

Diffusion of Moisture Through Optical Fiber Coatings

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Abstract—The strength of polymer-coated fused silica optical fiber is dependent on the ambient moisture because of stress corrosion. The diffusion rate of water vapor through the polymer coating can be estimated by monitoring the strength as a function of time after suddenly changing the ambient humidity. Not only is this technique a new way of sensing humidity, but it also allows estimation of the time needed for the coated fiber to equilibrate with its environment. A comparison has been made between the diffusion coefficients measured in this way and by monitoring the weight of free-standing polymer films as a function of time. Fickian diffusion has been assumed and is justified by the good agreement between the experiment and theory. The diffusion of water vapor both into and out of various polymers was investigated.

Index Terms—Coatings, diffusion equations, humidity measurements, reliability, stress measurement.

I. INTRODUCTION

THE STRENGTH of fused silica optical fiber depends on the activity of water at its surface due to the stress corrosion effect. Polymer coatings are always applied to optical fibers to protect them from mechanical damage during handling. Such coatings also act as a diffusion barrier to moisture reaching the glass surface from the surrounding environment. In addition to its mechanical protection role, it has been suggested that the coating's ability to reduce water transport might enhance the fiber's lifetime [1].

Moisture diffusivity in the coating has important practical implications. When modeling the lifetime of optical fibers based on proof testing, it is usually assumed that the service environment is the same as the proof test environment. Griffioen [2] points out that this will produce longer lifetime estimates if the proof test environment is less aggressive (colder and drier) than the service environment. Further, when a fiber is drawn, it experiences a dry environment characteristic of the draw furnace and takes some time to equilibrate with the ambient humidity [2]. Therefore, it is advisable to wait some time after drawing before proof testing to avoid the lifetime modeling being too optimistic. How long the wait needs to be is controlled by the diffusion coefficient of the moisture in the coating.

An approach for the determination of the diffusion coefficient of moisture through polymer coatings has been developed that involves monitoring the strength of fibers as a function of time after changing the ambient humidity [3], [4]. This is a novel way of sensing humidity and is feasible because the strength

of the fiber is sensitive to the concentration of the moisture at the glass/polymer interface. This dependence can be empirically described as follows [4]:

$$\sigma = A + Be^{-cH} \quad (1)$$

where

σ fiber's strength;
 H relative humidity;
 $A, B,$ and C fit parameters.

Besides measuring the diffusion coefficients, this technique also determines the equilibration time needed for the test environment to reach a steady state at the glass/polymer interface. Previous work, in which the diffusion coefficient of moisture was monitored in a similar way, was published by Bouten [5]. He monitored the strength of the fiber as a function of relative humidity in two ranges—60% to 100% relative humidity and from 42% to a vacuum of 10^{-4} Pa—and found that the diffusion coefficients determined from these two experiments were not the same. An explanation for this might be that his drying range extended past 20% RH, which is where a discontinuity in the strength versus humidity behavior was found by Duncan *et al.* [6]. Therefore, this drying experiment might be spanning two different kinetic regimes.

The diffusion coefficient or permeability (the diffusion coefficient multiplied by the solubility of the diffusant) of polymers is usually measured using flat films. Because the geometry of the film is easier to model than the cylindrical shape of the fiber coating, film samples are more convenient to work with. On the other hand, the curing conditions for the polymer when coated on the fiber in-line and when cast as a freestanding film are different and may result in different permeability or diffusion rates. Some of the numerous techniques for determining diffusion coefficients in polymer films are weight change, use of chemical labels that are detected optically, mass labels detected by Rutherford backscattering, Raman section probe, rotating-polarizer ellipsometer, birefringence, ultraviolet (UV) absorption, and optical density of thin layers [7]. Another more recent technique [7], [8] is to use infrared evanescent fields to determine the concentration of the diffusing species. This technique is feasible as long as the optical intensity is known as a function of the concentration of diffusant. A more detailed discussion on some of the measurement techniques can be found in books by Crank [9] and Vieth [10].

