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"Non-Fickian Moisture Diffusion in Polymeric Composites"

By

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Abstract

This article concerns the effects of non-Fickian water diffusion in fiber-reinforced polymeric composites. The departure from classical diffusion is attributed to the time-dependent response of the polymer, akin to viscoelastic mechanical response.

A formulation is provided to evaluate the coefficient of moisture diffusion and moisture profiles within the composite for the non-Fickian case. In addition, it is demonstrated that computed magnitudes of residual hygro-thermal stresses may differ by about 25% from predictions based upon classical diffusion.

1. Introduction

The diffusion of water in polymers and fiber-reinforced polymeric composites has been studied extensively for almost a century and a vast body of literature deals with that subject. A survey, primarily concerned with fiber-reinforced polymeric composites, was published recently (Weitsman, 1991).

The most prominent and common formulation of the diffusion process employs the well known Fick's law (Fick, 1855), whose one dimensional version reads

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2}, \qquad t > 0,\ -L \le z \le L. \tag{1}$$

The field equation (1) is accompanied by initial and boundary conditions

$$C(z,0) = C_i(z), \qquad -L \le z \le L, \tag{2}$$

and, say

$$C(\pm L,t) = C_L(t), \qquad t > 0. \tag{3}$$

In equations (1), (2) and (3), z and t are spatial coordinate and time, respectively, $C = C(z,t)$ is moisture content and D denotes the coefficient of moisture diffusion. In many cases the coefficient D is assumed constant, whereby the diffusion process is linear. The above assumption will be employed in the present work.

Consider, in addition, the special circumstance of an initially dry plate subjected to constant boundary conditions, namely,

$$C(z,0) = 0, \quad -L \le z \le L, \tag{2a}$$

$$C(\pm L,t) = C_0 H(t), \quad t > 0. \tag{3a}$$

where, $H(t)$ is the Heaviside step function.

Denote the solution to the unit step input (*i.e.*, $C_0 = 1$ in equation (3a)) by $C_H(z,t)$. The well known result, given in Crank (1975), reads:

$$C_H(z,t) = \sum_{n=0}^{\infty}(-1)^n \left[\operatorname{erfc}\left(\frac{2n+1-z/L}{2\sqrt{t^*}}\right) + \operatorname{erfc}\left(\frac{2n+1+z/L}{2\sqrt{t^*}}\right)\right]. \tag{4}$$

Integration across the thickness provides the weight gain $M_H(t)$, which corresponds to $C_H(z,t)$,

$$M_H(t) = 4L\sqrt{t^*} \cdot \left[\frac{1}{\sqrt{\pi}} + 2\sum_{n=1}^{\infty} \operatorname{ierfc}\left(\frac{n}{\sqrt{t^*}}\right)\right], \tag{5}$$

where

$$t^* = \frac{Dt}{L^2}, \tag{6}$$

erfc(z) is the complementary error function and ierfc(x) is its integral:

$$\mathrm{ierfc}\,(x) = \int_0^x \mathrm{erfc}\,(\xi) d\xi. \tag{7}$$

In view of linearity, the solution for $C_0 \neq 1$, as well as for $C(\pm L, t) = g(t)$, can be expressed by means of $C_H(z,t)$ and $M_H(t)$ in a straightforward manner (Crank, 1975).

Since data on moisture distribution are scarce and difficult to generate, the most readily available experimental information accounts for total weight gain. Before comparing weight gain data with model predictions, note the characteristic features of $M_H(t^*)$ when plotted vs. $\sqrt{t^*}$, as shown in Figure 1. Accordingly, the value of the initial slope is $4L/\sqrt{\pi}$, departures from linearity by $\pm 1\%$ do not occur until $\sqrt{t^*} \approx 0.557$, $M_H(t^*) \approx 0.62$, and saturation, to within $\pm 1\%$, occurs at $\sqrt{t^*} = 1.32$. It should be recognized that typical weight gain data exhibit scatter of at least $\pm 1\%$.

In addition, it is possible to infer the value of the diffusion coefficient D from $M_H(t)$ (Shen and Springer, 1981), we have

$$D = \frac{\pi}{16} \lim_{t \to 0} \frac{[M_H(t)]^2}{t}. \tag{8}$$

In this manner, knowledge of $M_H(t)$ enables the evaluation of $C(z,t)$, through retracing expression (4) from equation (5), and the computation of residual hygral stresses by means of well established analyses (Tsai and Hahn, 1980, Harper and Weitsman 1985, Weitsman, 1991).

Several uncertainties arise when moisture weight gain data do not correspond to the strictures exhibited in Figure 1, implying that the premises which led to $M_H(t)$ are not met by the polymeric composite material at hand. Such circumstances occur very frequently, with a typical example exhibited in Figure 2 for the case of Fiberite T300/1014 composite (Blikstad, *et al*, 1988). To accentuate the departures from "classical" predictions, which corresponds to equation (5), the data in Figure 2 are bracketed by two curves which conform to the format of Figure 1 (multiplied by two distinct constants C_0 to provide best fits with data at short and long times, respectively). For future reference, these curves are denoted by "Upper Fickian" and "Lower Fickian", respectively.

There are several plausible explanations for the causes for departure from a linear diffusion process (Weitsman, 1991). Of these, one rationale is motivated by considerations akin to the well known time dependent, viscoelastic response of polymers. Accordingly, the very same Gibbs free energy which gives rise to time-dependent mechanical response, predicts a diffusion process with time-dependent boundary conditions even under exposure to constant ambient environment (Weitsman, 1990).

This consideration will be employed in the present work, namely, we shall retain the field equation (1) and initial condition(2a) but will consider the boundary condition

$$C(\pm L, t) = f(t) \tag{9}$$

instead of (3a), *even though the ambient condition remains constant.*

The following issues will be addressed in the present work:

(a) Express the moisture distribution, $C(z,t)$, when moisture uptake $M(t)$ does not conform to expression (5).

(b) Establish a method to determine the value of the coefficient of moisture diffusion, D, when expression (5) — and thereby also equation (8) — no longer hold.

(c) Evaluate the effects of foregoing distribution $C(z,t)$ on residual stresses in composite laminates.

2. Diffusion with Boundary Conditions of Viscoelastic Type

It has been suggested (*e.g.*, Long and Richman, 1960) that departure from "classical" diffusion may be explained by replacing boundary condition (3a) with

$$C(\pm L,t) = \left[C_0 + C_1\left(1 - e^{-\beta t}\right)\right] H(t). \tag{10a}$$

More recently, it has been shown (Weitsman, 1990) that for viscoelastic materials, both creep compliance $S(t)$ and chemical potential $\mu(t)$ are expressible in Prony series forms, namely,

$$\mu(t) = \mu_0 + \sum_{n=1}^{N} \mu_n \left(1 - e^{-\beta_n t}\right).$$

This observation suggests that, in view of the time-dependent response of the polymer, one should consider the boundary condition

$$C(\pm L,t) = \left[C_0 + \sum_{n=1}^{N} C_n \left(1 - e^{-\beta_n t}\right)\right] H(t) \tag{10b}$$

of which (10a) accounts for the first term in the series. The above expression implies that equilibrium between the moisture content just inside the material and the chemical potential of the external vapor is established over an extended time — rather than instantaneously.

The solution to equation (1), with initial condition (2a) and boundary condition

$$C(\pm L,t) = \left(1 - e^{-\beta t}\right) H(t)$$

is well known (Crank, 1975). For future reference, it will be denoted by $\hat{C}(z,t;\beta)$. We have

$$\begin{aligned}\hat{C}(z,t;\beta) &= 1 - \exp(-\beta t)\cdot\frac{\cos z\sqrt{\beta D}}{\cos L\sqrt{\beta D}} - \\ &\quad -\frac{16\beta L^2}{\pi}\cdot\sum_{n=0}^{\infty}\frac{(-1)^n \exp\{-[(2n+1)\pi/2]^2 t^*\}}{(2n+1)[4\beta L^2 - D\pi(2n+1)^2]}\cos\frac{(2n+1)\pi z}{2L}.\end{aligned} \tag{11}$$

Upon integration across the thickness, the total weight gain corresponding to $\hat{C}(z,t;\beta)$ is

$$\hat{M}(t;\beta) = 2L \cdot \left\{ 1 - \exp(-\beta t)\sqrt{\frac{D}{\beta L^2}} \tan \sqrt{\frac{\beta L^2}{D}} - \right.$$
$$\left. - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\{-[(2n+1)\pi/2]^2 t^*\}}{(2n+1)^2\{1-(2n+1)^2[D\pi^2/(4\beta L^2)]\}} \right\}. \quad (12)$$

Consequently, the distribution and total weight gain due to boundary condition (10b) are

$$C(z,t) = C_0 C_H(z,t) + \sum_{n=1}^{N} C_n \hat{C}(z,t;\beta_n), \quad (13)$$

and

$$M(t) = C_0 M_H(t) + \sum_{n=1}^{N} C_n \hat{M}(t;\beta_n). \quad (14)$$

The latter expression should be correlated with experimental data.

3. Data Fitting

Since data contain experimental error and statistical scatter, it is advisable to smoothen the weight gain data, $M_{\text{exp}}(t)$, before affecting a match with expression (14).

Noting that for early times $M_H(t)$ is proportional to $\sqrt{t}$, we choose to fit the experimental data as follows,

$$M_{\text{fit}}(t) = \sum_{j=1}^{J} A_j t^{j/2}. \quad (15)$$

The coefficients A_j are determined by minimizing the square error, namely,

$$\frac{\partial}{\partial A_i} \int_0^{t_{\max}} \left[M_{\text{exp}}(t) - \sum_{j=1}^{J} A_j t^{j/2} \right]^2 dt = 0, \qquad (i = 1, 2, \cdots, J) \quad (16)$$

In equation (16), $t_{\max}$ denotes the duration of the moisture uptake experiment.

With A_j determined through expression (16) it is now necessary to express M_{fit} in the form (14). This task is accomplished in two steps.

