

The Effect of Diffusion Rates in Optical Fiber Polymer Coatings on Aging

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ABSTRACT

Optical fibers have been found to exhibit an accelerated rate of strength reduction during static fatigue and zero stress aging for long times in aggressive environments. This phenomenon has been commonly referred to as the fatigue and aging “knee”. The onset of the knee has been found to be highly variable and is sensitive to the polymer buffer coating. In past work we have shown that moisture vapor penetrates most polymer coatings on the time scale of minutes, which implies that the diffusion rate of small molecules is not the rate-determining step for aging. On the other hand, the diffusion of large molecules through the polymer coatings can take anywhere from weeks to years to reach the polymer / glass interface. The implication of this result is that large molecule diffusion might be the rate-determining step in aging. In the work presented here the diffusion of moisture and pH buffer solutions through various optical fiber coatings will be discussed. These results are correlated with the zero stress aging behavior of the same fibers.

Keywords: Optical fiber, strength, fatigue, reliability, diffusion, aging knee

1. INTRODUCTION

1.1 Equilibration

Before the effects of the environment on the strength of polymer coated optical fibers can be characterized, the glass surface of the optical fiber has to be in equilibrium with the testing environment. In order to ensure that the testing environment is the same as the environment at the glass surface, the fiber has to be equilibrated. In previous work^{1,2} the equilibration period (at 25°C) for moisture to reach the glass surface, which was within minutes, was determined by measuring the fiber strength as a function of time after the fiber was placed in a humid environment. Since mechanical testing of optical fiber is not only conducted in humid environments, but also in numerous liquid environments such as water and pH buffer solutions, proper equilibration times for these liquids need to be determined. pH buffer solutions consist of water and buffering ions, therefore by determining the equilibration period for these solutions the diffusion of water and the ions through the polymer coating can also be determined. In this paper the equilibration time for water and pH buffer solutions (at 25°C) are characterized for single acrylate, dual acrylate, and polyimide polymer coatings and as a result the diffusion of the buffering ions, which are larger than water molecules, can be studied.

1.2 The Fatigue and Aging “Knee”

Fused silica optical fiber exhibits what has been termed a “knee” in its zero stress aging and static fatigue behaviors. The knee represents an abrupt drop in the strength of the optical fiber after some time and a faster rate of strength degradation. Since this behavior affects the lifetime and handleability of optical fibers there is a need to understand why the knee occurs and how to delay its onset.

A possible explanation for the knee is that density fluctuations in the glass lead to non-uniform rates of dissolution, resulting in the formation of surface “pits” which act as stress concentrators³ and reduce the strength of the glass. Aged fiber surfaces have been characterized by scanning tunneling microscopy⁴ and atomic force microscopy⁵ which give direct evidence of surface roughening. Yuce *et al.*⁵ measured both the strength and surface roughness and arrived at the relationship that the strength had a simple power law dependence on the surface roughness.⁶

Even though there is evidence that the onset of the knee in water depends on the nature of the polymer coating,^{7,8,5,9} one straight forward explanation as to why this occurs has not been found. It has been suggested that the onset of the knee is delayed by better coating / glass adhesion.¹⁰ Whereas another possible explanation is that the polymer coating reduces the rate at which the corroding species reaches the surface. However, it has been shown that water vapor penetrates most

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polymer coatings within hours at room temperature,^{1,2} and therefore it is unlikely that the diffusion rate of small molecules (e.g. H₂O) can be the rate determining step for aging which occurs on the time scale of years.

The rate of diffusion of larger species through the coating might however be relevant to the aging behavior. Corrosion of the fiber surface produces large species (e.g. silicic acid) that must be removed from the surface for the process to continue. Such processes are hard to study directly. As an alternative approach, in this work we characterize how quickly the fiber strength equilibrates with various pH buffer solutions. These results are used to assess the diffusion rates of large ions, and the results are then compared to the zero stress aging behavior in pH 7 at 90°C.

2. EXPERIMENTAL PROCEDURE

2.1 Equilibration and diffusion

Three fiber specimens were used in this study; one with a single acrylate coating, one with a dual acrylate coating, and a polyimide coating. These fibers were placed in glass jars containing pH buffer solutions ranging from pH 1 to pH 12 at 25°C. The pH 1 to 10 buffer solutions were supplied by Fisher Scientific* and the pH 12 was obtained from LabChem Inc.** Table 1 lists the components of the pH buffer solutions.