A. Diffusion Models

Diffusion coefficients in polymer films can be measured by simply recording the weight of the film as a function of time after the environmental conditions are suddenly changed. The

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accumulated mass of the diffusing species at time t , M_t , is given by [11]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right) \quad (2)$$

where

- M_∞ mass that has entered after infinite time;
- D diffusion coefficient;
- $2l$ thickness of the film [see Fig. 1(a)].

To calculate the diffusion coefficient of moisture for the coated fiber, cylindrical symmetry must be used. In this work, the boundary conditions for this geometry were assumed to be that the outside concentration is a constant, $C(r = b, t) = C_1$, and that the glass/polymer interface is impermeable, $\partial C(r = a, t)/\partial r = 0$. The solution corresponding to these boundary conditions for the diffusion equation in cylindrical symmetry is [11]

$$1 - \frac{C(r, t)}{C_1} = \pi \sum_{n=1}^{\infty} \exp(-D\alpha_n^2 t) J_1(a\alpha_n) J_0(b\alpha_n) \times \left(\frac{Y_0(r\alpha_n) J_1(a\alpha_n) - J_0(r\alpha_n) Y_1(a\alpha_n)}{J_0(b\alpha_n)^2 - J_1(a\alpha_n)^2} \right) \quad (3)$$

where

- $C(r, t)$ concentration at a distance r from the center of the fiber at a time t ;
- D diffusion coefficient;
- a glass fiber radius;
- b coating outer radius [Fig. 1(b)];
- J_i and Y_i Bessel functions of order i , which may be approximated by polynomials as given by Abramowitz and Stegun [12];
- α_n n th positive root of

$$J_1(a\alpha) Y_0(b\alpha) - J_0(b\alpha) Y_1(a\alpha) = 0. \quad (4)$$

To obtain a diffusion coefficient, the concentration at the polymer/glass interface, $C(r = a, t) = C_0$, has to be known as a function of time. A simple way of measuring this concentration is to determine the strength of the fiber. Because the strength of the fiber depends on the activity (assumed proportional to concentration) of the moisture or water vapor present at the interface, as described by (1), the effective concentration of water vapor can be obtained from these results.

B. Types of Diffusion Behavior

The above model is based on the assumption that Fickian diffusion is taking place, i.e., D is a constant independent of concentration. Polymers show variability in their permeability and diffusion rates for different diffusing species. This is because the diffusion behavior is very sensitive to the diffusant and the temperature. Some polymers will tend to absorb the diffusing

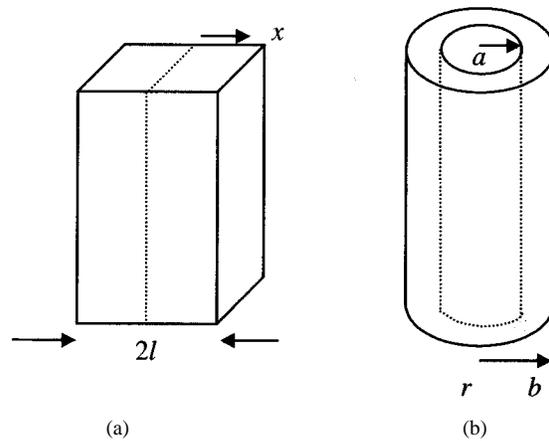


Fig. 1. The geometry for (a) polymer film and (b) coated fiber.

species and form clusters within their structure, in which case the behavior of diffusion in and out of the polymer will not be the same [8].

