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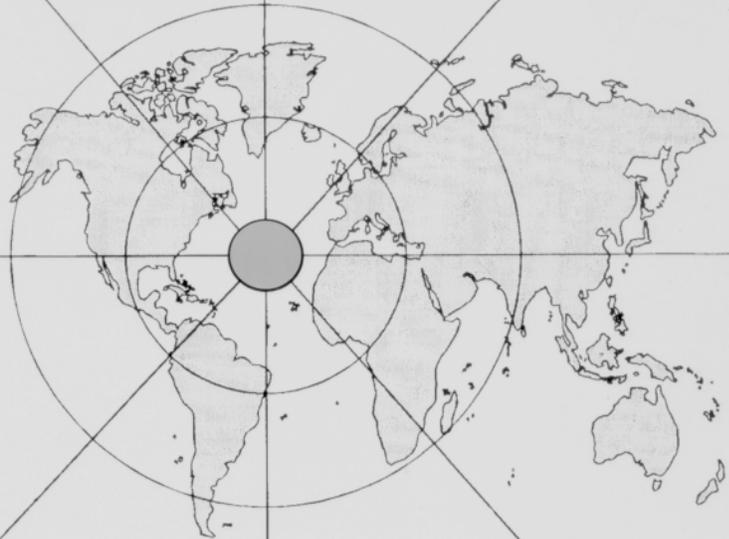
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J. L. Armstrong, M. J. Matthewson and C. R. Kurkjian

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Janet L. Armstrong,[1] M. John Matthewson,[1] Charles R. Kurkjian [2]

[1] Rutgers University, Piscataway, New Jersey
[2] Bell Communications Research, Morristown, New Jersey

ABSTRACT

A new technique for measuring the diffusion coefficients of water vapor through optical fiber polymer coatings has been developed which uses the relationship between the fiber strength and the water concentration at the glass surface. This technique is verified by comparison with standard weight gain/loss measurements performed on freestanding polymer films. A detailed analysis using an axisymmetric solution of the diffusion equation has been applied to the coated fiber geometry. A much simpler solution for a planar sheet was also used which gives similar results for the fiber, but is only an accurate analysis for the flat polymer films. In all of these cases 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 the polymers was investigated, and a slight difference in the behavior was observed for one coating.

INTRODUCTION

Since, the strength of polymer coated fibers depends on the water activity at the polymer/glass interface, the requirements for today's coatings is not only to provide mechanical protection, but also supposedly to prevent moisture from penetrating the coatings. It is believed that the coated fiber's lifetime will increase if water transport can be slowed. Studies are usually conducted on polymer films in order to determine the permeability or diffusion coefficients of water in the polymer coatings. This is a convenient and simple way of making these measurements, but the curing conditions for the polymer when coated on the fiber and when cast as a freestanding film are different and may result in a different permeability.

A different approach to determining the diffusion coefficient for the polymer coatings is to monitor the strength of the fibers as a function of time after changing the ambient humidity in the test environment.[1] This is a novel way of sensing humidity because the strength of the fiber is dependent on the concentration of the moisture at the glass/coating interface. This technique not only measures diffusion coefficients, but also determines the equilibration time needed for the test environment to fully reach the glass/polymer interface. There are some published data of this sort by Bouten,[2] and Kurkjian *et al.*.[1] Bouten measured the strength as the fiber equilibrated on moving from 60 to 100% relative humidity and drying from 42% to a vacuum of 10^{-4} Pa. He found the diffusion coefficients for those two experiments were not the same, but his drying range extended past the observed discontinuity in the strength *versus* humidity behavior reported by Duncan *et al.*.[3] Therefore, his drying experiment might be spanning two different kinetic regimes.

As mentioned earlier, most of the work performed in this field has been on polymer film samples. There are numerous techniques for determining diffusion coefficients in polymer films; one of the most popular and simplest ways is to measure the film's weight change as a function of time after it has been immersed in a particular environment.[4] Another technique[5,6] 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 concentration of diffusant.

