Enhanced fatigue and aging resistance using reactive powders in the optical fiber buffer coating

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ABSTRACT

We have shown in previous work that the addition of small quantities of colloidal silica to the UV-curable polymer coating of fused silica optical fiber causes a dramatic improvement in the fatigue and aging resistance both in aqueous and in constant humidity environments. The presence of silica in the coating inhibits the mechanisms responsible for the surface roughening that causes the fatigue knee and strength degradation during zero-stress aging. This work presents results which show the effect of higher concentrations of the silica additive (6 wt%) and of an adhesion promoting agent on both the rheological properties of the polymer coating and the fatigue and zero-stress aging behavior of the fiber. Viscosity measurements show thixotropic behavior which indicates that the silica particles tend to form a network structure in the prepolymer. Filtration of the prepolymer to remove large particles is hampered by this phenomenon. The fiber coated with the silica-containing polymer exhibits substantial improvement in the long term mechanical reliability compared to a reference fiber without additive in the coating.

1. INTRODUCTION

The correlation between increasing surface roughness and strength degradation during zero-stress aging in harsh conditions has now been well established.[1-4] Matthewson[5] suggested that differential etching rates on the fiber surface are responsible for the development of roughness, which then acts as a source of strength degrading defects; suppression (or, at least, partial inhibition) of surface dissolution has therefore a beneficial effect on fiber reliability.

Previous work showed that the addition of colloidal silica particles in the polymer coating dramatically improves the fatigue and aging behavior of fused silica optical fiber.[6-9] The effect on long term reliability of two concentrations has been studied and the results showed that the static fatigue lifetime of the fiber could be increased by a factor of 10 in humid air[6] by adding only 0.75 wt% of colloidal silica and by up to a factor of 400 in aqueous environment by adding 3 wt%.[7,9] The zero-stress aging results also exhibited substantial improvements. The effect of different surface area of the particles was also studied. Analysis of the fiber surface using atomic force microscopy revealed that the presence of the additive slows down the roughening process which occurs during aging[6,8], and this, in turn, corresponds to a reduction of the strength loss.[3] A possible mechanism was described by which the colloidal silica particles incorporated in the coating dissolve preferentially due to their higher solubility and reactivity and so protect the fiber sacrificially.

The first fiber fabricated with the additive exhibited two undesirable properties due to the crudity of the preparation techniques: there was large scatter in the fatigue data, especially in the post-knee region, and the

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tensile strength showed a low strength mode. These problems were minimized or solved by improving the mixing procedure of the silica additive with the prepolymer, and by filtering the prepolymer. As an alternative to filtration, a dual coating with the additive only in the secondary buffer was found to be most effective.[7,9] However, several questions were still unanswered after the previous experiments:

– Can a higher concentration of silica be mixed with the prepolymer, and does this produce further improvement in the mechanical properties of the fiber?

– Can the filtration process of the prepolymer with the additive be extended to micron sized meshes, so that the large particles responsible for the occurrence of occasional weak defects in the single coated fiber are totally eliminated?

– Does the presence of organic additives, such as wetting agents, improve the dispersion of the silica in the coating? Does it affect the coating and the fiber properties? (Good adhesion, which can be promoted by wetting agents, can be beneficial to the fatigue behavior,[10,11] although excessive adhesion may adversely affect the strippability of the fiber).

– Does the silica additive in the coating affect the optical properties?

This work presents results which address the questions listed above.

2. EXPERIMENTAL

2.1 Single *vs.* dual coating

From the point of view of practical applications, dual coating appears to be the most promising way to implement the use of silica-loaded polymer coatings. It has been shown[7,9] that tensile strength degradation can be avoided by using a dual coating. With the primary coating acting as a mechanical buffer there is no tensile strength degradation, but the fiber with the additive still does exhibit the beneficial effects due to the silica addition. A similar consideration can be made concerning optical properties: any possible contribution to optical loss by the additive is eliminated by the presence of a primary buffer without any additive. However, one of the aims of this work was to study the effect of silica-filled coatings on the properties of a waveguide in the case in which any possible negative effect due to the silica additive is maximized. This is why a single coating was used.

