Diffusion of Moisture Through Fatigue- and Aging-Resistant Polymer Coatings on Lightguide Fibers

Janet L. (Armstrong) Mrotek, M. John Matthewson, and Charles R. Kurkjian

***Abstract*—In previous work the diffusion rate of water vapor through the polymer coating on optical fiber was estimated by monitoring the strength as a function of time after suddenly changing the ambient humidity. This technique is used here to measure the diffusion of moisture both into and out of two novel fiber coatings. The first specimen is a dual-coated fiber with silica particles added to its secondary coating. It is shown that the improvement in this fiber's reliability is not due to the silica particles adsorbing/absorbing the moisture. The second fiber, coated with a fluorinated polymer, was designed to have higher fatigue resistance as a result of having a lower permeability to moisture. It is found that even though this fiber had higher than normal resistance to fatigue, the diffusion of moisture through this coating was not substantially different than through typical coatings used on fibers for telecommunications applications.**

***Index Terms*—Humidity diffusion, optical coatings, optical fiber reliability, stress measurement.**

I. Introduction

PREVIOUS work [1] described a method for determining the diffusion coefficient of moisture through polymer coatings on optical fibers by monitoring the strength of the fibers as a function of time after suddenly changing the ambient humidity. This is a novel way of sensing humidity and is feasible because the strength of the fiber is easily measured to high accuracy and is sensitive to the concentration of the moisture at the glass/polymer interface.

In this work, we use this technique to assess the importance of coating permeability to mechanical behavior. The technique has proved useful in probing and elucidating the mechanisms by which two different nonstandard coating materials impart improved mechanical performance.

Manuscript received October 25, 2002. This work was supported in part by Telcordia Technologies.

J. L. (Armstrong) Mrotek was with the Department of Ceramic and Materials Engineering, Rutgers University, Piscataway, NJ 08854. She is now with the Specialty Photonics Division, OFS, Somerset, NJ 08873 USA (e-mail: jmrotek@ofsoptics.com).

M. J. Matthewson is with the Department of Ceramic and Materials Engineering, Rutgers University, Piscataway, NJ 08854 USA (e-mail: mjohnm@fracture.rutgers.edu).

C. R. Kurkjian is with Department of Ceramic and Materials Engineering, Rutgers University, Piscataway, NJ 08854 USA, and also with the Materials Institute of Princeton University, Princeton, NJ 08544 USA (e-mail: ckurkjia@rci.rutgers.edu).

Digital Object Identifier 10.1109/JLT.2003.814930

A. Effect of Silica Particles in Coating

It has been shown that the addition of nano-sized silica particles to the coating has a beneficial effect on fiber reliability by greatly delaying the onset of the fatigue and aging "knees" [2]–[4]. The proposed mechanism for this effect is that the silica particles preferentially dissolve in the moisture present in the coating, thus reducing the rate at which the moisture corrodes the glass surface to give strength degrading roughness. Another possible mechanism is that the particles simply absorb the moisture in the coating, thus reducing the activity of water at the glass surface. Rondinella *et al.* [2], [3] argue that the quantity of silica in the coating is inadequate to explain the dramatic increase in lifetime and proposed that the mechanism involves preferential dissolution of the particles, which reduces the activity of the water at the fiber surface. If the silica particles retained significant amounts of water, the diffusion through the silica loaded coating would appear much slower. Here we measure the diffusion for two specimens identical except that one has 3 wt% silica particles incorporated in the secondary coating. The fiber with the 3 wt% silica particles in the coating has been shown to greatly delay the onset of strength degradation during zero stress aging and also to prolong the lifetime under a static stress by more than two orders of magnitude beyond the "fatigue knee" relative to a fiber with a standard coating [3].

B. Low Permeability and High n Coating

A sample of a fiber with a coating designed to have a lower permeability with the intent of yielding a higher value for the fatigue parameter n, was obtained from Alcatel. [5] The coating material incorporated fluorine either into the backbone or in a side chain of the polymer. Orcel *et al.* [5] reported the properties of this fiber sample including water permeability of 0.011 $\mathrm{g}\cdot\ \mathrm{cm}/\ \mathrm{m}^2\cdot 24\ \mathrm{h}\cdot\ \mathrm{mm\ Hg}$ and a static fatigue parameter of $n = 51$. In order to test their claim that the enhanced fatigue behavior results from lower permeability, we compare this fiber with a fiber with standard ultraviolet (UV)-acrylate coating. The diffusion of the moisture both into and out of these coatings was measured with the strength measurement technique discussed previously.

