Gradient-dependent Model for Moisture Diffusion in a Polymer Matrix Composite Laminate

CHO-LIANG TSAI*

Department of Construction Engineering, National Yunlin University of Science and Technology, Touliu, 640 Yunlin, Taiwan and Service Center of Construction Technology and Material Testing National Yunlin University of Science and Technology Touliu, 640 Yunlin, Taiwan

MING-CHANG CHENG

Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology, Touliu, 640 Yunlin Taiwan and Department of Mechanical Enginering, Southern Taiwan University of Technology, 710 Tainan, Taiwan

SHING-LIN CHANG

General Education Center, Southern Taiwan University of Technology, 710 Tainan, Taiwan

(Received July 27, 2005)
(Accepted January 4, 2006)

ABSTRACT: This study presents a new diffusion model named the gradient-dependent model. It is based on the strain-dependent model, a modification of Fick's diffusion model, and is employed to solve penetrant diffusion in a 2D-infinite plate with finite thickness. An immersion test is performed and analyzed for studying moisture diffusing through the surfaces of a polymer matrix composite laminate into the material and the induced in-plane expansion is measured. The hygric expansion is proportional to the moisture concentration, which can be derived from the gradient-dependent model involving parameters standing for the hygric property of the material. By fitting the theoretical solution of the hygric expansion to the data, the parameters for locating the penetrant front can be obtained and they are very important in describing the hygric behavior of the material.

KEY WORDS: diffusion, hygric expansion, moisture concentration, penetrant front.

*Author to whom correspondence should be addressed. E-mail: tsaicl@ce.yuntech.edu.tw

0021-9983/07/04 0419–16 $10.00/0 DOI: 10.1177/0021998306063794

INTRODUCTION

FICK FIRST PUT diffusion on a quantitative basis and published the pioneering Fick's diffusion model in 1855 [1]. Fick's hypothesis is that the rate of transfer of a diffusing substance, called a penetrant, through a unit area of a cross section of the media is proportional to the gradient of the penetrant concentration in diffusion direction but with the opposite sign. The model has been adopted in solving many diffusion cases, such as diffusions in semi-infinite domain and a 2D-infinite plate. However, all the solutions based on the model indicate that the penetrant concentration everywhere in the media material becomes non-zero immediately after the diffusion begins. If the location is deep and the diffusion duration is short, then the concentration is very low but non-zero. No penetrant molecules can possibly penetrate the media and reach the deeper part of the material without reasonable duration.

Frisch et al. [2] modified the model into a strain-dependent model by including the first derivative term of the penetrant concentration w.r.t. the diffusion coordinate into the governing equation of Fick's model, and solved two cases, diffusions in semi-infinite domain and a 2D-infinite plate with finite thickness [2,3]. Their solutions indicate that the penetrant penetrates the media progressively. The location of the penetrant front can be calculated from the solution which is the advancing front boundary of the diffusing penetrant [4].

However, Frisch et al.'s solution for diffusion in the 2D-infinite plate does not satisfy the condition that the penetrant concentration in the plate has to be symmetrical w.r.t. the center of the plate when the external conditions on both sides are the same. This study confirms that the strain-dependent model can never result in a symmetric solution for the case. However, if the sign of the first derivative term in the strain-depending model is dependent on the diffusion direction, then the model can yield a symmetric solution for the case. The modified model is called the gradient-dependent model.

An immersion test of unidirectional continuous fiber polymer matrix T700 carbon/epoxy composite laminate was conducted. In the experiment, dry composite laminates were immersed in water, and the data of their expansion in in-plane fiber's transverse direction induced by moisture absorption through both surfaces were obtained by the suspension method [5,6]. The hygric expansion is proportional to the average moisture concentration in the laminate, which can be calculated by the solution derived from theoretical diffusion model allowing the theoretical function of the hygric expansion to be derived [5,6]. The function involves parameters denoting the hygric property of the material. Based on least square curve fitting, the parameters can be obtained when adjusting them to optimize the fitting of the function to the data. The parameters are very important for describing the hygric property of the material to predict the hygric behavior of the laminate such as the induced hygric stress.

The theoretical function of the hygric expansion derived from Fick's model can fit the data very well. The gradient-dependent model only provides a limited improvement to the fitting, which is not the major concern of this study. The major contributions of this study are: (1) developing the delicate gradient-dependent diffusion model to calculate the penetrant front [3] (advancing boundary [1,4]), and (2) configuring the experimental and analysis process for obtaining the saturated hygric expansion strain, diffusivity, and gradient coefficient of a plate.

THEORETICAL BACKGROUND

The governing equation of Fick's model for one-dimensional penetrant diffusing in the media is given by

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

where c is the penetrant concentration in the media; t is the diffusion duration; D is the diffusivity, and x is the coordinate of diffusion direction. When the original of the coordinate x is set at the center of the plate (Figure 1), the solution of c for the penetrant diffusing through both surfaces into a 2D-infinite plate with thickness h is given by [1]

$$c(t,x) = c_\infty\left\{1 - \frac{4}{\pi}\sum_{n=1,3,5,\ldots}^{\infty}\left[\frac{(-1)^{(n-1)/2}}{n}e^{-(n\pi/h)^2 Dt}\cos\left(\frac{n\pi}{h}x\right)\right]\right\} \tag{2}$$

where c_∞ is the saturated concentration. The average concentration over the thickness is given by

$$\bar{c}(t) = c_\infty\left[1 - \frac{8}{\pi^2}\sum_{n=1,3,5,\ldots}^{\infty}\frac{1}{n^2}e^{-(n\pi/h)^2 Dt}\right]. \tag{3}$$

If the hygric expansion of the material is proportional to the concentration [6], then the in-plane hygric expansion strain of the plate is given by [6]

$$\varepsilon(t) = \varepsilon_\infty\left[1 - \frac{8}{\pi^2}\sum_{n=1,3,5,\ldots}^{\infty}\frac{1}{n^2}e^{-(n\pi/h)^2 Dt}\right] \tag{4}$$

