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Modeling of diffusion in the presence of damage in polymer matrix composites

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Abstract

It is now well known that Fick's Law is frequently inadequate for describing moisture diffusion in polymers and polymer composites. Non-Fickian or anomalous diffusion is likely to occur when a polymer composite laminate is subjected to external stresses that could give rise to internal damage in the form of matrix cracks. As a result, it is necessary to take into account the combined effects of temperature, stress, and damage in the construction of such a model. In this article, a modeling methodology based on irreversible thermodynamics applied within the framework of composite macro-mechanics is presented, that would allow characterization of non-Fickian diffusion coefficients from moisture-weight-gain data for laminated composites. A symmetric damage tensor based on continuum damage mechanics is incorporated in this model by invoking the principle of invariance with respect to coordinate transformations. For tractability, the diffusion-governing equations are simplified for the special case of a laminate, with uniformly distributed matrix cracks, that is subjected to a uniaxial tensile stress. The final form for effective diffusivity obtained from this derivation indicates that the effective diffusivity for this case is a quadratic function of crack density. A finite element procedure that extends this methodology to more complex shapes and boundary conditions is also presented. Comparisons with test data for a 5-harness satin textile composite are provided for model verifications.

Keywords: Diffusion; Damage; Composite; Micro-crack; Finite elements; Non-Fickian

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1. Introduction

The benefits of a light-weight polymer matrix composite (PMC) components to aircraft engines are now well known. Although thousands of PMC components are currently in service, barriers still exist to further implementation in more structurally critical and higher temperature applications. Most of these barriers are associated with the inability to accurately predict component lives, and therefore, component life-cycle costs. A fiber reinforced composite material with a polymer matrix will typically absorb moisture in a humid environment and at elevated temperatures. A combined exposure to heat and moisture affects a PMC in a variety of ways. First, the hygrothermal swelling causes a change in the residual stresses within

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the composite that could lead to micro-crack formation. These micro-cracks, in turn, provide fast diffusion paths and thus alter the moisture absorption characteristics of the laminate. Secondly, heat and humidity may cause the matrix to become plasticized thus causing an increase in the elongation to failure of the matrix. Thirdly, the chemical bond at the interface between fiber and matrix may be affected which in turn, would influence strength and toughness. Finally, in the event of cyclic heating and cooling with a sustained use-temperature above the boiling point of water, vaporization and out-gassing of absorbed moisture may take place leading to physical damage and chemical changes within the PMC, especially at temperatures greater than the T_g of the matrix. A continuous exposure to high moisture concentrations at the exposed surfaces of a PMC component could also lead to damage in the form of matrix cracking, dissolution, and peeling.

It is now widely recognized that cyclic moisture absorption and desorption plays a significant role in influencing the mechanical behavior, and therefore, long-term durability of polymers and PMC. Numerous diffusion models have been proposed over the years for modeling hygrothermal effects in PMC. The one, most frequently used by researchers is the one-dimensional Fickian model. Unfortunately, this model tends to overestimate the moisture absorption in panels for a short diffusion time (Shen and Springer, 1981). Some researchers have suggested that the deviation can be explained by a two-stage Fickian process (Gurtin and Yatomi, 1979; Carter and Kibler, 1978). Others claim that the diffusion process in a PMC is really non-Fickian (Shirrell et al., 1979; Weitsman, 1991). In reality, the nature of the diffusion process depends on the material and on the environmental conditions that the material is exposed to. For example, if the rate of viscoelastic relaxation in a polymer is comparable to the rate of moisture diffusion, then the diffusion is likely to be non-Fickian. In addition, the presence of strong temperature and stress gradients has been known to engender non-Fickian driving forces. The presence of damage in the form of matrix cracks could also lead to anomalous diffusion. Employing a rigorous thermodynamic approach, Weitsman (1987) developed a model for coupled damage and moisture transport in a transversely isotropic, fiber reinforced polymer composite. The damage entity was represented as a skew-symmetric tensor and was included in the model as an internal state variable. However, the model was mathematically complex and was not amenable to a simple closed-form solution.

In this article, theory of irreversible thermodynamics is applied within the framework of continuum mechanics to derive governing equations for diffusion in a PMC from first principles. A special form for Gibbs potential is formulated for an orthotropic material using stress, temperature, damage and moisture concentration as independent state variables. The resulting governing equations are capable of modeling the effect of interactions between complex stress, temperature, damage and moisture concentration on the diffusion process within an orthotropic material. The primary focus of this work is to model diffusion in the presence of a pre-existing state of damage; consequently damage evolution is not included in the present analysis for tractability. Because the mathematically complex nature of the governing equations precludes a closed-form solution, a variational formulation is used to derive the weak form of the non-linear governing equations that are then solved using the finite element method. This approach provides a significant improvement over solution methods reported in the literature for this type of problems. For model validation, the model predictions are compared with experimental data for the special case of isothermal diffusion in an unstressed 5-harness satin weave graphite/epoxy $[0/90/0/90]_s$ laminate with distributed matrix micro-cracks.

