is close to the theoretical strength of the material. Such fibers do fail by fracture and the failure process therefore includes nucleation as well as propagation of the crack. The details of this fatigue process are not clearly understood but reasonable reliability predictions can be made if an appropriate crack growth kinetics model is used to extrapolate to field conditions.⁴

However, anomalies in the fatigue behavior and strength degradation under zero-stress aging are not accounted for by the above model. It is now known that these phenomena are caused by surface corrosion of the silica glass leads to the formation of surface roughness or 'pits' which then act as a new source of stress concentrating defects. While it was originally thought that the pits are formed by surface dissolution, recently it has been shown that aging produces a surface layer on the fiber, presumably of hydrated silica, that is removed by immersion in hot sulfuric acid, but which is too weak to contribute to the fiber strength.⁵ The surface layer also forms on fibers aged bare. These results show that surface corrosion does not remove silica but does break up the glass network by hydrolysis of a surface layer. This suggests the possibility that the hydrated silica gel can be dehydrated to regain some of the original strength. This article investigates the effect of drying on the post-aging strength of fused silica optical fiber.

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2. EXPERIMENTAL

Three fused silica optical fibers (designated A, B and C) were aged for 5 days in 85°C pH 7 buffer and then placed in a desiccator over Drierite[‡] at room temperature for various periods of time. The specimens were then broken in liquid nitrogen using the two-point bending technique. Two-point bending determines the failure strain, ϵ_f ; the failure stress, σ_f , is calculated using:

$$\sigma_f = \epsilon_f E_0 (1 + \alpha \epsilon_f),$$

where $E_0 = 72.2$ GPa is the zero strain elastic modulus and $\alpha = 2.125$ is a factor that accounts for both the strain dependence of the modulus and the resulting shift in the position in the centroid when bending the fiber.⁶ In addition to testing all three fibers coated, the same experiments was performed on fiber C after its polymer coating had been removed by immersion in hot sulfuric acid. Fibers A and B have commercial dual polymer coatings while fiber C has a single coating of a formulation typical of commercial coatings *ca.* 1983.

The fiber strengths were determined after drying by measurement in liquid nitrogen in order to establish the intrinsic or inert strength. This is necessary because drying alone will cause the strength measured in non-inert conditions to increase simply because drying removes moisture from the fiber's environment; it is necessary to distinguish between apparent strengthening due to changes in moisture content of the environment, and true increases in the intrinsic strength. The fibers aged coated were tested coated in liquid nitrogen. Normally fibers tested in liquid nitrogen are stripped of their coating since the polymer embrittles at low temperature and can cause premature failure of the fiber. In these experiments, however, it was necessary to avoid stripping the coating since the stripping process might disturb or remove the silica gel layer that we are trying to strengthen by drying. Coating embrittlement does lead to unusually large scatter in the results for higher strength fiber (≥ 12 GPa) so that these results may somewhat reflect the mechanical state of the coating rather than the fiber. Two-point bending was used throughout for the strength measurement since it is the only convenient strength measurement technique that can test bare fiber and can break fiber immersed in liquid nitrogen.⁷

3. RESULTS AND DISCUSSION

Fig. 1 shows measurements of the liquid nitrogen strength of coated fibers A and B. The error bars represent a 95% confidence interval on the mean strength and each point is an average for 15 specimens. The tests were performed after aging for 5 days in 85°C pH 7 buffer, and after different periods of time in the desiccator. For reference, the unaged strength and the strength immediately after the aging process are also shown. We see that the aging causes a modest strength degradation of ~5%. However, after one day in the desiccator the strength recovers to slightly over the original strength. The apparent increase in strength to more than the original strength is surprising but may be an artifact caused by testing with the coating still on the fiber. It is possible that the aged coating is somewhat less brittle than the unaged material (its T_g may be lower due to hydrolysis of crosslinks) thus having a smaller influence on the measured strength.