Schlottner and Furlan [8] classified diffusion in polymers into three cases. The first, case I, is Fickian diffusion, which assumes that there are no changes in the polymer structure as a result of interactions with the diffusing species. This type of diffusion, which is based on the random walk with no interaction theory, occurs when the diffusion rate is slower than the polymer relaxation rate. Therefore, by the time the diffusion process is over, the polymer structure is no longer changing and does not react or interact further with the diffusant. This is the type of diffusion that is assumed in this paper. The second, case II, is based on strong interactions between the polymer and the diffusant. In this case, the diffusion is occurring so fast that there is no time for the polymer to relax. Because the polymer is still changing at the end of the diffusion process, there appear to be interactions occurring. In this type of diffusion, sharp boundaries appear between the polymer and the diffusing species. The third, case III, occurs when diffusion rates and relaxation rates occur on the same time scale. This type of diffusion is called non-Fickian or anomalous diffusion. One purpose of the work presented in this paper is to determine whether diffusion of moisture in typical optical fiber coatings is Fickian.

II. EXPERIMENTAL PROCEDURES

A. Films

The gravimetric method was used to measure the diffusion of moisture into and out of freestanding polymer films. Films with $\sim 80 \mu\text{m}$ (acrylate) and $\sim 140 \mu\text{m}$ (polyimide) thickness and $\sim 3 \text{ cm}^2$ surface area were suspended vertically from a balance arm. The weight ($\pm 10 \mu\text{g}$) of the films was monitored as a function of time with a computer-controlled balance.¹ Two humidity chambers were used in order to measure the diffusion of water moisture into or out of the films. The balance was placed inside one of the humidity chambers that was controlled to either 20 or $95 \pm 1\%$ relative humidity at a constant temperature of $25 \pm 0.1 \text{ }^\circ\text{C}$. The films were placed in another humidity chamber maintained at 95 or $20 \pm 1\%$, at a constant temperature

¹Sartorius Research, Germany.

of 25 ± 0.1 °C. If the chamber containing the balance was controlled to 95% humidity, then the chamber with the films was controlled to 20% and vice versa. The films were left overnight in this chamber and then moved to the humidity chamber containing the balance. The weight of the film was then measured as a function of time until an equilibrium weight was achieved.

To measure diffusion of water vapor into the films, i.e., “wetting,” one humidity chamber was set to 20% relative humidity and the other chamber containing the balance was set to 95%. The reverse humidity settings were utilized to measure diffusion of water vapor out of the films, i.e., “drying.” Although most optical fibers are coated with UV-curable acrylate polymers, there are some fibers that are coated with polyimide or silicone rubbers for specialty applications. Films of typical compositions of all three types of polymers were studied.

B. Fibers

A two-point bend apparatus [13] was used to measure the strength of the fiber and was operated with a constant faceplate velocity of $5000 \mu\text{m/s}$. These experiments were conducted in the same manner as the weight change experiments; namely, the fiber was equilibrated overnight in one humidity chamber before being broken after being rapidly placed in a second. Once the specimens were moved to the second chamber, the strength was measured until the equilibrium strength for the new environment was reached. This produced the strength of the fiber as a function of time in the test environment. To obtain diffusion coefficients, the strength was converted to an equivalent concentration or humidity at the glass surface. To make this conversion, a separate experiment was performed in which the equilibrated strength of the fibers at different humidity values in the range of 20–95% was measured. Twenty samples were broken at each humidity. By fitting (1) to those data, values for the fit parameters A , B , and C were found. By using this relationship [(1) with constant values], the strength measured in the diffusion experiments was converted to an equivalent humidity.

The fiber specimens investigated here were coated with one of the following: a single layer of UV-acrylate ($125 \mu\text{m}$ glass diameter and $250 \mu\text{m}$ overall diameter), a polyimide ($220 \mu\text{m}$ glass diameter and $245 \mu\text{m}$ overall diameter), and a silicone ($140 \mu\text{m}$ glass diameter and $261.5 \mu\text{m}$ overall diameter). While these polymers were not identical to the free-standing film specimens, they were of similar compositions.

