

# Aging behavior of optical fibers in aqueous environments

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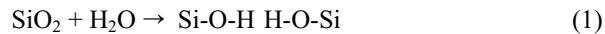
## ABSTRACT

Silica optical fibers drawn from a common preform and coated with specialty coatings were exposed to zero-stress aging in various aqueous environments for approximately ten months. The strength of the fiber samples was tracked with two-point bend testing. The onset of an aging “knee” was observed for some fiber samples while other coatings offered enhanced protection from the effects of moisture-induced strength degradation.

**Keywords:** optical fiber, aging, strength, reliability, environmental effects, coatings

## 1. INTRODUCTION

Zero-stress aging is defined as the process of fiber strength degradation in the absence of stress. In this respect, aging differs from fatigue which is defined as moisture-assisted crack growth under stress. Strength degradation under aging is considered to be controlled by increased surface roughness due to the dissolution of silica on the surface of a fiber by water corrosion.<sup>1</sup> Dissolution occurs when a polar species (water) ruptures the silicon-oxygen bond as illustrated in the following equation:



When the Si-O bond is stressed, static fatigue will occur and sub-critical crack growth will proceed until failure. Both aging and fatigue have been shown to exhibit a “knee”<sup>2</sup> where strength degradation proceeds at an accelerated rate below the knee. The aging “knee” is believed to represent a shift in the strength-limiting basis of the fiber from the fiber’s initial flaw distribution to increasing surface roughness caused by silica dissolution on the surface of the fiber.

The protective polymer coating applied to the silica optical fiber has a critical role in the aging characteristics of the fiber.<sup>3</sup> The role of the coating in strength preservation can be described as 1. preventing the diffusion of water to the glass surface<sup>4</sup> and 2. minimizing the mobility of water at the glass-coating interface. With regard to (1), if the corrosive effect of water can be segregated from the silica surface, aging cannot occur (although some minor strength degradation can occur due to atmospheric moisture attached to the glass surface before the coating is applied). This will depend on the permeability of the coating to water diffusion; only hermetic coatings are considered capable of completely preventing water from reaching the glass surface. For (2), the availability and activity of water at the glass-coating interface has both mechanical and chemical implications. If water is free to react with the silicon-oxygen bonds, the (Si-O-H) will be readily replaced with unreacted H<sub>2</sub>O to repeat the process. However, if the water is held tightly at the interface, it will become saturated and the dissolution process will slow. Since water diffusion and mobility at the glass-coating interface are both temperature-driven effects, the temperature of the environment will significantly affect the aging behavior of a fiber.

As optical fibers are used increasingly in specialty applications, the effect of aging on the long-term reliability of fibers has similarly grown in importance. This is a special concern for fibers in adverse environments<sup>5</sup> (e.g. oil well sensors) or in applications requiring extremely high reliability (e.g. medical fibers<sup>6</sup>). Although extensive research has been performed on the aging behavior of fibers, this work has focused almost exclusively on acrylate coatings used for telecommunication fibers<sup>7,8</sup> while only some limited studies have looked into the aging behavior of specialty

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coatings.<sup>9,10,11</sup> In a previous publication, the authors have detailed the results of an aging study on acrylate and polyimide-coated fiber samples.<sup>12</sup> In this paper, we also present and discuss the results of aging experiments on fibers coated with carbon, silicone, and HCS<sup>®</sup> protective coatings then soaked in saltwater, distilled water at room temperature, water at 50°C and water at 80°C. This is a continuation of an effort to understand the aging behavior and reliability of optical fibers with special coatings under various environmental conditions.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Sample preparation

Seven fiber samples were prepared for zero-stress aging, coated with:

- Acrylate
- Silicone
- Polyimide
- HCS<sup>®</sup> Hard Clad Silica
- Carbon-acrylate
- Carbon-silicone
- Carbon-polyimide