Fig. 2 shows the results for fiber C that had been aged and dried both coated and after removal of the coating using sulfuric acid at ~180°C. First, it is noted that the coated fiber has been degraded in strength much more severely by the aging than the bare fiber. This effect has been observed before⁸ and is thought due to differences in the surface roughening kinetics;

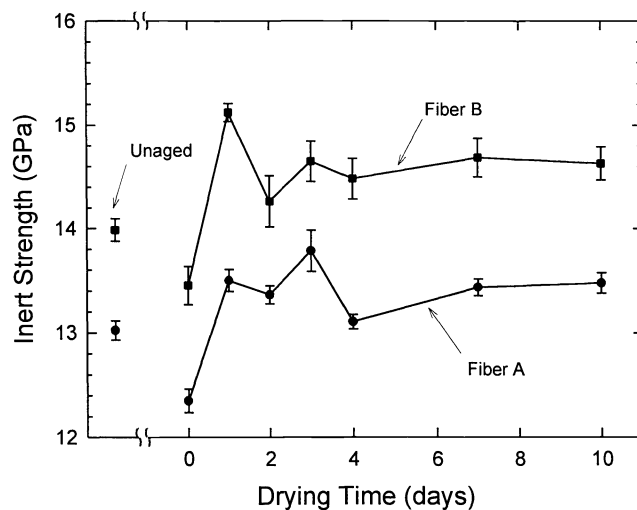


Fig. 1. Liquid nitrogen bending strength of fibers A and B before and after aging, and after drying.

[‡] Fisher Scientific, Pittsburgh, PA.

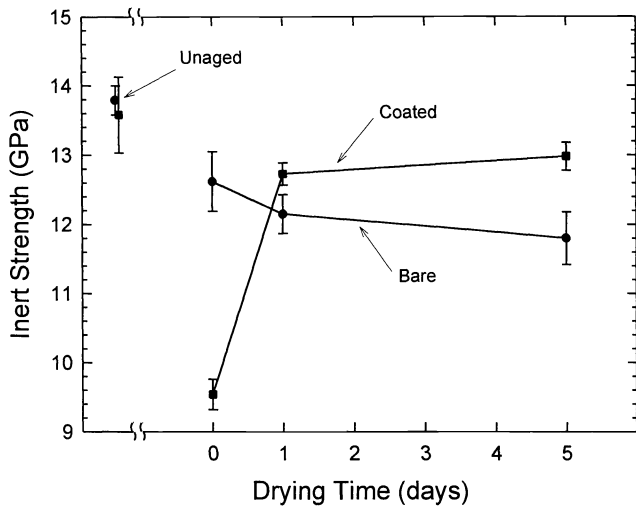


Fig. 2 Liquid nitrogen bending strength of fiber C before and after aging, and after drying. Results are shown for the fiber aged, dried and then tested both coated and after removal of the polymer coating in hot sulfuric acid.

of the coating. Given that, most, if not all, of the strength recovery observed in this fiber is real and is not an artifact of the coating. These results therefore provide more unequivocal evidence for strength recovery than the data of Fig. 1.

In contrast to coated fiber, the bare fiber behavior shown in Fig. 2 shows no strength recovery upon drying and perhaps shows slight continued degradation. It should be noted that the surface gel layer formed upon aging is also observed for fiber aged bare.⁵ Therefore, bare fiber should also have the potential for strength recovery but this is not observed. The reason for the difference in behavior of bare and coated fiber is not clear.

