

Water, Salt Water, and Alkaline Solution Uptake in Epoxy Thin Films

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ABSTRACT: As a means of characterizing the diffusion parameters of fiber reinforced polymer (FRP) composites within a relatively short time frame, the potential use of short term tests on epoxy films to predict the long-term behavior is investigated. Reference is made to the literature to assess the effectiveness of Fickian and anomalous diffusion models to describe solution uptake in epoxies. The influence of differing exposure conditions on the diffusion in epoxies, in particular the effect of solution type and temperature, are explored. Experimental results, where the solution uptake in desiccated (D) or undesiccated (U) thin films of a commercially available epoxy matrix subjected to water (W), salt water (SW), or alkali concrete pore solution (CPS) at either 20 or 60°C, are also presented. It was found that the type of solution did not significantly influence the diffusion behavior at 20°C and that the mass uptake profile was anomalous. Exposure to 60°C accelerated the initial diffusion behavior and appeared to raise the level of saturation. In spite of the accelerated approach, conclusive values of uptake at saturation remained elusive even at an exposure period of 5 years. This finding questions the viability of using short-term thin film results to predict the long-term mechanical performance of FRP materials. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1898–1908, 2013

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INTRODUCTION

The in-service lifetime of many civil engineering structures can be 50–100 years and so durable materials are essential. There has been a growing interest in the use of carbon fiber reinforced polymer (CFRP) reinforcement as internal passive or prestressed reinforcement for concrete. One promising application area is in marine environments where conventional steel reinforcement is susceptible to corrosion. But the challenge is to predict how the CFRP reinforcing materials will behave over the coming decades when embedded in concrete and exposed to aggressive solution environments.

Exposure to solutions can potentially change the FRP mechanical properties. The uptake of solutions in epoxy matrix FRPs is widely acknowledged as occurring in the matrix, while the carbon fibers are assumed impermeable in comparison.^{1–3} On entering the matrix, aqueous solutions chemically interact with the material. The epoxy is plasticized as the polymer chains are forced apart, resulting in macro-scale swelling⁴ and softening of the material that can then have an impact on resin-dominated properties such as the CFRP dowel strength.⁵ Experimental programs to investigate the effects of solution uptake on FRP tendon properties can be devised. However, the problem arises that cylindrical FRP tendons often have a relatively large diameter

and a high fiber volume fraction so the timeframe to conduct uptake tests to saturation on actual tendons becomes prohibitive. Therefore, the possibility of inferring the longer-term FRP tendon behavior from shorter-term thin film tests on epoxy-only samples provides a potential means to extrapolate the behavior. However, to do so, a number of inter-related research components are required. The first is to establish the baseline behavior of thin films exposed to appropriate solution environments. The time to saturation, repeatability, and reliability of the measurements, the modeling of the uptake behavior, and the scope for viably accelerating the uptake through the use of higher temperatures all need to be established. Once this baseline exists it is necessary to link the thin-film behavior to that of a CFRP tendon. The final piece is to then determine the relationship between the tendon mass uptake and the CFRP mechanical properties and thereby conclude whether these outcomes could be predicted on the basis of the thin film baseline measurements.

The focus of this article is to present the foundation step to establish the baseline moisture uptake behavior of thin films of epoxy subjected to solutions that may be typical in civil engineering concrete applications, namely, water, salt water, and concrete pore solution. This study will be conducted and critiqued with due recognition of the overarching aim which is to

use the thin film diffusion results to infer CFRP tendon mechanical properties. A companion paper will then discuss the additional modeling and experiments required to connect thin film results to predictions of the corresponding behavior in an FRP tendon.

DIFFUSION IN EPOXIES

Epoxyes are acknowledged to have attractive physical properties, such as a high strength, toughness, and chemical resistance^{6,7} which are desirable in civil engineering applications. An epoxy matrix is formed by curing an epoxy polymer with a hardener resulting in a crosslinked finished product.⁷ Epoxyes are permeable to aqueous solutions because of the free space that exists between the molecular chains into which water molecules can move.⁸ A further driver of aqueous solution uptake is the affinity between the hydroxyl (OH) polar groups on the crosslinked epoxy and the polar water molecules.⁹ The chemistry of an epoxy has been shown to have a substantial effect on moisture uptake. Wright has noted that water absorption may differ by a factor of ten between different resin types, and a factor of three for a single resin having different curing formulations.¹⁰ More specifically, diffusion in epoxyes has been shown to be a function of the ratio of resin to hardener⁹ and the density of hydrophilic groups.¹¹ As it is difficult to predict the exact nature of uptake in epoxyes, experimental observation is frequently used as a method of characterizing the durability. In particular, thin film specimens with a high ratio of surface area to volume are used to study diffusion. These specimens exhibit relatively rapid saturation and the thin-film moisture uptake measurements can be incorporated into relevant diffusion models to yield the desired material diffusion parameters in as short a time frame as possible.

The moisture uptake transport process in epoxyes is generally considered to be dominated by diffusion. However, the selection of an appropriate diffusion model to describe the behavior is a challenge and the most appropriate choice depends on many factors including the observed behavior and the required balance of model accuracy and mathematical complexity. In the following, both Fickian and anomalous models will be discussed in the context of unidirectional diffusion.

Fickian Diffusion

A Fickian diffusion model is a robust starting point given its prevalent use and widespread acceptance. Further details can be found in Crank.¹² Fick's first and second laws for one-dimensional diffusion are shown in eqs. (1) and (2).

$$F = -D \frac{\partial C}{\partial x} \quad (1)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

These expressions relate the rate of transfer of diffusing substance per unit area, F , to its concentration, C , in the direction of diffusion, x , perpendicular to the unit area considered. The diffusion coefficient, D , is a function of how permeable a given material is to a given solution over time, t . For a thin film, a common boundary condition is to assume that a material is initially dry and is then exposed to moisture of a constant concentration at its surface. The outermost layer of the material is

assumed to become immediately saturated and thereafter maintains a solution concentration of C_0 , at its surface. The incorporation of these boundary conditions leads to an expression for the solution concentration in the film at any position and time:

$$C(x, t) = C_0 - \frac{4C_0}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\left(\frac{-(2n+1)^2 \pi^2 Dt}{l^2}\right) \cos\left(\frac{(2n+1) \pi x}{l}\right), \quad -\frac{l}{2} \leq x \leq \frac{l}{2} \quad (3)$$