2.2 Coating preparation and fiber drawing

Three coating formulations were prepared, based on a commercially available single coating (Desolite® 950-133): a reference without any additive (designated "W0"), a formulation with 6 wt% of Cab-O-Sil M5 (designated "W6"), and one with 6 wt% of M5 plus 1 wt% of wetting agent (designated "W6+"). It is noted that the prepolymer used in this work already contains wetting agent; therefore, the formulation W6+ shows the effect of *excess* wetting agent on the coating preparation and the fiber properties.

All the sets of fiber for the mechanical testing were drawn from the same preform with the same diameter of 125 μm. The overall outer diameter for the coated fibers was 212 μm. In addition, three lengths of multimode optical waveguide were drawn using the same coating formulations; the core and clad diameters were 105 and 125 μm, respectively. The optical fiber was used only for the optical measurements.

The prepolymer preparation and fiber drawing procedures were similar to those adopted during previous work.[6-9] In particular, in order to reduce the scatter previously observed in the fatigue data, resulting from the poor dispersion of the silica particles in the coating, all the formulations with additive were immersed in an ultrasound bath at about 40°C for ~1 day to improve dispersion and aid in bubble removal.[7,9] After mixing the

additive, the W6 and W6+ prepolymers were subjected to viscosity measurements using a Couette concentric cylinder viscometer.

2.3 Filtration

The prepolymer with 6 wt% of additive (especially the formulation with the excess wetting agent W6+) required a longer preparation time than the formulations with lower amounts of additive, probably due to higher viscosity which slowed down the removal of the bubbles generated during mixing. One of the purposes of this work was to verify the possibility of filtering the coating with the additive through a narrow membrane (1 or 2 μm) in order to remove the impurity particles responsible for the weak defects observed in uniaxial tension. However, this was impossible because a gelatinous material which had formed in the prepolymer (presumably silica), clogged the filter membrane. This was particularly true for the W6+. The prepolymers with the additive were therefore filtered through a 20 μm membrane, similar to the "M5F" formulation described in previous work.[7,9]

2.4 Mechanical testing

The initial strength and the strength distribution of the fibers were measured in uniaxial tension. 20 specimens for each type of fiber were tested at room temperature in air with a crosshead speed of 500 $\mu m.s^{-1}$ corresponding to a constant stress rate of ~120 $MPa.s^{-1}$. The specimen gauge length was 300 mm, and the relative humidity was about 82%.

The static fatigue behavior was studied using the two-point bending technique.[12] 30 specimens were bent inside precision bore glass tubes for the three types of fiber at each applied stress; the breaks were detected acoustically. The testing environment was pH 7 buffer solution at 90°C.

The residual strength after zero-stress aging in pH 7 buffer solution at 90°C was measured using two-point bending[13] at room temperature at a constant stress rate of 60 $MPa.s^{-1}$. The data have been corrected to take into account small fluctuations in the ambient temperature.[14] The aging times were 0, 2, 4, 8, 24, 51, 96 and 245 hours. In the case of unaged fiber, the samples were soaked for about 48 hours in the test environment at room temperature in order to equilibrate the local environment at the fiber surface.[14] pH 7 buffer solution was used as the testing environment in order to maintain a chemically stable and reproducible environment.