III. RESULTS AND DISCUSSIONS

A. Film Study

The results of the weight change experiments for the acrylate and polyimide freestanding films are shown in Fig. 2. For clarity, the normalized weight change is shown

$$W_n = \frac{W_t - W_{\text{dry}}}{W_{\text{wet}} - W_{\text{dry}}} = \frac{M_t}{M_\infty} \quad (5)$$

where

- W_t weight of the film at time t ;
- W_{dry} equilibrated weight in the drier environment (20%);
- W_{wet} equilibrated weight in the wetter environment (95%).

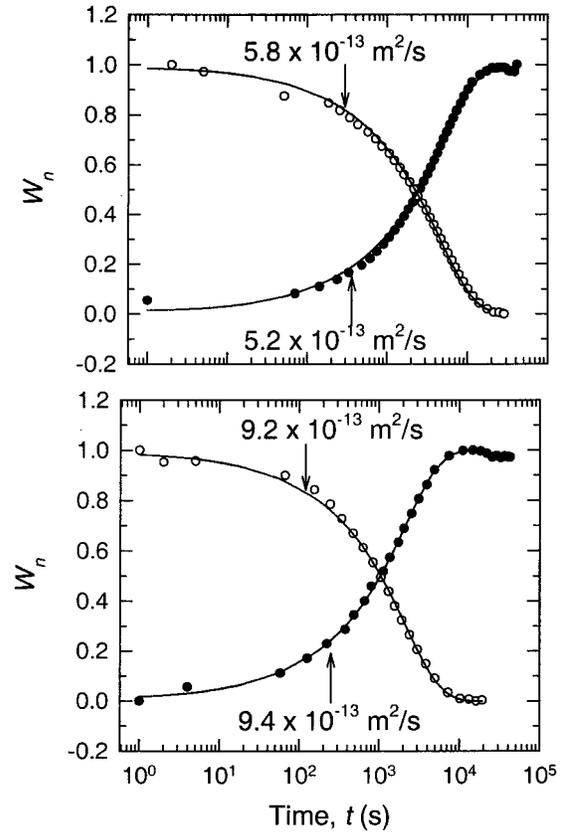


Fig. 2. Normalized film weight as a function of time after suddenly changing the ambient humidity for the diffusion of moisture into (\bullet) and out of (\circ) (a) acrylate film and (b) polyimide film. Solid lines are fits to the diffusion equation (3), and legends show the value of the diffusion coefficient determined by the fits.

The diffusion coefficients were found by fitting the data to (2). The diffusion coefficients of water in the acrylate film were found to be $D = (5.2 \pm 0.1) \times 10^{-13} \text{ m}^2/\text{s}$ for diffusion in or “wetting” and $D = (5.8 \pm 0.1) \times 10^{-13} \text{ m}^2/\text{s}$ for diffusion out, or “drying.” The small but statistically significant difference between these values indicates a slight deviation from Fickian behavior. The errors represent a 95% confidence interval. Values of $(9.4 \pm 0.4) \times 10^{-13} \text{ m}^2/\text{s}$ for wetting and $(9.2 \pm 0.3) \times 10^{-13} \text{ m}^2/\text{s}$ for drying were found for the polyimide film; this behavior appears Fickian. Ogawa and Nagata [14] obtained a similar diffusion coefficient of $2 \times 10^{-13} \text{ m}^2/\text{s}$ for water in a polyimide film using a weighting technique that utilized thermogravimetric analysis.

Gravimetric measurements on the silicone film could not be made for two reasons. First, the film was too weak to be hung on the balance, and second, the diffusion into the film occurred too fast to be measured. As a result, the diffusion coefficients for this silicone film could not be obtained and are not shown here.