The percentage mass increase of a specimen can be calculated from the concentration profile, e.g., measured in moles/cm³ within the material. The key linking term is the effective molar mass of the relevant solution M_{eff} . The relationship between solution concentration in a material at saturation, C_0 , and the percentage mass increase in the specimen at saturation, M_{∞} , is shown in eq. (4).

$$M_{\infty} = 100 \frac{\text{Mass of molecules}}{\text{Dry mass}} = 100 \frac{C_0 M_{\text{eff}}}{\rho_r} \quad (4)$$

The mass uptake at time t , M_t , can be calculated using relationships between solution concentration and mass uptake and integrating the concentration gradient over the specimen thickness [eqs. (3) and (4)] to give:

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{\frac{-D(2n+1)^2 \pi^2 t}{l^2}\right\} \quad (5)$$

In addition, Crank¹² showed that for thin film specimens, the diffusion coefficient of a material can be determined directly from the initially linear relationship between solution uptake and the square root of time:

$$\frac{M_t}{M_{\infty}} = \frac{4}{l} \sqrt{\frac{Dt}{\pi}} \Rightarrow D = \left(\frac{M_t}{\sqrt{t}}\right)^2 \frac{\pi l^2}{16M_{\infty}^2} \quad (6)$$

According to Fickian diffusion, this expression should hold until the specimens are at least 60% saturated after which the percentage mass increase should become concave against the abscissa¹³ as shown schematically in Figure 1.

Non-Fickian Diffusion

Two principal causes of non-Fickian, or anomalous, diffusion of moisture in epoxyes are severe degradation, which encompasses macro-scale breakdown, or milder solution-polymer interactions. Severe degradation is shown indicatively in Figure 1 but will not be investigated in detail in this study. The possibility of degradation nevertheless remains a consideration, in particular, with some of the higher temperature studies reported later. Anomalous diffusion due to solution-polymer interactions can be attributed to two phenomena which can be inter-related: the chemical interaction between the diffusing solution and the polymer, and the relaxation of the epoxy structure. In Fickian diffusion, the former mechanism is not taken into account and any relaxation of the material due to solution uptake is assumed to occur much more rapidly than the rate of diffusion.¹² Yet in practice, during the uptake of aqueous solutions into epoxyes, there is simultaneous diffusion and hydrogen bonding occurring and the material will swell and relax at a limited rate.

A number of experimental investigations have reported anomalous diffusion attributed to milder solution-polymer

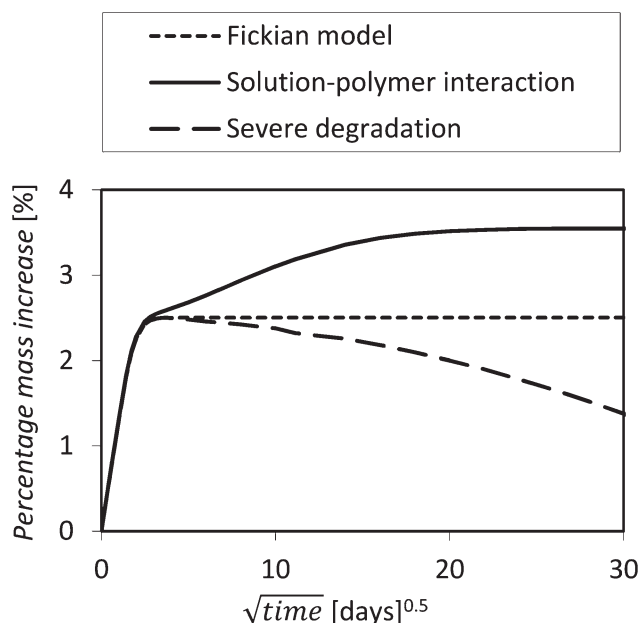


Figure 1. Illustrations of differing types of uptake behavior in epoxies.

interactions where the uptake behavior is seen to “drift” upwards (Figure 1) after an initially linear relationship between percentage mass increase and the square root of time.^{2,9,14–21} The degree of this behavior may even be dependent on the geometry of the test specimens.²² The upward drift has been observed to proceed at a considerably slower rate than the initial behavior which greatly prolongs the time to saturation. As a result, the majority of the aforementioned experimental investigations do not observe saturation in the epoxies studied.

Anomalous Diffusion Modeling

Attempts have been made to model anomalous diffusion in epoxies. The most common categories of model used are time-dependent,^{15,23} concentration-dependent,²⁰ relaxation-dependent,^{2,9,12,15,17,19} methods or methods that assign dual-phases to either the polymer (Jacob–Jones model)^{14,15} the moisture (Langmuir model),¹⁸ or uptake process in general.^{22,24} All of these methods rely on experimental observation in order to specify suitable parameters for anomalous diffusion models. Glaskova et al.¹⁵ quantified the effectiveness of a number of the above techniques for a selected epoxy, and found the Langmuir and relaxation models to be particularly effective. In the following, the Langmuir method was selected to model anomalous diffusion due to its reported effectiveness,^{15,16,18} its basis on scientific principle and its ability in principle to forecast percentage mass increase at saturation from a set of experimental results where saturation has not yet occurred.

Langmuir Diffusion Modeling

The Langmuir model considers the effect of diffusing molecules interacting with the epoxy polymer simultaneously with the occurrence of diffusion. As diffusing molecules move through the polymer they may become bound, with a probability γ , and bound molecules may again become free to diffuse, with probability, β . Thus, the Fickian diffusion process is simultaneously augmented with molecules becoming free, and diminished with molecules

becoming bound. Carter and Kibler¹⁸ are widely acknowledged as having formulated the model proposed in 1978, though a similar approach was described by Crank¹² in 1975. A summary of the Langmuir model outlined by Carter and Kibler¹⁸ follows.

