

Measurement of Diffusion Coefficient of Oxygen in FRP Using Luminescence Quenching

by

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Abstract

A new method for determining diffusion and permeation coefficients of oxygen in polymers was recently developed that utilizes luminescence quenching. This technique is faster and simpler than other existing methods such as steady-state diffusion across a membrane (ASTM standard⁷), and accumulation into a volume.

Two diffusion experiments were performed. In the first, termed film-on-sensor technique, polymer was directly cast on a luminescence sensor film (PtTFPP dispersed in a very thin polystyrene matrix on glass), allowing for measurement of the concentration at the polymer/sensor boundary. In the second, termed dye-in-polymer technique, the dye was dispersed into the polymer, which was cast directly on the glass slide. In both cases, change in luminescence was monitored using an inverted fluorescence microscope, to measure oxygen concentration. Unsteady-state diffusion of oxygen in the polymer was modeled using Fick's law and the Stern-Volmer equation for luminescence quenching, to extract diffusion and permeation coefficients. Diffusion coefficients measured for Polydimethylsiloxane (PDMS) matches well with the value given in literature. New and preliminary data for Epoxy and FRP are promising.

Introduction

Several studies have independently confirmed¹⁻⁶ that fiber reinforced polymer (FRP) wraps can slow down the corrosion rate of reinforcing steel in concrete. While the mechanism for this reduction is not fully understood, it has been speculated that since FRP is a barrier element, it reduces the ingress of deleterious elements responsible for corrosion. Of these, oxygen is

the most critical. Thus, determination of the diffusion behavior of oxygen through FRP is of considerable importance.

Information on gas diffusion coefficient in polymers is also of great practical value in the food packaging industry. A number of techniques have been proposed that include ASTM methods⁷, gravimetric sorption⁸ and accumulation volume technique^{9, 10}. Most of these techniques require homogeneous free-standing thin films of uniform thickness. If the thickness of the film is large and the oxygen diffusion coefficient small, the time required to experimentally determine the diffusion coefficient can be considerable. As the minimum FRP thickness is much greater than the polymer film used in the food packaging industry available techniques for measuring oxygen diffusion coefficients are not suitable.

In the present work we used a method for determining diffusion coefficients of oxygen in polymers based on luminescence quenching. The luminescence of some fluorophores quench in the presence of oxygen. This technique is faster and simpler than other existing methods. In most cases reported in the literature¹¹⁻¹⁴, a dye is directly dispersed in the polymer. Initially, this polymer is equilibrated at a particular oxygen concentration and then exposed to a higher ("diffuse-in experiment") or lower oxygen concentration ("diffusion-out experiment"). In all previous studies, the average oxygen concentration change in the polymer was monitored by studying the average intensity change of the fluorophore using a spectrofluorometer.

For most fluorophores, intensity quenching is proportional to the concentration of oxygen. When the fluorophore is homogeneously dispersed in the polymer matrix, the luminescence quenching due to changes in O₂ concentration can be modeled by the Stern-Volmer (SV) equation:

$$I_0 / I - 1 = k_{sv} p_{O_2} \quad (1)$$

where

I₀: intensity at the absence of oxygen k_{sv}: SV constant
and p_{O₂}: partial pressure of oxygen.

However, many sensors do not follow the linear SV curve due to the heterogeneous dispersion of dye in the film. Recently, it was reported¹⁵⁻¹⁷ that only the homogeneous regions of the sensor follow the linearity of the SV equation. Our present work focused on the measurement of oxygen diffusion coefficient in polymers using fluorescence sensor with a fluorescence microscope. The use of the fluorescence microscope allowed us to investigate the spatial distribution of the SV response of the sensor at different oxygen

concentrations at the microscopic level. Then, response from the homogeneous regions was analyzed to calculate the oxygen diffusion coefficient.

Our paper discusses the measurement of diffusion coefficients by two methods. In case of the film on sensor method, the polymer was laminated on the sensor. Concentration change in the polymer was sensed by the luminescence sensor. In the second method, the dye was dispersed in the polymer.