The fiber strength, which was obtained from the average of 10 to 20 samples, was monitored as a function of time ranging from 10 seconds to around one year. These results were obtained in order to establish firstly the equilibration times and secondly the relationship between the final strength and pH. These measurements were made in two-point bending with a constant faceplate velocity of 5000 μm/s.¹¹ The strength was monitored as a function of time in distilled water for the dual acrylate and polyimide coated fiber.

Table 1. The components in the pH buffering solutions.

pH	Components
1, 2	H ₂ O, KCl, and HCl
4	H ₂ O and KHC ₈ H ₄ O ₄
6, 7, 8	H ₂ O, KH ₂ PO ₄ , and NaOH
10	H ₂ O, K ₂ CO ₃ , K ₃ BO ₃ , and KOH
12	H ₂ O, Na ₂ HPO ₄ , and NaOH

2.2 Zero stress aging

The fibers were immersed in test tubes containing pH 7 buffer and were then placed into a water bath that was controlled at 90 ± 1°C. Samples were withdrawn for aging times ranging from one hour to approximately four months, and their strength was measured in two-point bending at a faceplate velocity of 5000 μm/s. Some samples were stripped of their coating in ~200°C sulfuric acid so that the glass surface morphology could be studied using atomic force microscopy (AFM). The AFM used was a Digital Instruments*** NanoScope IIIa AFM run in contact mode. A 2 x 2 μm area of each image was analyzed to extract roughness data.

3. RESULTS

3.1 Equilibration in pH buffer solution

Figure 1 shows the strength as a function of time in distilled water for the dual acrylate and polyimide coated fiber. Upon comparing these results with the humidity diffusion results,² it is found that equilibration is achieved on the same time scale, which is within a few hours.

Figure 2 shows a schematic of how the strength is expected to behave as a function of immersion time in the various pH buffer solutions. The initial strength is characteristic of the ambient environment that the fiber was in before it was placed in the pH buffer solution (i.e. laboratory air). Then, as the water in the pH buffer solution diffuses through the coating, the strength of the fiber correspondingly drops until the water diffusion process is completed (after a few hours). At this time a

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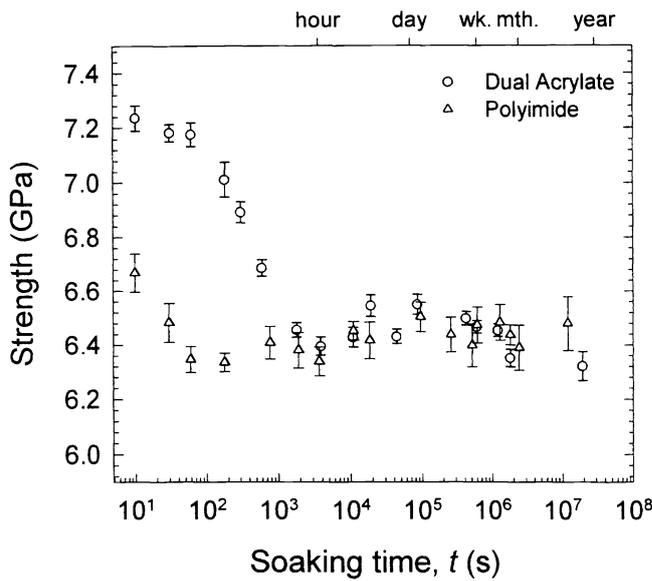


Figure 1. Comparison of the stress *versus* soaking time in distilled water for dual acrylate and polyimide coated fibers.

strength falls as water penetrates the coating, then starts to increase after a day and levels off after about a week. This increase in strength is expected since the strength of silica is higher at low pH.¹² The strength then remains relatively constant out to about a month after which the strength drops implying that zero stress aging has occurred. The diffusion coefficient that was calculated by using the cylindrical solution to the diffusion equation² and assuming that pH equilibrium was reached after one week is on the order of $10^{-14} \text{ m}^2/\text{s}$, whereas the diffusion coefficient of water in this coating is $\sim 5 \times 10^{-13} \text{ m}^2/\text{s}$.² The same behavior was not observed for the pH 12 single acrylate results. A difficulty in the work shown here is that the distinction between the ions reaching the glass surface and zero stress aging is hard to make. This is particularly so since at high pH the strength would decrease both due to ions reaching the glass surface and due to aging.