The model assumes that molecules of solution entering a material are free, i.e., unbound, and can proceed to diffuse in a Fickian-like manner with an associated diffusion coefficient D_L . The concentration of free molecules at a given position is denoted as n rather than C . At any given time and position within the material, there is a probability (γ), that free molecules will become bound to the epoxy. The concentration of bound molecules at any point is denoted by N and there is a probability (β) that bound molecules will become free. At equilibrium, the relationship between free molecule concentration (n_∞) and bound molecule concentration (N_∞) is:

$$\gamma n_\infty = \beta N_\infty \quad (7)$$

The binding and freeing of molecules proceeds throughout the diffusion process, and so reduces and augments, respectively, the concentration of free molecules that are able to diffuse from any given point where:

$$D_L \frac{\partial^2 n}{\partial x^2} = \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} \quad (8)$$

$$\frac{\partial N}{\partial t} = \gamma n - \beta N \quad (9)$$

An exact solution for the concentration of free and bound molecules within a thin film, of thickness l , of initially dry material exposed to moisture at a constant concentration is derived in Ref. 18. A simplified approximation for the relative mass uptake, valid when 2γ and 2β are much smaller than κ is presented as:

$$\begin{aligned} \frac{M_t}{M_\infty} = & \frac{\beta}{\gamma + \beta} \exp(-\gamma t) \left[1 - \frac{8}{\pi^2} \sum_{p=1}^{\infty (\text{odd})} \frac{\exp(-\kappa p^2 t)}{p^2} \right] \\ & + \frac{\beta}{\gamma + \beta} [\exp(-\beta t) - \exp(-\gamma t)] + [1 - \exp(-\beta t)], \end{aligned} \quad (10)$$

$$2\gamma, 2\beta \ll \kappa$$

where

$$\kappa = \frac{\pi^2 D_L}{l^2} \quad (11)$$

The Langmuir type relationship between solution concentration at saturation and percentage mass increase in a thin film is:

$$M_\infty = \frac{100 M_{\text{eff}} (n_\infty + N_\infty)}{\rho_r} \quad (12)$$

Two further approximations can be used in conjunction with eq. (10). When exposure times are short, and uptake proceeds linearly with the square root of time,

$$M_t \approx \frac{4}{\pi^{3/2}} \left(\frac{\beta}{\gamma + \beta} \right) M_\infty \sqrt{\kappa t}, \quad 2\gamma, 2\beta \ll \kappa, \quad t < 0.7 / \kappa \quad (13)$$

is a valid approximation. When exposure times are sufficiently long, corresponding to post-linear uptake behavior, and κt is large compared to unity, the uptake behavior can be approximated as:

Table I. Experimental Evaluation of Diffusion Parameters for Epoxies in Salt Solutions

	Water parameters	Temperature	Salt solution concentration % wt	Ratio $M_{\infty,SW}/M_{\infty,W}$	Ratio D_{SW}/D_W (Fickian)	Comments
Kahraman and Al-Harhi ²⁵	$M_{\infty,W} \approx 9\%$ (300 days) $D_W \approx 3.46 \times 10^{-5} \text{ cm}^2/\text{day}$	Room	0.01	0.85	0.92	
		Room	0.1	0.79	1.06	
		Room	2.8	0.69	1.58	
		Room	5.5	0.60	1.39	
Tai and Szklarska-Smialowska ²⁶	$M_{\infty,W} = 7.5\%$ (49 days)	Room	0.010	0.77	No data	Results for "Adhesive A"
		Room	0.10	0.59	No data	
		Room	2.8	0.58	No data	
		Room	3.5	0.23	No data	
Chin et al. ²⁷	$M_{\infty,W} = 1.42\%$ (≈ 20 days) $D_W = 4.85 \times 10^{-5} \text{ cm}^2/\text{day}$	22°C	3.5	1.26	1.96	
		60°C	3.5	0.965	0.63	
Yang et al. ²⁸	$M_{\infty,W(\text{stage } 1)} = 0.76\%$ $M_{\text{max},W} = 0.83\%$ (1080 days) $D_{W(\text{stage } 1)} = 2.95 \times 10^{-5} \text{ cm}^2/\text{day}$	23°C	5	$\left. \begin{matrix} 0.26 \text{ (stage 1)} \\ \left\{ \begin{matrix} M_{\text{max},SW} \\ M_{\text{max},W} \end{matrix} \right\} = 0.35 \end{matrix} \right\}$	1.8 (stage 1)	Two stage Fickian model
Soulier et al. ³	$M_{\infty,W} = 2.7\%$ $D_W = 3.72 \times 10^{-4} \text{ cm}^2/\text{day}$	37°C	0.9	0.98	0.97	
		37°C	3.5	0.94	No data	
		37°C	7	0.93	0.98	
		37°C	15	0.87	0.82	
		37°C	35	0.69	0.90	

$$M_t \approx M_{\infty} \left[1 - \frac{\gamma}{\gamma + \beta} \exp(-\beta t) \right], \quad 2\gamma, 2\beta \ll \kappa, \quad t \gg 1/\kappa \tag{14}$$

By differentiating eq. (14), β and then γ can be calculated from experimental data of the mass uptake with time where:

$$-\left(\frac{dM_t}{dt}\right)^{-1} \frac{d^2 M_t}{dt^2} \approx \text{constant} = \beta \tag{15}$$

$$\exp(-\beta t) \left[\beta \left(\frac{dM_t}{dt}\right)^{-1} M_t + 1 \right] \approx \text{constant} = 1 + \beta/\gamma \tag{16}$$

SOLUTION DEPENDENCY

Of particular interest in this study is the effect of the solution on the moisture uptake. Common in-service conditions for FRP tendons include exposure to water (W), salt water (SW), and concrete pore solution (CPS) and thus a review of experimental studies relating to the behavior of epoxies subjected to similar environments was undertaken.^{25–29} Unless otherwise stated, Fickian models were used by the cited authors to infer the diffusion coefficients.

Water and Salt water

Table I compares the diffusion coefficients and percentage mass increase at saturation in epoxies when submerged in either water or salt water solutions. With the exception of the 22°C results from Ref.27, the findings suggest that the presence of sodium chloride salts in the diffusing water acts to decrease the percentage mass increase at saturation. The cited reasoning^{25,26,28} for the reduction was due to reverse osmosis occurring when water absorbed into a composite forms an electrolyte as it dissolves water-soluble substances within the polymer. Chin et al.²⁷ also noted that when studying solution uptake in salt water solutions at 60°C, mass loss associated with serious degradation was observed, which was not evident in epoxies exposed to water at equivalent temperatures. This indicates that salt solutions can precipitate more serious material degradation at higher temperatures.