Consider first the step-wise increasing boundary condition

$$C(\pm L,t) = C_0 H(t) + \sum_{k=1}^{K} C_k^H H(t-t_k),$$

to which corresponds the total weight gain

$$M(t) = C_0 M_H(t) + \sum_{k=1}^{K} C_k^H M_H(t-t_k) H(t-t_k). \tag{17}$$

The quantities C_0, C_k^H and t_k $(k = 1,2,\cdots,K)$ in equation (17) can be selected in a manner which yields $M(t) - M_{\text{fit}}(t) < \delta_{\text{cr}}$ at all times t, with δ_{cr} a prescribed tolerance. It is advisable to select δ_{cr} to be smaller than a typical discrepancy between $M_{\text{exp}}(t)$ and $M_{\text{fit}}(t)$.

The proposed procedure is to select C_0 in equation (17) which, in view of equation (5), would yield $M(t) = M_{\text{fit}}$ at the first time step, *i.e.*,

$$C_0 = \frac{M_{\text{fit}}(\Delta t)}{4}\sqrt{\frac{\pi}{D\Delta t}},$$

where Δt is the selected time step.

Then, retain $M(t) = C_0 M_H(t)$ until such time $t = \bar{t}_1$ when $M_{\text{fit}}(\bar{t}_1) - C_0 M_H(\bar{t}_1) = \delta \approx \delta_{\text{cr}}$. In view of equation (5), this discrepancy at $t = \bar{t}_1$ is overcome by introducing a step increment in the boundary condition at some earlier time t_1 of magnitude

$$C_1^H = \frac{\delta}{4}\sqrt{\frac{\pi}{D(\bar{t}_1 - t_1)}}.$$

The combined effect of $C_0 M_H(t) + C_1^H M_H(t-t_1)$ is now compared with $M_{\text{exp}}(t)$ until such time $\bar{t}_2$ when they differ by δ_{cr}, at which stage another incremental step is added to the boundary condition at an earlier time t_2 of magnitude C_2^H analogous to C_1^H. The procedure is repeated until the entire range of $M_{\exp}(t)$ is covered. The amplitudes of the incremental steps are given by

$$C_k^H = \frac{\delta}{4}\sqrt{\frac{\pi}{D(\bar{t}_k - t_k)}}. \tag{18}$$

In our computations, we found it is expedient to select t_k to coincide with $\bar{t}_{k-1}$ (with $t_1 = 0$).

With known C_k^H and t_k ($k = 1, 2, \cdots, K$), it is possible to convert the step-wise incrementing boundary condition

$$C(\pm L, t) = \sum_{k=1}^{K} C_k^H H(t - t_k). \tag{19}$$

to the continuous Prony series form

$$C(\pm L, t) = \sum_{n=1}^{N} C_n \left(1 - \mathrm{e}^{-\beta_n t}\right). \tag{20}$$

Employing a least square fit, we have

$$\frac{\partial}{\partial C_i}\int_0^{t_{\max}} \left[\sum_{k=1}^{K} C_k^H H(t - t_k) - \sum_{n=1}^{N} C_n \left(1 - \mathrm{e}^{-\beta_n t}\right)\right]^2 dt = 0. \tag{21}$$

Equation (21) results in an $N \times N$ system of linear algebraic equations in C_n

$$a_{ij} C_j = b_i \tag{22}$$

where

$$a_{ij} = t_{\max} - \frac{1 - \mathrm{e}^{-\beta_i t_{\max}}}{\beta_i} - \frac{1 - \mathrm{e}^{-\beta_j t_{\max}}}{\beta_j} + \frac{1 - \mathrm{e}^{-(\beta_i + \beta_j) t_{\max}}}{\beta_i + \beta_j}, \tag{23}$$

$$b_i = \sum_{k=1}^{K} C_k^H \left[(t_{\max} - t_k) + \frac{1}{\beta_i}\left(\mathrm{e}^{-\beta_i t_{\max}} - \mathrm{e}^{-\beta_i t_k}\right)\right]. \tag{24}$$

It should be noted that the above procedure provides some latitude in the selection of t_k ($k = 1, 2, \cdots, K$) and β_j ($j = 1, 2, \cdots, N$). Although no hard and fast rule seems to be available, it is advisable to select β_j which cover the spectrum of experimental time, preferably two — but at least one — values of β per time decade.

It may appear that the employment of the intermediate series (19) is redundant and that the values of C_n in equation (20) can be obtained directly through a least square fit of

$$\frac{\partial}{\partial C_j}\int_0^{t_{\max}}\left[M_{\text{fit}}(t) - C_0 M_H(t) - \sum_{n=1}^{N} C_n \hat{M}(t;\beta_n)\right]^2 dt = 0, \tag{25}$$

which yields an $N \times N$ system of linear algebraic equations

$$\hat{a}_{ij} C_j = \hat{b}_i \tag{26}$$

to determine C_j.

In this circumstance we have

$$\hat{a}_{ij} = \int_0^{t_{\max}} \hat{M}(t;\beta_i)\hat{M}(t;\beta_j)dt, \tag{27}$$

and

$$\hat{b}_i = \int_0^{t_{\max}} \left[M_{\text{fit}}(t) - C_0 M_H(t)\right] \hat{M}(t;\beta_i)dt. \tag{28}$$

Unfortunately, the numerical evaluation of $\hat{a}_{ij}$ and $\hat{b}_i$ involves compounded effects of truncation errors and, most critically, yields an ill-conditioned matrix $\hat{a}_{ij}$. The latter difficulty arises from the fact that rows and columns in the $\hat{a}_{ij}$ matrix consist of elements of very close magnitudes.

In many circumstances moisture uptake data do not seem to approach an equilibrium value, regardless of the duration of exposure, and $M(t)$ tends to increase according to $M(t) \sim Kt^p$ as $t >> 1$. It can be shown that this circumstance is commensurate with a time dependent boundary condition

$$C(\pm L, t) = C_0 t^p H(t). \tag{29}$$

To prove this, let $\overline{C}(z,s)$ denote the Laplace transform of $C(z,t)$, then, since

$$\overline{C}(\pm L, s) = C_0 \frac{\Gamma(p+1)}{s^{p+1}},$$

it can be shown that

$$\overline{C}(z,s) = \frac{C_0\Gamma(p+1)}{s^{p+1}} \cdot \frac{\cosh qz}{\cosh qL} \tag{30}$$

where $q = \sqrt{s/D}$.

Consequently, the Laplace transform, $\overline{M}(s)$, of the total weight gain $M(t)$ is

$$\overline{M}(s) = \frac{2C_0\Gamma(p+1)}{s^{p+1}} \cdot \frac{\tanh qL}{q}. \tag{31}$$

Although it seems impossible to express $M(t)$ analytically[1], its asymptotic value for $t >> 1$ is readily obtainable from

$$\lim_{s\to 0} \overline{M}(s) = \frac{2LC_0\Gamma(p+1)}{s^{p+1}},$$

which yields

$$\lim_{t\to\infty} M(t) = 2LC_0t^p. \tag{32}$$

4. Evaluation of the Coefficient of Moisture Diffusion

In all previous computations, it was implicitly assumed that the value of the coefficient of moisture diffusion D is known. However,

[1] An exception occurs for the important circumstance $p = 1/2$, which corresponds to $M(t) \sim A\sqrt{t}$ as $t \to \infty$. In this case both $C(z,t)$ and $M(t)$ have the following analytical expressions (see Appendix)

$$C(z,t) = C_0\sqrt{t}\left[1 + \frac{8}{\pi^2\sqrt{t^*}}\sum_{n=0}^{\infty}\frac{(-1)^{n+1}}{(2n+1)^2}\,\mathrm{F}\left(\frac{(2n+1)\pi}{2}\sqrt{t^*}\right)\cos\frac{(2n+1)\pi z}{2L}\right],$$

$$M(t) = 2LC_0\sqrt{t}\left[1 - \frac{16}{\pi^3\sqrt{t^*}}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^3}\,\mathrm{F}\left(\frac{(2n+1)\pi}{2}\sqrt{t^*}\right)\right].$$

where $F(\xi)$ denotes Dawson's integral (Olver, 1974) defined by

$$F(\xi) = \mathrm{e}^{-\xi^2}\int_0^{\xi}\mathrm{e}^{u^2}\,du.$$

when experimental weight gain data do not fit the format shown in Figure 1, expression (8) does not apply and D is unknown.

Assume as before that departure from classical diffusion are attributable strictly to the time-dependence of the boundary condition, namely,

$$C(\pm L, t) = C_0[1 + f(t)]H(t) \tag{33}$$

with $f(0) = 0$.

Therefore,

$$M(t) = C_0 \left\{ M_H(t) + \int_0^t M_H(t-\tau)\frac{df(\tau)}{d\tau}d\tau \right\}. \tag{34}$$

Let $\tilde{g}(s)$ denote the Carson transform of $g(t)$, namely,

$$\tilde{g}(s) = s\int_0^\infty e^{-st}g(t)dt,$$

then

$$\tilde{M}(s) = C_0\left[\tilde{M}_H(s) + \tilde{M}_H(s)\tilde{f}(s)\right],$$

whence

$$\tilde{f}(s) = \frac{1}{C_0}\frac{\tilde{M}(s)}{\tilde{M}_H(s)} - 1. \tag{35}$$

Note that at this stage, C_0, $f(t)$ (whereby also $\tilde{f}(s)$) as well as D are unknown. However, $\tilde{M}_H(s)$ is known analytically (Crank, 1975), namely,

$$\tilde{M}_H(s) = 2\sqrt{\frac{D}{s}}\tanh\sqrt{\frac{s}{D}}L. \tag{36}$$

In addition, $\tilde{M}(s)$, which is the Carson transform of the weight gain data, can be computed numerically.

By hypothesis, $f(t)$ is independent of the sample thickness L. Therefore, consider two sets of weight gain data $M(t;L_1)$ and $M(t;L_2)$ associated with thicknesses L_1 and L_2, respectively. Equation (35) yields

$$\frac{\tilde{M}(s;L_1;D)}{\tilde{M}(s;L_2;D)} = \frac{\tilde{M}_H(s;L_1)}{\tilde{M}_H(s;L_2)}. \tag{37}$$

Note that equation (37) contains the unknown D alone and does not include $\tilde{f}(s)$ and C_0.