To minimize variations in strength that may arise from different preform or drawing conditions, all fiber was drawn from the same preform; in addition, the furnace temperature, draw speed, draw tension, and fiber size were all held constant. With the exception of the HCS fiber sample, all samples were pulled from the same draw furnace. The glass size was held at 125µm for all samples. Because of the characteristics of the coatings tested, the coating thickness varied between samples.

| Coating type     | Coating thickness |
|------------------|-------------------|
| Acrylate         | 37 µm             |
| Silicone         | 60 µm             |
| Polyimide        | 7 µm              |
| HCS              | 11 µm             |
| Carbon-acrylate  | ≈400Å + 37 µm     |
| Carbon-silicone  | ≈400Å + 60 µm     |
| Carbon-polyimide | ≈400Å + 7 µm      |

Table 1. Coating types and thicknesses.

The acrylate fiber sample was coated with a secondary acrylate coating only for direct comparison of the chemical reaction of this coating versus other homogenous coatings. Both the acrylate and HCS fluoroacrylate fiber coatings were applied and cured with ultraviolet (UV) radiation. The silicone and polyimide coatings were cured with thermal ovens; the silicone sample cures by polymerization while the polyimide sample is cured via solvent evaporation followed by imidization. The carbon samples are prepared by pyrolysis of a hydrocarbon gas on the surface of the fiber, resulting in a very thin graphitic layer chemically bonded to the surface of the glass.

### 2.2 Zero-stress aging

All samples were cut into approximately thirty 25 cm samples and placed into temperature baths controlled to an accuracy of +/- 2°C. One end of the fibers was attached to the side of the temperature bath and kept out of the soaking environment; strength testing was performed only on the portion of fiber that was submerged. The samples were soaked under zero-stress in the following solutions:

- Distilled water at room temperature
- Saltwater\* at room temperature
- Distilled water @ 50°C
- Distilled water @ 80°C

### 2.3 Two-point bend strength testing

Samples were removed from soaking tanks at defined intervals and tested with two-point bend strength testing set at a 4%/minute strain rate. The fiber samples were tested within several minutes after removal from the tanks and were not dried except to remove surface water immediately before strength testing. Two-point bend testing was chosen because it focuses on the intrinsic strength-controlling flaw distribution of the fiber rather than the larger extrinsic (or “weakest link”) flaws found with tensile testing. In addition, many strength measurements can be made with a small sample.

## 3. DATA AND DISCUSSION

Before aging, the baseline strength and fatigue values were established for the seven fiber types. Strength values are based on 20 measurements; dynamic fatigue values are calculated from fibers strained at 25%, 2.5%, and 0.25%/minute:

|                  | Median strength (GPa) | Range (GPa) | Dynamic fatigue “n <sub>d</sub> ” value |
|------------------|-----------------------|-------------|-----------------------------------------|
| Acrylate         | 6.39                  | 0.76        | 20                                      |
| Carbon-acrylate  | 4.06                  | 0.25        | >100                                    |
| Polyimide        | 6.93                  | 0.31        | 22                                      |
| Carbon-polyimide | 4.12                  | 0.20        | >100                                    |
| Silicone         | 7.06                  | 0.59        | 20                                      |
| Carbon-silicone  | 4.08                  | 0.27        | >100                                    |
| HCS              | 6.55                  | 0.30        | 21                                      |

Table 2. Baseline strength, range, and fatigue values.