2. Model development

The Gibbs potential for an orthotropic material subjected to applied stress and internal damage must be expressed in a polynomial form that remains invariant to coordinate transformations. Such a polynomial can be mathematically expressed as a combination of invariant terms obtained from the so-called irreducible integrity bases (Adkins, 1959; Talreja, 1994). The irreducible integrity bases for an orthotropic material are,

$$\bar{\sigma}_{11}, \bar{\sigma}_{22}, \bar{\sigma}_{33}, d_{11}, d_{22}, d_{33}, \bar{\sigma}_{23}^2, \bar{\sigma}_{13}^2, \bar{\sigma}_{12}^2, \bar{\sigma}_{23}\bar{\sigma}_{13}\bar{\sigma}_{12}, d_{23}^2, d_{13}^2, d_{12}^2, d_{23}d_{13}d_{12},$$
$$\bar{\sigma}_{23}d_{23}, \bar{\sigma}_{13}d_{13}, \bar{\sigma}_{12}d_{12}, d_{23}\bar{\sigma}_{13}\bar{\sigma}_{12}, d_{13}\bar{\sigma}_{12}\bar{\sigma}_{23}, d_{12}\bar{\sigma}_{23}\bar{\sigma}_{13}, \bar{\sigma}_{23}d_{13}d_{12}, \bar{\sigma}_{13}d_{12}d_{23}, \bar{\sigma}_{12}d_{23}d_{13}, \tag{1}$$

where the normalized stress

$$\bar{\sigma}_{ij} = \frac{\sigma_{ij}}{\sigma_f},$$

where σ_f is the ultimate stress in a material principal direction, the damage tensor d_{ij} is a symmetric tensor of the second rank.

The chemical potential of moisture in the polymer is given by

$$\mu = \rho_s \frac{\partial \phi}{\partial m}, \tag{2}$$

where, ϕ is Gibbs potential, ρ_s is the mass density of the polymeric solid, and "m" is the moisture concentration. It should be noted that in this treatment the moisture concentration "m" is assumed to be a scalar valued variable with the same value in all symmetry directions. Conservation of diffusing mass within a unit volume of the polymer requires

$$\frac{\partial m}{\partial t} = -\frac{\partial f_i}{\partial X_i}, \quad i = 1, 3, \tag{3}$$

where, in the absence of temperature, stress and damage gradients, moisture flux f_i for orthotropic symmetry is assumed to be of the form,

$$f_i = -D_i \frac{\partial \mu}{\partial X_i}, \tag{4}$$

where D_i are the diffusion coefficients in the lamina material principal directions. It should be noted that repeated indices do not imply summation in Eq. (4). Combining Eqs. (2)–(4), gives the governing equation for diffusion in a anisotropic medium,

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial X_i}\left(D_i \frac{\partial \mu}{\partial X_i}\right), \quad i = 1, 3. \tag{5}$$

Please note that repeated indices imply summation in Eq. (5).

2.1. Special case

Consider a laminate with intralaminar cracks oriented perpendicular to the X_1 axis, subjected to an in-plane uniaxial loading in the X_1 direction under isothermal conditions as schematically shown in Fig. 1. For the special case of uniaxial loading, the states of stress and damage reduce to

$$\bar{\sigma}_{22} = \bar{\sigma}_{33} = \bar{\sigma}_{13} = \bar{\sigma}_{23} = \bar{\sigma}_{12} = 0,$$

$$d_{22} = d_{33} = d_{13} = d_{23} = d_{12} = 0.$$

Based on a definition of the damage originally proposed by Talreja (1994), it can be shown that the non-zero damage component d_{11} is given by

$$d_{11} = \frac{\kappa(m, T) t_c^2 \delta_1}{t}. \tag{6}$$

In Eq. (6), $\kappa(m,T)$ is an experimentally determined influence parameter that incorporates the constraining influence of moisture concentration (m), temperature (T), ply orientation, and fiber architecture on crack