Consider a data fit according to equation (15), whose Carson transform is given by

$$\tilde{M}(s) = \sum_{j=1}^{J} \frac{A_j}{s^{j/2}} \Gamma(\frac{j}{2}+1). \tag{38}$$

Consequently, it is possible to compute the ratio

$$\rho_k = \rho(s_k) = \frac{\tilde{M}(s_k; L_1; D)}{\tilde{M}(s_k; L_2; D)}$$

at distinct values of transform parameter $s = s_k$ ($k = 1, 2, \cdots, K$) and express the ratio

$$r_k(D) = r(s_k, D) = \frac{\tanh\sqrt{s_k L_2^2/D}}{\tanh\sqrt{s_k L_1^2/D}},$$

which corresponds to the right hand side of equation (37).

The value of D can be determined from the best least square fit obtained from

$$\frac{d}{dD} \sum_{k=1}^{K} [\rho_k - r_k(D)]^2 = 0, \tag{39}$$

namely,

$$\sum_{k=1}^{K} [\rho_k - r_k(D)] r_k'(D) = 0, \tag{40}$$

where,

$$\begin{aligned} r_k'(D) \quad = \quad & \left(-\frac{\sqrt{s_k/D}}{2D}\right) [L_2 \mathrm{cth}(L_1\sqrt{s_k/D}) \mathrm{sech}^2(L_2\sqrt{s_k/D}) - \\ & -L_1 \mathrm{csch}^2(L_1\sqrt{s_k/D}) \tanh(L_1\sqrt{s_k/D})]. \end{aligned}$$

Denote

$$g_k(D) \quad = \quad \left(-\frac{2D}{\sqrt{s_k/D}}\right) r_k'(D)$$

$$= L_2 \text{cth}(L_1\sqrt{s_k/D}) \text{sech}^2(L_2\sqrt{s_k/D}) -$$
$$-L_1 \text{csch}^2(L_1\sqrt{s_k/D}) \tanh(L_1\sqrt{s_k/D}), \tag{41}$$

then, since $D \neq 0$, eqn.(40) is equivalent to

$$\sum_{k=1}^{K} [\rho_k - r_k(D)] g_k(D) = 0. \tag{42}$$

This equation can be solved numerically for D. In the sequel, Newton's Iteration Method will be employed.

Newton's Iteration Method starts with a suitably chosen initial value $D^{(0)}$ and employs iteration until attaining convergence within a prescribed tolerance. In the present case, the n^{th} iterative value, $D^{(n)}$, is related to the $(n-1)^{\text{st}}$ value as follows:

$$D^{(n)} = D^{(n-1)} - \frac{\sum_{k=1}^{K} [\rho_k - r_k(D^{(n-1)})] g_k(D^{(n-1)})}{\left\{ \sum_{k=1}^{K} [\rho_k - r_k(D)] g_k(D) \right\}' \Big|_{D=D^{(n-1)}}}. \tag{43}$$

The denominator in equation (43) can be expressed as

$$\left\{ \sum_{k=1}^{K} [\rho_k - r_k(D)] g_k(D) \right\}' = \sum_{k=1}^{K} \left\{ [\rho_k - r_k(D)] g_k'(D) + \frac{s_k}{2D} g_k^2(D) \right\}$$

where

$$g_k'(D) = \left(-\frac{\sqrt{s_k/D}}{D} \right) \cdot \left\{ \text{cth}(L_1\sqrt{s_k/D}) \tanh(L_2\sqrt{s_k/D}) \left[\frac{L_1^2}{\sinh^2(L_1\sqrt{s_k/D})} - \right. \right.$$
$$\left. \left. - \frac{L_2^2}{\cosh^2(L_2\sqrt{s_k/D})} \right] - \frac{L_1 L_2}{\sinh^2(L_1\sqrt{s_k/D}) \cosh^2(L_2\sqrt{s_k/D})} \right\}.$$

5. Moisture Effects on Residual Stresses

To demonstrate the significance of non-Fickian diffusion on residual stresses in composite materials, consider the case of a $[0_2^\circ/90_2^\circ]_S$

symmetric lay-up. The basic stress-strain relation for the cross-ply laminate are (Harper and Weitsman, 1985):

For the 0° layers,

$$\begin{aligned}\sigma_x(z,t) &= Q_L[\epsilon_x^0(t) + z\kappa_x(t) - \alpha_L \Delta T - \beta_L C_e(z,t)] \\ &\quad + Q_{LT}[\epsilon_y^0(t) + z\kappa_y(t) - \alpha_T \Delta T - \beta_T C_e(z,t)],\end{aligned} \tag{44}$$

$$\begin{aligned}\sigma_y(z,t) &= Q_{LT}[\epsilon_x^0(t) + z\kappa_x(t) - \alpha_L \Delta T - \beta_L C_e(z,t)] \\ &\quad + Q_T[\epsilon_y^0(t) + z\kappa_y(t) - \alpha_T \Delta T - \beta_T C_e(z,t)],\end{aligned} \tag{45}$$

where subscripts L and T denote the the directions along and perpendicular to the fibers respectively, x and y denote the length and width directions of the laminate respectively, α's are the thermal expansion coefficients and β's the moisture swollen coefficient, ΔT is the temperature variation, $C_e(z,t)$ the effective moisture concentration.

For the 90° layers, the stresses can be obtained by interchanging subscripts L and T.

In the above equations, ϵ^0 and κ are determined in terms of the external applied loads. In the absence of such loads we have

$$N_x(t) = \int_{-L}^{L} \sigma_x(z,t)dz = 0, \tag{46}$$

$$N_y(t) = \int_{-L}^{L} \sigma_y(z,t)dz = 0, \tag{47}$$

$$M_x(t) = \int_{-L}^{L} \sigma_x(z,t)zdz = 0, \tag{48}$$

$$M_y(t) = \int_{-L}^{L} \sigma_y(z,t)zdz = 0. \tag{49}$$

Substitution of the appropriate stress expressions into eqns.(46)–(49) yields, after some manipulations, the following results:

$$\begin{aligned}\epsilon_x^0(t) &= \frac{h}{\Delta}\{(Q_L + Q_T)[hP\Delta T(t) + RG(t) + SF(t)] \\ &\quad - Q_{LT}L[hP\Delta T(t) + RF(t) + SG(t)]\},\end{aligned} \tag{50}$$

$$\begin{aligned}\epsilon_y^0(t) &= \frac{h}{\Delta}\{Q_L + Q_T)[hP\Delta T(t) + RF(t) + SG(t)] \\ &\quad - Q_{LT}L[hP\Delta T(t) + RG(t) + SF(t)]\},\end{aligned} \tag{51}$$

$$\kappa_x(t) = \kappa_y(t) = 0, \tag{52}$$

where

$$\Delta = h^2(Q_L + Q_T)(Q_L + Q_T) - (Q_{LT}L)^2, \quad F(t) = \int_0^h C_e(z,t)dz,$$

$$G(t) = \int_h^L C_e(z,t)dz, \quad P = Q_L\alpha_L + Q_{LT}\alpha_T + Q_{LT}\alpha_L + Q_T\alpha_T,$$

$$R = Q_L\beta_L + Q_{LT}\beta_T, \quad S = Q_{LT}\beta_L + Q_T\beta_T, \quad C_e(z,t) = C(z,t) - C_{\text{th}},$$

C_{th} denotes the threshold moisture concentration below which no swelling effect is observed and h is the common thicknesses of 90° and 0° laminae group, while — as before — $2L$ is the total thickness of the laminate.

6. Computational Results

The moisture weight gain data of Figure 2 were fitted by foregoing numerical scheme with a smooth curve $M_{\text{fit}}(t)$ according to equation (15) and subsequently with $M(t)$ according to equation (14) and (5).

Those computations yielded a six-term fit with $A_1 = 0.23281$, $A_2 = 0.010999$, $A_3 = -7.2414 \times 10^{-3}$, $A_4 = 1.5040 \times 10^{-4}$, $A_5 = -1.3487 \times 10^{-6}$, $A_6 = 4.4508 \times 10^{-9}$ for M_{fit} and the resulting curve is shown by the solid line in Figure 4. The smooth curve of M_{fit} was subsequently represented by $M(t)$ of equation (14) with $\delta = 0.01M_\infty$. This representation is shown in Figure 4.

Afterward, the data were represented by $M(t)$ as expressed by equation (5) with $C_0 = 0.7$ and $N = 7$, $C_1 = 0.098605$, $C_2 = 0.021929$, $C_3 = -0.083097$, $C_4 = 0.27450$, $C_5 = -0.55194$, $C_6 = 1.7834$, $C_7 = -1.5819$ and $\beta_1 = 1/10$, $\beta_2 = 1/50$, $\beta_3 = 1/100$, $\beta_4 = 1/500$, $\beta_5 = 1/1000$, $\beta_6 = 1/5000$, $\beta_7 = 1/10000$ (β in hours^{-1}).

In all above computation, we took $D = 3.2 \times 10^{-4}$ mm^2/hour.

The resulting curves for $M(t)$ are indistinguishable from $M_{\text{fit}}(t)$ and coincide with the solid line shown in Figure 2.

For purpose of comparison, the data of Figure 2 were bracketed by two curves of the form $C_0 M_H(t)$. The value of $C_0 = 1.12 \times 10^{-2}$, with $D = 3.2 \times 10^{-4}$ mm^2/hour, provide a "Lower Fickian Fit", while $C_0 = 1.32 \times 10^{-2}$, with $D = 1.7 \times 10^{-4}$ mm^2/hour, gave an "Upper Fickian Fit" to the data. These curves are shown by dashed lines in Figure 2.

Employing the aforementioned values of C_i and β_i $(i = 1, 2, \cdots, 8)$ and $C_0 = 0.7 \times 10^{-2}$, the distributions $C(z,t)$ were computed at times $t = 500, 3600$ and 8000 hours. Results are shown in Figures 5 through 7, where moisture profiles associated with both "Upper" and "Lower" Fickian data fits are shown for comparison.

Residual hygro-thermal stresses were evaluated according to equations (44) and (45). The computations employed the manufacturer's data (ICI data sheet) which gave $h = 0.127$mm, $E_L = 148$ GPa and $E_T = 11$GPa. In the absence of further details, we assumed a Poisson ratio $\nu_{LT} = 0.28$. The above quantities were converted to the stiffness utilized in equations (44) and (45) as follows (Tsai and Hahn, 1980): $\nu_{TL} = \nu_{LT} \dfrac{E_T}{E_L}$, $Q_L = \dfrac{E_L}{1 - \nu_{LT}\nu_{TL}}$, $Q_T = \dfrac{E_T}{1 - \nu_{LT}\nu_{TL}}$, $Q_{LT} = \dfrac{\nu_{LT} E_T}{1 - \nu_{LT}\nu_{TL}}$.