Figure 1 shows the two geometries that are investigated here. For the case of a planar film of thickness $2l$, the time dependent solution to the diffusion equation, where both surface concentrations are constant, $C(|x| = l, t) = C_1$, and the initial concentration distribution within the film, $C(|x| < l, t = 0) = C_2$, is uniform, the concentration profile is given by:[7]

$$\left(\frac{C(x,t) - C_2}{C_1 - C_2}\right) = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1} \times \cdots$$
$$\exp\left\{\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right\}\cos\left(\frac{(2n+1)\pi x}{2l}\right). \quad (1)$$

While Eq. 1 is directly applicable to the planar film, it can be used as an approximate solution for the cylindrical coating, Figure 1b, where $l = b - a$, and the glass/coating interface is at $x = a$.[1]

Diffusion coefficients in polymer films can be measured by simply recording the weight of the film as a function of time after the environment is suddenly changed. The accumulated mass of the diffusing species at time t, M_t, is given by:[7]

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

where M_∞ is the mass that has entered after infinite time.

For completeness, the full solution of the diffusion equation in cylindrical symmetry has

Figure 1: The geometry for the (a) polymer film and (b) coated fiber.

also been used. Assuming the outside concentration is a constant, $C(r = b, t) = C_1$, and that glass/polymer interface is impermeable, $\partial C(r = a, t)/\partial r = 0$, the solution to the diffusion equation is:[7]

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

J and Y are the Bessel functions, and α_n is the nth positive root of:

$$J_1(a\alpha)Y_o(b\alpha) - J_o(b\alpha)Y_1(a\alpha) = 0. \quad (4)$$

In order to obtain a diffusion coefficient, the concentration at the polymer/glass interface, $C(r = a, t) = C_o$, has to be known as a function of time. A simple way of measuring this concentration is to determine the strength of the fiber as a function of time after the ambient humidity is suddenly changed. Since the strength of the fiber depends on the amount of the water vapor present at the interface, the effective concentration or humidity can be obtained from these results.

The above model is based on the assumption that Fickian diffusion is taking place. Polymers show considerable variability in their permeability to various diffusing species and the diffusion is often not Fickian.[5] Some polymers will tend to absorb the diffusing species and form clusters within their structure in which case

the concentration profile for diffusion in and out of the polymer will not be symmetrical. In this paper, the water vapor diffusion coefficients in both polymer films and coatings are measured and compared to show that measuring the strength of the fiber is a valid and useful technique. The symmetry of the diffusion both in and out of the coating was used to evaluate the importance of accumulation. Finally, a special strength enhancing fiber coating is studied to determine if it shows different permeability characteristics.[8,9]

EXPERIMENTAL PROCEDURES

Diffusion into freestanding polymer films was studied by using two humidity chambers. A computer controlled precision balance was placed inside one of the humidity chambers that were controlled at $25 \pm 0.1°C$ and either 20 or $95 \pm 1.0\%$ relative humidity. The films were left overnight in the other humidity chamber that was controlled to $25 \pm 0.1°C$ and either 95 or $20 \pm 1.0\%$ relative humidity respectively. For example, if the film was left overnight in 25°C and 20% relative humidity, the chamber with the balance in it was set to 25°C and 95% relative humidity. Then the film was placed in the high humidity chamber and the weight was measured as a function of time. This particular experiment measures diffusion of water vapor into the film. The reverse experiment measures diffusion of water vapor out of the film. Polyimide and acrylate films were studied.

A two-point bend apparatus[10] was used to measure the strength of the fiber and was operated with a constant faceplate velocity of 5000 μm/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 in a second. Specimens were broken until an equilibrium strength was reached. This produced the strength of the fiber as a function of time in the test environment. In order to determine diffusion coefficients the strength data have to be converted to an equivalent concentration or humidity at the glass surface. This conversion is performed by measuring the equilibrated strength as a function of humidity in the range of 25 to 95%. This was achieved by leaving the fibers overnight at 25°C in a set humidity in order to ensure the fibers were equilibrated with their test environment. Twenty samples were broken in each humidity.

The fiber coatings investigated here were a single layer of UV-acrylate (125 μm glass diameter and 250 μm overall diameter) and a polyimide (220 μm glass diameter and 245 μm overall diameter). Also, two dual layer UV-acrylate coated fibers were studied which were identical except that one had 3 wt.% of silica particles incorporated in the secondary coating (125 μm glass diameter, 185 μm primary coating and 250 μm overall diameter).