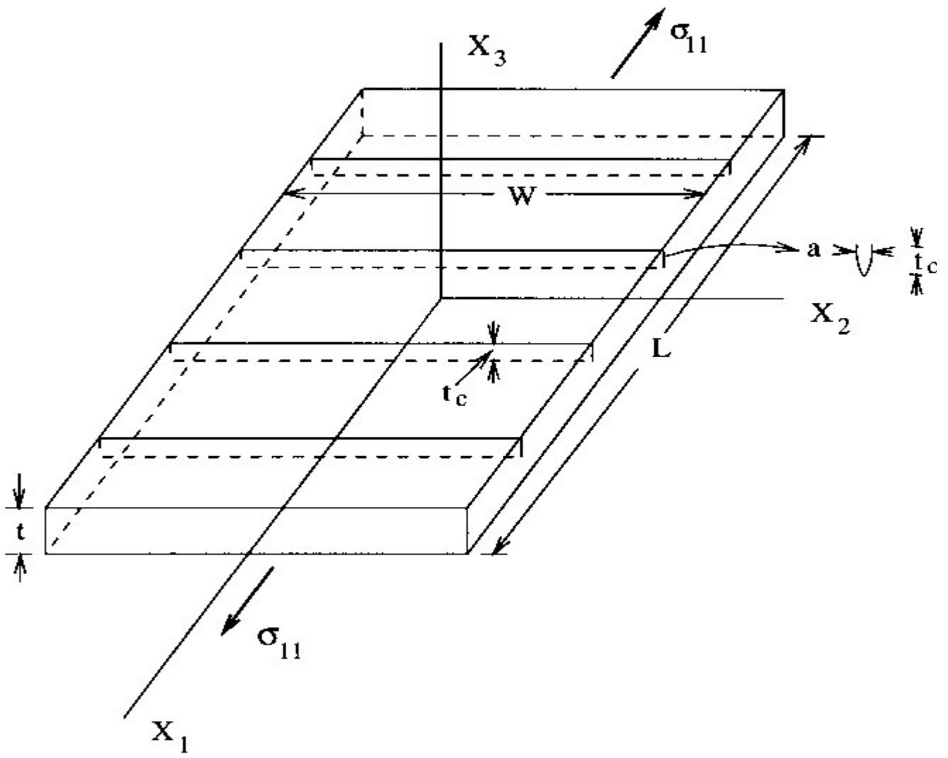

Fig. 1. Schematic of a micro-cracked laminate under uniaxial stress state.

opening displacement; t_c is the crack size, t is the total thickness of the laminate, and δ_1 is the crack density in the X_1-direction as depicted in Fig. 1.

Using the irreducible integrity bases from Eq. (1) and assuming that terms beyond second-order in uniaxial stress and damage can be neglected, the Gibbs potential becomes

$$\rho_s\phi = \hat{C}_0 + \hat{C}_1\bar{\sigma}_{11} + \hat{C}_2 d_{11} + \hat{C}_3\bar{\sigma}_{11}^2 + \hat{C}_4\bar{\sigma}_{11}d_{11} + \hat{C}_5 d_{11}^2 + \hat{C}_6\bar{\sigma}_{11}^2 d_{11} + \hat{C}_7\bar{\sigma}_{11}d_{11}^2. \tag{7}$$

In Eq. (7), the $\hat{C}_i$ are thermodynamic coefficients that could be expressed, in general, as functions of temperature (T) and concentration (m). In this manner, concentration and temperature are implicitly included in the polynomial expansion of Gibbs potential as state variables.

The chemical potential of moisture in the polymer for this special case is

$$\begin{aligned}\mu &= \rho_s\frac{\partial\phi}{\partial m}\\ &= \rho_s\left[\frac{\partial\hat{C}_0}{\partial m} + \frac{\partial\hat{C}_1}{\partial m}\bar{\sigma}_{11} + \hat{C}_1\frac{\partial\bar{\sigma}_{11}}{\partial m} + \frac{\partial\hat{C}_2}{\partial m}d_{11} + \hat{C}_2\frac{\partial d_{11}}{\partial m} + \frac{\partial\hat{C}_3}{\partial m}\bar{\sigma}_{11}^2 + 2\hat{C}_3\bar{\sigma}_{11}\frac{\partial\bar{\sigma}_{11}}{\partial m} + \frac{\partial\hat{C}_4}{\partial m}\bar{\sigma}_{11}d_{11}\right.\\ &\quad + \hat{C}_4 d_{11}\frac{\partial\bar{\sigma}_{11}}{\partial m} + \hat{C}_4\bar{\sigma}_{11}\frac{\partial d_{11}}{\partial m} + \frac{\partial\hat{C}_5}{\partial m}d_{11}^2 + 2\hat{C}_5 d_{11}\frac{\partial d_{11}}{\partial m} + \frac{\partial\hat{C}_6}{\partial m}\bar{\sigma}_{11}^2 d_{11} + 2\hat{C}_6\bar{\sigma}_{11}d_{11}\frac{\partial\bar{\sigma}_{11}}{\partial m} + \hat{C}_6\bar{\sigma}_{11}^2\frac{\partial d_{11}}{\partial m}\\ &\quad \left. + \frac{\partial\hat{C}_7}{\partial m}\bar{\sigma}_{11}d_{11}^2 + \hat{C}_7 d_{11}^2\frac{\partial\bar{\sigma}_{11}}{\partial m} + 2\hat{C}_7\bar{\sigma}_{11}d_{11}\frac{\partial d_{11}}{\partial m}\right].\end{aligned} \tag{8}$$

Because chemical potential is, in general, a function of σ_{11}, d_{11}, T, and m, therefore,

$$\frac{\partial \mu}{\partial X_i} = \frac{\partial \mu}{\partial m}\frac{\partial m}{\partial X_i} + \frac{\partial \mu}{\partial T}\frac{\partial T}{\partial X_i} + \frac{\partial \mu}{\partial \bar{\sigma}_{11}}\frac{\partial \bar{\sigma}_{11}}{\partial X_i} + \frac{\partial \mu}{\partial d_{11}}\frac{\partial d_{11}}{\partial X_i}.$$