There are no clear trends as to the effects of salt water solution on diffusivity. Kahraman and Al-Harhi²⁵ attribute an increased diffusivity to the ability of the salt solutions to form micro-cavities in the epoxies. Room temperature results for 3.5%²⁷ or 5%²⁸ salt concentration solutions also suggest a higher diffusivity when compared with water. In contrast, the similarity of the measured diffusivity in water and salt water solutions led

Table II. Experimental Evaluation of Diffusion Parameters for Epoxies in Alkaline Solutions

	Water parameters	Temp	pH	Solution details	$\frac{M_{\infty,CPS}}{M_{\infty,W}}$	D_{CPS}/D_W	Comments
Chin et al. ²⁷	$M_{\infty,W} = 1.42\%$ (≈ 20 days) $D_W = 4.58 \times 10^{-5}$ cm ² /day	22°C	13.5	NaOH: 0.68% wt KOH: 1.8% wt Ca(OH) ₂ : 0.5% wt	1.15	1.26	
	$M_{\infty,W} = 2.00\%$ (≈ 17 days) $D_W = 1.18 \times 10^{-3}$ cm ² /day	60°C			0.94	0.72	
Yang et al. ²⁸	$M_{\infty,W(\text{stage } 1)} = 0.76\%$ $M_{max,W} = 0.83\%$ (1080 days) $D_{W(\text{stage } 1)} = 2.95 \times 10^{-5}$ cm ² /day	23°C	8.5	Concrete leachate	$\left. \begin{array}{l} 0.88 \text{ (stage 1)} \\ \left\{ \frac{M_{max,CPS}}{M_{max,W}} = 1.84 \right\} \end{array} \right\}$	1.29 (stage 1)	Two stage Fickian model
Tsotsis and Lee ²⁹	$M_{\infty,W} = 6.6\%$ $D_W = 1.78 \times 10^{-2}$ cm ² /day	100°C	8.5	Ca(OH) ₂	≈ 1	≈ 1	Epoxy specimens containing carbon fibres
		100°C	10.5	Ca(OH) ₂	≈ 1	≈ 1	

Soulier et al.³ to infer from their experimental findings that the diffusion was concentration independent.

As the literature is inconclusive, it seems that the presence of salts in an aqueous exposure environment could either increase or decrease the rate of uptake and equilibrium moisture content, depending on the specific chemistry of the epoxy, cure cycle, cure state, and exposure temperature.

Alkaline Solutions

Experiments investigating the effect of alkalinity on diffusion in epoxy matrices (Table II) have generally found it to either have no effect²⁹ (although these tests were conducted on composites), or to increase both the diffusivity and percentage mass increase in the material at saturation. Yang et al.²⁸ stated that greater matrix deterioration was the reason for the observed higher percentage mass increase at saturation in the alkali solutions. Furthermore, at elevated temperatures, alkali solutions have been seen to precipitate serious material degradation not seen in specimens exposed to water at the same temperature²⁷ which, as with salt water solution, suggests that alkali solutions can precipitate more serious material degradation at higher temperatures.

EXPERIMENTAL

The significance of the exact nature of the diffusing solution is evaluated by considering absorption of water, salt water, and concrete pore solution in thin films of epoxy materials. Additional factors taken into consideration include the initial moisture content and the effect of temperature. In the following, the thin film preparation and the relevant preconditioning and exposure conditions of the experimental specimens will be detailed.

Epoxy Sample Preparation

The epoxy studied was an EPR4434/EPH943. The EPR4434 resin consists of 25–50% 1,6-hexanediol diglycidyl ether, 25–50% methylenedianiline and 25–50%, bisphenol F diglycidyl ether (DGEBF). The EPH943 hardener is 100% isophoronediamine.

Thin films were prepared in an aluminium alloy plate containing a machined flat channel of width 40 mm, length 160 mm, and nominal depth 0.3 mm. Quantities of resin and hardener were weighed out according to the proprietary mixing ratio, and thoroughly mixed. The mixture was degassed at an absolute pressure of 1.5 kPa. A quantity of the epoxy was deposited towards one end of the mould and, in accordance with the ASTM standard D 823-87,³⁰ a hand-held drawdown method was used to spread the epoxy evenly over the channel. The films were cured in an oven using a proprietary curing cycle. The exact details of the cure cycle are confidential but during the curing process the films were heated to a maximum temperature of 195°C. Given the adhesive, brittle nature of epoxies, demolding thin films of the material without damaging them was a challenge. The technique developed was to demold the specimens by cutting the hot, ductile epoxy away from the sides of the channel with a scalpel, before prising a thin aluminium shim between the mould and the film strip. After the film strip had cooled to ambient temperature, it was scored using a scalpel then snapped into individual specimens. The glass transition temperature (T_g) values measured from two differential scanning calorimetry (DSC) tests were 132.9 and 141.0°C, which compared favorably to the values reported by the manufacturer of between 135.5 and 145°C measured by dynamic mechanical thermal analysis (DMTA).

To investigate the influence of initial moisture in the specimen on the uptake characteristics, some samples were preconditioned using desiccation to remove any moisture in the sample. The desiccated thin film samples were placed in a desiccator at a room temperature of approximately 20°C.