B. Strength Measurement Results

Fig. 3 shows the raw data for strength as a function of time after changing the ambient environment for the acrylate, polyimide, and silicone-coated fibers. As stated earlier, the diffusion coefficients cannot be directly obtained from strength data since

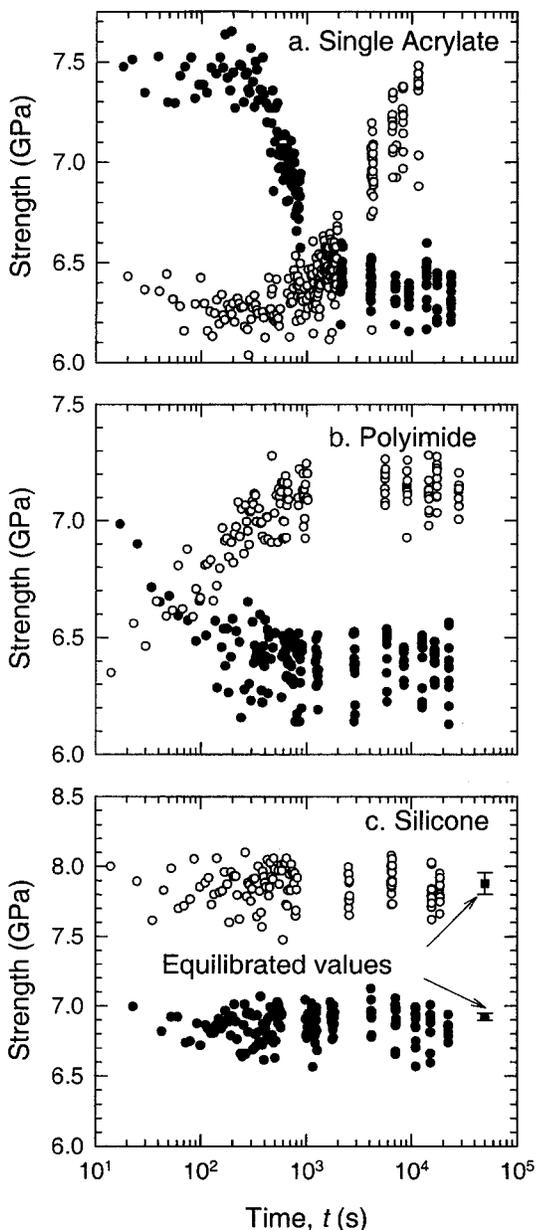


Fig. 3. Strength as a function of time after suddenly changing the ambient humidity for the diffusion of moisture into (●) and out of (○) single-acrylate-coated fibers, polyimide-coated fibers, and silicone-coated fibers.

strength is a nonlinear function of humidity. The strength must first be converted to the corresponding effective humidity at the glass/polymer interface. This conversion was performed by fitting the equilibrated strengths at various humidities to (1), as shown in Fig. 4. This equation was then used to map the results in Fig. 3 into effective humidity at the fiber surface, i.e., the value of the ambient humidity that gives the same *equilibrated* strength. For easier analysis of the data, the normalized effective humidity H_n is calculated