RESULTS AND DISCUSSION

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

$$W_n = \frac{W_t - W_{dry}}{W_{wet} - W_{dry}} , \qquad (5)$$

where W_t is the weight at time t, W_{dry} is the weight in the drier environment, (20%), and W_{wet} is the weight in the wetter environment, (95%). The normalized accumulated weight is then equal to Eq. 2. The diffusion coefficients for the films were found by fitting the data to this equation. Measured values of $D = (5.17 \pm 0.12) \times 10^{-13}$ m²/s for diffusion into, "wetting", and $(5.79 \pm 0.13) \times 10^{-13}$ m²/s for diffusion out of, "drying", the acrylate film were found. A value of $(9.40 \pm 0.35) \times 10^{-13}$ m²/s was found for wetting and $(9.24 \pm 0.29) \times 10^{-13}$ m²/s for drying of the polyimide film. The errors represent a 95% confidence interval. There appears to be a slight accumulation in the acrylate layer, since
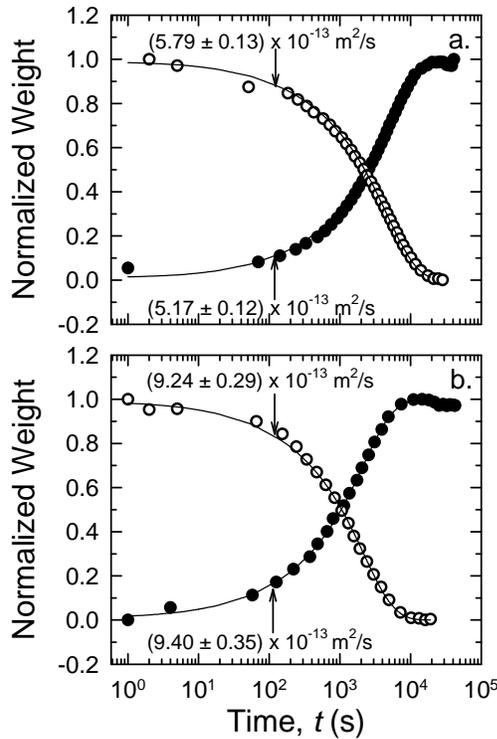
Figure 2: The predicted fit (solid lines) from Eq. 2 and the diffusion into (●) and out of (○) (a) acrylate film and (b) polyimide film.

the diffusion coefficients for drying and wetting within 95% confidence are slightly different.

Figure 3 shows the raw strength data for the acrylate and polyimide coatings. The diffusion coefficients cannot be directly obtained from this graph. The strength must 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 the following empirical equation:

$$\sigma = A + B e^{-CH} , \qquad (6)$$

where σ is the strength, $A, B,$ and C are constants, and H is the relative humidity expressed as a percentage. Figure 4 shows Eq. 6 fitted to the strength data for acrylate and polyimide coated fibers. This equation is then used to map the results in Figure 4 into the normalized humidity, defined by:
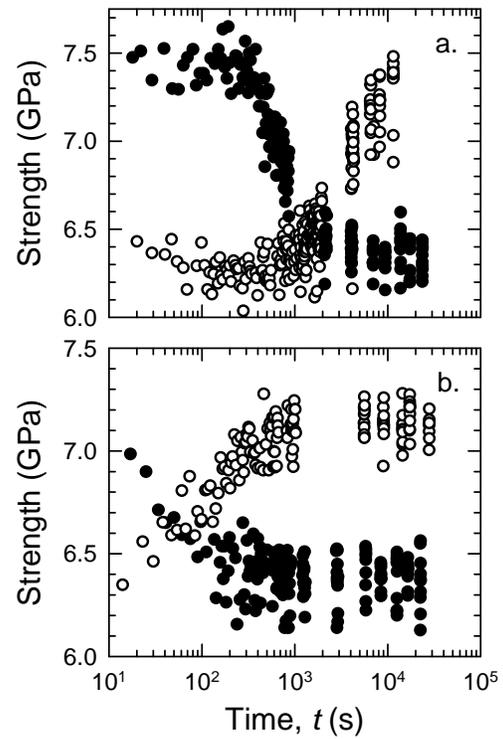
Figure 3: Diffusion into (●) and out of (○) (a) acrylate coated fiber and (b) polyimide coated fiber.