### 3.1 Acrylate

The aging behavior of the acrylate fiber is summarized in the following graph and table (for clarity, the 50°C water data is omitted from the following graphs; also all graphs use a similar strength range for comparison):

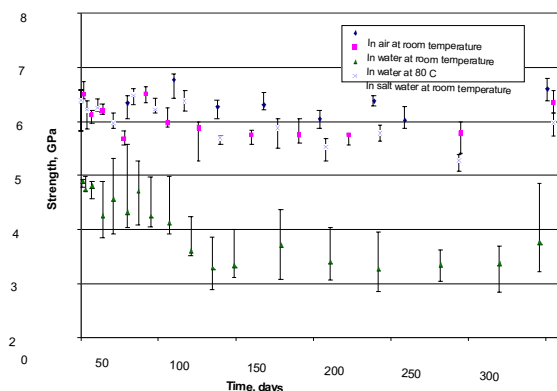


Fig. 1. Acrylate fiber aging behavior.

| Acrylate fiber strength after ≈300 days | Median strength (GPa) | $\sigma / \sigma_0$ (Final strength / baseline strength) | Range (GPa) |
|-----------------------------------------|-----------------------|----------------------------------------------------------|-------------|
| Initial                                 | 6.39                  |                                                          | 0.49        |
| Air @ room temperature                  | 6.60                  | 103%                                                     | 0.41        |
| Water @ RT                              | 6.34                  | 99%                                                      | 0.41        |
| Saltwater @ RT                          | 5.97                  | 93.5%                                                    | 0.42        |
| Water @ 50C                             | 4.45                  | 69.7%                                                    | 0.39        |
| Water @ 80C                             | 3.78                  | 59.2%                                                    | 1.62        |

Table 3. Acrylate fiber aging data.

\* Instant Ocean, Aquarium Systems, Mentor, OH

As the graph indicates, the acrylate fiber dropped below 80% of its original strength after only one day of aging at 80°C, suggesting that the acrylate coating offers little protection as a moisture barrier. After two weeks at 80°C, the strength data started to exhibit a marked increase in data variability with ranges (max-min) often > 1 GPa (145 kpsi). At day 85, the acrylate strength dropped to a low of 3.3 GPa (478 kpsi) whereupon no further significant strength degradation occurred.

### 3.2 Polyimide

The polyimide fiber experienced a similar drop in strength at 80°C. However, as the graph below indicates, the degradation was much more gradual than the acrylate fiber with a tighter data range.

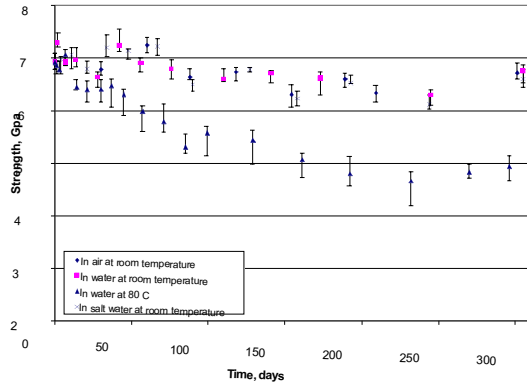


Fig. 2. Polyimide fiber aging behavior.

Similar to the acrylate fiber, the polyimide fiber soaked at 80°C reached some minimum strength around day 200, whereupon no further degradation in strength was evident. The polyimide fiber exhibited a minor strength drop in room temperature water and saltwater and (like acrylate) the 50°C aging behavior tended to fall between room temperature water and the 80°C water data.

### 3.3 Silicone

The silicone used for the fiber samples is characterized as “hydrophobic” by the coating manufacturer and this fiber type exhibited the best resistance to aging of all the non-carbon samples:

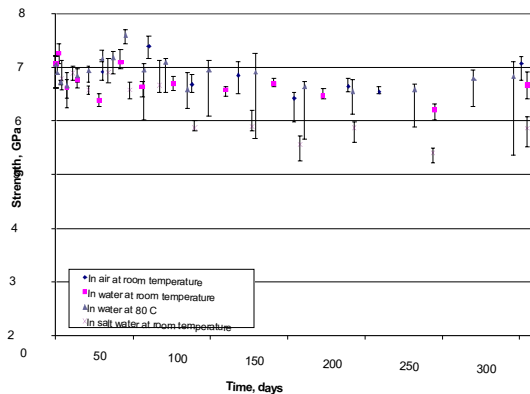


Fig. 3. Silicone fiber aging behavior.