$$H_n = \frac{H_t - H_{low}}{H_{high} - H_{low}} \quad (6)$$

where

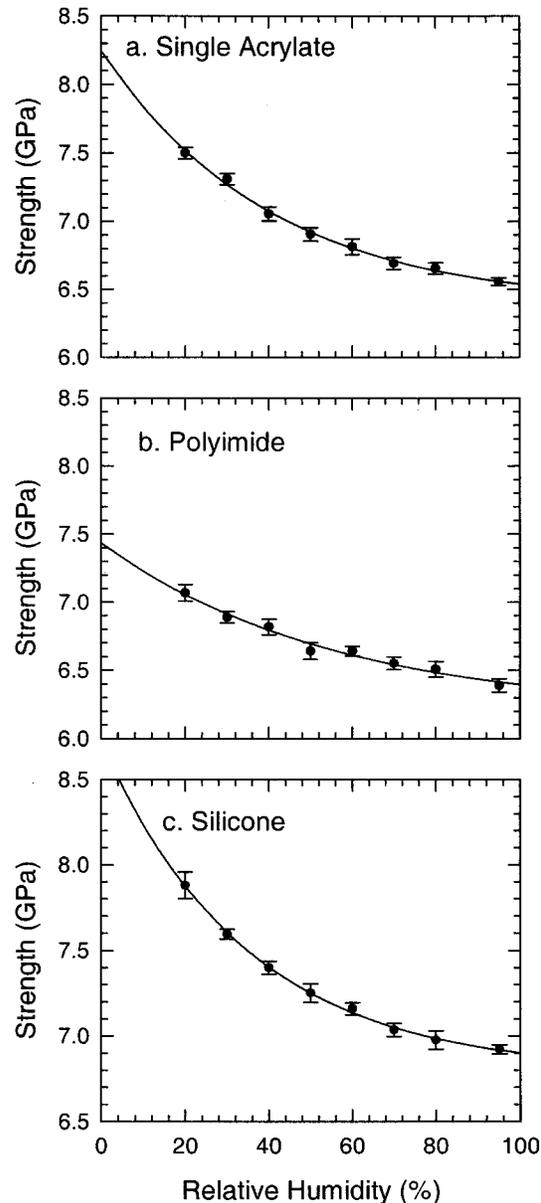


Fig. 4. The equilibrium strength (at 25 °C) as a function of humidity. Solid lines are fits to (1).

- H_t effective relative humidity at time t ;
- H_{low} lowest relative humidity (20%);
- H_{high} highest relative humidity (95%).

The results for the effective relative humidity are shown in Fig. 5 together with the fits of (3) to the data and the calculated diffusion coefficients. The diffusion coefficients are for the acrylate $6.6 \pm 0.6 \times 10^{-13} \text{ m}^2/\text{s}$ (drying) and $9.2 \pm 1.0 \times 10^{-13} \text{ m}^2/\text{s}$ (wetting) and for the polyimide $8 \pm 4 \times 10^{-13} \text{ m}^2/\text{s}$ (drying) and $12 \pm 4 \times 10^{-13} \text{ m}^2/\text{s}$ (wetting).

In the silicone coating [Fig. 3(c)], the diffusion occurred in less time than it took to make the first strength measurement (~ 10 s). Based on this information, the actual diffusion coefficient cannot be measured, but a lower limit can be placed on it, which is $D \geq 10^{-11} \text{ m}^2/\text{s}$. This value was calculated assuming that the diffusion process took 10 s to be completed. Crank and

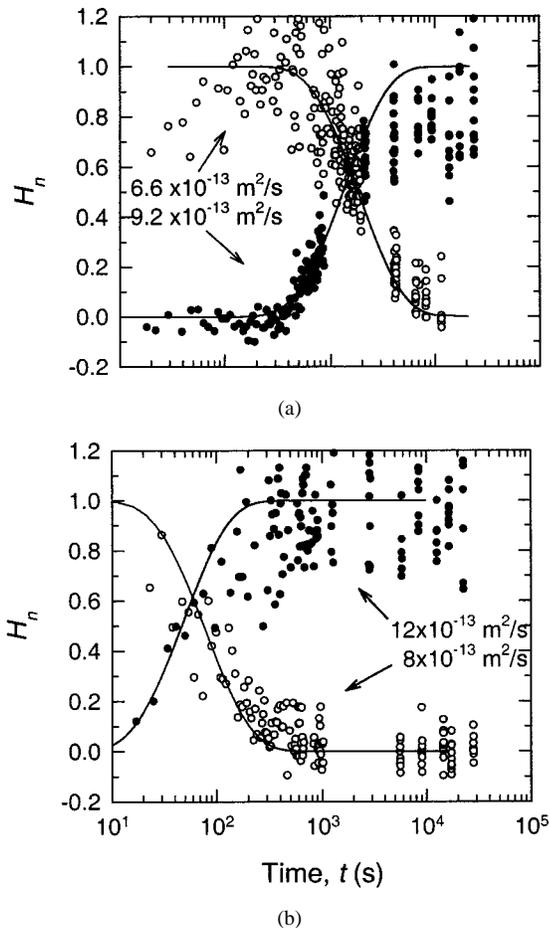


Fig. 5. Normalized effective humidity at the glass surface H_n as a function of time after suddenly changing the ambient humidity. Results are the diffusion into (\bullet) and out of (\circ) (a) acrylate-coated fiber and (b) polyimide-coated fiber.