Moisture Uptake

The samples of the epoxy matrix were submerged in either distilled water (W), salt water (SW), or an alkaline solution to simulate exposure to concrete pore solution (CPS). The salt water and concrete pore solutions were formulated as described

Table III. Experimental Evaluation of Thin Film Epoxy Specimens

Notation	Dimensions (mm)	Desiccation	Age at testing	Series	SW	W	CPS	20°	60°	No. samples
SW-20-U-F	40 × 35 × 0.3398	N	≤6 days	1	X			X		5
W-20-U-F	40 × 35 × 0.3415	N	≤6 days	1		X		X		5
CPS-20-U-F	40 × 35 × 0.3393	N	≤6 days	1			X	X		5
SW-20-D-F	38 × 18 × 0.3488	Y	2 years	3	X			X		3
SW-60-D-F	38 × 18 × 0.3359	Y	2 years	3	X				X	3

by Chin et al.²⁷ The salt water solution comprised of 3.5% by mass sodium chloride and deionized water. Unfortunately, there is no general consensus in the literature about the chemical composition of concrete pore solution (Table II). The concrete pore solution used here comprised of 0.68% by mass sodium hydroxide (NaOH), 1.8% by mass potassium hydroxide (KOH), and 0.5% by mass calcium hydroxide Ca(OH)₂ based on Ref. 27. Tests showed the pH of the solution to be 13.5. However, it was noted that the concentration of Ca(OH)₂ was much higher than that noted in the baseline Christensen³¹ reference. Despite this discrepancy, even at the lower concentration, experiments showed that the Ca(OH)₂ was in excess of that required for saturation.

The thickness of each film was measured in seven places using a Universal Horizontal Microscope of 100 nm resolution. The dry samples were then weighed, before being submerged in individual containers of W, SW, or CPS and stored at either 20°C in a temperature controlled lab or placed in an oven maintained at 60°C for the duration of the test. Gravimetric sorption was used to measure the solution uptake: the films were removed from solution, rinsed in deionized water, blotted dry, then weighed before being returned to solution. This method was repeated twice for each film at each time interval. The percentage mass increase at time t , M_t , based on the measured mass, m_t for each film was calculated as:

$$M_t = 100 \left[\frac{m_t - m_0}{m_0} \right] \quad (17)$$

M_∞ can be measured experimentally from a specimen's mass at saturation (m_∞) and its dry mass (m_0) where:

$$M_\infty = 100 \left[\frac{m_\infty - m_0}{m_0} \right] \quad (18)$$

When calculating the mass uptake in the salt water solution, it was assumed the solution was a homogeneous mixture of dissociated water molecules, aqueous sodium ions and aqueous chloride ions. This may not strictly be the case. However, by formulating models based on macro effects of diffusion, i.e., the experimentally observed mass increase behavior, it is possible to simplify the modeling without the need to consider this in-depth aspect of diffusion chemistry. Thus an average molecule mass was calculated based on the ratios of molecules per liter of solution.

Experimental Series and Results

The experimental program is summarized in Table III. The notation used to denote each sample is a prefix of two letters

which denote the solution type where W = water, SW = salt water, and CPS = concrete pore solution, followed by the numerical value of the temperature, either 20°C or 60°C, a further letter indicates the initial moisture state where U = undesiccated and D = desiccated and the final "F" indicates that the sample is a film. Hence SW-20-U-F would be a non-desiccated thin film sample subjected to salt water at 20°C. The average thin film dimensions, including the film thickness, are also shown in Table III. As discussed, the main parameters were the initial moisture condition (with or without desiccation), the exposure conditions and the temperature. The mass uptake results are plotted in Figure 2 where each data point represents the average of either five or three specimens (Table III). Error bars illustrate 95% confidence limits assuming a normal distribution of data.

The measurements for the desiccated and undesiccated specimens were taken over an initial period of around 100 and 500 days, respectively. Even after this time, the films did not appear to be saturated. An opportunity then arose to take a further set of readings after around 800 and 1800 days exposure of the desiccated and undesiccated specimens, respectively. Although some of the 60°C samples had dried out and had to be discarded, these later, albeit limited, readings will be used to give an indication of the robustness of the predictions and observations based on the initial measurement period.

By considering the undesiccated specimens subjected to different exposure conditions, the uptake behavior appears to be solution-independent for the most part, with the solution uptake generally greater in water than in salt water or concrete pore solution at 20°C. After the initial linear relationship between percentage mass increase and the square root of time, a pronounced "upward drift" is evident suggesting Langmuir-type diffusion is occurring.

The effect of desiccation can be determined by comparing SW-20-U-F and SW-20-D-F. The desiccated results had a higher mass uptake at a given time and seemed to display a smaller scatter. Based on the 100 day results, the temperature comparison (SW-20-D-F and SW-60-D-F) suggested that although the initial uptake slopes differed, the specimens were converging to similar values with increasing saturation. However, the later readings at 800 days exposure show a marked divergence in mass uptake suggesting the higher temperature exposure increased the propensity for uptake. As the experiments progressed, it was noted that the films exposed at 60°C darkened in appearance, whereas the films exposed at 20°C did not.