In a separate study¹³ bare fiber (stripped dual acrylate coated fiber) strength was measured in various pH buffer solutions. Since the coating of the fiber has been removed, water and the buffering ions can reach the glass surface immediately. Therefore the coated fiber strength should approach this strength as equilibration is reached. The strength of the bare fiber in pH 4 and pH 12 is shown in Figures 3 and 4 respectively. It is important to note that the bare fiber strength should only be compared with the dual acrylate coated fiber results, since the glass of the other two fibers may not be exactly the same. A result of comparing the bare and dual acrylate coated fiber strength is that it appears that somewhere between a month and a year zero stress aging has occurred in pH 4 (Figure 3). On the other hand, in pH 12, the dual acrylate strength never reaches the bare fiber strength.

“water diffusion plateau” should be observed, which should be at the same strength for all buffer solutions. After some further time the buffering ions start to reach the glass surface and so change the pH at there from 7 towards the pH of the buffering solution. The strength behavior is expected to change at this time since for low pH the strength should start to increase, whereas in high pH, the strength should start to decrease. A plateau should be observed when the ion diffusion process is completed. After some additional time the strength is expected to drop for all of the pH buffer solutions because zero stress aging is occurring.

The initial drop in strength and the water diffusion plateau were observed for all three specimens in all of the pH buffer solutions. The results for pH 4 and 12 are shown in Figures 3 and 4 respectively. The water plateau extends from approximately one hour to somewhere between a week to a month. The behavior is best illustrated for the single coated acrylate fiber in pH 4 (Figure 3). In this particular case the

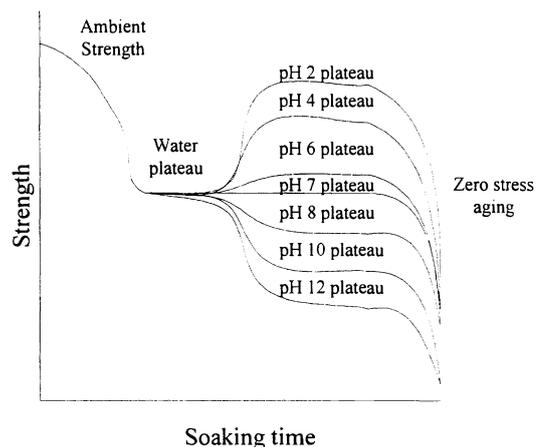


Figure 2. Expected variation of strength with soaking time in various pH buffer solutions.

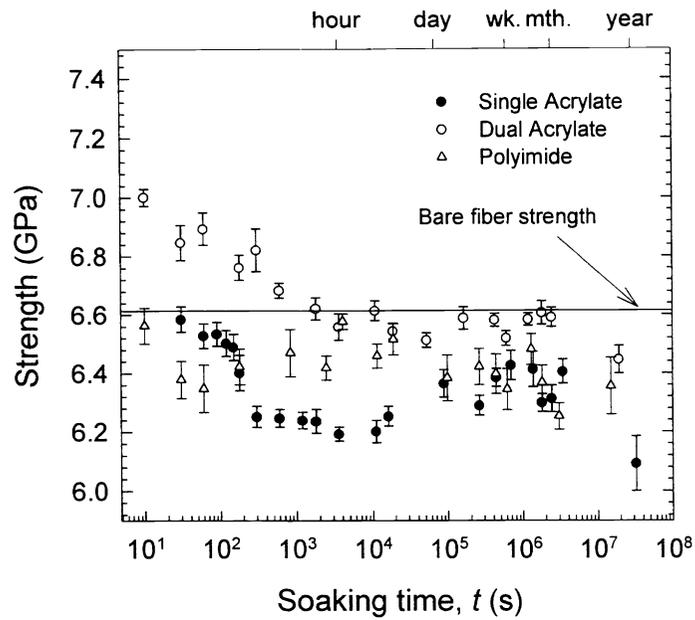


Figure 3. Comparison of the stress *versus* soaking time in pH 4 buffer for single acrylate, dual acrylate, and polyimide coated fibers. The bare fiber strength is for 30s immersion in pH 4 buffer.¹³