We combined the SV equation with Fick's law of diffusion to extract the diffusion coefficient from experimental data.

Experimental Procedure

Luminescence oxygen sensors were prepared by spin coating a dilute solution (1.3283e-004 mol/liter) of the oxygen sensing dye Platinum Tetrakis (pentafluorophenyl) porphyrin (PtTFPP) (Frontier Scientific, Inc., Logan UT) dispersed in polystyrene/toluene on a 1mm thick, 19mm diameter circular glass slide. The spinning speed was maintained at 1000 rpm for 60 seconds. Then it was cured at room temperature for 1 hour and subsequently at 120 °C for 5 hours.

The oxygen diffusion coefficient was measured for a PDMS film with a known oxygen diffusion coefficient to validate the technique.

An epoxy solution was prepared by mixing 100 ml of component A and 42 ml of component B for 5 minutes in accordance with the manufacturer's instructions. For the film on sensor method, the epoxy or PDMS (Sylgard 184, Dow Corning) were directly cast on the 19 mm fluorescent sensor. PDMS was cured for 1 hour at 120°C. In the case of GFRP and CFRP, the fibers were first cut into 19 mm diameter circles. Then, they were saturated with epoxy and cast on the sensor films. Epoxy, GFRP and CFRP films were cured at room temperature for 7 days.

For the dye in polymer technique, the epoxy samples were prepared by dispersing 1 mg PtTFPP dye in 20 ml epoxy and then casting this solution on glass and curing it.

A Leica DMI 4000B Inverted Research Fluorescence Microscope equipped with Leica DFC340 FX CCD camera was used in this study. Fluorescence microscopy was carried out with a neutral red filter set (Chroma Technology, HQ535/50x exciter and HQ645/75m emitter). Image Pro-plus 6 with Scope Pro 6 (Media Cybernetics, Inc) software was used for capturing and analyzing the images. To minimize photobleaching of the fluorescent sensors, Scope Pro

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software was used to control the shutter. The specimen was only exposed to light while taking images with the lamp intensity maintained at 10% of its maximum.

To calibrate the luminescence sensor according to SV equation it was exposed to different known concentrations of oxygen and then intensity change was studied by the fluorescence microscope. Calibration experiment was carried out by attaching the sensor to a chamber where it was flushed with different concentrations of oxygen.

A stainless steel diffusion cell was constructed for measuring the diffusion characteristics in polymers. In case of the film on sensor experiment and the dye in polymer film experiment, the film containing dye or the film attached to the sensor was placed in a stainless steel chamber. The surface of this film was continuously flushed with oxygen or nitrogen. In all cases, the polymer film was first equilibrated with air and then exposed to zero concentration of oxygen (N₂ atmosphere). Luminescence intensity changes measured changes in oxygen concentration at the sensor/polymer film boundary in the film-on-sensor technique, and average oxygen concentration in the polymer in the dye-in-polymer technique.

The diffusion cell was mounted on the microscope stage (Figure 1) in such a way that the sensor faced the illumination source and detector. To ensure that the sensor film was within the focal length of objectives, a new microscope stage was designed and fabricated

Analysis

In this work, diffusion of gas through a polymer material is described by Fick's law, which in one dimension is written in the form

$$\frac{\delta C}{\delta t} = D \left(\frac{\delta^2 C}{\delta x^2} \right) \quad (2)$$

for constant diffusivity. Here, $C(x,t)$ is the concentration at the position x at time t and D is the diffusion coefficient of the gas in the material. The solution to this equation depends on the boundary conditions at the edges of the film.