Furthermore, we assumed hygrothermal properties similar to those of AS4/3502 (Harper and Weitsman, 1985). We thus took $\beta_L = 0$, $\beta_T = 3.24 \times 10^{-3}/1\%$ moisture weight gain, $C_{\text{th}} = 0.1\%$, $\Delta T = -180°C$, $\alpha_L = -0.02 \times 10^{-6}/°C$, $\alpha_T = 27.5 \times 10^{-6}/°C$.

Results of the hygro-thermal residual stresses are shown in Figures 8–13.

It can be noted from the above results that, at early stages, although all the predicted moisture distributions correspond to the same total moisture weight gain, they yield distinct stress distributions. At later stages, as the moisture distribution tends be uniform, the predicted residual stresses are basically proportional to the predicted total moisture weight gain. At some locations, the Fickian predictions may differ by as much as 20–30% from the non-Fickian values.

Furthermore, at the early stages, the stresses are closer to the lower Fickian fit since the boundary moisture saturation level is closer to the lower bound, while at later stages, as the moisture saturation level increases, the stresses are closer to those which correspond to the upper bound. In any case, it is worth noting that the lower and upper Fickian fits on the moisture distribution give lower and upper bounds of the resulting hygro-thermal stress predictions.

7. Conclusions

In principle, the diffusion process of water in polymers and polymeric composites may depart from the idealizations inherent in the classical formulation of Fick. Although there are abundant reasons for that departure, the current work focused on correlating non-Fickian weight gain data with a time-dependent boundary condition, as motivated by the viscoelastic response of polymers.

It is shown that non-Fickian aspects of the moisture absorption process have significant effects on the resulting hygro-thermal stresses in composite materials. The current work reveals the sensitivity of the residual hygro-thermal stresses to a boundary condition of a viscoelastic type, exhibiting discrepancies of about 20–30%.

For a diffusion process whose lower and upper Fickian fits can be found, is it safe to say that the residual stresses which correspond to those two cases provide bounds for the non-Fickian case, resulting in good engineering estimates for the residual stresses in laminates.

However, for an accurate assessment, non-Fickian analysis is needed and the formulations presented in this work provide a systematic method to treat this case.

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Appendix:

The Analytical Solution to the Diffusion Problems with Boundary Condition $C(\pm L, t) = C_0\sqrt{t}H(t)$

Employing the notation of section 3, the transformed governing equation for the diffusion problem is:

$$\frac{d^2\overline{C}}{dz^2} - \frac{s}{D}\overline{C} = 0 \tag{A.1}$$

The solutions in the transformed space are

$$\overline{C} = C_0\frac{\sqrt{\pi}}{2}\frac{\cosh qz}{\sqrt{s^3}\cosh qL}, \tag{A.2}$$

$$\overline{M}(s) = C_0\sqrt{\pi D}\frac{\tanh qL}{s^2}. \tag{A.3}$$

For simplicity in future use, we denote, in eqn.(A.2),

$$\overline{y}(s) = \frac{\cosh qz}{s\cosh qL}. \tag{A.4}$$

Generally, if $\overline{y}(s)$ can be expressed as

$$\overline{y}(s) = \frac{f(s)}{g(s)} \tag{A.5}$$

where $f(s)$ and $g(s)$ are polynomials of s, and if the degree of $g(s)$ is higher than that of $f(s)$, then $\overline{y}(s)$ can be further expressed as

$$\overline{y}(s) = \sum_{n=1}^{N}\frac{f(a_n)}{g'(a_n)}\cdot\frac{1}{s-a_n}, \tag{A.6}$$

where, a_n are zero points of $g(s)$ and N is the degree of $g(s)$.

In the present case, $f(s) = \cosh qz$, and $g(s) = s\cosh qL$.

Since

$$\cosh z = \left(1+\frac{4z^2}{\pi^2}\right)\cdot\left(1+\frac{4z^2}{3^2\pi^2}\right)\cdot\left(1+\frac{4z^2}{5^2\pi^2}\right)\cdots, \tag{A.7}$$

and $g(s)$ is indeed one degree higher than that of $f(s)$. Furthermore, a_n can be solved from the equation

$$s \cosh qL = 0 \tag{A.8}$$

to give

$$a_{00} = 0, \tag{A.9}$$

and

$$q_n L = \pm \frac{(2n+1)\pi i}{2}, \tag{A.10}$$

hence

$$a_n = -\frac{D(2n+1)^2\pi^2}{4L^2}, \qquad (n = 0, 1, 2, \cdots). \tag{A.11}$$

Thus $\overline{C}(s)$ can be rewritten as:

$$\overline{C}(s) = C_0 \frac{\sqrt{\pi}}{2} \left[\frac{f(0)}{g'(0)} \frac{1}{s^{3/2}} + \sum_{n=0}^{\infty} \frac{f(a_n)}{g'(a_n)} \frac{1}{\sqrt{s}(s-a_n)} \right]. \tag{A.12}$$

Although each value of a_n corresponds to two values (+ or −) of q_n in equation (A.10), the choice of any specific sign is immaterial, since either one would yield the same results for the present problem. Selecting the positive sign we obtain

$$f(s) = \cosh qz, \tag{A.13}$$

$$f(0) = \cosh 0 = 1, \tag{A.14}$$

$$f(a_n) = \cos \frac{(2n+1)\pi z}{2L}; \tag{A.15}$$

$$g'(s) = \cosh qL + \frac{1}{2} qL \sinh qL, \tag{A.16}$$

$$g'(0) = \cosh 0 = 1, \tag{A.17}$$

$$g'(a_n) = \frac{(2n+1)\pi}{4}(-1)^{n+1}. \tag{A.18}$$

In inverting $\overline{C}(s)$ as expressed in eqn.(A.12), we note that the inverse of

$$\overline{f}(s) = \frac{1}{\sqrt{s}(s-a)} \tag{A.19}$$

is

$$f(t) = \frac{1}{\sqrt{a}} \, e^{-at} \operatorname{erf}(\sqrt{at}). \tag{A.20}$$

On the other hand, the so called Dawson's integral has an alternative expression (Olver, 1974)

$$\mathrm{F}(\xi) = \frac{\sqrt{\pi}}{2i}\,\mathrm{e}^{-\xi^2}\,\mathrm{erf}(\xi i) = \mathrm{e}^{-\xi^2}\int_0^{\xi} \mathrm{e}^{u^2}\,du. \tag{A.21}$$

Comparing (A.20) with (A.21), then substituting the above result into eqn.(A.12)we obtain:

$$C(z,t) = C_0\sqrt{t}\left[1 + \frac{8}{\pi^2\sqrt{t^*}}\sum_{n=0}^{\infty}\frac{(-1)^{n+1}}{(2n+1)^2}\,\mathrm{F}\left(\frac{(2n+1)\pi}{2}\sqrt{t^*}\right)\cos\frac{(2n+1)\pi z}{2L}\right]. \tag{A.22}$$

The total moisture weight gain can be readily computed from the integration of the above expression to yield

$$M(t) = 2LC_0\sqrt{t}\left[1 - \frac{16}{\pi^3\sqrt{t^*}}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^3}\,\mathrm{F}\left(\frac{(2n+1)\pi}{2}\sqrt{t^*}\right)\right]. \tag{A.23}$$

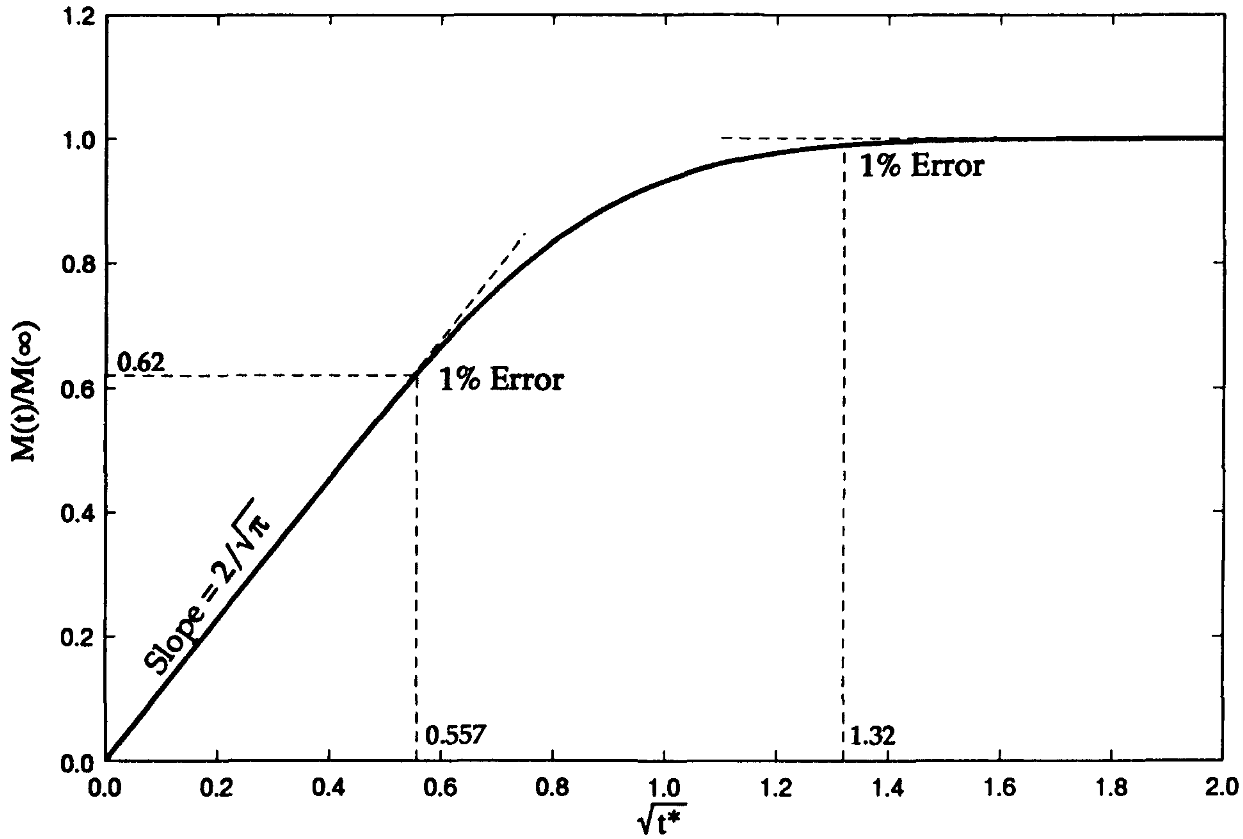

Figure 1. The total weight gain $M(t)/M(\infty)$ vs. $\sqrt{t^*}$ according to Fick's Law, with locations where departures from straight lines exceed 1%. $M(\infty) = 2L$ for the case of unit boundary condition.