3. RESULTS AND DISCUSSION

3.1 Viscosity measurements

Fig. 1 shows the results of viscosity measurements performed on the W6 prepolymer (similar behavior was observed for W6+ prepolymer). Two cycles with shear rate increasing up to 100 s^{-1} and then decreasing to 1 s^{-1} were performed, with a time interval of 1 hour between them. The W6 prepolymer exhibits thixotropic behavior in the first cycle ("Cycle I" in Fig. 1); the viscosity decreases with shear rate, indicating that structure in the prepolymer, probably chains of silica particles, have formed, but break down at high shear. Substantial hysteresis is observed for decreasing shear rates indicating that the structure does not reform on the time scale of the experiment. After 1 hour ("Cycle II" in Fig. 1), the prepolymer shows a slightly dilatant behavior with little

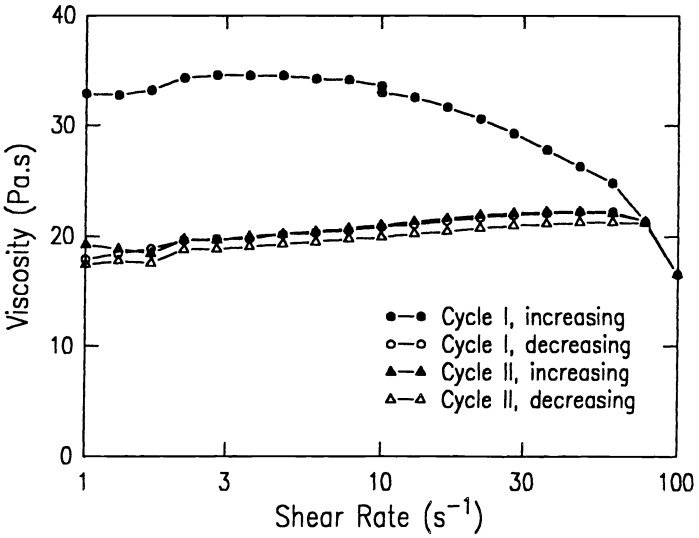

Fig. 1 Viscosity measurements on W6 prepolymer.

hysteresis, indicating that the structure does not reform on the time scale of one hour. This behavior is in marked contrast with that of the W0 prepolymer, which behaves as a slightly pseudoplastic, nearly Newtonian fluid (*i.e.* slight shear thinning but without hysteresis).

3.2 Tensile strength

Fig. 2 shows a Weibull plot of the tensile strength data for the W0, W6, and W6+ fiber. The W0 fiber exhibits unimodal behavior (although one weak specimen was observed for W0, such weak specimens are not representative of this fiber). The two fibers with the additive exhibit a well defined low strength mode, which, as previously suggested,[6-9] is due to the presence of weak defects on the fiber surface probably created by mechanical interaction between large impurity particles in the coating and the fiber surface. Foreign particles could easily contaminate the prepolymer during mixing of the silica additive, and filtration through a 20 μm membrane does not completely eliminate this source of defects. The mean value of the tensile strength is 4.22±0.32 GPa for W0, 4.13±0.26 GPa for W6, and 4.18±0.22 GPa for W6+ fibers. By eliminating the low strength mode specimens, the values are 4.38±0.02 GPa for W0, 4.44±0.02 GPa for W6, and 4.44±0.04 GPa for W6+, with corresponding values of the Weibull modulus of 121, 120 and 84. All the error bars represent a 95% confidence interval.

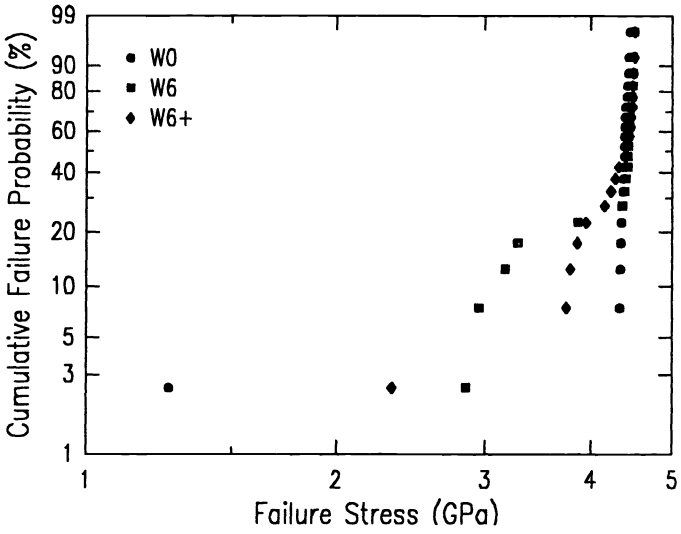

Fig. 2 Weibull probability plot for tensile strength data of W0, W6, and W6+ fibers.