For the special case of uniform stress, damage, and temperature distributions, only the moisture gradient term is dominant and Eq. (4) can be written as

$$\begin{aligned}
D_i \frac{\partial \mu}{\partial X_i} &= D_i\left(\frac{\partial \mu}{\partial m}\right)\left(\frac{\partial m}{\partial X_i}\right) \\
&= \rho_{\mathrm{s}} D_i \left[\frac{\partial^2 \hat{C}_0}{\partial m^2}. + \frac{\partial^2 \hat{C}_1}{\partial m^2}\bar{\sigma}_{11} + 2\frac{\partial \hat{C}_1}{\partial m}\frac{\partial \bar{\sigma}_{11}}{\partial m} + \hat{C}_1 \frac{\partial^2 \bar{\sigma}_{11}}{\partial m^2} + \frac{\partial^2 \hat{C}_2}{\partial m^2} d_{11} + 2\frac{\partial \hat{C}_2}{\partial m}\frac{\partial d_{11}}{\partial m} + \hat{C}_2 \frac{\partial^2 d_{11}}{\partial m^2} \right. \\
&\quad + \frac{\partial^2 \hat{C}_3}{\partial m^2}\bar{\sigma}_{11}^2 + 4\bar{\sigma}_{11}\frac{\partial \hat{C}_3}{\partial m}\frac{\partial \bar{\sigma}_{11}}{\partial m} + 2\hat{C}_3\left(\frac{\partial \bar{\sigma}_{11}}{\partial m}\right)^2 + 2\hat{C}_3\bar{\sigma}_{11}\frac{\partial^2 \bar{\sigma}_{11}}{\partial m^2} + \frac{\partial^2 \hat{C}_4}{\partial m^2}\bar{\sigma}_{11} d_{11} + \frac{\partial \hat{C}_4}{\partial m}\frac{\partial \bar{\sigma}_{11}}{\partial m} d_{11} \\
&\quad + \frac{\partial \hat{C}_4}{\partial m}\bar{\sigma}_{11}\frac{\partial d_{11}}{\partial m} + \frac{\partial \hat{C}_4}{\partial m} d_{11}\frac{\partial \bar{\sigma}_{11}}{\partial m} + \hat{C}_4\frac{\partial d_{11}}{\partial m}\frac{\partial \bar{\sigma}_{11}}{\partial m} + \hat{C}_4 d_{11}\frac{\partial^2 \bar{\sigma}_{11}}{\partial m^2} + \frac{\partial \hat{C}_4}{\partial m}\bar{\sigma}_{11}\frac{\partial d_{11}}{\partial m} + \hat{C}_4\frac{\partial \bar{\sigma}_{11}}{\partial m}\frac{\partial d_{11}}{\partial m} \\
&\quad + \hat{C}_4\bar{\sigma}_{11}\frac{\partial^2 d_{11}}{\partial m^2} + \frac{\partial^2 \hat{C}_5}{\partial m^2} d_{11}^2 + 4 d_{11}\frac{\partial \hat{C}_5}{\partial m}\frac{\partial d_{11}}{\partial m} + 2\hat{C}_5\left(\frac{\partial d_{11}}{\partial m}\right)^2 + 2\hat{C}_5 d_{11}\frac{\partial^2 d_{11}}{\partial m^2} + \frac{\partial^2 \hat{C}_6}{\partial m^2}\bar{\sigma}_{11}^2 d_{11} \\
&\quad + 2\frac{\partial \hat{C}_6}{\partial m}\bar{\sigma}_{11} d_{11}\frac{\partial \bar{\sigma}_{11}}{\partial m} + \frac{\partial \hat{C}_6}{\partial m}\bar{\sigma}_{11}^2\frac{\partial d_{11}}{\partial m} + 2\frac{\partial \hat{C}_6}{\partial m}\bar{\sigma}_{11} d_{11}\frac{\partial \bar{\sigma}_{11}}{\partial m} + 2\hat{C}_6 d_{11}\left(\frac{\partial \bar{\sigma}_{11}}{\partial m}\right)^2 + 2\hat{C}_6\bar{\sigma}_{11}\frac{\partial \bar{\sigma}_{11}}{\partial m}\frac{\partial d_{11}}{\partial m} \\
&\quad + 2\hat{C}_6\bar{\sigma}_{11} d_{11}\frac{\partial^2 \bar{\sigma}_{11}}{\partial m^2} + \frac{\partial \hat{C}_6}{\partial m}\bar{\sigma}_{11}^2\frac{\partial d_{11}}{\partial m} + 2\hat{C}_6\bar{\sigma}_{11}\frac{\partial \bar{\sigma}_{11}}{\partial m}\frac{\partial d_{11}}{\partial m} + \hat{C}_6\bar{\sigma}_{11}^2\frac{\partial^2 d_{11}}{\partial m^2} + \frac{\partial^2 \hat{C}_7}{\partial m^2}\bar{\sigma}_{11} d_{11}^2 \\
&\quad + \frac{\partial \hat{C}_7}{\partial m}\frac{\partial \bar{\sigma}_{11}}{\partial m} d_{11}^2 + 2\frac{\partial \hat{C}_7}{\partial m}\bar{\sigma}_{11} d_{11}\frac{\partial d_{11}}{\partial m} + \frac{\partial \hat{C}_7}{\partial m} d_{11}^2\frac{\partial \bar{\sigma}_{11}}{\partial m} + 2\hat{C}_7 d_{11}\frac{\partial \bar{\sigma}_{11}}{\partial m}\frac{\partial d_{11}}{\partial m} + \hat{C}_7 d_{11}^2\frac{\partial^2 \bar{\sigma}_{11}}{\partial m^2} \\
&\quad \left. + 2\frac{\partial \hat{C}_7}{\partial m}\bar{\sigma}_{11} d_{11}\frac{\partial d_{11}}{\partial m} + 2\hat{C}_7\frac{\partial \bar{\sigma}_{11}}{\partial m} d_{11}\frac{\partial d_{11}}{\partial m} + 2\hat{C}_7\bar{\sigma}_{11}\left(\frac{\partial d_{11}}{\partial m}\right)^2 + 2\hat{C}_7\bar{\sigma}_{11} d_{11}\frac{\partial^2 d_{11}}{\partial m^2} \right] \left(\frac{\partial m}{\partial X_i}\right).
\end{aligned} \tag{9}$$