Proctor Whitney and Johnson¹¹ measured the strength of silica fibers over a wide range of temperatures and found that the fibers were slightly stronger in liquid helium (4 K) than in liquid nitrogen (77 K). One possible interpretation of this result is that there is still some fatigue in liquid nitrogen and that such conditions are not truly inert. If this were the case, then any strengthening (measured in liquid nitrogen) observed upon drying might be, at least partially, caused by removal of moisture rather than a real increase in inert strength. Such an effect is unlikely to be large enough to explain the substantial strength recovery shown in Fig. 2. However, in order to demonstrate this, the liquid nitrogen strength of unaged fiber C has been determined as a function of drying time and the results are shown in Fig. 3. No increase in strength with drying is observed, although the scatter in the results is large indicating that coating embrittlement is taking place. While

bare fiber corrodes over its whole surface while coated fiber corrodes only at points of weak adhesion of the coating.⁹ Since surface roughening is caused by differential corrosion rates from point to point on the surface, the coated fiber with patchy adhesion can produce the faster degradation.¹⁰

Drying of coated fiber C produces substantial strength recovery, 80% of the strength loss produced by aging is recovered after only one day drying. These results are not caused by coating effects; the scatter in the strengths of the aged fiber (whether dried or not) is much lower than the unaged fiber and is typical of the scatter observed for fiber tested at higher temperatures. Since the scatter in the unaged fiber strength is large, it is likely that the coating is failing at ~13 to 14 GPa and so causing some premature failure. However, the aged strength of 9.5 GPa is much less than any strength observed before aging and so must be a good measure of the fiber strength, irrespective

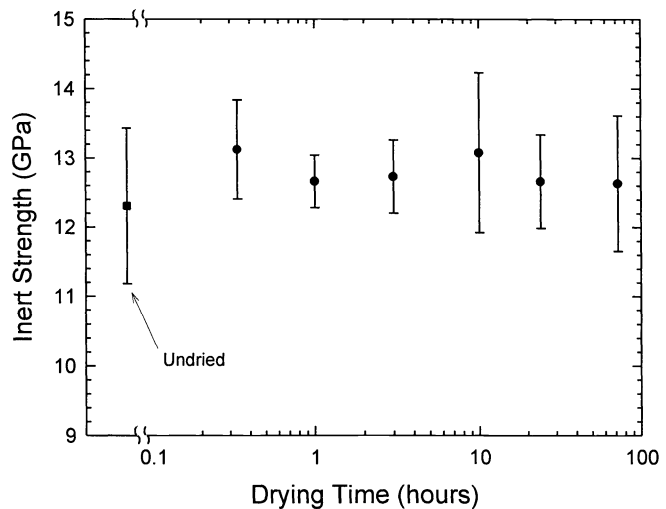


Fig. 3. Liquid nitrogen bending strength of unaged fiber C as a function of drying time.

embrittlement might mask any increase in strength with drying, it is unlikely that it could completely mask a 40% strength increase similar to that observed in Fig. 2.

Strength degradation occurs on the time scale of hours or more in 100°C water but takes decades or more at 25°C; the effective activation energy for this process is $\sim 90 \text{ kJ}\cdot\text{mol}^{-1}$.¹² In contrast, we observe strength recovery upon drying at room temperature in less than a day. It is perhaps surprising that the reverse degradation reaction occurs much more rapidly than the forward degradation reaction. The mechanism we propose here for the strength recovery is condensation or polymerization of silica gel to reform load-bearing solid silica. From the literature on silica gel, it is known that the condensation reaction is very sensitive to pH and to the nature of any ionic species present. Activation energies for polymerization in the range of 35 to 65 $\text{kJ}\cdot\text{mol}^{-1}$ have been observed;¹³ these relatively low values explain why the strengthening can occur rapidly at room temperature. However, the overall kinetics of degradation dominate under wet conditions and this must be due to the relatively high concentration of both reactants, namely water and surface siloxane bonds.

4. CONCLUSIONS

Some of the strength loss of polymer coated fibers caused by zero-stress aging in harsh environments can be recovered by exposure to a very dry environment. This phenomenon is thought to be due to reconstitution of solid silica from the hydrated gel layer formed during the aging process. Bare fiber did not exhibit strength recovery with similar treatment.

5. ACKNOWLEDGMENTS

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