3.3 Static fatigue

Fig. 3 shows the static fatigue behavior of the three types of fiber measured using two-point bending. The arrows represent experiments still running at the time of writing, namely two tubes of W6 fiber (at applied stresses of 1.88 and 1.70 GPa) and one of W6+ (at 1.70 GPa). Both types of formulation with the additive exhibit substantial improvements in the lifetime compared with the W0 fiber. As described before, the additives delay the onset of the fatigue knee, but do not affect the region before the knee. The maximum lifetime ratio observed between W6 and W0 fiber is (at the time of writing) more than 200 at an applied stress of 1.88 GPa. It is not possible at this time to estimate the final maximum lifetime ratio, because after approximately 2 months none of the specimens in each of the tubes at applied stress levels still in progress have broken. This is in marked contrast with the W0 fiber, which at the same applied stresses exhibits times of failure of ~ 10 *hours*. The improvement obtained for the W6+ fiber is less than for the W6 fiber; in fact, all the specimens of W6+ at 1.88 GPa

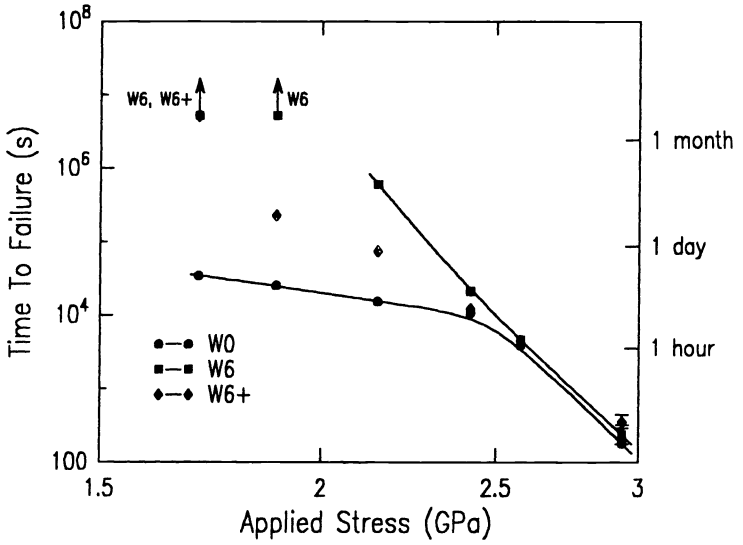

Fig. 3 Static fatigue in two-point bending of W0, W6, and W6+ fibers in pH 7 at 90°C.

broke after slightly more than 63 hours, while the W6 specimens are still surviving after 2 months without any failures. This indicates that the excess wetting agent reduces the efficacy of the additive.

3.4 Zero-stress aging

Fig. 4 shows the residual strength of the W0, W6, and W6+ fibers after zero-stress aging in pH 7 buffer solution at 90°C. Each point on the figure corresponds to the average of 10 specimens and the error bars represent a 95% confidence interval. In the case of unaged fiber, 20 specimens have been broken for each point. The unaged strength of the three fibers is statistically indistinguishable, but the W6 fiber exhibits higher residual strength for all the aging times. After 10 days, the W6 fiber has lost approximately 20% of the initial strength, while W0 and W6+ fibers have lost ~40%. It is noted that the residual strength of the W6+ fiber differs little from that of the W0 fiber.