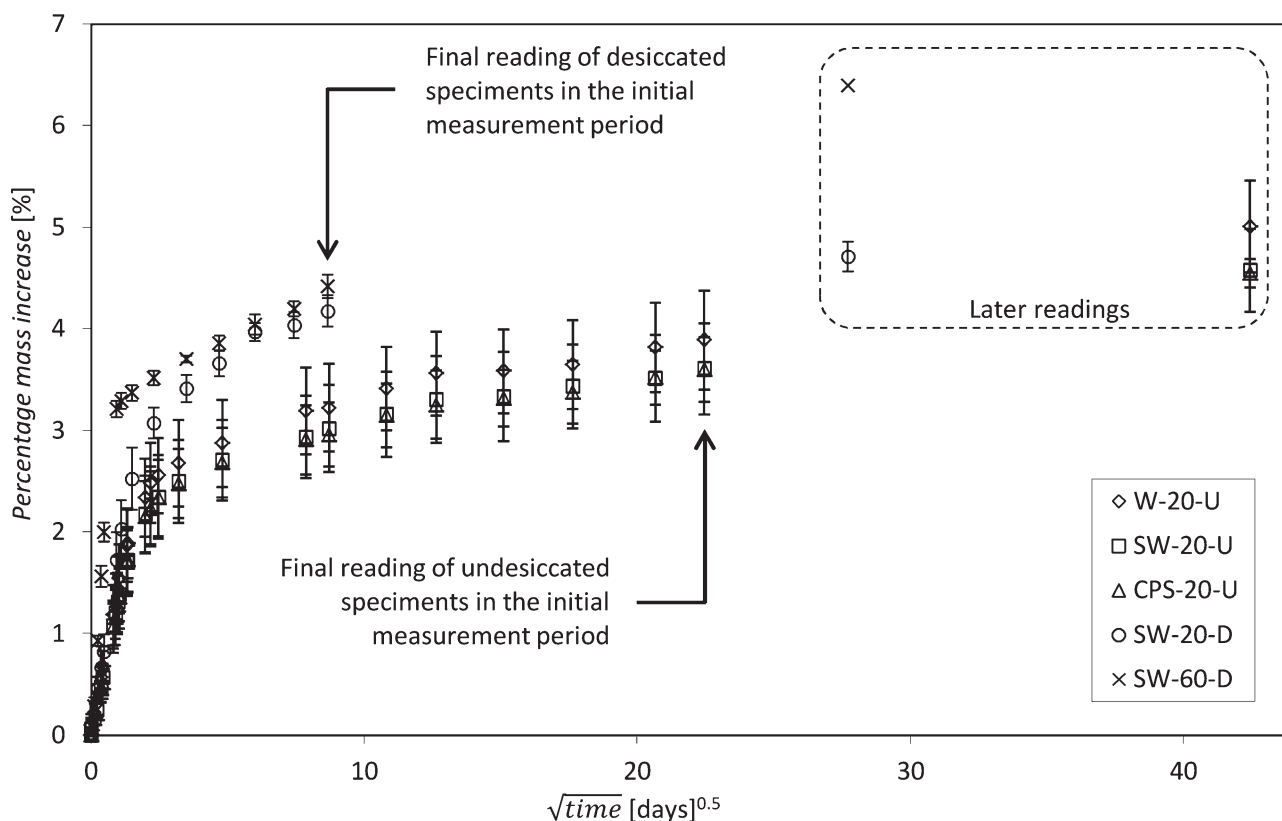


Figure 2. Thin film experimental results for the percentage mass increase with time.

However, no visual cracking in the films exposed at 60°C could be observed in optical microscope images taken at 20 and 50× magnification at 450 days.

DIFFUSION MODELING

Both the Fickian and Langmuir diffusion parameters were calculated from the experimental results based on the initial measurement period. In the Fickian model, the two necessary parameters to obtain are the percentage mass increase at saturation (M_∞) and the diffusion coefficient (D). The diffusion coefficient is calculated from the initial linear slope of the experimental data curves shown in Figure 2. A least squares analysis was used to obtain the best fit. The diffusion coefficient can then be calculated by rearranging eq. (6) and substituting in M_∞ , which is taken to correspond to the mass uptake reading at either 100 days (for the desiccated specimens) or 500 days (for the undessicated specimens), and the calculated best fit value of the slope.

The first step in constructing a Langmuir model to describe the experimental results is to obtain the parameters β and γ based on eqs. (15) and (16). To obtain β from the experimental results, Carter and Kibler¹⁸ describe fitting a curve through the experimental results at longer times but further details were not provided. In a review of other studies that have utilized the Langmuir method, the description of how the Langmuir parameters were inferred was either omitted, Ref. 32 made reference

to Carter and Kibler, or regression techniques were cited.^{33,34} Suri and Perreux,³⁴ who used a non-linear regression to fit of the experimental data, highlighted that there are accuracy problems in calculating β using “highly unstable” numerical derivatives. Bonniau and Bunsell³⁵ used a minimum variances method, that solves four simultaneous equations expressed in terms of β , γ , D , and M_∞ . Though they found the method to be effective, it does require the experimental observation of M_∞ , which is a prohibitive restraint when saturation tends to occur only after extended periods of time.

In this study, two methods were subsequently employed and compared to evaluate the β and γ coefficients. The first was a numerical point-by-point method where average values of β and γ were calculated from the experimental data. The second method used the Simplex algorithm to evaluate a nonlinear regression fit to the experimental data. The benefit of the numerical method was its simplicity. However, the non-uniform spacing of the data points and the experimental scatter presented difficulties in accurately calculating the first and second derivatives at each experimental data point. The result was a considerable fluctuation in what should be constant values of γ and β . Given these limitations, a nonlinear regression approach was preferred and an equation of the form:

$$M_t \approx A + B \exp(-\lambda t), \quad 2\gamma, 2\beta \ll \kappa, \quad t \gg 1/\kappa \quad (19)$$

was sought to satisfy the exponential long term behavior approximation during the initial measurement period. The

Table IV. Relative Fickian Diffusion Parameters for Thin Films Exposed to Water, Salt Water and CPS at 20°C

Water parameters	Salt solution details	$M_{\infty,SW}/M_{\infty,W}$	D_{SW}/D_W	CPS solution details	$M_{\infty,CPS}/M_{\infty,W}$	D_{CPS}/D_W
$M_{\infty,W} = 3.893\%$ $D_W = 3.074 \times 10^{-5}$ (cm^2/day)	3.5% wt	0.925	0.99	NaOH: 0.68 % wt KOH: 1.8 % wt $\text{Ca}(\text{OH})_2$: 0.5 % wt	0.924	0.990

parameters A , B , and λ were evaluated by minimizing the least squares error of eq. (14) to the experimental data points using the Simplex algorithm, implemented in MATLAB by X. S. Yang. From these values, β could be calculated directly from λ , and subsequent parameters γ , $M_{\infty,L}$, κ , and D_L were then determined. The solutions were checked to ensure the validity of the Langmuir modeling namely that, the values of γ and β should be much smaller than κ , $t \gg 1/\kappa$ and that only data points were used that lie at times when the approximation converges with the governing behavior equation.

One drawback of the regression analysis is that minimizing the square of the error does not necessarily accurately represent the trend in the later data points, an important aspect of forecasting future behavior. Therefore, there can be a scenario where the model predicts that saturation has all but occurred but the trend in the last few data points suggests otherwise. The calculated Langmuir parameters from the regression fit also depend on the time of the selected starting mass uptake point since,

when earlier data points are discounted, greater weighting is effectively put on the later points, and the predicted percentage mass increase at saturation then rises.

Modeling Results and Calculated Parameters

In Table IV, the 20 °C Fickian diffusion parameters for the salt water and concrete pore solution are calculated relative to the water results to facilitate comparison with results in the literature. The salt water results seem to be similar to those obtained by Soulier et al.³ for a solution with a similar concentration. However, whereas a number of researchers found that $M_{\infty,CPS}/M_{\infty,W}$ was greater than 1 (Table II), in this study, this ratio was slightly less than 1.