$$RH_n = \frac{RH_t - RH_{low}}{RH_{high} - RH_{low}} , \qquad (7)$$

where RH_t is the relative humidity at time t, RH_{low} is the lowest relative humidity, and RH_{high} is the highest relative humidity. The results are shown in Figure 5. If a planar geometry is assumed for the coating, the normalized humidity is given by equation 1. This equation has been fitted to the data (dashed lines), and the best-fit diffusion coefficients were obtained by regression analysis. The cylindrically symmetric solution, Eq. 3, has been calculated for the same best fit values of the diffusion coefficients and is shown (solid lines) in Figure 5. The difference between the two solutions is dependent on the ratio of the outer and inner radii of the coating. This ratio is small for the polyimide coating so the difference between the planar and cylindrical solutions is negligible. That ratio is approximately two for the acrylate coating, but the difference is still relatively small. For bigger radii ratios, the

planar solution will not provide an adequate description.

Similar values for the diffusion coefficients were found both when weighing the freestanding films (Figure 2) and from the strength measurement technique (Figure 5). The diffusion coefficient was found to be slightly higher in the polyimide for both techniques. This validates the strength measurement technique, and it should be noted again that this technique determines the *in situ* diffusion coefficient for the real coating, rather than a model sheet specimen. However, the diffusion coefficient is not measured as accurately with this technique because of the inherent variability in the strength. This makes it harder to measure small changes in strength, whereas small changes in weight can be measured accurately. This is aggravated by only having a limited experimental time before the half-life of the diffusion (where the

normalized humidity is 0.5) is reached. As a result the standard error in the estimates of the diffusion coefficients are approximately three times higher than for the gravimetric technique. However, the ~ 10% error is acceptable for most purposes. Figure 5b 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 did not produce reliable error estimates in this case. The stress measurement technique is therefore not useful for a half-life below about 50 s.

Another result shown in Figure 5a is that the diffusion in and out of the coating is not symmetrical. There is some slight deviation. This implies that the water vapor may be
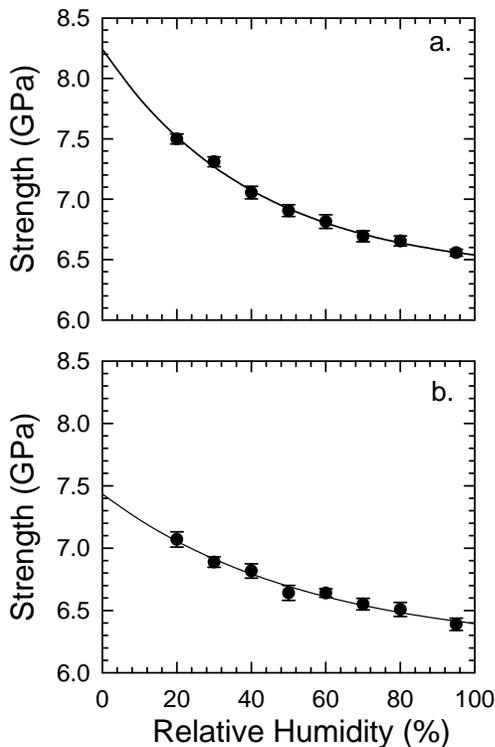
Figure 4: The equilibrium strength (at 25°C) as a function of humidity for (a) acrylate coated fiber and (b) polyimide coated fiber.
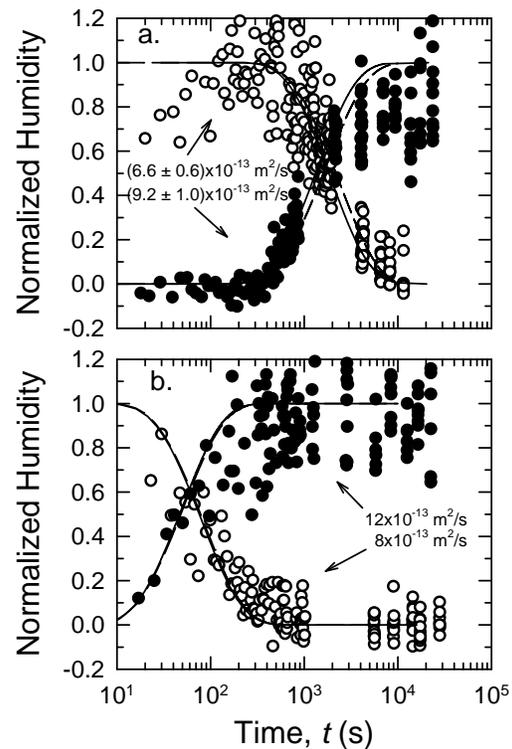
Figure 5: A cylindrical fit, Eq. 3, (solid lines), and a planar fit, Eq. 1, (dashed lines) to the diffusion into (●) and out of (○) (a) acrylate coated fiber and (b) polyimide coated fiber.