For the special stress-free case, where $\bar{\sigma}_{11} = 0$, Eq. (9) becomes

$$\begin{aligned}
D_i \frac{\partial \mu}{\partial X_i} &= \rho_{\mathrm{s}} D_i \left[\frac{\partial^2 \hat{C}_0}{\partial m^2} + \frac{\partial^2 \hat{C}_2}{\partial m^2} d_{11} + 2\frac{\partial \hat{C}_2}{\partial m}\frac{\partial d_{11}}{\partial m} + \hat{C}_2\frac{\partial^2 d_{11}}{\partial m^2} + \frac{\partial^2 \hat{C}_5}{\partial m^2} d_{11}^2 \right. \\
&\quad \left. + 4 d_{11}\frac{\partial \hat{C}_5}{\partial m}\frac{\partial d_{11}}{\partial m} + 2\hat{C}_5\left(\frac{\partial d_{11}}{\partial m}\right)^2 + 2\hat{C}_5 d_{11}\frac{\partial^2 d_{11}}{\partial m^2} \right] \left(\frac{\partial m}{\partial X_i}\right) \\
&= \rho_{\mathrm{s}} D_i \left[\left\{ \frac{\partial^2 \hat{C}_0}{\partial m^2} + 2\frac{\partial \hat{C}_2}{\partial m}\frac{\partial d_{11}}{\partial m} + \hat{C}_2\frac{\partial^2 d_{11}}{\partial m^2} + 2\hat{C}_5\left(\frac{\partial d_{11}}{\partial m}\right)^2 \right\} \right. \\
&\quad \left. + \left\{ \frac{\partial^2 \hat{C}_2}{\partial m^2} + 4\frac{\partial \hat{C}_5}{\partial m}\frac{\partial d_{11}}{\partial m} + 2\hat{C}_5\frac{\partial^2 d_{11}}{\partial m^2} \right\} d_{11} + \left\{ \frac{\partial^2 \hat{C}_5}{\partial m^2} \right\} d_{11}^2 \right] \left(\frac{\partial m}{\partial X_i}\right).
\end{aligned} \tag{10}$$

If, for conceptual simplification, it is assumed that swelling due to moisture absorption influences only the opening displacement without significantly affecting either the crack size, t_{c}, or the crack density, δ_1, then,

$$\frac{\partial}{\partial m}\left(\frac{\kappa t_{\mathrm{c}} \delta_1}{t}\right) = \frac{t_{\mathrm{c}}^2 \delta_1}{t}\frac{\partial \kappa}{\partial m}. \tag{11}$$

Taking the definitions of damage and its derivative given, respectively, by Eqs. (6) and (11) and substituting into Eq. (10) results in the final expression for moisture flux,

$$D_i \frac{\partial \mu}{\partial X_i} = \bar{D}_i \frac{\partial m}{\partial X_i},$$

where, each orthotropic component of effective diffusivity ($\bar{D}_i$) can be obtained as a quadratic function of the crack density given by

$$\begin{aligned}\bar{D}_i = \rho_s D_i \Bigg[& \left\{ \frac{\partial^2 \hat{C}_0}{\partial m^2} + 2\frac{t_c^2}{t}\frac{\partial \hat{C}_2}{\partial m}\frac{\partial \kappa}{\partial m}\delta_1 + \hat{C}_2 \frac{t_c^2}{t}\frac{\partial^2\kappa}{\partial m^2}\delta_1 + 2\hat{C}_5\left(\frac{t_c^2}{t}\right)^2\left(\frac{\partial\kappa}{\partial m}\right)^2\delta_1^2 \right\} \\ & + \left\{ \frac{\partial^2 \hat{C}_2}{\partial m^2} + 4\frac{t_c^2}{t}\frac{\partial \hat{C}_5}{\partial m}\frac{\partial\kappa}{\partial m}\delta_1 + 2\hat{C}_5\frac{t_c^2}{t}\frac{\partial^2\kappa}{\partial m^2}\delta_1\right\}\kappa\frac{t_c^2}{t}\delta_1 + \left\{\frac{\partial^2\hat{C}_5}{\partial m^2}\right\}\left(\kappa^2\frac{t_c^4}{t^2}\right)\delta_1^2\Bigg] \\ = {} & C_0 + C_1\delta_1 + C_2\delta_1^2, \end{aligned} \tag{12}$$