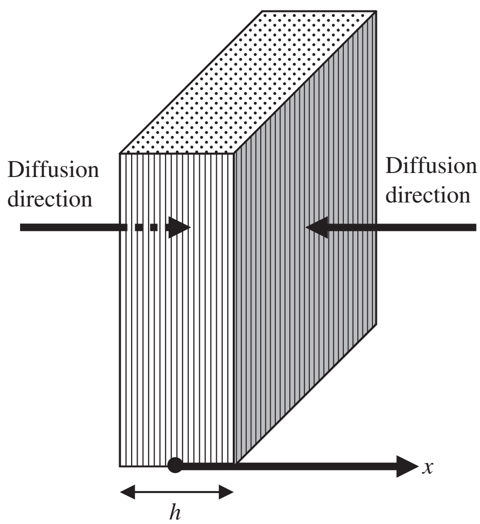

Figure 1. *Penetrant diffusing through both surfaces into a 2D-infinite plate with thickness h.*

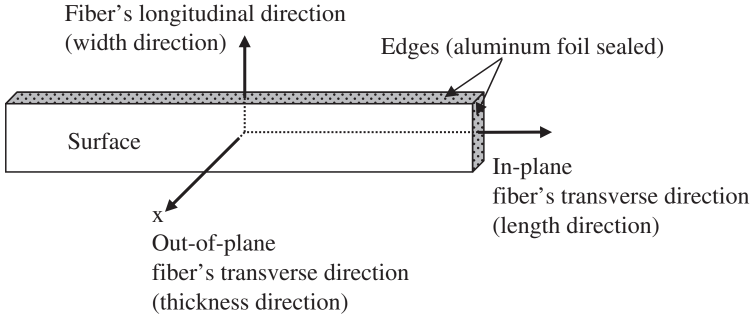

Figure 2. *Three principal directions of an unidirectional composite laminate.*

where ε_∞ is the saturated hygric strain. For an unidirectional composite laminate, the hygric strain in the fiber direction is extremely small [5,6]. This study focuses on the hygric expansion in the in-plane fiber's transverse direction due to moisture absorption through both surfaces, which can be measured by the suspension method [6] (Figure 2). The values of ε_∞ and D can be derived by fitting Equation (4) to the data of the hygric expansion strain.

However, the penetrant needs time to reach the core part of the media material [1], indicating that Equation (2) is improper because it shows that immediately after the diffusion begins, the c at the center of the plate ($x = 0$) becomes non-zero, regardless of how small t is and how large h is. The value of c is very small but definitely non-zero. This result implies that very few molecules of the penetrant can penetrate the material and reach the deepest core part of the plate in no time as the diffusion begins, and that cannot be true.

This problem could not be solved until Frisch et al. published a different model [2,3]. A first-order derivative term was included in Equation (1), producing

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - \nu\frac{\partial c}{\partial x} \tag{5}$$

where ν is the coefficient for the first-order derivative term of c w.r.t. x, gradient coefficient. The model was named the strain-dependent model. Two cases were solved using the model, diffusions in semi-infinite domain and a 2D-infinite plate with finite thickness. The solutions indicate an advancing boundary [1], showing that the penetrant front moves progressively deeper into the inner part of the material. Nevertheless, the solution for the second case does not satisfy the condition that the penetrant concentration should be symmetric w.r.t. the center of the plate when the conditions on both sides are the same. The details of solving this case are reconsidered herein.

To solve Equation (5), let $c(t, x) = T(t)X(x)$, where T is a function of t and X is a function of x. Equation (5) becomes

$$\dot{T}X = DTX'' - \nu TX' \tag{6}$$

$$\frac{\dot{T}}{T} = \frac{DX'' - nX'}{X} = -k, \quad k\text{: constant} \tag{7}$$

$$\begin{cases} \dot{T} + kT = 0 \\ DX'' - nX' + kX = 0 \end{cases} \tag{8}$$

For $k = 0$,

$$\begin{cases} T = K_1, \quad K_1: \text{ constant} \\ X = K_2 \text{ or } K_3 e^{(\nu/D)x}, \quad K_2, K_3: \text{ constants} \end{cases} \tag{9}$$

$$c(t,x) = K_1 K_2 + K_1 K_3 e^{(n/D)x} = \alpha_0 + \alpha_1 e^{(n/D)x}, \quad \alpha_0, \alpha_1: \text{ constants.} \tag{10}$$

For $k \neq 0$, and $k = \nu^2/4D$ or $\sqrt{\nu^2 - 4Dk} = 0$

$$\begin{cases} T = K_4 e^{-kt} = K_4 e^{\left(-\nu^2/4D\right)x}, \quad K_4: \text{ constant} \\ X = K_5 e^{(\nu/2D)x} \text{ or } K_6 x e^{(\nu/2D)x}, \quad K_5, K_6: \text{ constants} \end{cases} \tag{11}$$

$$\begin{aligned} c(t,x) &= K_4 K_5 e^{-\left(\nu^2/4D\right)t + (\nu/2D)x} + K_4 K_6 x e^{\left(\nu^2/4D\right)t + (\nu/2D)x} \\ &= \alpha_2 e^{-\left(\nu^2/4D\right)t + (\nu/2D)x} + \alpha_3 x e^{-\left(\nu^2/4D\right)t + (\nu/2D)x}, \quad \alpha_2, \alpha_3: \text{ constants.} \end{aligned} \tag{12}$$