| Polyimide fiber strength after ≈300 days | Median strength (GPa) | $\sigma / \sigma_0$ | Range (GPa) |
|------------------------------------------|-----------------------|---------------------|-------------|
| Initial                                  | 6.93                  |                     | 0.31        |
| Air @ room temperature                   | 6.72                  | 97.1%               | 0.31        |
| Water @ RT                               | 6.75                  | 97.5%               | 0.43        |
| Saltwater @ RT                           | 6.60                  | 95.3%               | 0.26        |
| Water @ 50C                              | 6.08                  | 87.8%               | 0.44        |
| Water @ 80C                              | 4.94                  | 71.3%               | 0.49        |

Table 4. Polyimide fiber aging data

| Silicone fiber strength after ≈300 days | Median strength (GPa) | $\sigma / \sigma_0$ | Range (GPa) |
|-----------------------------------------|-----------------------|---------------------|-------------|
| Initial                                 | 7.06                  |                     | 0.59        |
| Air @ room temperature                  | 7.07                  | 100%                | 0.44        |
| Water @ RT                              | 6.66                  | 94.3%               | 0.51        |
| Saltwater @ RT                          | 5.86                  | 83.1%               | 0.55        |
| Water @ 50C                             | 6.62                  | 93.8%               | 0.55        |
| Water @ 80C                             | 6.84                  | 96.9%               | 1.49        |

Table 5. Silicone fiber aging data.

The silicone fiber samples, however, exhibited a greater sensitivity to saltwater than the other fiber samples, losing about one-fifth of its original strength over the course of the experiment. The reason for this degradation is unclear, but may be related to a chemical reaction between the basic saltwater (pH≈8.5) and the silicone coating.

### 3.4 Hard Clad Silica (HCS®)

The Hard Clad Silica (HCS) fiber exhibited very little strength degradation over the course of the test, retaining over 90% of its initial strength even in the most aggressive test.

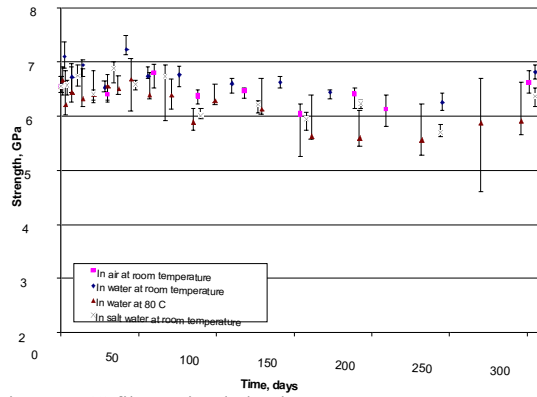


Fig. 4. HCS fiber aging behavior.

| HCS fiber strength after ≈300 days | Median strength (GPa) | $\sigma / \sigma_0$ | Range (GPa) |
|------------------------------------|-----------------------|---------------------|-------------|
| Initial                            | 6.55                  |                     | 0.30        |
| Air @ room temperature             | 6.61                  | 100%                | 0.41        |
| Water @ RT                         | 6.81                  | 104%                | 0.26        |
| Saltwater @ RT                     | 6.36                  | 97.2%               | 0.36        |
| Water @ 50C                        | 6.45                  | 98.5%               | 0.47        |
| Water @ 80C                        | 5.92                  | 90.3%               | 0.97        |

Table 6. HCS fiber aging data.

This fluorinated acrylate polymer coating is used as an optical cladding, but these results indicate that the HCS also serves as a good barrier against the effects of aging.