where,

$$C_0(m,T) = \rho_s D_i \frac{\partial^2 \hat{C}_0}{\partial m^2}, \tag{13}$$

$$C_1(m,T) = \rho_s D_i \left(\frac{t_c^2}{t}\right)\left[\kappa\frac{\partial^2 \hat{C}_2}{\partial m^2}. + 2\frac{\partial \hat{C}_2}{\partial m}\frac{\partial\kappa}{\partial m} + \hat{C}_2\frac{\partial^2\kappa}{\partial m^2}\right], \tag{14}$$

$$C_2(m,T) = \rho_s D_i \left(\frac{t_c^2}{t}\right)^2\left[2\hat{C}_5\left(\frac{\partial\kappa}{\partial m}\right)^2 + \kappa\left\{4\frac{\partial \hat{C}_5}{\partial m}\frac{\partial\kappa}{\partial m} + 2\hat{C}_5\frac{\partial^2\kappa}{\partial m^2}\right\} + \kappa^2\frac{\partial^2\hat{C}_5}{\partial m^2}\right]. \tag{15}$$

Substituting Eq. (12) into Eq. (5) yields the governing equation for moisture diffusion in an orthotropic laminate subjected to zero stress and uniform intralaminar damage,

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial X_i}\left[\left(C_0 + C_1\delta_1 + C_2\delta_1^2\right)\frac{\partial m}{\partial X_i}\right]. \tag{16}$$

As defined in Eqs. (13)–(15), the damage coefficients C_0, C_1, C_2, depend on polymer density, polymer diffusivity, moisture concentration, temperature, and the ratio t_c^2/t. These coefficients can be characterized from absorption experiments on pre-cracked laminate specimens as discussed in the "Model verification" Section 4.

For modeling absorption and/or desorption in a laminate in the through-thickness, i.e., in the X_3 direction, Eq. (16) reduces to

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial X_3}\left[\left(C_0 + C_1\delta_1 + C_2\delta_1^2\right)\frac{\partial m}{\partial X_3}\right]. \tag{17}$$

3. Finite element formulation

In order to extend the simple one-dimensional analytical model in Eq. (17) to more complex shapes and boundary conditions, a three-dimensional finite element code (NOVA-3D) was developed. The variational (weak) form of Eq. (16) in three dimensions is given by,

$$\int_{V^{(e)}}\left[u\frac{\partial m^t}{\partial t} + D^t\frac{\partial u}{\partial X_i}\frac{\partial m^t}{\partial X_i}\right]\mathrm{d}V - \int_{A^{(e)}}\left[u\left(D^t\frac{\partial m^t}{\partial X_i}\right)n_i\right]\mathrm{d}A = 0, \tag{18}$$

where, u is an admissible variational test function. Based on the variational statement, the diffusion boundary conditions can now be identified as,

$$\left(D^{\mathrm{t}}\frac{\partial m^{\mathrm{t}}}{\partial X_i}\right)n_i + \hat{q} = 0 \quad \text{on } A_1^{(\mathrm{e})} \quad \text{(specified solvent flux)},$$

$$m = \hat{m} \quad \text{on } A_2^{(\mathrm{e})} \quad \text{(specified concentration)},$$

where $A_1^{(\mathrm{e})} + A_2^{(\mathrm{e})} = A^{(\mathrm{e})}$ and n_i are the components of the unit outward normal at the boundary. Thus,

$$\int_{V^{(\mathrm{e})}}\left[u\frac{\partial m^{\mathrm{t}}}{\partial t} + D^{\mathrm{t}}\frac{\partial u}{\partial X_i}\frac{\partial m^{\mathrm{t}}}{\partial X_i}\right]\mathrm{d}V = -\int_{A_1^{(\mathrm{e})}} u\hat{q}\,\mathrm{d}A. \tag{19}$$

A standard finite element interpolation of the concentration field over each element is given by

$$m(X_i, t) = \sum_{j=1}^{N} N_j(X_i)\, m_j(t), \tag{20}$$

where, m_j are the nodal concentrations, N_j are the interpolation functions and N is the number of nodes per element. Substituting Eq. (20) into Eq. (19) and employing matrix notation, Eq. (19) becomes

$$\lfloor T^{(\mathrm{e})}\rfloor\{\dot{m}\} + \lfloor K^{(\mathrm{e})}\rfloor\{m\} = \{F^{(\mathrm{e})}\}, \tag{21}$$

where, the superscript (e) is used to denote that the equations are satisfied over each element and

$$T_{jk}^{\mathrm{e}} = \int_{V^{(\mathrm{e})}} (N_j N_k)\,\mathrm{d}V,$$

$$K_{jk}^{\mathrm{e}} = \int_{V^{(\mathrm{e})}} \left\{D^{\mathrm{t}}\frac{\partial N_j}{\partial X_i}\frac{\partial N_k}{\partial X_i}\right\}\mathrm{d}V,$$

$$F_j^{\mathrm{e}} = -\int_{A_1^{(\mathrm{e})}} N_j\hat{q}\,\mathrm{d}A, \qquad i = 1,3 \text{ and } j,k = 1,N.$$