interacting with the polymer. Slight asymmetry was also observed in the planar films (Figure 2a), but the sense is reversed. It is not clear whether this asymmetry is significant. The polyimide films (Figure 2b) appear to be symmetrical, but because of the large error found in Figure 5b for the strength technique, no conclusions can be drawn.

Effect of silica particles in coating

We have studied the affect of having colloidal silica particles incorporated in the outer layer of the dual coated fiber. In previous work, the silica particles were found to have a beneficial effect on fiber reliability by greatly delaying the onset of the fatigue and aging "knees".[8,9] The particles preferentially dissolve in moisture thus reducing the activity of the water at the glass surface, which results in a reduction of the corrosion rate of the glass. One possible mechanism that has been suggested for the particles is that they simply absorb the ambient moisture, thus keeping the fiber surface drier. However, Rondinella *et al.*[8,9] argue that the quantity of silica in the coating is inadequate to explain the dramatic increase in lifetime. We provide direct evidence for this assertion here, since if the silica particles were absorbing significant amounts of water, the diffusion through silica-loaded coating would appear much slower using the strength measurement technique. We have compared two fiber specimens; one with 3 wt.% of silica particles in the secondary coating and a second identical specimen, drawn at the same time using the same polymer, but without the silica particles. Since both specimens have a dual coating, it is only possible to determine an effective overall diffusion coefficient for both layers.[1] However, if the diffusion coefficient of the second layer is substantially changed by the presence of the silica particles, this would be readily apparent. The normalized humidity *versus* time for both of these specimens is shown in Figure 6. The data were fitted to the cylindrically symmetric solution of the diffusion equation (3) and for both

specimens the diffusion in both directions is the same; namely $D = 3 \times 10^{-12}$ m^2/s. Since the silica additive has no effect on the rate of diffusion, this shows that the silica does not act as a sink for water. As suggested in the earlier work, this shows that the mechanism by which the powder delays the onset of fatigue and aging knees does not involve gettering the water.[8,9]

CONCLUSIONS

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 comparable diffusion coefficients to the more commonly used film weighing technique. It is however, more meaningful because it is an *in*
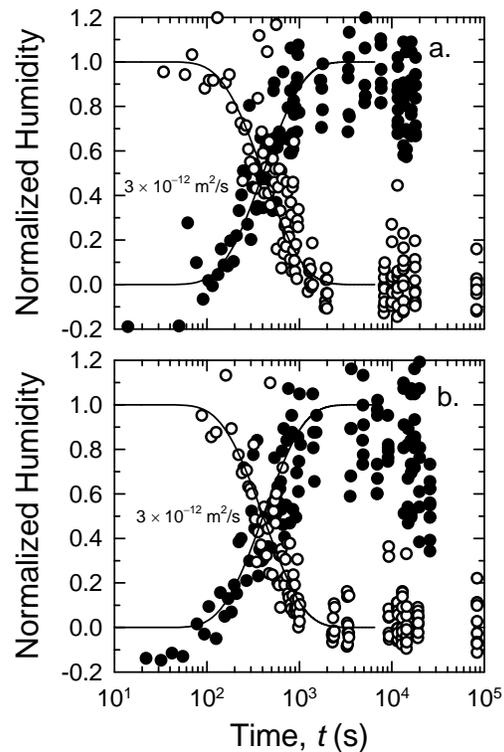
Figure 6: The diffusion, in the range from 30 – 95% *RH* at 25°C, into (●) and out of (○) a dual coated fiber with (a) 0 wt% silica and (b) 3 wt% silica added to the secondary coating.