For $k \neq 0$, and $\nu^2 - 4Dk < 0$

$$\begin{cases} T = K_7 e^{-kt}, \quad K_7: \text{ constant} \\ X = K_8 e^{(\nu/2D)x} \sin\left(\dfrac{\sqrt{4Dk - \nu^2}}{2D} x\right) \text{ or } K_9 e^{(\nu/2D)x} \cos\left(\dfrac{\sqrt{4Dk - \nu^2}}{2D} x\right) \\ \qquad K_8, K_9: \text{ constants} \end{cases} \tag{13}$$

$$\begin{aligned} c(t,x) &= K_7 K_8 e^{-kt + (\nu/2D)x} \sin\left(\frac{\sqrt{4Dk - \nu^2}}{2D} x\right) + K_7\, K_9 e^{-kt + (\nu/2D)x} \cos\left(\frac{\sqrt{4Dk - \nu^2}}{2D} x\right) \\ &= \alpha_4 e^{-kt + (\nu/2D)x} \sin\left(\frac{\sqrt{4Dk - \nu^2}}{2D} x\right) + \alpha_5 e^{-kt + (\nu/2D)x} \cos\left(\frac{\sqrt{4Dk - \nu^2}}{2D} x\right) \\ &\qquad \alpha_4, \alpha_5: \text{ constants.} \end{aligned} \tag{14}$$

For multiple values of k, k_n, $n = 1$ to ∞,

$$c(t,x) = \sum_{n=1}^{\infty} \left[\alpha_{4n} e^{-k_n t + (\nu/2D)x} \sin\left(\frac{\sqrt{4Dk_n - \nu^2}}{2D} x\right) + \alpha_{5n} e^{-k_n t + (\nu/2D)x} \cos\left(\frac{\sqrt{4Dk_n - \nu^2}}{2D} x\right) \right]$$
$$k_n, \alpha_{4n}, \alpha_{5n}: \text{ constants.} \tag{15}$$

For $k \neq 0$, and $\nu^2 - 4Dk > 0$

$$\begin{cases} T = K_{10} e^{-kt}, \quad K_{10}: \text{ constant} \\ X = K_{11} e^{\left(\nu + \sqrt{\nu^2 - 4Dk}/2D\right)x} \text{ or } K_{12} e^{\left(\nu - \sqrt{\nu^2 - 4Dk}/2D\right)x}, \quad K_{12}, K_{13}: \text{ constants} \end{cases} \tag{16}$$

$$\begin{aligned} c(t,x) &= K_{10} K_{11} e^{-kt + \left(\nu + \sqrt{\nu^2 - 4Dk}/2D\right)x} + K_{10} K12 e^{-kt + \left(\nu - \sqrt{\nu^2 - 4Dk}/2D\right)x} \\ &= \alpha_6 e^{-kt + \left(\nu + \sqrt{\nu^2 - 4Dk}/2D\right)x} + \alpha_7 e^{-kt + \left(\nu - \sqrt{\nu^2 - 4Dk}/2D\right)x}, \quad \alpha_6, \alpha_7: \text{ constants.} \end{aligned} \tag{17}$$

For multiple values of k, k_n, $n = -1$ to $-\infty$,

$$c(t,x) = \sum_{n=-1}^{-\infty} \left(\alpha_{6n} e^{-k_n t + \left(\nu + \sqrt{\nu^2 - 4Dk_n}/2D\right)x} + \alpha_{7n} e^{-k_n t + \left(\nu - \sqrt{\nu^2 - 4Dk_n}/2D\right)x}\right), \quad k_n, \alpha_{6n}, \alpha_{7n}: \text{ constants.} \tag{18}$$

The general form of c is the combination of Equations (10), (12), (15), and (18).

$$\begin{aligned} c(t,x) = {} & \alpha_0 + \alpha_1 e^{(\nu/D)x} + \alpha_2 e^{-\left(\nu^2/4D\right)t + (\nu/2D)x} + \alpha_3 x e^{-\left(\nu^2/4D\right)t + (\nu/2D)x} \\ & + \sum_{n=1}^{\infty} \left[\alpha_{4n} e^{-k_n t + (\nu/2D)x} \sin\left(\frac{\sqrt{4Dk_n - \nu^2}}{2D} x\right) + \alpha_{5n} e^{-k_n t + (\nu/2D)x} \cos\left(\frac{\sqrt{4Dk_n - \nu^2}}{2D} x\right) \right] \\ & + \sum_{n=-1}^{-n} \left(\alpha_{6n} e^{-k_n t + \left(\nu + \sqrt{\nu^2 - 4Dk_n}/2D\right)x} + \alpha_{7n} e^{-k_n t + \left(\nu + \sqrt{\nu^2 - 4Dk_n}/2D\right)x} \right). \end{aligned} \tag{19}$$

When $t \to \infty$, c should approach a steady saturated state. Consequently, k_n and D cannot be negative, unless the terms involving t do not exist. In the studied case, moisture diffuses through both surfaces into a 2D-infinite dry plate with thickness h which is immersed in water. If the original of the x-coordinate is set at the center of the plate and its direction is defined as perpendicular to the plate, then the distribution of the moisture inside the plate should be symmetric w.r.t. x (Figures 1 and 2). However, it is impossible to derive a symmetric solution from Equation (5), because if c is symmetric, $\partial c/\partial t$ and $\partial^2 c/\partial x^2$ must be symmetric, but $\partial c/\partial x$ must be anti-symmetric. An equation cannot have both non-trivial symmetric and anti-symmetric functions. To keep the form of Equation (5) and make the solution symmetric, the equation must be redefined as

$$\frac{\partial c}{\partial t} = \begin{cases} \text{Diffusion is in positive } x\text{-direction. } (x < 0 \text{ for the studied case.}) \\ \qquad D\dfrac{\partial^2 c}{\partial x^2} - \nu\dfrac{\partial c}{\partial x} \\ \text{Diffusion is in negative } x\text{-direction. } (x > 0 \text{ for the studied case.}) \\ \qquad D\dfrac{\partial^2 c}{\partial x^2} + \nu\dfrac{\partial c}{\partial x}. \end{cases} \tag{20}$$