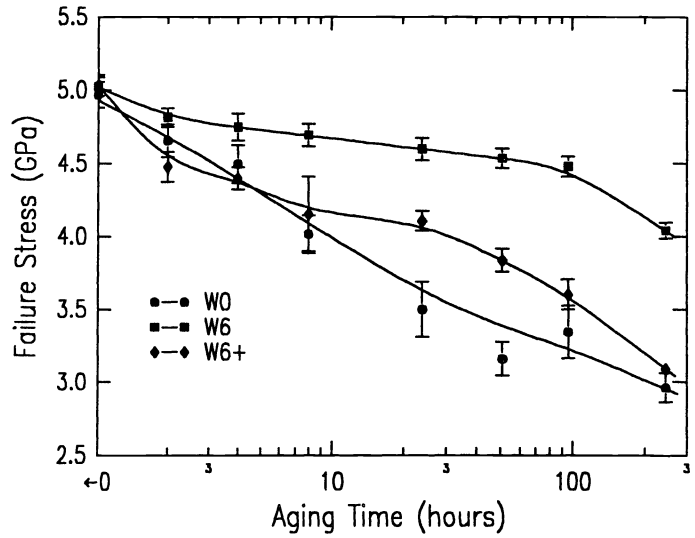

Fig. 4 Residual strength in two-point bending of W0, W6, and W6+ fibers after zero-stress aging in pH 7 at 90°C.

3.5 Optical measurements

Optical attenuation measurements were made between wavelengths of 800 to 1600 nm using the cutback method on various lengths. Fig. 5 shows typical results for measurements on 2 and 496 m for the W0, W6, and W6+ fibers. There is no significant difference between them, though, unfortunately, a lossy preform was used giving a minimum loss of ~ 10 db.km^{-1}. From the curves in Fig. 5 it can be noted that if the coating additives contribute to the loss it is no more than 1 db.km^{-1}. While this does not prove that optical loss is not a problem, it does show that there is no dramatic contribution to the loss. For telecommunication applications, the added loss in a single mode fiber should be much less than 0.01 db.km^{-1}. It should be emphasized that these are single coated fibers but with the additive in the secondary buffer no contribution is expected.

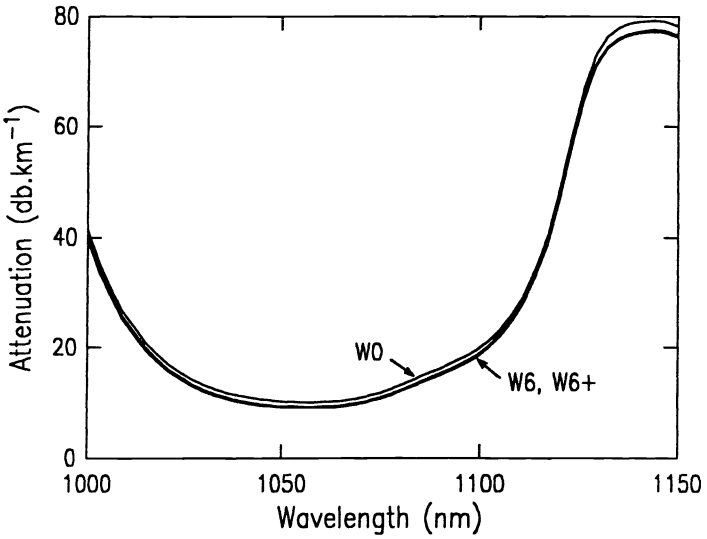

Fig. 5 Optical attenuation of W0, W6, and W6+ fibers measured using the cutback technique.

4. CONCLUSIONS

This work shows that it is possible to add 6 wt% to the polymer coating of fused silica optical fiber and obtain substantial improvements in the long term mechanical properties. We expect to observe further improvements in static fatigue behavior compared to previous results of specimens with lower concentrations, but at the time of writing some experiments are still in progress and therefore it is not possible to determine the final lifetime increase. A lifetime ratio of more that 200 times compared to the fiber without additive has been already obtained. Zero-stress aging experiments exhibited similar positive results. The zero-stress aging results (and, to a lesser extent, the static fatigue results) show that the presence of excess wetting agent in the coating

does not produce any further improvement than the silica additive alone; on the contrary, it appears to limit the beneficial effect due to the silica particles.