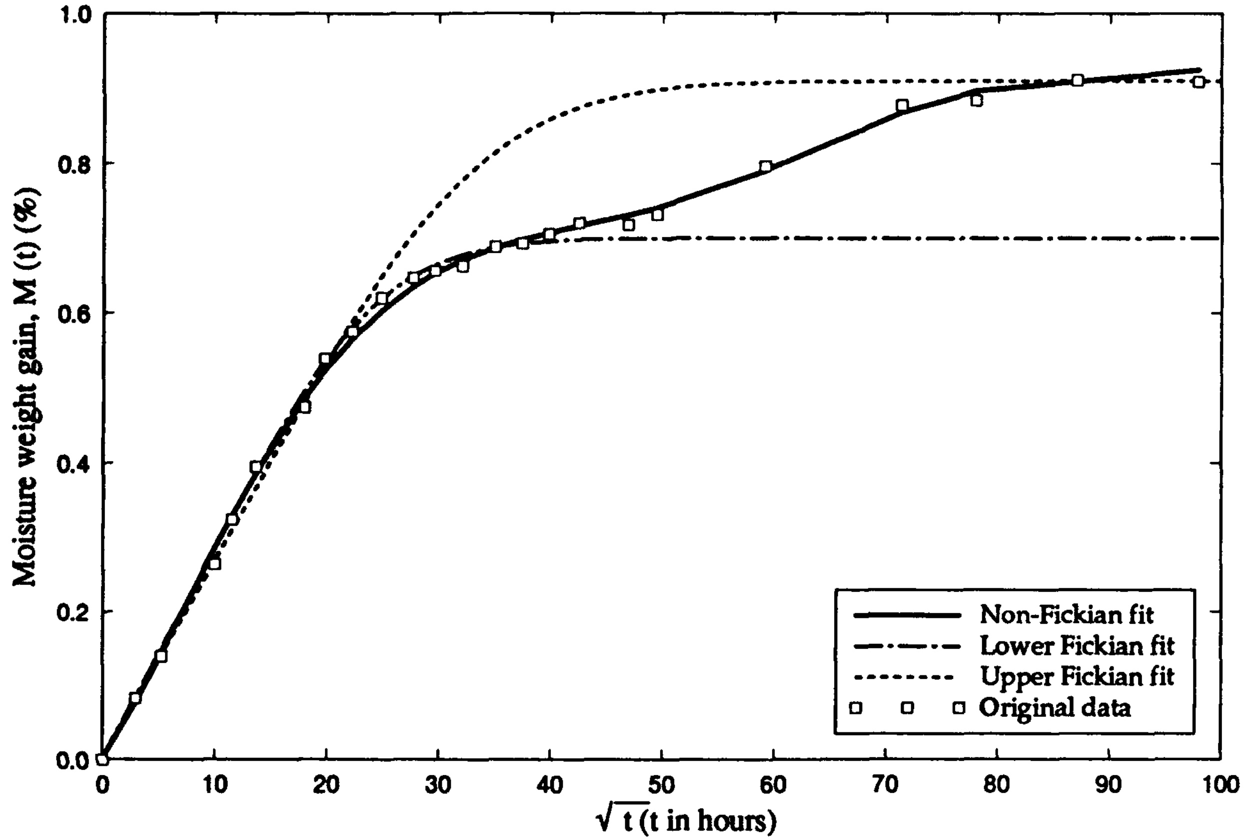

Figure 2. The total moisture weight gain data and the theoretical predictions by non-Fickian fitting and Fickian fittings with two different saturation levels.

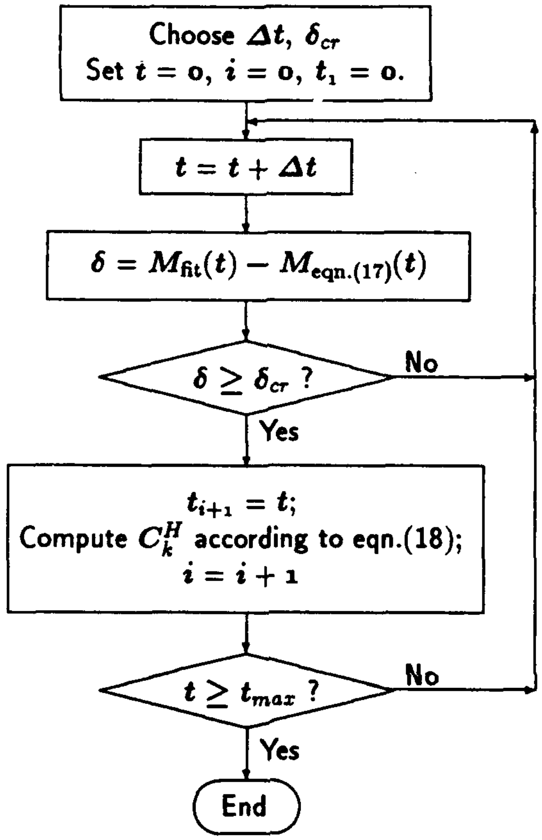

Figure 3: Flow chart for presenting the boundary condition as sequence of step functions.

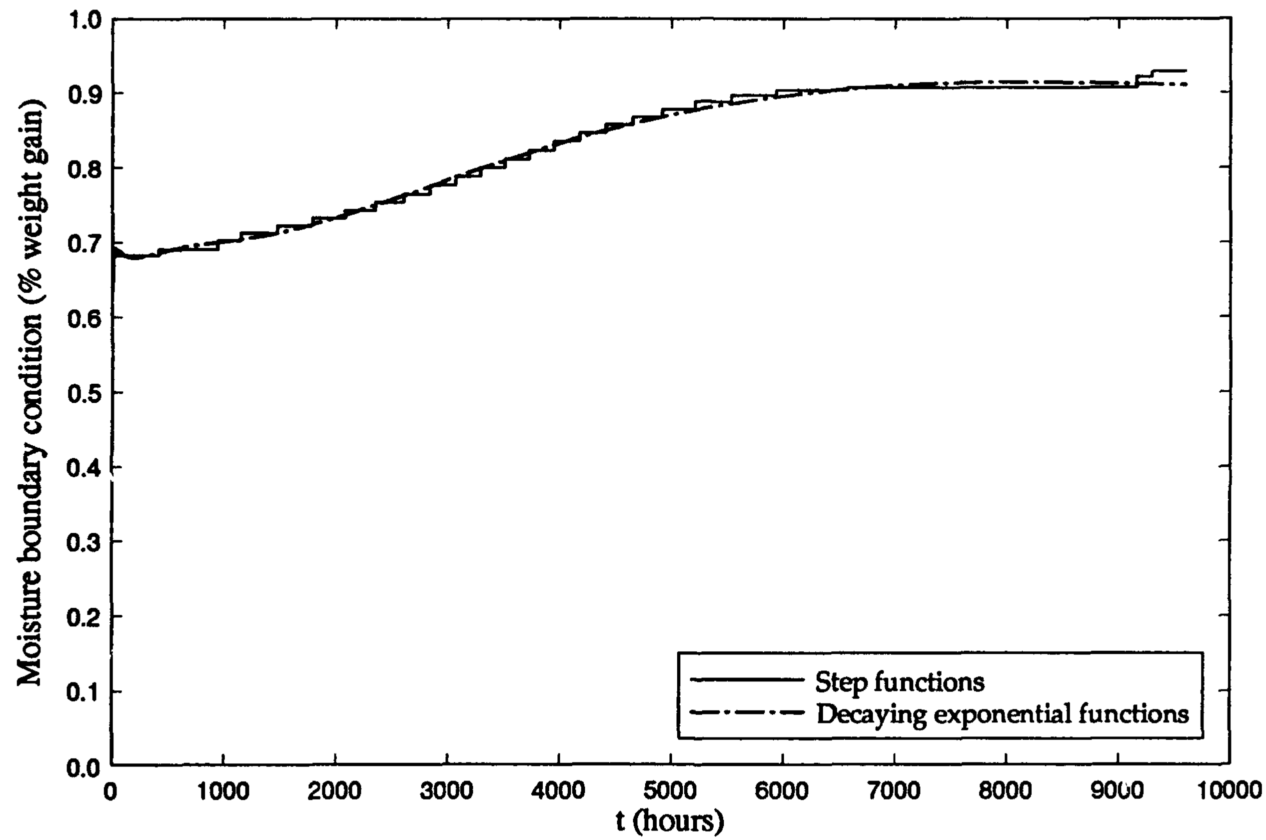

Figure 4. The boundary condition represented by a series of step functions and by a series of decaying exponential functions.