The time derivative $\{\dot{m}\}$ is approximated using a standard theta family of approximations, yielding at time t_n and t_{n+1},

$$\lfloor A^{(\mathrm{e})}\rfloor\{m\}_{n+1} + \lfloor B^{(\mathrm{e})}\rfloor\{m\}_n = \{P^{(\mathrm{e})}\}_n, \tag{22}$$

where

$$\lfloor A^{(\mathrm{e})}\rfloor = \lfloor T^{(\mathrm{e})}\rfloor + \theta\Delta t_{n+1}\lfloor K^{(\mathrm{e})}\rfloor,$$

$$\lfloor B^{(\mathrm{e})}\rfloor = \lfloor T^{(\mathrm{e})}\rfloor + (1-\theta)\Delta t_{n+1}\lfloor K^{(\mathrm{e})}\rfloor,$$

$$\{P^{(\mathrm{e})}\} = \Delta t_{n+1}\lfloor\theta\{F^{(\mathrm{e})}\}_{n+1} + (1-\theta)\{F^{(\mathrm{e})}\}_n\rfloor.$$

Eq. (22) is solved using a value of $\theta = 0.5$, which corresponds to the Crank–Nicholson scheme and is unconditionally stable. Note that for $n = 1$, the value of the starting concentration in Eq. (22) is known from the initial conditions.

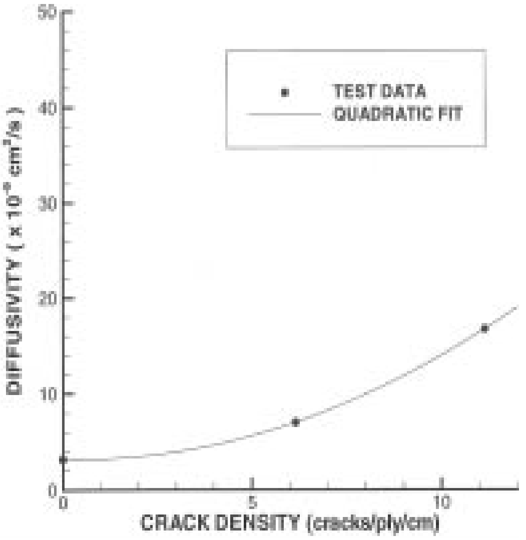

Fig. 2. Change in diffusivity with micro-crack density.

4. Model verifications

In order to characterize the model coefficients and perform preliminary model verifications, moisture-weight-gain data for graphite/epoxy 5-harness satin $[0/90/0/90]_s$ laminate with different micro-crack densities were obtained from hygrothermal tests performed elsewhere. [1] Specifically, test specimens were mechanically pre-cracked by uniaxial fatigue as well as static loading and then exposed to 75% relative humidity at 40°C. The crack densities reported for the specimens were 6.142 cracks per ply per cm for the static load case and 11.142 cracks per ply per cm for the fatigue load case, respectively. An un-cracked specimen was also included in the test matrix as the control specimen. The specimens were not subjected to any applied mechanical stress during absorption. The effective diffusivity for each test specimen was extracted from weight gain data using standard analytical procedure (Shen and Springer, 1981).

A quadratic least-squares curve-fit to the diffusivity data is shown by the solid line in Fig. 2. The values of the damage coefficients defined in Eq. (12) were obtained using this procedure for this case and are given as $C_0 = 3.184 \times 10^{-09}$ cm^2/s, $C_1 = -1.036 \times 10^{-10}$ cm^3/s, and $C_2 = 1.184 \times 10^{-10}$ cm^4/s. The corresponding equation for through-thickness diffusivity as a function of crack density is given by

$$D_3 = 3.184 \times 10^{-09} - 1.036 \times 10^{-10}\delta_1 + 1.184 \times 10^{-10}\delta_1^2 \text{ cm}^2/\text{s}. \quad (23)$$

It should be noted that although the linear damage coefficient C_1 has a negative value, the over-all value of the diffusivity is, for all practical purposes, a monotonically increasing function of crack density as evidenced in Fig. 2.

Moisture-weight-gain curves predicted by the model using the quadratic diffusivity–damage relation given by Eq. (23) combined with the diffusion governing Eq. (17), and its comparison with test data are shown in Figs. 3–5. The results shown in Fig. 3 correspond to an undamaged specimen. The moisture data shown in Fig. 4 correspond to a micro-crack density of 6.142 cracks per ply per cm, and those in Fig. 5 correspond to a micro-crack density of 11.142 cracks per ply per cm. A reasonable agreement between

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[1] Private communications, Pratt and Whitney aircraft, West Palm Beach, FL.

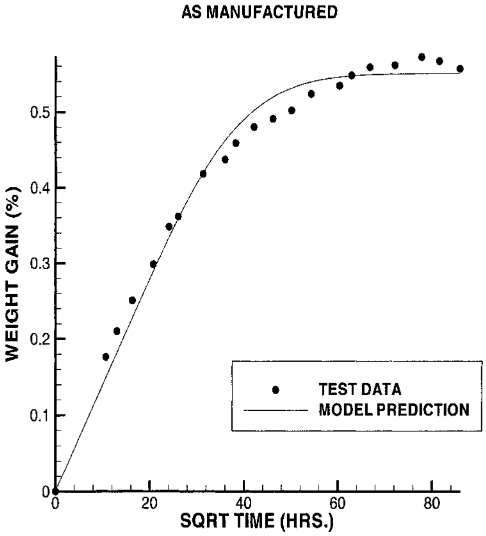

Fig. 3. Predicted vs. measured weight-gain for $\delta_1 = 0$ cracks per ply per cm.