A concentration of silica of 6 wt% affects the rheology of the prepolymer. Viscosity measurements showed thixotropic behavior, which indicates the presence of a structure in the prepolymer (probably chain networks of silica). These chains break down by increasing the shear and do not reform on a time scale of 1 hour. A gelatinous material was directly observed while trying to filter the coating through a 2 μm sized membrane. The filtration through such a narrow membrane proved impossible but the prepolymer was successfully filtered through a 20 μm membrane. As previously found,[7,9] this does not entirely remove the large particles which cause the low strength mode observed in uniaxial tension; more work is necessary to solve this problem. Vigorous stirring before filtration and application of the coating onto the fiber should remedy these difficulties.

Preliminary optical measurements show that the presence of silica in the primary buffer does not increase the optical loss, but only to a resolution of ~1 db.km^{-1} (no losses are expected if the additive is put in a secondary buffer). Further measurements on low loss fiber are necessary in order to verify that the silica additive has a negligible contribution to the optical attenuation.

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. H. H. Yuce, R. S. Robinson and P. L. Key, "A Scanning Tunneling Microscope Study of Optical Fiber Corrosion," *OFC'90 Tech. Digest,* post deadline paper PD14, San Francisco, CA, (1990).
2. R. S. Robinson and H. H. Yuce, "Scanning tunneling microscopy study of optical fiber corrosion: surface roughness contribution to zero-stress aging" *J. Am. Ceram. Soc.*, **74** [4] 814-18.
3. H. H. Yuce, J. P. Varachi and P. L. Key, "Effect of stress free aging on mechanical characteristics of optical fibers," Ceramic Trans. **20** 191-203 (1991).
4. H. H. Yuce, J. P. Varachi Jr., J. P. Kilmer, C. R. Kurkjian and M. J. Matthewson, "Optical fiber corrosion: coating contribution to zero-stress aging" post deadline paper PD21, San Jose, CA, (1992).
5. M. J. Matthewson, "Optical fiber reliability models," *Proc. SPIE*, **CR50**, in press.
6. M. J. Matthewson, V. V. Rondinella and C. R. Kurkjian "The influence of solubility on the reliability of optical fiber", *Proc. SPIE,* **1791** 52-60 (1992).
7. M. J. Matthewson, H. H. Yuce, V. V. Rondinella, P. R. Foy and J. R. Hamblin "Effect of silica particles in the polymer coating on the fatigue and aging behavior of fused silica optical fiber" *OFC/IOOC '93 Tech. Digest* **4** postdeadline paper PD21, 87-90, OSA, Washington DC, (1993).
8. V. V. Rondinella, M. J. Matthewson and C. R. Kurkjian, "Coating additives for improved mechanical reliability of optical fiber," *J. Am. Ceram. Soc.*, in press.
9. V. V. Rondinella and M. J. Matthewson, "Effect of concentration and particle size on the fatigue of optical fiber with silica doped coatings", unpublished results.
10. T. S. Wei and B. J. Skutnik, "Effect of coating on fatigue behavior of optical fiber," *J. Non-Cryst. Solids,* **102** 100-105 (1988).
11. J. P. Clarkin, B. J. Skutnik and B. D. Munsey, "Enhanced strength and fatigue resistance of silica fibers with hard polymeric coatings," *J. Non-Cryst. Solids*, **102** 106-111 (1988).
12. M. J. Matthewson and C. R. Kurkjian, "Static fatigue of optical fibers in bending," *J. Am. Ceram. Soc.*, **70** [9] 662-668 (1987).
13. M. J. Matthewson, C. R. Kurkjian and S. T. Gulati, "Strength measurement of optical fibers by bending," *J. Am. Ceram. Soc.*, **69** [11] 815-821 (1986).
14. V. V. Rondinella and M. J. Matthewson, "Effect of loading mode and coating on dynamic fatigue of optical fiber in two-point bending," *J. Am. Ceram. Soc.*, **76** [1] 139-144 (1993).