II. Experimental Procedures

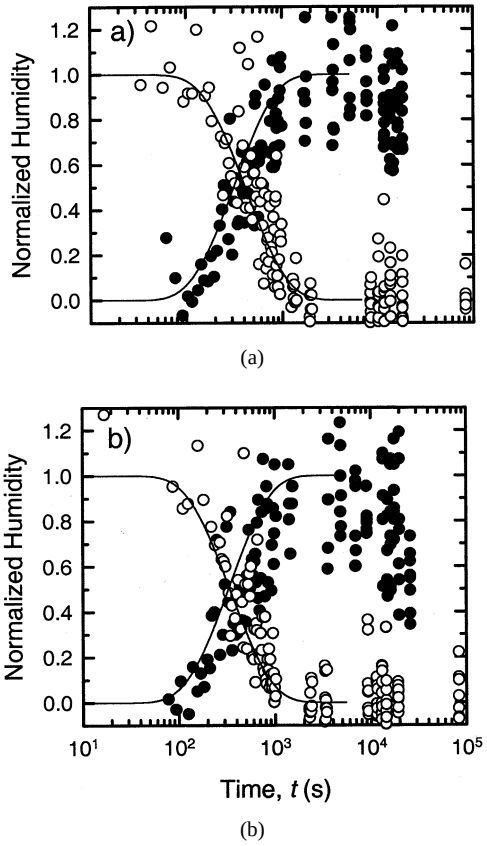
A two-point bend apparatus [6] was used to measure the strength of the fibers and was operated with a constant faceplate velocity of 5000 μm/s. The fiber was equilibrated overnight in a humidity chamber. It was then rapidly placed in a second chamber at a different humidity. Once the specimens were moved to the second chamber, the strength of the fibers was measured as a function of time until the equilibrium strength for the new environment was reached. The strength data were then converted to an equivalent humidity at the glass surface and the time evolution of the humidity was then fitted to the diffusion equation to determine the diffusion coefficient [1]. All the specimens examined here have dual polymer coatings. The strength measurement technique for determining diffusion coefficients cannot distinguish between the coating layers, but results in a composite value for both layers [7].

III. Results and Discussions

The equivalent humidity at the glass surface (normalized to the initial and final humidity *q.v.* [1]) versus time, for the specimen with 3 wt% of silica and its reference specimen, are shown in Fig. 1. The data were fitted to the cylindrically symmetric solution to the diffusion equation [1] and the resulting diffusion coefficients are shown in Table I. For both specimens (within the 95% confidence interval) the coefficients in either direction are the same. The silica powder does not act as a significant sink for water since the apparent diffusion coefficient is sensibly the same as for the control without powder. Also the diffusion profiles closely follow the shape for Fickian diffusion. As suggested in the earlier work, [2]–[4] this shows that the mechanism by which the silica particles delay the onset of fatigue and aging knees does not involve gettering of the water.

A possible explanation for the similarity between the diffusion coefficients for the two specimens is that the fibers have been exposed to ambient air for three years so that perhaps all the silica particles were already hydrolyzed and thus could no longer act as water getters compared with the freshly draw fiber. This is not the case since, as shown in Fig. 2, upon remeasuring the zero stress aging behavior, it was observed that the onset of the knee for the 3 wt% fiber was still further out in time. The more recent data appear stronger than the original data [8] because they were measured in two-point bending at a faster faceplate velocity than the original data. Even though the strengths were measured at difference faceplate velocities the trends in the strength with aging time are the same.

The results for the fluorinated-coated fiber are shown in Fig. 3. The diffusion coefficients are found to be, $D_{\text{wetting}} = (1.7 \pm 0.2) \times 10^{-12}$ m^2/s and $D_{\text{drying}} = (0.9 \pm 0.2) \times 10^{-12}$ m^2/s, which are significantly different from each other. This might imply that the chemical potential of water is not a linear function of concentration, but that the activity coefficient increases with concentration. Of more relevance here the diffusion coefficient for this coating is $\sim 1/2$ that of the control coating (Table I). Nonetheless, Fig. 3 shows that this coating can be equilibrated with ambient moisture on the time scale of hours, so it is hard to see how the coating



(a)

(b)

Fig. 1. Diffusion, in the range from 30–95% *RH* at 25 °C, into, i.e., wet (•) and out of, i.e., dry (◯) a dual-coated fiber with (a) 0 wt% silica and (b) 3 wt% silica added to the secondary coating.