Film on sensor model:

For the film on sensor experiment when the upstream of the film is maintained as pure nitrogen and initially, the film conditioned with air, the solution for Fick's second law combined with the Stern-Volmer equation is¹⁴

$$\left(\frac{I_{air}}{I} - 1 \right) = \left(\frac{I_{air}}{I_0} - 1 \right) \left(1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-\frac{D(2n+1)^2 \pi^2 t}{4l^2} \right) \right) \quad (3)$$

Dye dispersed in polymer specimen:

For the diffusion out experiment, the spatial and temporal profile of the concentration C in the film is derived from Fick's law of diffusion with the following boundary conditions¹¹

$$\rho(x,0) = 1 \quad (4)$$

$$\text{where } \rho(x,t) = c(x,t) / c_{eq} \quad (5)$$

$$\rho(0,t) = 0 \quad (6)$$

Zero flux at $x=l$

Temporal and spatial profile of concentration is given by

$$\rho(x,t) = \frac{4}{\pi} \sum_{n=odd}^{\infty} \left[\frac{1}{n} \exp\left(-\frac{n^2 \pi^2 D t}{4l^2}\right) \sin\left(\frac{n\pi x}{2l}\right) \right] \quad (7)$$

Using the Stern-Volmer equation, one can write

$$I(t) = \frac{I_0}{l} \int_0^l \frac{dx}{1 + B\rho(x,t)} \quad (8)$$

$$\text{Where } B = I_0 / I_{eq} - 1 \quad (9)$$

$$\frac{I(t)}{I_{eq}} = \frac{(B+1)}{l} \int_0^l \frac{dx}{1 + B\rho(x,t)} \quad (10)$$

Fitting equation 10 to experimental data allowed for the extraction of the diffusion coefficient D in this work.

Result and Discussion

The luminescence sensor was first calibrated according to the SV equation. It was found from the SV analysis that, though the dye was not homogeneously dispersed (Figure 2), the data obtained from all the different regions (from low intensity to high intensity) followed the linearity of SV equation. But k_{sv} was different for the different regions. The photobleaching effect was relatively higher in the high-intensity region where the dye was aggregated, than in the other region. K_{SV} values for different regions are given in Table 1.

Table 1: Stern Volmer data for sensors

	Average intensity	Region 1	Region 2	Region 3	Region 4
K_{sv}	12.52 atm ⁻¹	12.52 atm ⁻¹	13.28 Atm ⁻¹	13.28 atm ⁻¹	14.42 Atm ⁻¹
Regression Coeff.	.9995	.9995	.9979	.9979	.9983

Based on the above findings, the luminescence intensity change of one homogeneous region of the sensor was monitored for evaluating the oxygen diffusion coefficient in polymer.

In case of both the film on sensor and the dye dispersed in polymer techniques the polymer surface which was initially in equilibrium with air was flushed with nitrogen. As oxygen diffused out from the polymer, *COMPOSITES & POLYCON 2007*

its concentration change at the polymer sensor boundary was sensed by fluorophore in case of the film on sensor method. Images of the sensor were taken simultaneously. A background image was acquired for same experimental setup without the fluorophore. Background intensity was subtracted from the experimental data. Then, response from the homogeneous region of the sensor was analyzed for recording intensity change with respect to time as oxygen diffused out from the polymer film. In case of the dye dispersed in polymer experiment, the average intensity change of the polymer was observed. The thickness of the polymer film on sensor was measured using digital calipers.

For proving this technique, it was used first to measure the diffusion coefficient of oxygen in PDMS. Experimental data fitted with the diffusion model (equation 3) are given in Figure 3. A range of diffusion coefficients are reported in literature for PDMS. Our data for PDMS fall within this range.

Oxygen diffusion data for epoxy were measured by dispersing dye in epoxy. Figure 4 shows the experimental data and the fitted diffusion model (equation 8) to it. The diffusion coefficient for epoxy was found to be of the order of 10^{-11} m²/sec. Preliminary experimental data for GFRP are promising. The diffusion coefficient obtained for GFRP is smaller than the diffusion coefficient obtained for epoxy. This may be due to the fact that glass fibers are impermeable to oxygen so increasing the fiber content in FRP decreases the oxygen diffusion coefficient. However, more experiments are required before detailed conclusions about oxygen diffusion behavior in FRP can be drawn.