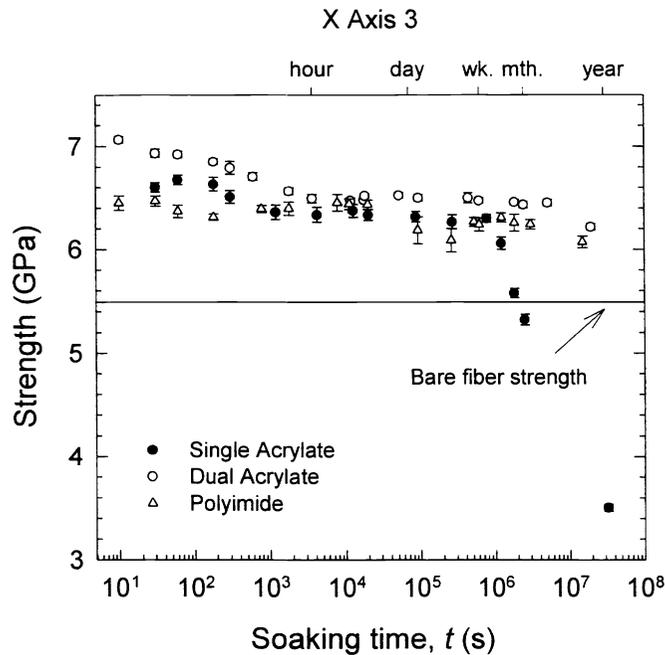


Figure 4. Comparison of the strength *versus* soaking time in pH 12 buffer for single acrylate, dual acrylate and polyimide coated fibers. The bare fiber strength is for 30s immersion in pH 12 buffer.¹³

Another comparison that can be made is between the strength in distilled water (Figure 1) with the strength in the different pH solutions (Figures 3 and 4). Since pH buffer solutions consist of water and buffering ions, any differences observed in these figures would be the result of the ions reaching the glass surface. If the ions had reached the glass / polymer interface in a year, the diffusion coefficient for the dual acrylate coated fiber, which was calculated from the cylindrical solution to the diffusion equation,² would be on the order of $\sim 10^{-16}$ m²/s, whereas the diffusion coefficient for water is $\sim 2 \times 10^{-12}$ m²/s in this coating.²

The pH and distilled water results for the polyimide coated fibers (Figures 1, 3, and 4) are not significantly different, and no significant changes in strength were measured after the initial water plateau. This implies that the buffering ions are not getting through this coating. Assuming that the ions would have reached the glass / polymer surface in a year the diffusion coefficient would be on the order of 10^{-19} m²/s, whereas the moisture diffusion rate is $\sim 9 \times 10^{-13}$ m²/s in this coating.²

The main difference between the moisture diffusion and the pH buffer solution diffusion is the size of the diffusing species. In Table 2 the approximate effective ionic radii in aqueous solutions at 25°C are shown.¹⁴ The smallest ion in the buffer solutions is three times larger than a water molecule. In general, larger diffusing species require larger openings in the polymer structure. Since forming or finding larger openings in the structure requires more energy, the activation energy for the diffusion of larger molecules increases and results in a decrease in the diffusion rate.¹⁵

Table 2. Approximate Effective Ionic Radii for buffer ions.¹⁴

Ion	Effect radius (nm)
H ₂ O	0.1
K ⁺	0.3
OH ⁻	0.35
Na ⁺ , H ₂ PO ₄ ⁻ , HPO ₄ ⁻²	0.4
CO ₃ ⁻²	0.45
H ⁺	0.9

The rate of diffusion of pH buffer ions through the polymer coatings was found in some cases to be more than eight orders of magnitude slower than the moisture diffusion. This implies that the equilibration time for room temperature testing of coated fibers in pH buffer solutions can range from a week to beyond a year. Also, it is often not possible to distinguish between equilibration and room temperature zero stress aging. Therefore it is suggested that room temperature tests in pH buffer solutions should be conducted on bare fibers rather than coated fiber in order to evaluate the effect of pH on strength (unless, of course, the purpose of the experiment is to study diffusion through the coating).

3.2 Zero stress aging results

The zero stress aging behavior for the three fibers is shown in Figure 5, and the AFM results for these fibers are shown in Figures 6 to 8. The strength of the single acrylate coated fiber shows a rapid drop in strength upon aging. This should correspond to an increase in the surface roughness, which is indeed seen in Figure 6. During aging of this particular fiber, the coating turned a dark brown and started to fall off after about two weeks. This observation might explain the modest increase in strength that is observed at two weeks.

The dual acrylate coated fiber starts to show effects of aging after about a week and after four months the strength has significantly dropped (Figure 5). The surface roughness, which is shown in Figure 7, correspondingly increases with aging.