TABLE I
Diffusion Coefficients

Type of Coating	D_{WETTING} (m^2/s)	D_{DRYING} (m^2/s)
Control UV-Acrylate	$(3.9 \pm 0.7) \times 10^{-12}$	$(2.9 \pm 0.3) \times 10^{-12}$
3 wt% silica in Secondary	$(3.7 \pm 1.0) \times 10^{-12}$	$(3.6 \pm 0.4) \times 10^{-12}$
Low Permeability and High n	$(1.7 \pm 0.2) \times 10^{-12}$	$(0.9 \pm 0.2) \times 10^{-12}$

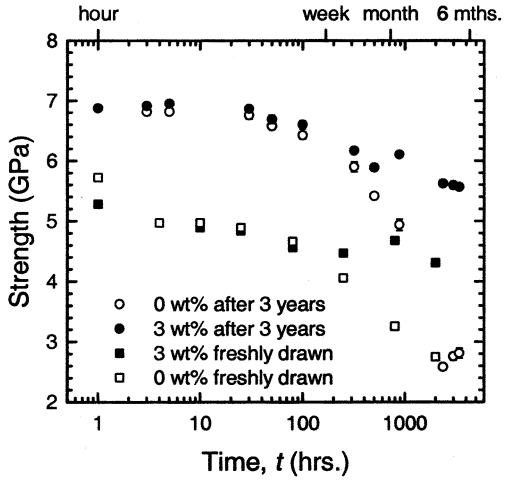


Fig. 2. Strength versus aging time in pH 7 buffer solution at 90 °C that was measured within a year after it was drawn (squares) [8] and after three years (circles).

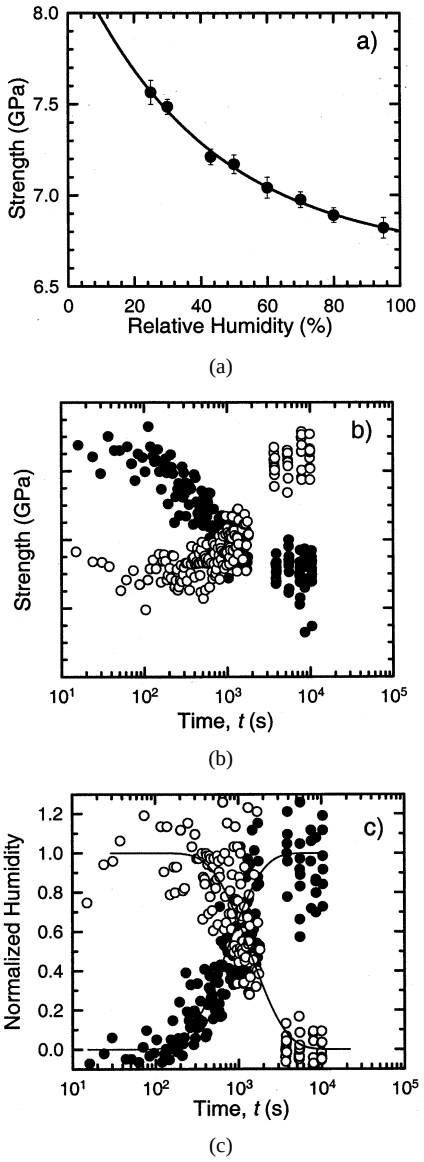


Fig. 3. "Low permeability" Alcatel fiber . (a) Strength as a function of relative humidity. (b) Strength as a function of time after changing humidity, where (•) is for wetting, i.e., going from 25% to 95% RH at 25 °C and (◯) is for drying, i.e., going from 95% to 25% RH at 25 °C. (c) Normalized humidity as a function of time.

permeability can affect strength or fatigue for a properly equilibrated specimen.

To confirm the claimed high value for n for this fiber [5], we have measured n in dynamic fatigue (Fig. 4) yielding a value of 30.3 ± 1.7. Though significantly lower then the static value reported $n = 51$ [5], this is still higher than the commonly found value of around 20. Fig. 4 also shows data for the same fiber after the removal of the coating using hot sulfuric acid ($\sim 200^{\circ}$C). These data yield a value of $n = 25.7 \pm 1.1$ verifying that the coating does indeed appear to increase n since n drops upon removal of the polymer. The reason for this is still not known, but it must be because this coating changes the chemical environment at the glass surface, e.g., by decreasing the pH locally. Our results do, however, suggest that it is ***not*** because of a reduced rate of water diffusion.

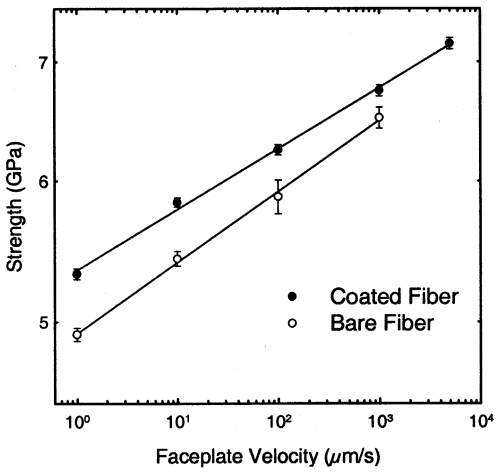


Fig. 4. Strength versus faceplate velocity at 50% relative humidity and 25 °C for the fluorinated coated fiber.