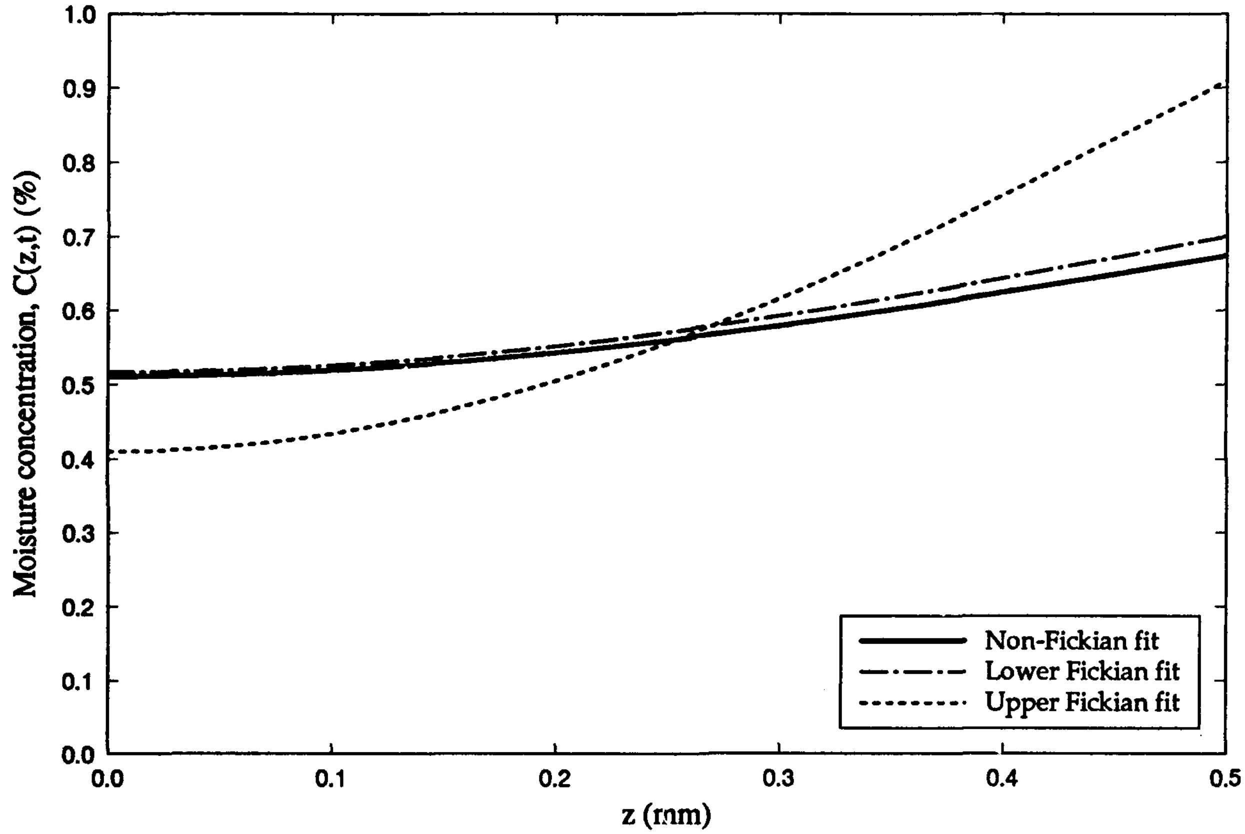

Figure 5. Moisture distribution across the laminate's thickness direction predicted by the non-Fickian fit and the "upper" and "lower" Fickian fits. (500 hours)

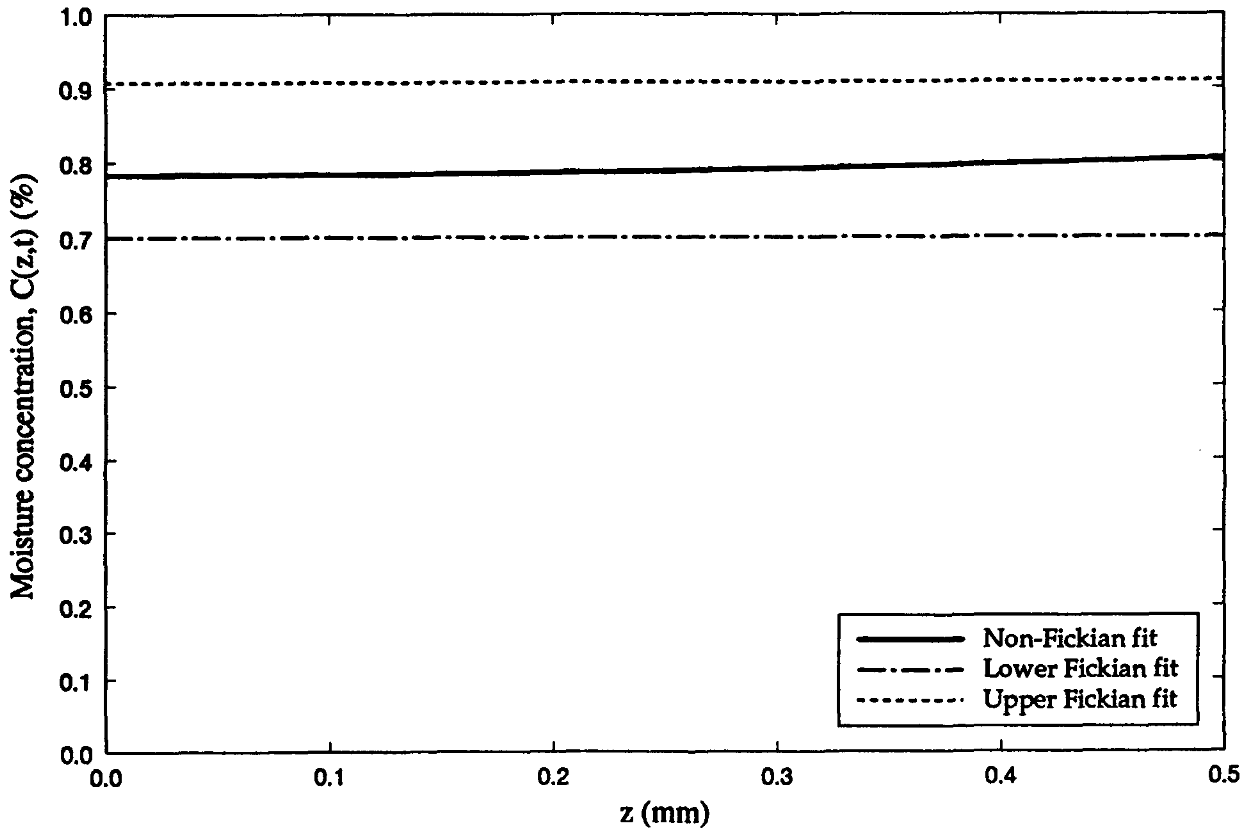

Figure 6. Moisture distribution across the laminate's thickness direction predicted by the non-Fickian fit and the "upper" and "lower" Fickian fits. (3600 hours)

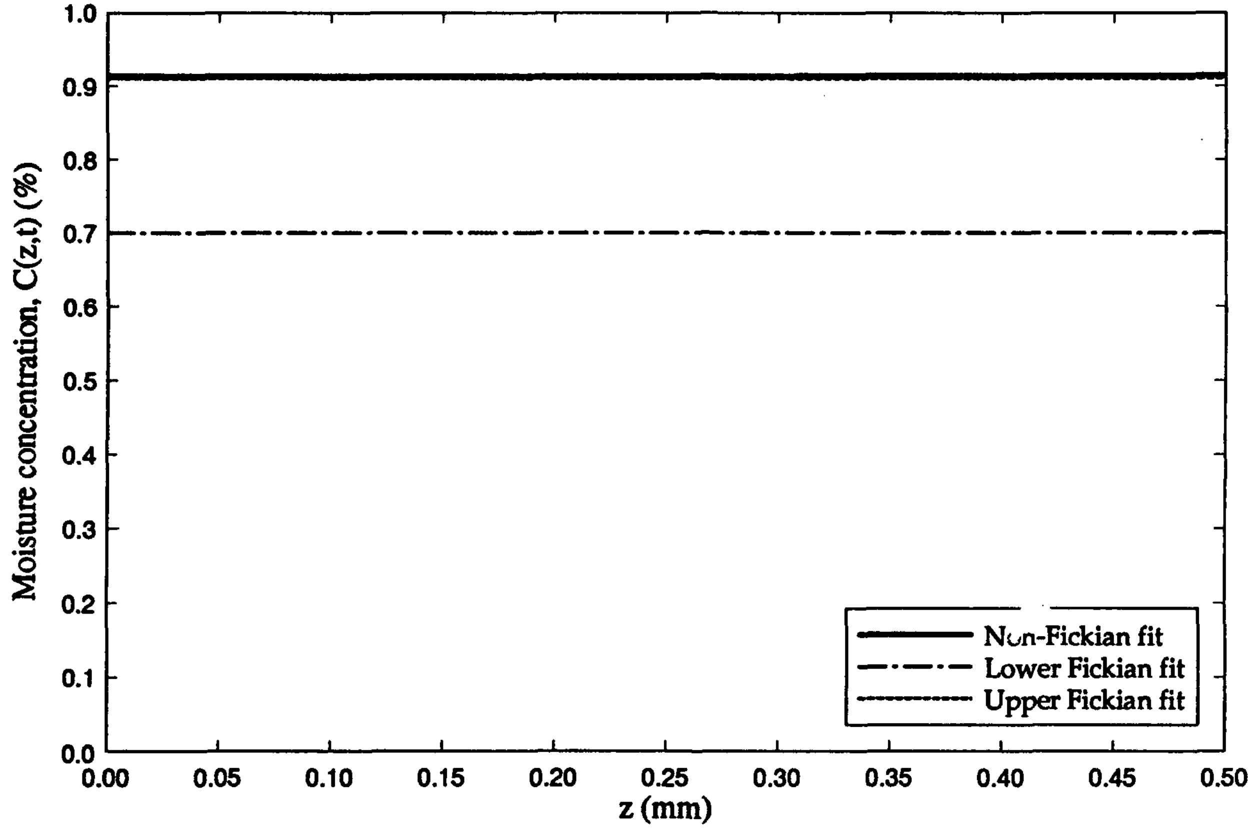

Figure 7. Moisture distribution across the laminate's thickness predicted by the non-Fickian fit and the "upper" and "lower" Fickian fits. (8000 hours)