This model is named the gradient-dependent model, implying that the $D\partial^2 c/\partial x^2$ always helps $\partial c/\partial t$, while $\partial c/\partial x$ retards the $\partial c/\partial t$ when the diffusion is in the positive direction of the x-coordinate, but accelerates it when the diffusion is in the negative x-coordinate direction. Equation (19) is then just for $x < 0$ part of the plate in the studied case. For $x > 0$, Equation (19) becomes

$$\begin{aligned} c = {} & \alpha_0 + \alpha_1 e^{-(\nu/D)x} + \alpha_2 e^{-\left(\nu^2/4D\right)t - (\nu/2D)x} + \alpha_3 x e^{-\left(\nu^2/4D\right)t - (\nu/2D)x} \\ & + \sum_{n=1}^{\infty} \left[\alpha_{4n} e^{-k_n t - (\nu/2D)x} \sin\left(\frac{\sqrt{4Dk_n - \nu^2}}{2D} x\right) + \alpha_{5n} e^{-k_n t - (\nu/2D)x} \cos\left(\frac{\sqrt{4Dk_n - \nu^2}}{2D} x\right) \right] \\ & + \sum_{n=-1}^{-n} \left(\alpha_{6n} e^{-k_n t + \left(-\nu + \sqrt{\nu^2 - 4Dk_n}/2D\right)x} + \alpha_{7n} e^{-k_n t + \left(-\nu - \sqrt{\nu^2 - 4Dk_n}/2D\right)x} \right). \end{aligned} \tag{21}$$

Even though the 4th, 5th, 7th, and 8th terms still make c in Equations (19) and (21) not symmetric, meaning $\alpha_3, \alpha_{4n}, \alpha_{6n}$, and α_{7n} must vanish. Equations (19) and (21) then become

$$c(t,x) = \alpha_0 + \alpha_1 e^{-(\nu/D)|x|} + \alpha_2 e^{-\left(\nu^2/4D\right)t-(\nu/2D)|x|} + \sum_{n=1}^{\infty}\left[\alpha_{5n} e^{-k_n t-(\nu/2D)|x|}\cos\left(\frac{\sqrt{4Dk_n-\nu^2}}{2D}x\right)\right]. \tag{22}$$

To satisfy the condition that $c(\infty, x) = c_\infty$, let $\alpha_0 = c_\infty$, $\alpha_1 = 0$. Equation (22) becomes

$$c(t,x) = c_\infty + \alpha_2 e^{-\left(\nu^2/4D\right)t-(\nu/2D)|x|} + \sum_{n=1}^{\infty}\left[\alpha_{5n} e^{-k_n t-(\nu/2D)|x|}\cos\left(\frac{\sqrt{4Dk_n-\nu^2}}{2D}x\right)\right]. \tag{23}$$

Rearranging Equation (23) yields

$$e^{(\nu/2D)|x|}[c(t,x) - c_\infty] = \alpha_2 e^{-\left(\nu^2/4D\right)t} + \sum_{n=1}^{\infty}\left[\alpha_{5n} e^{-k_n t}\cos\left(\frac{\sqrt{4Dk_n-\nu^2}}{2D}x\right)\right]. \tag{24}$$

When $t = 0$,

$$e^{(\nu/2D)|x|}[c(0,x) - c_\infty] = \alpha_2 + \sum_{n=1}^{\infty}\left[\alpha_{5n}\cos\left(\frac{\sqrt{4Dk_n-\nu^2}}{2D}x\right)\right]. \tag{25}$$

The plate is initially dry, except for the surfaces which are assumed to become saturated immediately after the diffusion starts. To cover this initiation condition,

$$c(0,x) = 0, -\frac{h}{2} < x < \frac{h}{2} \tag{26}$$

and to satisfy the boundary condition that $c(t,\pm h/2) = c_\infty$, a periodical function with a period $2h$ is defined.

$$c_p(x) = \begin{cases} c_\infty\left[1 + e^{(\nu/2D)(h-2x)}\right], & \frac{h}{2} < x < h \\ 0, & -\frac{h}{2} < x < \frac{h}{2} \\ c_\infty\left[1 + e^{(\nu/2D)(h+2x)}\right], & -h < x < -\frac{h}{2}. \end{cases} \tag{27}$$

Replacing $c(0, x)$ in Equation (25) with $c_p(x)$ of Equation (27), we get

$$e^{(\nu/2D)|x|}[c_p(x) - c_\infty] = \begin{cases} c_\infty e^{(\nu/2D)(h-x)}, & \frac{h}{2} < x < h \\ -c_\infty e^{(\nu/2D)|x|}, & -\frac{h}{2} < x < \frac{h}{2} \\ c_\infty e^{(\nu/2D)(h+x)}, & -h < x < -\frac{h}{2}. \end{cases} \tag{28}$$

Equation (28) can be expressed by Fourier series as

$$e^{(\nu/2D)|x|}\left[c_p(x) - c_\infty\right] = a_0 + \sum_{n=1}^{\infty}\left[a_n \cos\left(\frac{2n\pi}{2h}x\right)\right] \tag{29}$$

where

$$a_0 = \frac{1}{2h}\int_{-h}^{h} e^{(\nu/2D)|x|}\left[c_p(x) - c_\infty\right]\mathrm{d}x = 0 \tag{30}$$

$$\begin{aligned} a_n &= \frac{1}{h}\int_{-h}^{h} e^{(\nu/2D)|x|}\left[c_p(x) - c_\infty\right]\cos\left(\frac{n\pi}{h}x\right)\mathrm{d}x \\ &= -c_\infty\frac{2}{h}\int_0^{h/2} e^{(\nu/2D)x}\cos\left(\frac{n\pi}{h}x\right)\mathrm{d}x + c_\infty\frac{2}{h}\int_{h/2}^{h} e^{(\nu/2D)(h-x)}\cos\left(\frac{n\pi}{h}x\right)\mathrm{d}x. \end{aligned} \tag{31}$$

Let $z = h - x$ in the second term of Equation (31).

$$a_n = -c_\infty\frac{2}{h}\int_0^{h/2} e^{(\nu/2D)x}\cos\left(\frac{n\pi}{h}x\right)\mathrm{d}x + c_\infty\frac{2}{h}\int_0^{h/2} e^{(\nu/2D)z}\cos\left(n\pi - \frac{n\pi}{h}z\right)\mathrm{d}z. \tag{32}$$