Table 2. Diffusion data for PDMS and epoxy

	Thickness	Diffusion coefficient (m ² /sec)	
		Calculated	Literature
PDMS film (Syl-gard 184)	0.8 mm	1.84e-9	0.54e-9 to 3.4e-9 ¹⁸
Epoxy	2.7mm	4.9194e-011	

Conclusions

Diffusion of oxygen through FRP is a critical parameter that determines its performance in corrosion repair. A fluorescence microscopy technique has been developed to measure diffusion and permeation coefficients of oxygen in FRP. In this method, a heterogeneous luminescence sensor can be used by monitoring the S-V response at the microscopic level.

Data for PDMS compared well with values reported in the literature. Preliminary, new data for epoxy and FRP materials are order-of-magnitude meaningful.

Acknowledgements

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Figures:

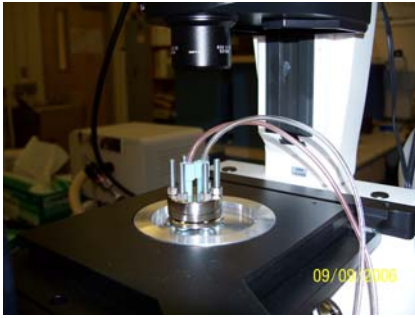


Figure 1: Diffusion cell positioning in inverted fluorescent microscope

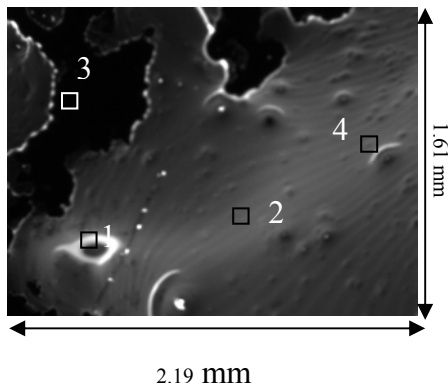


Figure 2: Image of luminescence sensor at 0% oxygen (0 to 5000 intensity in arb. units)

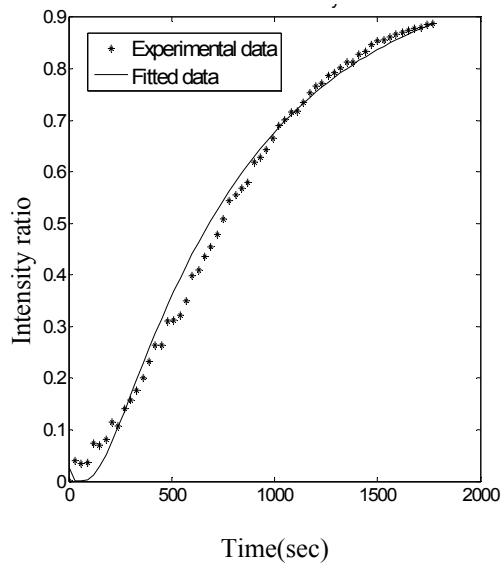


Figure 3: Experimental data and fitted data for the 0.8 mm thick PDMS film.

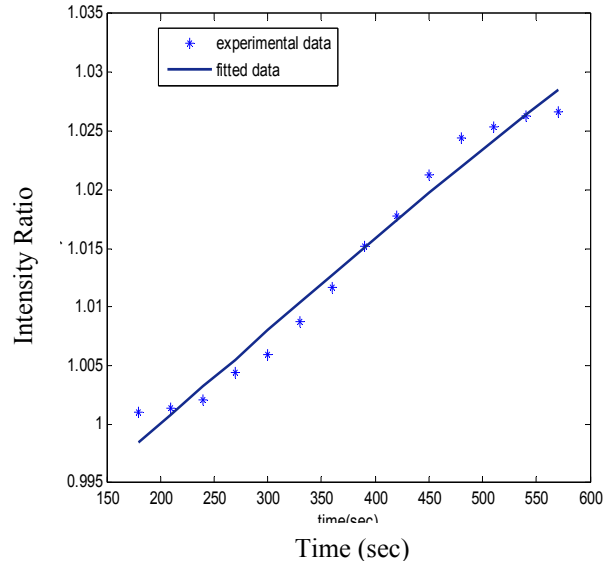


Figure 4: Experimental and fitted data for 2.7 mm thick epoxy film.

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