situ measurement that does not rely on the assumption that the film has seen the same cure conditions (and hence has the same properties) as the real coating. However, the precision with which the diffusion coefficient can be determined is somewhat lower and is limited to coatings with diffusion times greater than about 50 s.

For all of the coatings studied here, moisture penetrates on a time scale of $\sim 10^2$ to 10^3 seconds. It is therefore unlikely that water permeability 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 years).

Here we have used the cylindrically symmetric solution to the diffusion equation to accurately describe diffusion through the cylindrical shell. However, a simple planar sheet solution gives results with acceptable precision for coating outer to inner diameter ratios of less than approximately two.

Under the conditions used here, the diffusion is accurately described by Fickian behavior. We also show that the diffusion is not affected by a few weight percent of colloidal silica particles in the coating, which has significance for how these particles improve fiber reliability.

ACKNOWLEDGEMENT

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Janet L. Armstrong
Rutgers University
Dept. of Ceramic and Materials Eng.
607 Taylor Road
Piscataway, New Jersey 08854-8065

Janet Armstrong received her BS and MS in Ceramic Engineering from Rutgers University in 1995 and 1997 respectively. She is currently

pursuing her PhD in Ceramic Engineering at Rutgers University. Her thesis work consists of investigating the mechanical reliability of optical materials. She has been jointly working at Bellcore in Morristown, NJ and Rutgers University.
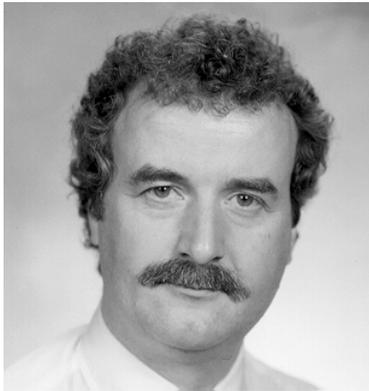
Dr. M John Matthewson
Rutgers University
Dept. of Ceramic and Materials Eng.
607 Taylor Road
Piscataway, New Jersey 08854-8065
mjohnm@fracture.rutgers.edu

John Matthewson received his BA degree in Theoretical Physics in 1975 and his MA and PhD degrees in Physics in 1978, all from Cambridge University. Since then he has worked in the Cambridge University Computer Laboratory, AT&T Bell Laboratories and IBM Almaden Research Center. He is now an Associate Professor in the Fiber Optic Materials Research Program at Rutgers University where his research group is concerned with strength and fatigue of optical materials in general and oxide and non-oxide fibers in particular.
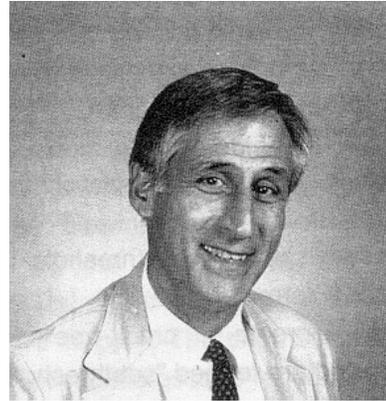
Dr. Charles R. Kurkjian
Bell Communications Research
445 South Street
Morristown, New Jersey 07960

Chuck Kurkjian is a member of the Fiber Media and Components Reliability Group at Bellcore in Morristown, NJ. He spent 35 years at Bell Labs involved in various aspects of glass and glass fiber research, and since joining Bellcore in 1994 he has concentrated on issues of mechanical reliability of lightguide fiber, cable, and optical components. He graduated from Rutgers University in 1952 and M.I.T. in 1955 with degrees in Ceramics.