For $n = 1, 3, 5, \ldots,$

$$a_n = -c_\infty 2\frac{e^{(\nu h/4D)}(n\pi/2)(-1)^{((n-1)/2)} - (\nu h/4D)}{(\nu h/4D)^2 + (n\pi/2)^2}. \tag{33}$$

For $n = 2, 4, 6, \ldots,$

$$a_n = 0. \tag{34}$$

From Equations (25) and (29), $\alpha_2 = a_0 = 0$, $\alpha_{5n,n=2,4,6\ldots} = a_{n,n=2,4,6,\ldots} = 0$, $\alpha_{5n,n=1,3,5\ldots} = a_{n,n=1,3,5,\ldots}$, and

$$k_n = \left[\left(\frac{\nu h}{4D}\right)^2 + \left(\frac{n\pi}{2}\right)^2\right]\frac{D}{(h/2)^2}. \tag{35}$$

Equation (23) then becomes

$$\begin{aligned} c(t,x) = c_\infty\Bigg\{1 - 2\sum_{n=1,3,5,\ldots}^{\infty}\Bigg[&\frac{e^{(\nu h/4D)}(n\pi/2)(-1)^{(n-1)/2} - (\nu h/4D)}{(\nu h/4D)^2 + (n\pi/2)^2} \\ &\times e^{-[(\nu h/4D)^2 + (n\pi/2)^2]\left(D/(h/2)^2\right)t - (\nu/2D)|x|}\cos\left(\frac{n\pi}{h}x\right)\Bigg]\Bigg\} \geq 0. \end{aligned} \tag{36}$$

Equation (27) is delicately designed to produce Equation (28), which is anti-symmetric w.r.t. $x = -h/2$ in the area $-h < x < 0$ and also anti-symmetric w.r.t. $x = h/2$ in the area $0 < x < h$, but symmetric w.r.t. $x = 0$ in the period $-2h < x < 2h$. Consequently, $a_{n,n=2,4,6,\ldots} = 0$ in Equation (29) to make c in Equation (36) satisfy the boundary condition that $c(t, \pm h/2) = c_\infty$.

If $\nu = 0$, then Equation (36) becomes Equation (2). Mathematically when $\nu \neq 0$, it is possible that $c(t,x)$ calculated from Equation (36) may be negative in some center area if t is not longer that certain critical value, $c(t, x) < 0$ in $-x_0 < x < x_0$ and $c(t, x) > 0$ in $-h/2 < x < x_0$ and $x_0 < x < h/2$, where x_0 stands for the coordinate of the penetrant front. However, a negative moisture concentration does not have any physical sense. Let $c(t, x) = 0$ when $-x_0 < x < x_0$ is representing the dry area around the center of the plate. In this case, the plate is partially wet. When t is big enough, $c(t, x)$ is positive everywhere in the plate even at the deepest center, indicating that the plate is thoroughly wet, but not saturated until $t \to \infty$.

Based on Equation (36), t can be solved numerically by letting $c(t, x_0) = 0$ for a given x_0, which is the diffusion duration required for the penetrant to reach location x_0.

$$0 = 1 - 2\sum_{n=1,3,5,\ldots}^{\infty}\left[\frac{e^{(\nu h/4D)}(n\pi/2)(-1)^{((n-1)/2)} - (\nu h/4D)}{(\nu h/4D)^2 + (n\pi/2)^2} \times e^{-\left[(\nu h/4D)^2 + (n\pi/2)^2\right]\left(D/(h/2)^2\right)t - (\nu/2D)x_0} \cos\left(\frac{n\pi}{h}x_0\right)\right]. \tag{37}$$

Let $x_0 = 0$ in Equation (37), then

$$0 = 1 - 2\sum_{n=1,3,5,\ldots}^{\infty}\left[\frac{e^{(\nu h/4D)}(n\pi/2)(-1)^{((n-1)/2)} - (\nu h/4D)}{(\nu h/4D)^2 + (n\pi/2)^2} e^{-\left[(\nu h/4D)^2 + (n\pi/2)^2\right]\left(D/(h/2)^2\right)t_c}\right] \tag{38}$$

where t_c is the critical diffusion duration required for the penetrant to reach the center of the plate. Reversely, x_0 can be solved from Equation (37) for a given t smaller than t_c.

The average concentration in the plate is given by

$$\bar{c}(t) = \frac{\int_{-h/2}^{h/2} c(t,x)\,\mathrm{d}x}{h}. \tag{39}$$

When $t < t_c$, Equation (39) becomes

$$\bar{c}(t) = c_\infty\left\{1 - \frac{2x_0}{h} - 2\sum_{n=1,3,5,\ldots}^{\infty}\left[\frac{\left[e^{(\nu h/4D)}(n\pi/2)(-1)^{((n-1)/2)} - (\nu h/4D)\right]}{\left[(\nu h/4D)^2 + (n\pi/2)^2\right]^2} \left\{e^{-(\nu h/4D)}(n\pi/2)(-1)^{((n-1)/2)} + e^{-(\nu/2D)x_0}\left[(\nu h/4D)\cos((n\pi/h)x_0) - (n\pi/2)\sin((n\pi/h)x_0)\right]\right\} e^{-\left[(\nu h/4D)^2 + (n\pi/2)^2\right]\left(D/(h/2)^2\right)t}\right]\right\}. \tag{40}$$

When $t > t_c$, Equation (39) becomes

$$\bar{c}(t) = c_\infty \left\{ 1 - 2 \sum_{n=1,3,5,\ldots}^{\infty} \left[\frac{\left[e^{\nu h/4D} n\pi/2(-1)^{(n-1)/2} - (\nu h/4D)\right]\left[e^{-(\nu h/4D)} n\pi/2(-1)^{(n-1)/2} + \nu h/4D\right]}{\left[(\nu h/4D)^2 + (n\pi/2)^2\right]^2} e^{-\left[(\nu h/4D)^2 + (n\pi/2)^2\right]\left(D/\left((h/2)^2\right)\right)t} \right] \right\}. \tag{41}$$

If $\nu = 0$, then Equations (40) and (41) become Equation (3).