IV. Conclusion

We have used a technique based on strength measurements to estimate the *in situ* diffusion coefficient of moisture through optical fiber coatings. This technique was used to examine possible mechanisms by which two specific coatings improved mechanical performance. It was shown that the diffusion of moisture is not affected by a few weight percent of colloidal silica particles in the secondary coating on an optical fiber. This rules out a drying effect as the mechanism for the improvement of the fiber's reliability and is consistent with the earlier suggestions that the particles work by lowering the activity of the moisture at the fiber surface. The "low permeability" and high n fiber fabricated by Alcatel was found to have a higher n than most typical fibers, but diffusion coefficients were on the same order of magnitude as for a typical dual-coated fiber.

References

[1] J. L. Mrotek, M. J. Matthewson, and C. R. Kurkjian, "Diffusion of moisture through optical fiber coatings," *J. Lightwave Technol.*, vol. 19, pp. 988–993, July 2001.

[2] V. V. Rondinella, M. J. Matthewson, and C. R. Kurkjian, "Coating additives for improved mechanical reliability of optical fiber," *J. Am. Ceram. Soc.*, vol. 77, no. 1, pp. 73–80, 1994.

[3] V. V. Rondinella, M. J. Matthewson, P. R. Foy, S. R. Schmid, and V. Krongauz, "Enhanced fatigue and aging resistance using reactive powders in the optical fiber buffer coating," in *Proc. Soc. Photo-Opt. Instrum. Eng.*, vol. 2074, 1993, pp. 46–51.

[4] Y.-S. Shiue, M. J. Matthewson, P. R. Stupak, and M. J. O'Connor, "Coating additives for enhanced mechanical reliability of fused silica optical fibers: Effect on mechanical and optical performance," in *Proc. SPIE*, vol. 4215, 2000, pp. 129–133.

[5] G. Orcel, J. Y. Boniort, J. Y. Barraud, and R. J. Overton, "Hermetic and polymeric coatings for military and commercial applications," in *Int. Wire & Cable Symp. Proc.*, 1995, pp. 330–334.

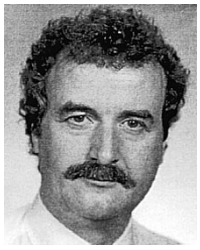
[6] M. J. Matthewson, C. R. Kurkjian, and S. T. Gulati, "Strength measurement of optical fibers by bending," *J. Am. Ceram. Soc.*, vol. 69, no. 11, pp. 815–821, 1986.

[7] J. L. Mrotek, M. J. Matthewson, and C. R. Kurkjian, "Modeling of diffusion through optical fiber coatings," in *Proc. Soc. Photo-Opt. Instrum. Eng.*, vol. 4215, 2000, pp. 144–149.

[8] D. J. Morgan, M. J. Matthewson, P. Stupak, and B. Bellerive, "Corrosion-resistant coatings on silica fibers," *Am. Ceram. Soc. Bull.*, vol. 73, no. 3, p. 245, Apr. 1996.

Janet L. (Armstrong) Mrotek received the B.S., M.S., and Ph.D. degrees in ceramic and materials engineering from Rutgers University, Piscataway, NJ, in 1995, 1997, and 1999, respectively. Her thesis work, which was done jointly at Telcordia (Bellcore), Morristown, NJ, and Rutgers University, consisted of investigating the mechanical reliability of optical materials.

She is currently a Member of the Technical Staff at the Specialty Photonics Division, OFS (formerly Lucent Technologies, SFD), Somerset, NJ.



M. John Matthewson received the B.A. degree in theoretical physics and the M.A. and Ph.D. degrees in physics from Cambridge University, Cambridge, U.K., in 1975 and 1978, respectively, for his work at the Cavendish Laboratory on contact mechanics and impact erosion.

He continued his work in this area concurrently as the Goldsmiths' Junior Research Fellow at Churchill College, Cambridge, U.K., and as a Science Research Council Postdoctoral Fellow until 1981. He then spent nearly three years in the Computer Laboratory of the University of Cambridge, advising on the use of personal computers in research. After two years at AT&T Bell Laboratories as a Postdoctoral Member of Technical Staff, he moved to the IBM Almaden Research Center, San Jose, CA, in 1986. He has been at Rutgers University, Piscataway, NJ, since 1989, where he is now Professor of Ceramic Science and Engineering. His research group is principally concerned with the strength, fatigue, and mechanical reliability of optical materials, as well as numerical modeling of materials processing. He has published more than 80 papers, most of them in these fields.

Charles R. Kurkjian retired from Bell Laboratories in 1994 after 35 years. During that time, he conducted research on glasses and glass lightguides. He spent the following five years at Telcordia Technologies (formerly Bellcore). He is now associated with the Department of Ceramics and Material Engineering at Rutgers University, Piscataway, NJ, and the Materials Institute at Princeton University, Princeton, NJ.