### 3.5 Carbon

The carbon-coated fiber samples exhibited very similar behavior during aging so that, for the sake of space, all the carbon data are grouped in the graph below:

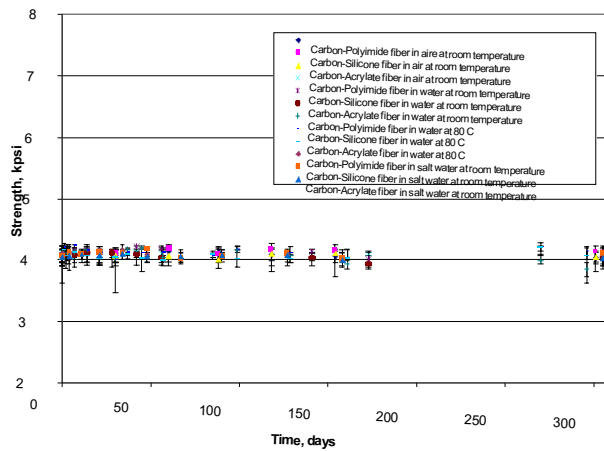


Fig. 5. Carbon-fiber aging behavior.

In sharp contrast to the aging behavior of the non-carbon fiber samples, the strength of these samples remains unchanged at ≈4.1 GPa (600 kpsi) regardless of the polymer coating applied over the carbon or the environmental conditions of the aging test. This indicates that, in addition to the protection offered against fiber fatigue, the hermetic carbon layer serves as a barrier against the effects of aging.

As the fiber strength data show, the temperature of the aqueous environment will have an impact on both the degree of strength degradation and the variation of the sample data:

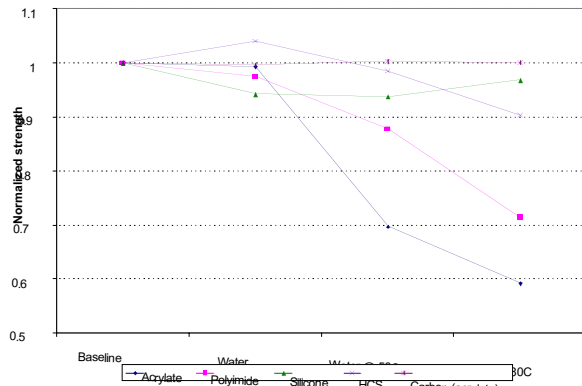


Fig. 6. Effect of water temperature on fiber strength after  $\approx 300$  days aging.

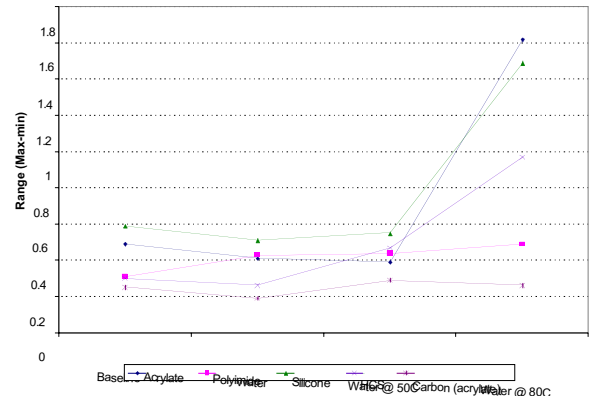


Fig. 7. Effect of water temperature on range after  $\approx 300$  days aging.

When the aging data for the most aggressive aging test ( $80^{\circ}\text{C}$  water) is plotted on a log-time chart, the aging “knee” becomes evident for the acrylate and polyimide fiber samples:

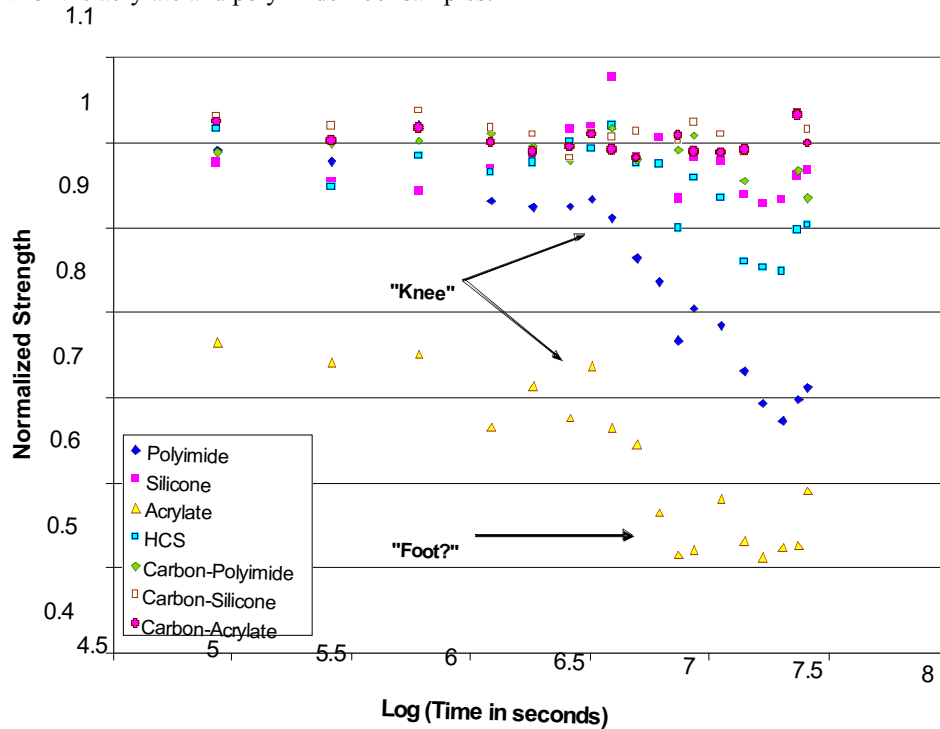


Fig. 8. Normalized fiber strength v. log time (seconds) for fibers soaked in  $80^{\circ}\text{C}$  water

The acrylate data also suggest that there may be a limit to strength degradation during zero-stress aging. After the sharp drop in strength at the “knee”, the acrylate fiber did not continue to lose strength for the final six months of soaking in  $80^{\circ}\text{C}$  water. This would suggest that aging follows the surface pit model<sup>13</sup> (a.k.a. “blunt pit model”<sup>14</sup>) where surface

flaws on the fiber are “blunted” with time even as the corrosive effect of water is roughening the glass surface. As a result, the fiber strength theoretically approaches some minimum between the effects of surface roughening and crack blunting. This would suggest that after the accelerated strength drop of the aging “knee” there is a flattened-out “foot” where no further degradation occurs. However, as figure 8 indicates, the aging behavior of a particular fiber – and the formation of a “knee” or “foot” – is dependent on the coating used over the glass fiber.

The characteristics of the coatings used in this study, such as water permeability and adhesion, clearly have a variable effect on the availability and activity of water at the glass-coating interface. The correlation between these coating parameters and the aging behavior of optical fibers is a topic for further research.

#### 4. CONCLUSIONS

Fiber samples with various protective coatings were drawn from a common preform under similar drawing conditions. The samples were then submerged in different aqueous environments under zero-stress aging conditions for approximately ten months and the following observations were made:

- An aging “knee” was observed for both the acrylate and polyimide fiber samples in the most aggressive aging environment of 80°C water. The aging behavior of the acrylate fiber sample suggests that after the accelerated strength degradation of the “knee”, there is a minimum strength after aging (a “foot”) caused by crack blunting and a reduction in the effect of water-induced corrosion.
- To the knowledge of the authors, this is the first aging study to use a common glass preform to directly compare the effect of different fiber coatings on aging behavior. However, additional research is required to directly compare the fiber coating characteristics (e.g. glass adhesion) to aging behavior.
- Strength degradation by aging can be minimized with a water-resistant coating like silicone, or eliminated with a hermetic coating like carbon.

#### ACKNOWLEDGEMENTS

The authors would like to thank Dawn Zak for compiling strength data and Richard Heinemann for setting up the test equipment.

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