Park [9] reported a moisture diffusion coefficient of 7×10^{-9} m^2/s , which is indeed greater than 10^{-11} m^2/s [9].

Similar values for the diffusion coefficients were found both when weighing the freestanding films (Fig. 2) and from the strength measurement technique (Fig. 5). The diffusion coefficient was found to be slightly higher in the polyimide than the acrylate for both techniques. This validates the strength measurement technique. It should be noted again that this technique determines the *in situ* diffusion coefficient for the real coating, rather than for a model sheet specimen. However, the diffusion coefficient is not measured as accurately with this technique because of the inherent variability in the strength; it is harder to measure small changes in strength than small changes in weight. This is aggravated by only having a limited experimental time before the half-life of the diffusion process is reached (where the normalized effective humidity is 0.5). As a result, the standard error in the estimates of the diffusion coefficients made here is approximately three times higher than for the gravimetric technique. Fig. 5(b) illustrates a limitation in the strength measurement technique. Since the polyimide is so thin (12.5 μm), the diffusion does not allow enough time to make many measurements before the half-life. As a result, the half-life is not well defined and fitting to the data produced large error estimates. The stress measurement technique is therefore not accurate for a diffusion half-life below about 50 s.

Another result shown in Fig. 5(a) is that the diffusion into and out of the acrylate coating is slightly asymmetrical with diffusion of moisture out of the polymer apparently occurring slightly slower. This slight deviation from Fickian behavior implies that the water vapor may be interacting with the polymer. A slight asymmetry was also observed in the planar films [Fig. 2(a)], but the sense is reversed. It is therefore not clear whether this asymmetry is significant. The polyimide films [Fig. 2(b)] appear to be symmetrical, but because of the large error found in Fig. 5(b) for the strength technique, no conclusions can be drawn on this matter. The assumption of Fickian diffusion is valid for this work, since the diffusion equation used here, which assumes Fickian diffusion, fit the data rather well.

Orcel *et al.* [1] have found correlation between the strength degradation observed in fused silica optical fibers exposed to aggressive environments and the permeability of the coatings. They therefore suggest that coating permeability is a controlling factor in the degradation. However, in this work, it is shown that moisture penetrates the coating within 10^1 to 10^3 s. This is rapid compared to the service life of an optical fiber, which is typically $\sim 10^9$ s (25 y). It is therefore unlikely that permeability of moisture is a controlling factor, though the permeability of other species might be [15].

IV. CONCLUSION

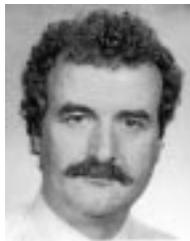
Diffusion coefficients for water in polymer coatings on optical fiber can be measured by monitoring the strength of the fibers as a function of time after the ambient humidity is suddenly changed. This technique gives diffusion coefficients that are comparable to those obtained with the more commonly used film weighing technique. It is, however, more meaningful to optical fiber strength and reliability because it is an *in situ* measurement that does not rely on the assumption that the film used in the gravimetric technique has the same cure conditions (and hence has the same properties) as the actual coating. However, the precision with which the diffusion coefficient can be determined is somewhat lower and is limited to coatings with a diffusion half-life greater than ~ 50 s.

For all of the coatings studied here, moisture penetrates on a time scale of $\sim 10^2$ to 10^3 s. It is therefore unlikely that the diffusivity of water in the coating is a controlling factor in how the coating influences the fiber reliability on the time scale of $\sim 10^9$ s (~ 25 y).

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