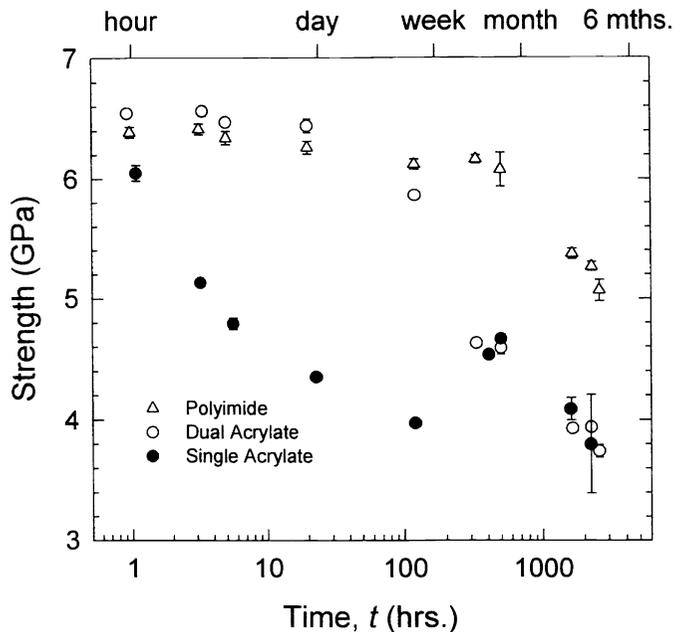


Figure 5. Zero stress aging in pH 7 buffer solution at 90°C for polyimide, dual acrylate, and single acrylate coated fibers.

The onset of the aging knee for the polyimide coated fiber is not observed until 2 months and even after four months the strength is not as low as the acrylates (Figure 5). This is explained by the observation that the polyimide coated fiber shows a relatively small increase in roughness with aging time (Figure 8).

4. DISCUSSION

Since the buffering ions are at least three times as large as a water molecule, a channel or hole in polymer structure that is approximately three times larger will be needed for diffusion to take place. The moisture diffusion results² found that the coating structure had a negligible effect on the moisture diffusion rates, in contrast to the results shown here for the pH buffer solutions. This implies that the diffusion of large molecules is highly dependent on the structure of the coating.

The results described here show some correlation between the diffusion behavior and the zero stress aging behavior. The single acrylate coated fiber showed the most rapid ionic diffusion times ($D \sim 10^{-14} \text{ m}^2/\text{s}$) and the fastest aging behavior. As stated earlier the onset of the knee in water has been found to vary with different types of polymer coatings,^{7,8,5,16} whereas the diffusion of the water through various coatings is not significantly different.² A possible explanation is that the occurrence of the knee depends on the dissolution rate of the glass surface, which directly depends on how fast the dissolution product can be removed through the coating. Since the size of the dissolution product is larger than a water molecule, the rate at which it can diffuse out of the coating may be dependent on the coating. Therefore the formation of the knee, which is not dependent on how fast the water can get to the glass surface, would depend on the diffusion rate of the dissolution product out of the coating.

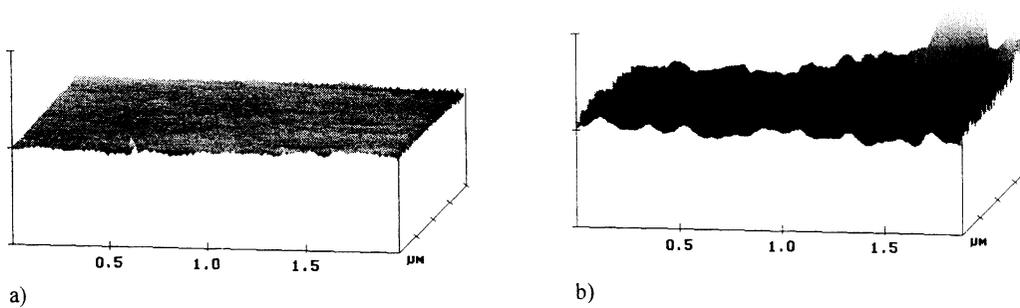


Figure 6. AFM images for the zero stress aged (90°C, pH 7) single coated acrylate fiber where a) aged for 1 hour, ($x = 0.5 \mu\text{m}/\text{div}$, $y = 25 \text{ nm}/\text{div}$), Roughness (Ra) = 0.3 nm, rms = 0.5 nm and b) aged for 3 months ($x = 0.5 \mu\text{m}/\text{div}$, $y = 20 \text{ nm}/\text{div}$), Roughness (Ra)=1.7 nm, rms = 3.4 nm.