Since the general shape of the uptake curves were broadly similar across solutions, only the salt water results will be presented here to highlight the differences between the Langmuir and Fickian predictions. Figure 3 compares the long term predictions of the two models based on the initial measurement period. As expected, this figure shows that by dictating the

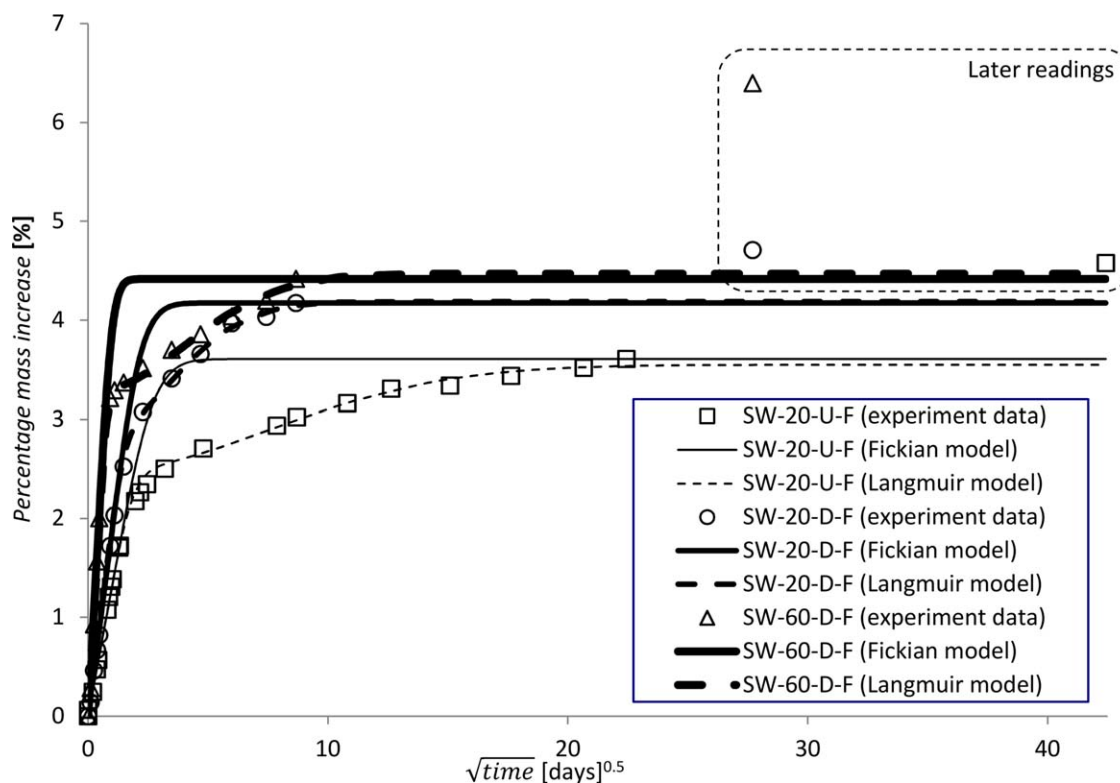


Figure 3. Fickian and Langmuir predictions for long-term mass uptake behavior. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Fickian and Langmuir Diffusion Parameters for Thin Films Exposed to Salt Water

Diffusion type		SW-20-U-F	SW-20-D-F	SW-60-D-F
Fickian	$D_{e,F}$ (cm ² /day)	2.999×10^{-5}	4.820×10^{-5}	2.187×10^{-4}
	$M_{\infty,F}$ (%)	3.599	4.174	4.416
Langmuir	β (day ⁻¹)	0.008873	0.04726	0.03139
	γ (day ⁻¹)	0.003910	0.02420	0.01163
	$((\beta+\gamma)/\gamma)^2$	2.076	2.286	1.878
	$D_{e,L}$ (cm ² /day)	6.432×10^{-5}	1.095×10^{-4}	4.008×10^{-4}
	$M_{\infty,L}$ (%)	3.549	4.188	4.470

percentage mass increase at a given time, there is a good agreement between the experimental results and the Fickian model at that juncture and the agreement is also good in the initial linear portion of the curve. However, at intermediate times, the Fickian model considerably overestimates the percentage mass increase. Furthermore, the later measurements show that, as further uptake continues to occur, the Fickian model underestimates the true percentage mass increase at saturation. In general, the Langmuir model appears to be a better predictor than the Fickian model as an indicator of the experimental data during the initial measurement phase. But again, the longer-term mass increases were underestimated in light of the 800 and 1800 day findings. The calculated diffusion parameters for the initial measurement periods are shown in Table V where the mass uptake at “saturation” is denoted as $M_{\infty,F}$ and $M_{\infty,L}$ and the diffusion coefficients $D_{e,F}$ and $D_{e,L}$ for the Fickian and Langmuir models, respectively.

Initial Moisture Content

It is of note that the parameters differ depending on whether the films were desiccated or not. The desiccated result is a purer measurement, but it is of interest to investigate how undesiccated results could be adjusted accordingly. With the desiccated specimens it was found that most of the mass loss occurred in the first couple of days of desiccation and after 19 days, where the mass readings had become more stable, the average mass loss was 1.40%. The undesiccated specimens were made in a series of batches, and stored in a laboratory with an average relative humidity of 45% for no more than 6 days before testing began. Carter and Kibler¹⁸ proposed a knockdown factor to account for humidity and suggests that the mass uptake after exposure to 45% RH would be one-third of that of the submerged saturated mass uptake in water. Using the desiccated mass at saturation, this also gives an expected moisture uptake of 1.39% which is consistent with the measured desiccation results. A positive correlation between the magnitude of the drift and the relative humidity was reported in all studies in which it was a variable.^{2,9,15,17}

If the drying process is assumed not to have had a major effect on the behavior, then the diffusion coefficients for the desiccated and undesiccated films each at 20°C should be the same. The discrepancy in Table V is caused by the differing times at which the diffusion coefficients were calculated based on available data: after 500 days exposure for the undesiccated films, and 100 days exposure for the desiccated films. Calculation of

the diffusion coefficient for undesiccated films after a comparable period of exposure of approximately 100 days yields a Fickian diffusion coefficient of 4.499×10^{-5} cm²/day, significantly more similar to that of the desiccated films.