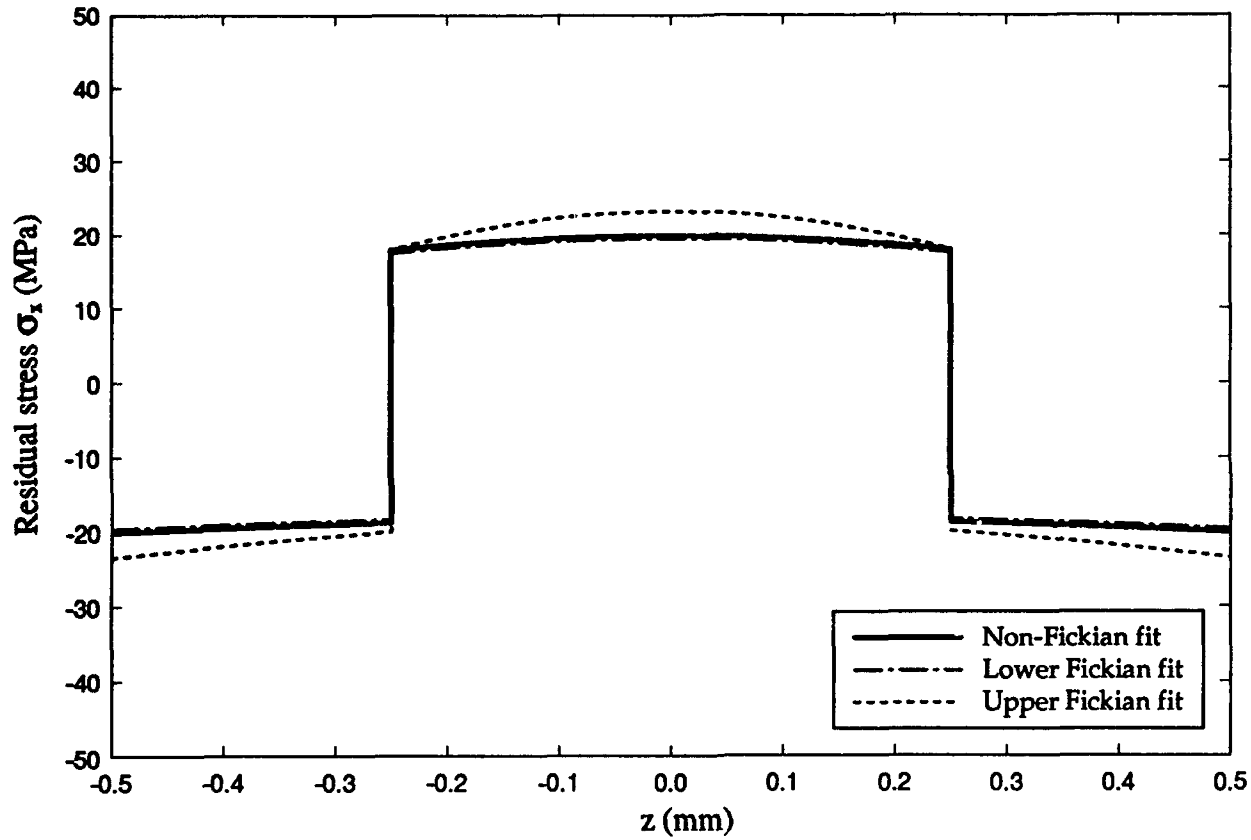

Figure 8. The residual hygro-thermal stress σ_x across the thickness of a $[0_2/90_2]_S$ laminate at t = 500 hours.

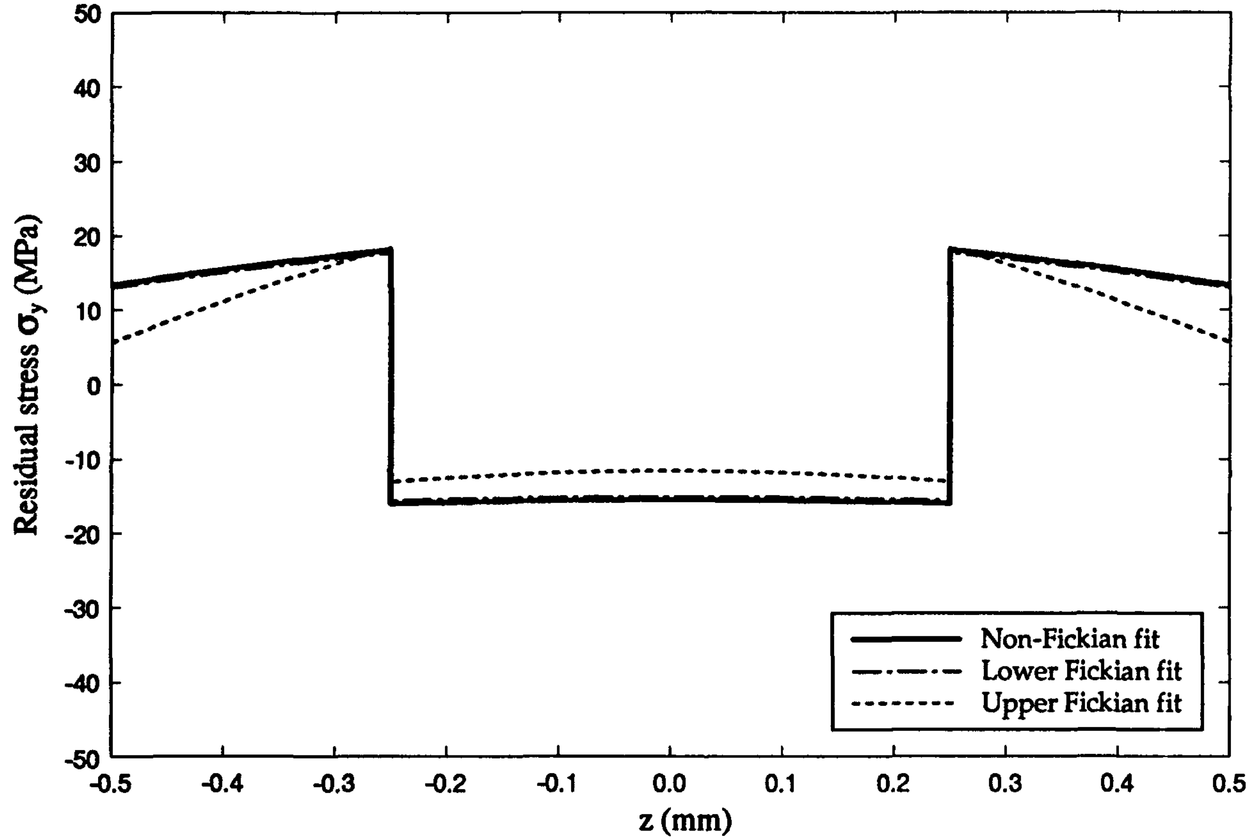

Figure 9. The residual hygro-thermal stress σ_y across the thickness of a $[0_2/90_2]_S$ laminate at t = 500 hours.

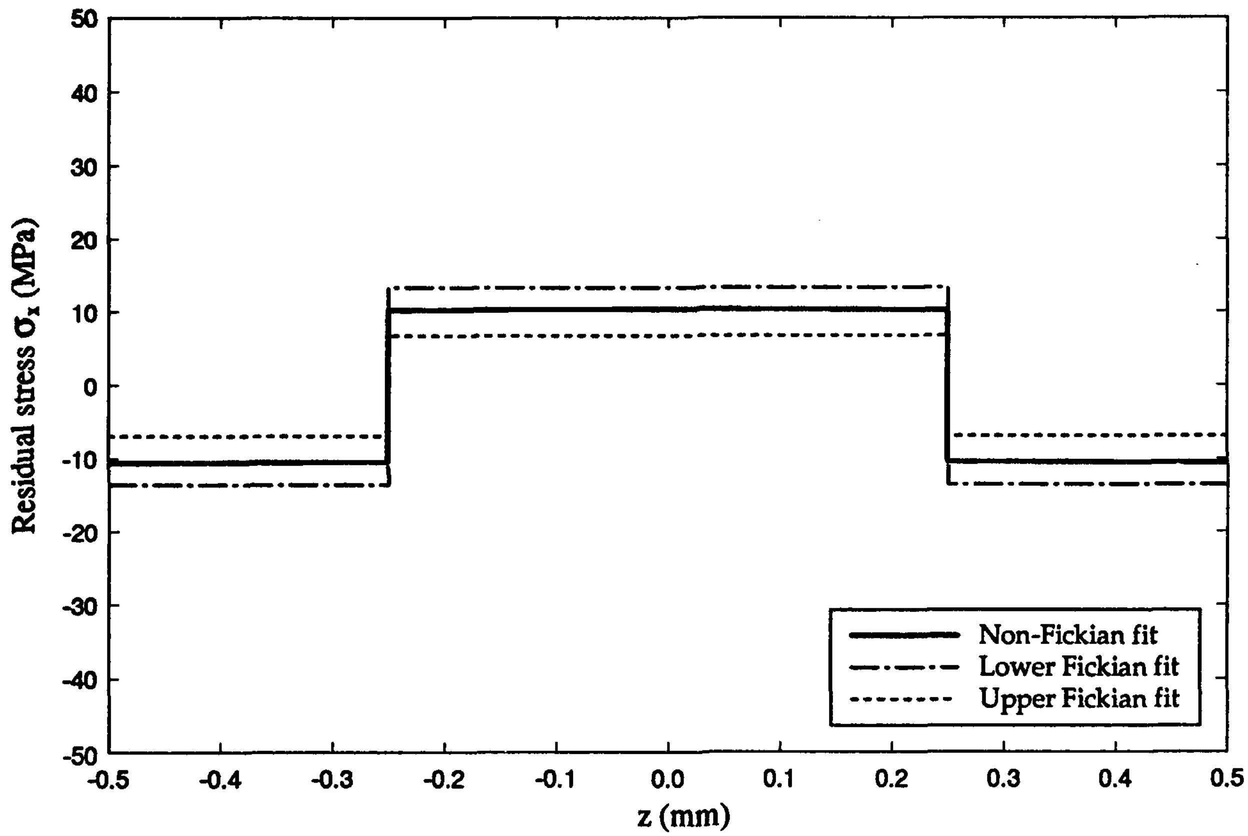

Figure 10. The residual hygro-thermal stress σ_x across the thickness of a $[0_2/90_2]_S$ laminate at t = 3600 hours.