Assuming that the hygric expansion strain of the material is proportional to its concentration [6], the hygric expansion strain of the plate in the in-plane direction becomes

$$\varepsilon(t) = \varepsilon_\infty \left\{ 1 - (2x_0/h) - 2 \sum_{n=1,3,5,\ldots}^{\infty} \left[\frac{\left[e^{(\nu h/4D)}(n\pi/2)(-1)^{((n-1)/2)} - (\nu h/4D)\right]}{\left[(\nu h/4D)^2 + (n\pi/2)^2\right]^2} \left\{ e^{-(\nu h/4D)}(n\pi/2)(-1)^{((n-1)/2)} + e^{-(\nu/2D)x_0}\left[(\nu h/4D)\cos\left(\frac{n\pi}{h}x_0\right) - (n\pi/2)\sin\left(\frac{n\pi}{h}x_0\right)\right]\right\} e^{-[(\nu h/4D)^2 + (n\pi/2)^2]\left(D/(h/2)^2\right)t} \right] \right\} \tag{42}$$

for $t < t_c$, and

$$\varepsilon(t) = \varepsilon_\infty \left\{ 1 - 2 \sum_{n=1,3,5,\ldots}^{\infty} \left[\frac{[e^{\nu h/4D} n\pi/2(-1)^{(n-1)/2} - (\nu h/4D)][e^{-(\nu h/4D)} n\pi/2(-1)^{(n-1)/2} + \nu h/4D]}{\left[(\nu h/4D)^2 + (n\pi/2)^2\right]^2} e^{-\left[((\nu h/4D))^2 + (n\pi/2)^2\right](D/(h/2)^2)t} \right] \right\} \tag{43}$$

for $t > t_c$.

EXPERIMENT AND ANALYSIS

An immersion test was performed on four-ply 0.057 cm thick unidirectional continuous fiber T700 carbon/epoxy composite laminates. Six square specimens, 20 cm long and 4 cm wide, were prepared such that the fiber of the laminate is in the width direction (Figure 2). The specimens were dried at 80°C for a week before the experiment to ensure that no moisture remained inside. All the edges were sealed by a 0.05 mm thick aluminum foil to ensure that no moisture diffused into the laminate through the edges to match the theory assumption. The aluminum foil was glued to the edges of each specimen by using silicon to make diffusion occur only through both surfaces not through the edges [6].

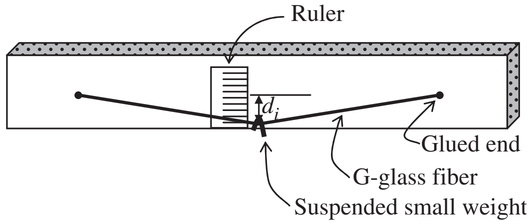

Figure 3. *Specimen with a piece of G-glass fiber glued on its surface for measuring hygric strain.*

The data of hygric expansion strain of the specimens immersed in water were collected using the suspending method [6]. A piece of G-glass fiber was attached horizontally to the surface of each specimen by gluing both its ends. The G-glass fiber, with a nine-micron filament diameter supplied by Ovens-Corning that would not expand by absorbing moisture was employed as a tool for measuring the hygric expansion strain of the laminate. A tiny weight of around 1mg was hung at the center of the fiber to stretch it. A piece of ruler, hung on the surface of the specimen but behind the fiber, was applied as a dimension reference (Figure 3). The specimens were held such that the width direction was vertical and the length direction was horizontal (Figure 4).

The horizontal distance between the glued ends of the fiber was around 18 cm, and the deflection at the center was around 0.5 cm. The exact length of the fiber can be calculated easily by Pythagorean relation. When the laminate with the fiber was immersed in water in a transparent container, it started to absorb water, expand, and pull the two glued ends of the fiber slightly apart. Since the total length of the fiber never changed, the deflection at the center of the fiber had to decrease. The deflection at the center of the fiber was recorded by a camera with a zoom-up lens. When $t = t_i$ and the deflection at the center of the fiber is given by d_i, the hygric expansion strain in the horizontal direction of the laminate is given by

$$e_i = \frac{\sqrt{(w_0/2)^2 + d_0^2 - d_i^2}}{w_0/2} - 1 \tag{44}$$

where d_0 is the initial deflection at the center of the fiber, and w_0 is the initial distance between the glued ends of the fiber.

Let ε_i be the theoretical hygric expansion strain calculated from Equation (4) or Equations (42) and (43) when $t = t_i$. The error between e_i and ε_i is given by

$$E_i = e_i - \varepsilon_i. \tag{45}$$

The sum of the error square is given by

$$\mathrm{SSE} = \sum_{i=1}^{n} E_i^2 = \sum_{i=1}^{n} (e_i - \varepsilon_i)^2. \tag{46}$$

When adopting Fick's model, Equation (4) is used to calculate ε_i in Equation (46), and D and ε_∞ can be obtained through minimizing the SSE. When the gradient-dependent model

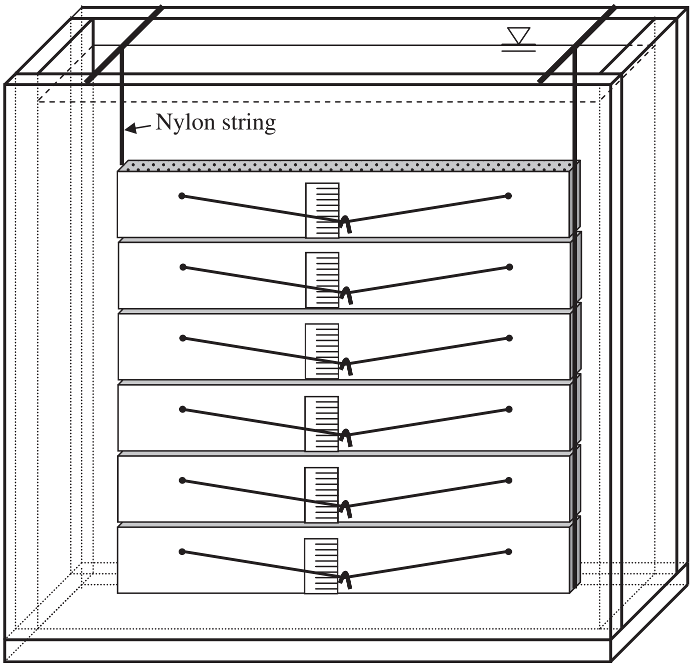

Figure 4. *Specimens immersed in water in a rectangular glass container.*

Table 1. Diffusivity and gradient coefficient in out-of-plane fiber's transverse direction, and saturated hygric strain in in-plane fiber's transverse direction of T700 carbon/epoxy composite laminate for Fick's diffusion model and gradient-depending diffusion model.