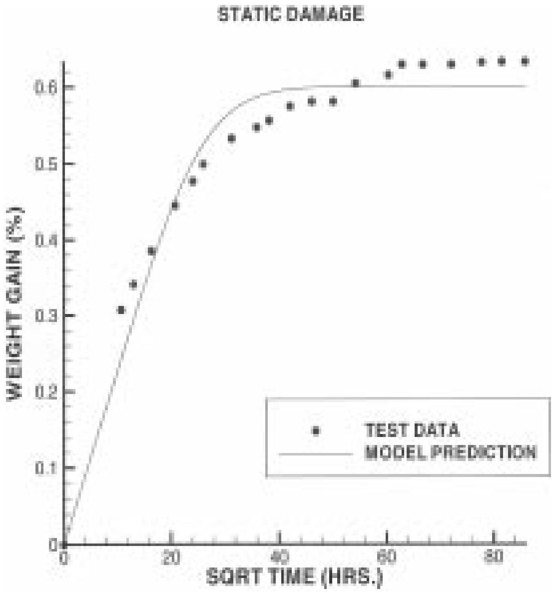

Fig. 4. Predicted vs. measured weight-gain for $\delta_1 = 6.142$ cracks per ply per cm.

model predictions and test data is observed for all three cases for the duration of the tests. Although these results do not conclusively prove that laminate diffusivity is a quadratic function of crack density, it does confirm that retaining only up to the quadratic terms in damage in the expansion of the Gibbs potential is an acceptable modeling approximation for the material system under consideration. As anticipated, the moisture uptake curves predicted by the finite element model for the simple one-dimensional case agree exactly with the analytical model predictions and are not separately presented in Figs. 3–5.

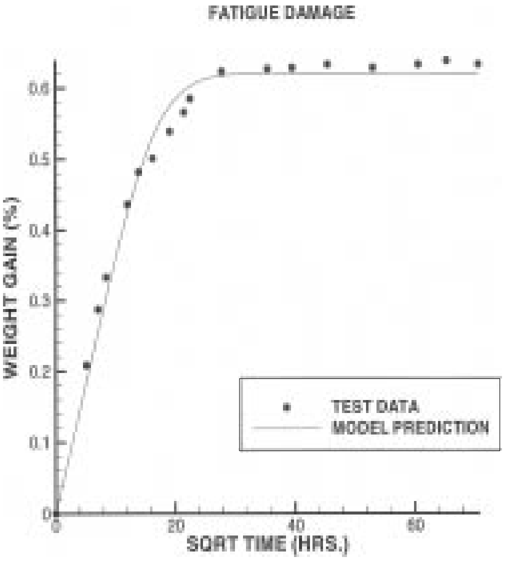

Fig. 5. Predicted vs. measured weight-gain for $\delta_1 = 11.142$ cracks per ply per cm.

5. Discussion and conclusions

A modeling methodology based on irreversible thermodynamics developed within the framework of composite macro-mechanics was presented to allow characterization of non-Fickian diffusion coefficients from moisture-weight-gain data for laminated composites with damage. A symmetric damage tensor based on continuum damage mechanics was incorporated in this model by invoking the principle of invariance with respect to coordinate transformations. To maintain tractability, the diffusion–governing equations were simplified for the special case of a laminate with uniform matrix cracks that is subjected to a uniaxial tensile stress state. A finite element procedure that extends this methodology to more complex shapes and boundary conditions was also presented. Because of the macro-mechanics formulation employed in developing this model, the model is currently restricted to the study of overall laminate absorption/desorption characteristics in the presence of non-evolving damage states. An alternative approach that considers the more detailed physical aspects of moisture ingress into a micro-cracked laminate can be found in Roy and Bandorawalla (1999).

The material coefficients needed to model the effect of matrix micro-cracking on laminate diffusivity were evaluated by using hygrothermal test data for a $[0/90/0/90]_s$ graphite/epoxy 5-harness satin textile composite. The moisture-weight-gain curves predicted by using a quadratic diffusivity–damage relation yielded good correlation with test data. Although these observations do not conclusively prove that the laminate diffusivity is indeed a quadratic function of crack density, it does indicate that retaining only up to the quadratic terms in damage in the expansion of the Gibbs potential is an acceptable modeling approximation for the material system under consideration. The primary purpose of this article is to establish a theoretical framework for using the proposed modeling approach to characterize and eventually, to predict absorption and desorption in micro-cracked laminates. The formulation presented in this article is deemed to provide a small, yet positive step towards that goal. Additional hygrothermal tests on specimens subjected to combined stress and damage states at different temperature and humidity levels are currently underway to comprehensively evaluate the accuracy of the proposed model when these data become available.

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