The Langmuir parameters reflect a certain concentration dependency of initial moisture content since the percentage of bound and unbound molecules potentially change with concentration. This can be seen in Table V where the ratios of $[(\gamma + \beta)/\gamma]^2$ for the desiccated and non-desiccated samples are compared.

Temperature

The desiccated diffusivity at 60°C was found to be approximately four times that at 20°C. At 100 days, the mass uptake at both temperatures was found to differ by only 6% but after 800 days the difference was 36%. Work by others has found the degree of non-Fickian behavior to be temperature dependent and, as the exposure temperature increases, so does the strength of the upward drift.^{2,9,16,21} At higher temperatures (Roy *et al.*²³ at 70°C and Popineau *et al.*¹⁶ at 60°C) the corresponding increase in upward drift can cause a sufficient shortening in the period taken to reach saturation such that a Fickian prediction of uptake behavior is a better representation than at lower temperatures. However, this behavior may also be the result of some breakdown of the polymer resulting in a decrease in mass which offsets any upwards drift. In this study, the higher temperature uptake at 60°C was anomalous which contradicts these findings. The experimental trends are more consistent with the 3-year deionized water exposure results from Ref. 28 where the maximum mass uptake in thin films at 60°C (6.38%) was found to be much greater than at 37.8°C (1.86%) and 23°C (0.83%).

DISCUSSION

The highest mass uptake in the thin films was noted after exposure to water but broadly speaking the salt water, water, and concrete pore solution 20°C uptake results were similar. The influence of the solution type did not appear to be time-dependent but the mass in the thin films did continue to increase with time. Marked differences between the mass uptake at the end of the initial measurement period at 100 (≈0.3 years) or 500 days (≈1.4 years), and the later readings at 800 (≈2.2 years) or 1800 days (≈4.9 years) were noted.

The dependency of the calculated diffusion parameters on the mass at saturation is an issue in terms of developing model

predictions. Using diffusion parameters obtained from the initial measurement period, neither the Fickian nor the Langmuir models gave an accurate prediction of the later readings, even when exposure was accelerated at 60°C. It has also been noted elsewhere that even after 36 months of exposure, final equilibrium may not have been reached.²⁸ This means that the parameters reported here, and, in many studies, elsewhere, can only be considered as approximate and are highly dependent on the length of time over which the solution uptake is measured. Unfortunately, the need to leave the thin films for extended periods of time negates the advantages of using thin films as a means to identify parameters in a short timeframe. Therefore, while the thin film tests can be used as a powerful relative measure to identify solution dependency, the value for the long-term extrapolation of the performance of a CFRP requires further investigation.

The desiccated results had less scatter than the undessicated results but the effect of the initial equilibrium moisture content in the thin film on the mass uptake was inconclusive. It would be expected that the initial moisture content would represent an offset in terms of the total percentage mass increase. From the trend of the mass uptake readings, e.g., after 800 days for the desiccated and 1500 days for the undessicated films were similar ($\approx 4.5\%$), it is not yet clear whether the initial moisture content is insignificant compared to the uptake capacity of the thin films at saturation.

The use of higher temperatures seemed to accelerate the uptake in the early stages of exposure and again in the later stages of exposure. The difference between the initial measurement period results and the later readings was more striking in the case of 60°C exposure than for 20°C which suggests that the uptake mechanisms depend on the exposure temperature. Additional temperatures should be tested to investigate the relationship between the diffusion and temperature and to develop Arrhenius plots. However, the reason for using higher temperatures was primarily to accelerate the uptake and thereby shorten the required length of time for the experiments. Therefore, a temperature dependency limits the viability of using short-term accelerated thin film measurements unless they can provide an indication of the long-term performance of a CFRP tendon subjected to lower temperatures.

Chemical testing of the samples at each stage of the experimental program, e.g., after curing, after heating to 60°C and after immersion in solution, would help to identify any chemical changes in the thin films and to quantify the relationship between the chemical composition and the observed behavior. This should be the subject of future work. A further question is whether thin film uptake results can be reliably extrapolated to predict the mechanical performance of a CFRP tendon. This is also an area for further study.

CONCLUSIONS

Solution uptake in epoxies has been found to depend on the exposure temperature, the solution type, and the matrix material. The behavior can be modeled as Fickian or using anomalous, Non-Fickian, diffusion models. The uptake behavior of thin

films is widely used to determine the relevant diffusion parameters.

In the tests reported here, the type of solution, either water, salt water, or a concrete pore solution, did not have a significant effect on the solution uptake. Anomalous diffusion was observed in the epoxy at 20 and 60°C, although no mass loss, associated with severe degradation, was observed. To observe saturation experimentally, the use of higher temperatures (60°C) as a means of acceleration, led to a higher initial diffusion coefficient, and a higher mass uptake, than that obtained in specimens exposed to 20°C. However, work by others suggests that higher temperatures may alter the nature of diffusion in composites. It is preferable to desiccate specimens prior to testing, as this allows the true value, rather than perceived value, of moisture content at saturation to be observed. Nonetheless, the initial moisture content may not be significant compared to the uptake capacity of the thin films at saturation.

Using the experimental results, Fickian and Langmuir diffusion parameters were calculated for the epoxy at 20 and 60°C. A Fickian model gave a poor approximation to the uptake behavior at intermediate times and was sensitive to the value used for the mass at saturation. The Langmuir diffusion model was found to more effectively model the anomalous diffusion in the epoxy. A regression analysis was used to determine the Langmuir parameters but one limitation was that, although the regression analysis minimizes the error between the predicted behavior and the experimental results, the later trends in experimental points are not necessarily accurately represented which will affect the predicted mass at saturation.

In spite of the accelerated approach, conclusive values of uptake at saturation remained elusive even at an exposure period of 5 years. This finding questions the viability of using short-term thin film results to predict the long-term mechanical performance of FRP materials.

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