	$D \pm$ S.D. ($\times 10^{-5}$ cm^2/day)	$\varepsilon_\infty \pm$ S.D.	$\nu \pm$ S.D. (cm/day)
Fick's model	1.70 ± 0.20	0.0021 ± 0.0002	–
Gradient-depending model	1.40 ± 0.20	0.0021 ± 0.0002	0.0009 ± 0.0001

is adopted, the values of D, ε_∞, and ν can be derived in the same way. A commercial software is employed to minimize the SSE numerically for obtaining the parameters.

Based on the data of the six specimens, the values of D and ε_∞ for Fick's model, D, ε_∞, and ν for the gradient-dependent model, and their standard deviations are listed in Table 1. A typical set of the hygric expansion strain is displayed in Figure 5. By fitting Equation (4) based on Fick's model to the data, the SSE is smaller than 6×10^{-9}. The fitted values tend to be slightly too low when $t < 15$ days, too high when 15 days $< t <$ 50 days, and too low when $t > 50$ days. The mismatch is no larger than 0.6×10^{-4} which is much smaller than the standard deviation of ε_∞, 2×10^{-4}. The fitting is very good. Nevertheless, the same mismatch trend occurs in every single data set. When fitting Equations (42) and (43) to the data, the SSE is smaller than 5.5×10^{-9}. Numerically, the improvement in the SSE is very limited, but the previous mismatch trend disappears. The fitting becomes excellent.

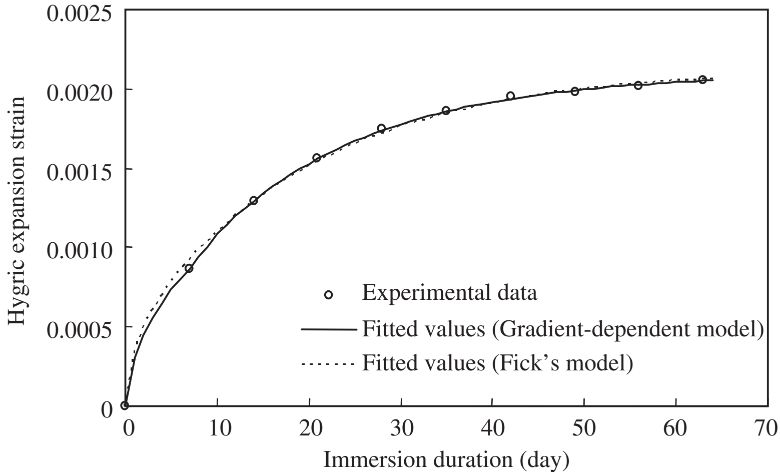

Figure 5. *Experimental data of hygric expansion strain vs immersion duration of T700 carbon/epoxy composite laminate in immersion test.*

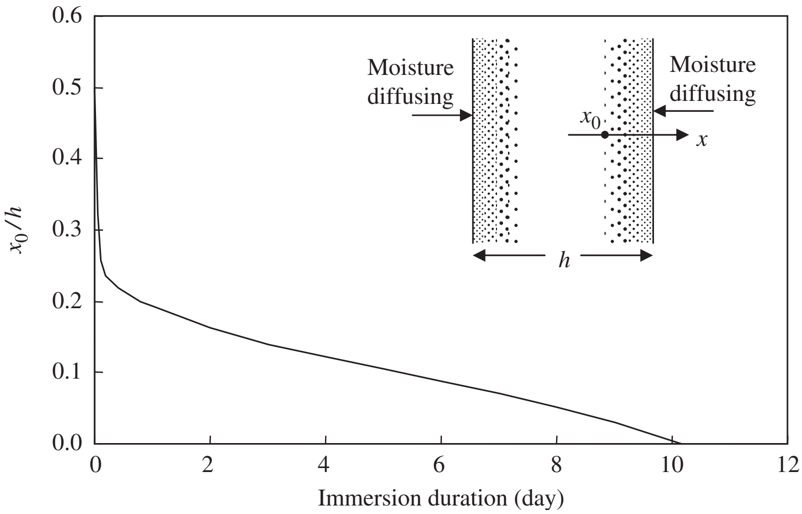

Figure 6. *Theoretically predicted coordinate of moisture front over thickness of specimen vs immersion duration of 0.057 cm thick unidirectional T700 carbon/epoxy composite laminate in immersion test.*

One of the most important functions of the developed model is to locate the penetrant front, which is the deepest location where penetrant reaches. Figure 6 shows the theoretically predicted coordinate of the moisture front versus diffusion duration based on the values of Table 1. The analysis indicates that the moisture thrusted into the material by around 0.15 mm deep in the first 5 h, slowed down later, and took 10.18 days to travel 0.285 mm to reach the center of the laminate making the laminate thoroughly wet. Verifying the predicted moisture front experimentally in such a thin laminate is a challenge in our future work. Figure 7 shows the distribution of the moisture concentration in the laminate.