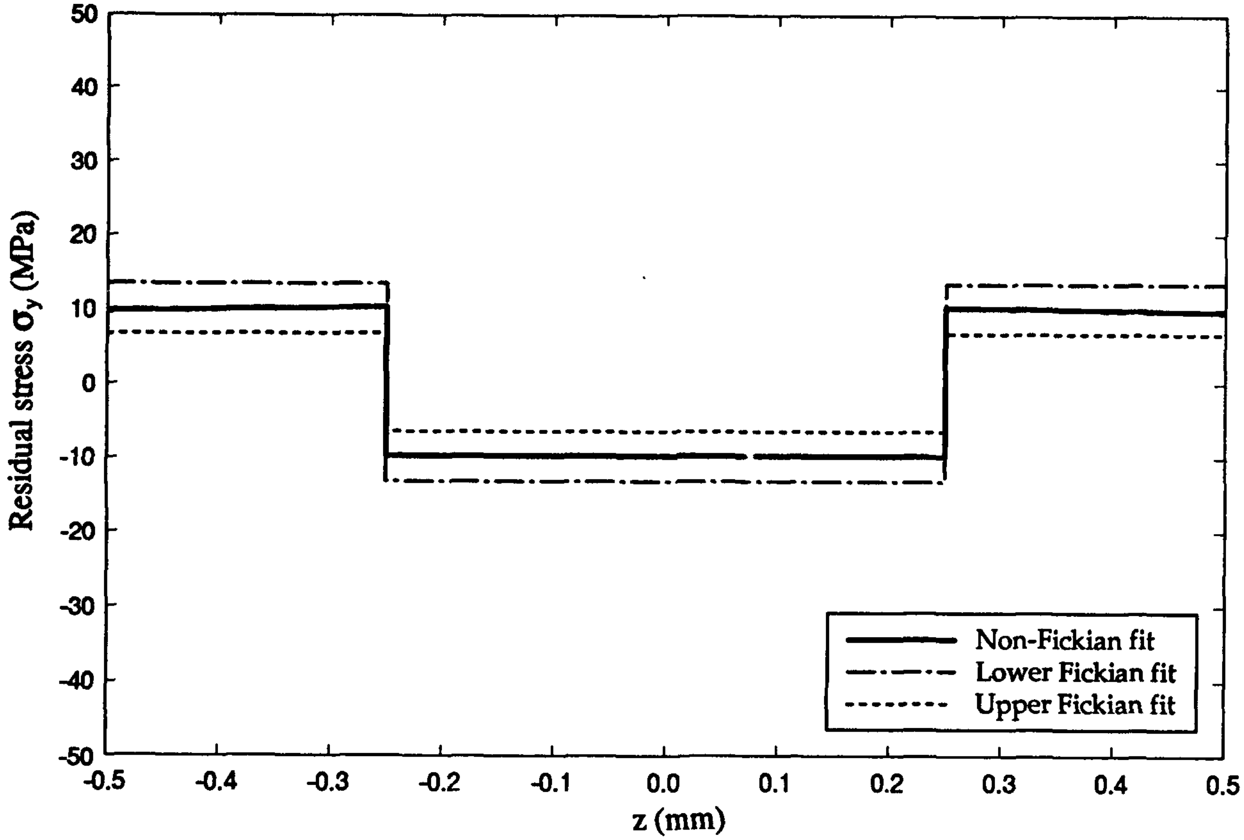

Figure 11. The residual hygro-thermal stress σ_y across the thickness of a $[0_2/90_2]_S$ laminate at t = 3600 hours.

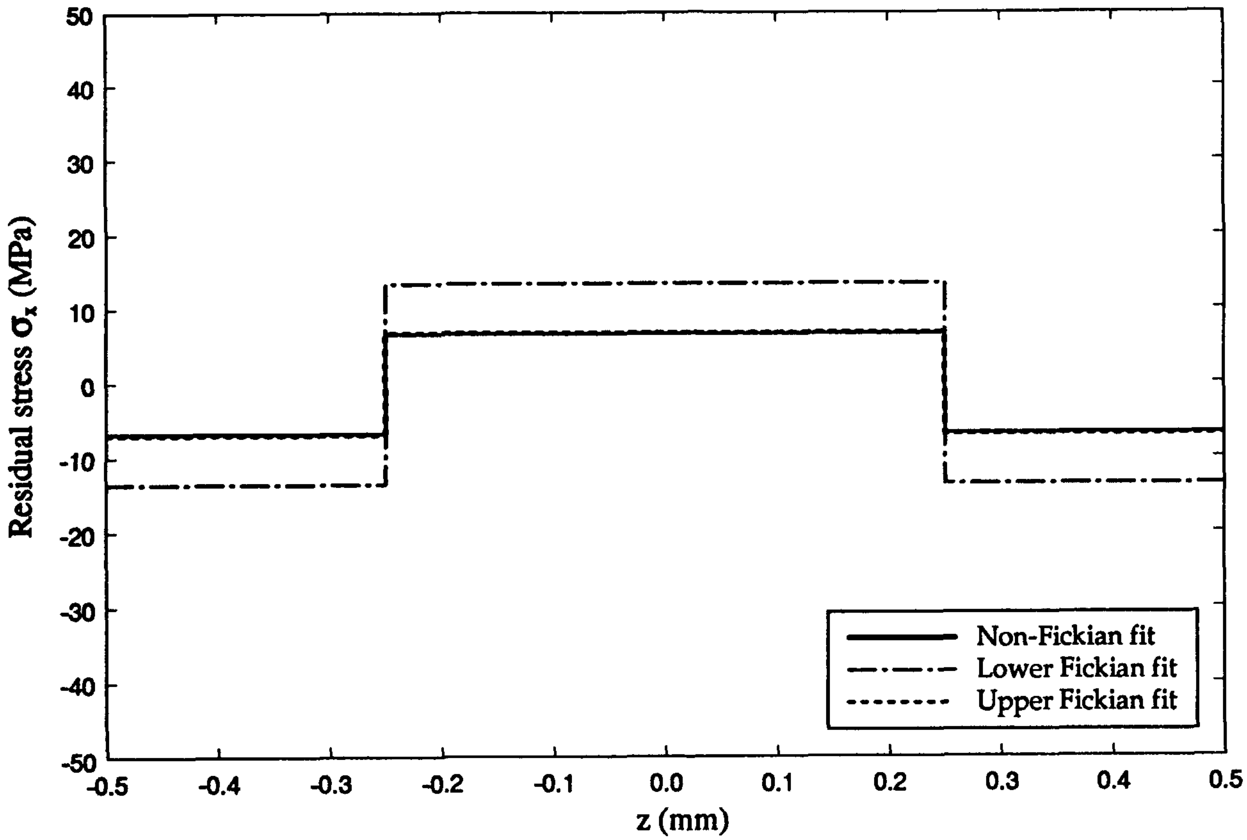

Figure 12. The residual hygro-thermal stress σ_x across the thickness of a $[0_2/90_2]_S$ laminate at t = 8000 hours.

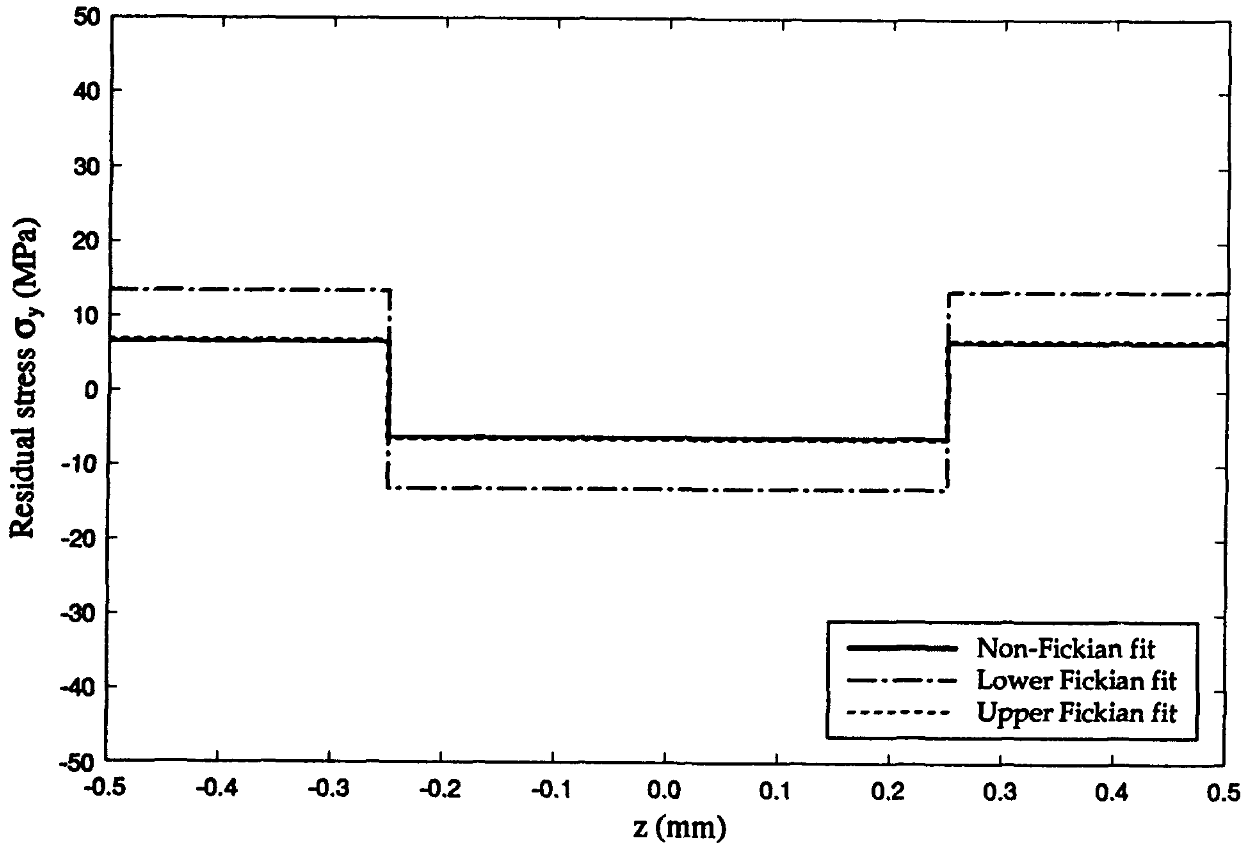

Figure 13. The residual hygro-thermal stress σ_y across the thickness of a $[0_2/90_2]_S$ laminate at t = 8000 hours.