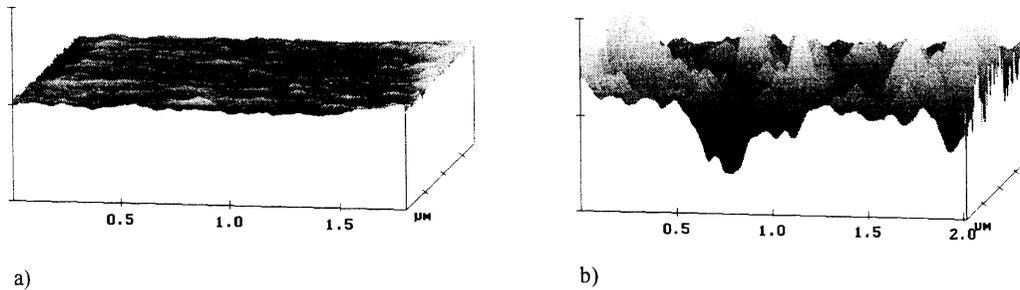


Figure 7. AFM images of zero stress aged (90°C, pH 7) dual acrylate coated fiber where a) aged for 1 hour, ($x = 0.5 \mu\text{m}/\text{div}$, $y = 25 \text{ nm}/\text{div}$), Roughness (Ra) = 0.4 nm, rms = 0.6 nm and b) aged for 4 months, ($x = 0.5 \mu\text{m}/\text{div}$, $y = 25 \text{ nm}/\text{div}$), Roughness (Ra) = 3.3 nm, rms = 4.5 nm.

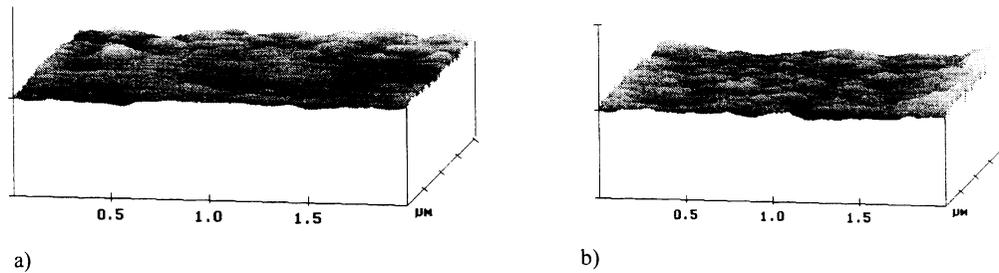


Figure 8. AFM images of the zero stress aged (90°C, pH 7) polyimide coated fibers where a) aged for 1 hour, ($x = 0.5 \mu\text{m}/\text{div}$, $y = 25 \text{ nm}/\text{div}$), Roughness (Ra) = 0.5 nm, rms = 0.7 nm and b) aged for 4 months, ($x = 0.5 \mu\text{m}/\text{div}$, $y = 25 \text{ nm}/\text{div}$), Roughness (Ra) = 0.7 nm, rms = 0.9 nm.

5. CONCLUSIONS

The diffusion of ions through polymer coatings has been monitored by measuring the strength of the fiber as a function of soaking time. Of the three coatings studied here, *i.e.* single acrylate, dual acrylate, and polyimide, an equilibration time was only observed for the single acrylate coated fiber in pH 4 corresponding to a diffusion coefficient on the order of $\sim 10^{-14} \text{ m}^2/\text{s}$.

The aging behavior for the fibers was found to parallel their diffusion behavior. For example, the single acrylate that showed the fastest ion diffusion rate also aged the fastest. This implies that the diffusion rate of large molecules, unlike the moisture diffusion rate, might be a controlling factor for the reliability of optical fibers.

A possible explanation for why the onset of the knee in water depends on the nature of the polymer coating is that it depends on how fast the glass surface dissolves. Our results show that the diffusion rates of species which are larger than a water molecule are highly dependent on the polymer coating. Therefore, the diffusion rate of the dissolution product (which is larger than a water molecule) away from the glass surface should also be dependent on the coating. The onset of the knee is therefore expected to correlate with the diffusion rate of large species and not with the diffusion rate of water, and hence on the transport properties of large species through the polymer coating.

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