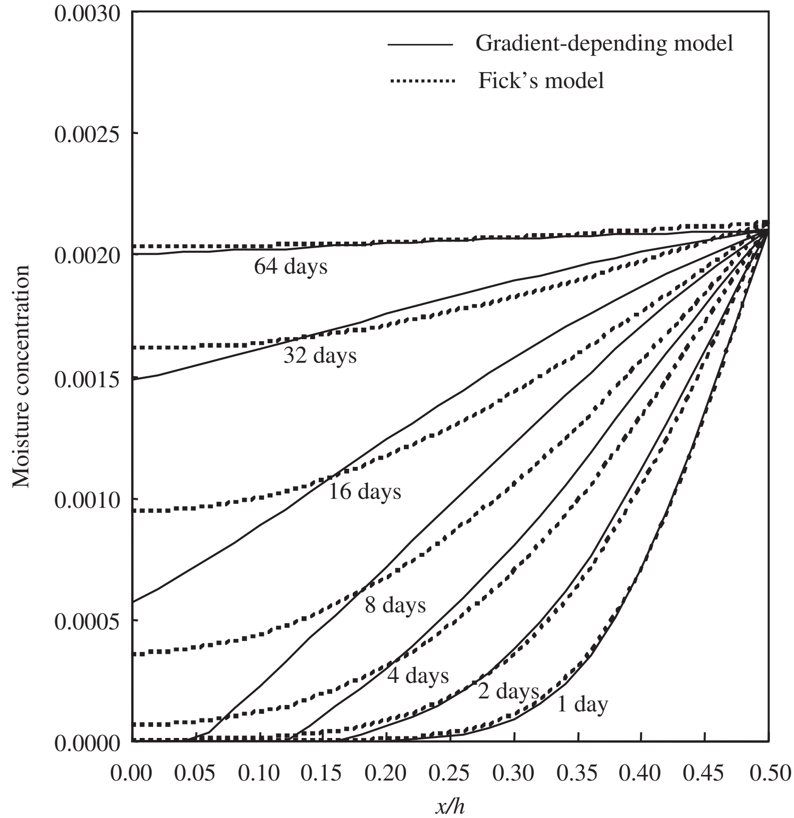

Figure 7. *Distribution of moisture concentration for 0.057 cm thick unidirectional T700 carbon/epoxy composite laminate in immersion test.*

CONCLUSIONS AND DISCUSSIONS

An immersion test of a composite laminate was conducted by using the suspension method, and the data were analyzed by Fick's model and the developed gradient-dependent model. Both models describe well the overall hygric expansion behavior of the laminate.

The gradient-dependent model is a refinement of Fick's model taking into consideration the sensitivity and dependency of diffusion on concentration gradient and its sign. The theoretical solution of concentration in the plate is derived based on the proposed model for the case of diffusion in a 2D-infinite plate, which clearly locates the penetrant front that does not exist in the solution based on Fick's conventional model.

The dynamic location of the penetrant front is a very important index indicating how deep the penetrant penetrates into the media material. Locating penetrant front can solve many practical problems, such as how long moisture will penetrate the protecting concrete and reach the reinforcing steel to induce corrosion in a reinforced concrete structure immersed in salty water, how many years a composite black box can protect the record of a crushed aircraft in water, how fast molecules of medicine can penetrate the human skin into the human body, etc if all related parameters can be obtained. Characterizing the parameters for the model in each case will be one of the main issues for employing the model in real case.

Results of this work indicate an interesting phenomenon that when a dry carbon/epoxy laminate is immersed in water, the moisture will penetrate instantly into the laminate to certain depth first, and then diffuse slowly toward the center of the laminate. This phenomenon is named moisture shock, similar to thermal shock. Studying the details of the moisture shock based on the proposed model is important in the future for quantifying penetrant absorption and the effects on the media of the early diffusion stage, such as how much, how deep, and how fast the penetrant thrusts into the media, how much stress is induced in the media, why the diffusion rate slows down later, and what mechanism dominates the thrust.

NOMENCLATURE

a_0, a_n = coefficients for constant and cosine terms of Fourier series
c = penetrant (moisture) concentration
c_∞ = saturated penetrant (moisture) concentration
$\bar{c}$ = average penetrant (moisture) concentration over the thickness of the plate
c_p = a periodical function with a period of $2h$
d_i = deflection at the center of the fiber
d_0 = initial d_i
D = diffusivity
e = experimental ε
e_i = experimental ε_i
E_i = error between e_i and ε_i
h = thickness of the plate
k = constant
k_{1-12} = constants
n = index for a series
SSE = summation of the E_i square
t = diffusion duration
t_c = critical t when the penetrant reaches the center of the plate
T = a function of t
w_0 = initial distance between the glued ends of the fiber
x = coordinate of diffusion direction
x_0 = coordinate of the penetrant front
X = a function of x
$z = h - x$
α_{1-7} = constants
α_{4n-7n} = constants
ε = in-plane hygric expansion strain of the plate
$\varepsilon_i = \varepsilon$ when $t = t_i$
ε_∞ = saturated ε
ν = gradient coefficient

ACKNOWLEDGMENTS

The authors would like to thank Professor I. M. Daniel at Northwestern University (USA) for his encouragement and supply of materials for preliminary test.

REFERENCES

1. Crank, J. (1975). *The Mathematics of Diffusion*, **2nd edn**, Oxford University Press USA, NY, USA.
2. Frisch, H.L., Wang, T.T. and Kwei, T.K. (1969). Diffusion in Glassy Polymers II, *Journal of Polymer Science: Part A-2*, **7**(12): 879–887.
3. Wang, T.T., Kwei, T.K. and Frisch, H.L. (1969). Diffusion in Glassy Polymers III, *Journal of Polymer Science: Part A-2*, **7**(5): 2019–2028.
4. Kwei, T.K. and Zupko, H.M. (1969). Diffusion in Glassy Polymers I, *Journal of Polymer Science: Part A-2*, **7**(5): 867–877.
5. Tsai, C.-L., Cheng, M.-C., Hwang, S.-F. and Tsai, Y.-S. (2004). Characterizing the Hygric Behavior of Composites by Suspending Method, *Journal of Composite Materials*, **38**(9): 757–768.
6. Daniel, I.M. and Ishai, O. (1994). *Engineering Mechanics of Composite Materials*, Oxford University Press Inc., New York.