Equivalent moisture diffusion coefficient of fiber reinforced composites

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Abstract. Total diffusion time and the total moisture absorption amount were proposed as the measurement standards of equivalent coefficients for composites moisture diffusion with impermeable fibers. Representative volume element (RVE) models and 2D transient finite element models of unidirectional fiber reinforced composites were established and the accuracy of the RVE model for calculating the equivalent diffusivity was verified. The influences of fiber volume fraction, fiber arrangement and interfaces on the equivalent moisture diffusivity were investigated using the RVE models. The results show that the equivalent moisture diffusivity decreases with the increase of fiber volume fraction. The equivalent moisture diffusivity of random fiber distribution is smaller than that of the periodic fibers distribution, and this difference can be neglected when the fiber volume fraction is relative small. The interfaces with higher diffusivity than matrix will apparently increase the composites diffusivity.

1. Introduction

Fiber reinforced resin composites are increasingly used in aerospace, transportation, civil and marine applications owing to their special properties including high specific strength, high specific stiffness and excellent physical and chemical properties. Composite materials may be exposed to environmental loads during service, resulting in weakened performance. Among them, moisture is one of the important factors that cause the decreasing of composites properties. Studying the water diffusion properties of composite materials is the primary task before assessing their long-term behavior.

Theoretical models and the steady-state finite element models have been proposed to predict the equivalent diffusivity of unidirectional composites. Shen [2] and Halpin [3] drew an analogy between the diffusion process and the heat conduction, giving an analytical expression of equivalent diffusivity for the unidirectional composites. Whitcomb [4] established a steady-state finite element diffusion model and studied the effects of fiber volume fractions. Based on the Halpin model, Gueribiz [5] proposed a self-consistent theoretical model and predicted the effects of fiber volume components, interfaces and voids on the equivalent diffusivity. Rocha [6] established a multi-scale FE diffusion model for unidirectional composite. However, moisture diffusing into composites is a transient process and thus the accuracy of steady state FE model may be questionable [7]. Y. Joliff [8] and M. Meng [9] studied the influence of interfaces on the equivalent diffusivity using 2D transient FE model.

The previous steady-state FE models [4, 5] contain a flux-isolated boundary condition which is inconsistent with the actual situation. Meanwhile, the equivalent diffusivity calculated by the steady-state model is smaller than that calculated by the transient FE model at the same fiber fraction [4, 5, 9]. In this paper, we propose the total diffusion time and the total moisture absorption amount as the measurement standards of equivalent coefficients for composites with impermeable fibers. A RVE FE
model for diffusion was established and verified by the transient model and was then used to analyze the effects of fiber volume fraction, fiber arrangement and interfaces on the composites diffusivity.

2. Numerical models

2.1. Concept of equivalence

A Fickian kinetic can be used to an infinite plane sheet in diffusion \(^{[10]}\):

\[
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ -\frac{Dt}{l^2} \pi^2(2n+1)^2 \right]
\]  

(1)

where, \(M_t\) is the water mass fraction which diffuses at the time \(t\), \(M_\infty\) is the saturated water mass fraction which diffuses after infinite time, \(D\) is the diffusivity and \(l\) the plate thickness. The moisture absorption curve will be linear part at initial time and the diffusivity can be expressed as Eq. (2):

\[
D = \pi \left( \frac{l}{4M_\infty} \right) \left[ M_t - M_\infty \right] \left( \sqrt{l_2} - \sqrt{l_1} \right)^2
\]  

(2)

The relationship between the saturation water concentration and the water mass fraction for pure resin can be expressed by Eq. (3):

\[
C_m = \frac{D_m M_\infty}{18 \times 10^{-3}}
\]  

(3)

where, \(C_m\) is the saturation water concentration and \(\rho_m\) is the density of pure resin.

Assume that the diffusivity and solubility of the polymeric composites’ matrix are \(D_m\) and \(C_m\), respectively. The existence of impermeable fibers change the diffusion path of water, thus the diffusivity and the amount of absorbed water decreased. As shown in Figure 1, in this paper, we extend the concept of “diffusion equivalence” for composite materials to including both the diffusivity and the solubility: the moisture absorption curves of the original composites model and of the effective model should be coincident. Under this requirement, the equivalent diffusivity \(D_{\text{eff}}\) can be calculated by Eq. (3), and the equivalent solubility \(C_{\text{eff}}\) can be expressed by Eq. (4):

\[
C_{\text{eff}} = C_m V_m
\]  

(4)

in which, \(V_m\) is the matrix percentage of the composites.

Figure 1. Equivalence of diffusion

2.2. 2D transient model

Commercial FE software Abaqus\textsuperscript{\textregistered} was implemented to simulating the water diffusion process. Transient diffusion FE model was firstly established to calculate the composites equivalent coefficient. As shown in Figure 2 (a), the 2D FE model has length of 990μm and width of 90μm. 275 fibers with diameter of 15μm are randomly distributed to the model, occupying 54.5% of the volume fraction. The fibers are not modeled realistically because of its impermeability and this simplification has been verified \(^{[1]}\).\(^{[8]}\). Linear quadrilateral element DC2D4 was used in the model. The converged analysis has been conducted and element size of 1μm will be used in the following simulations. Diffusivity of 0.741μm\(^2\)/s, and solubility of 3.94% are input to the model, while the solubility was calculated as 2845mol/m\(^3\) according to Eq. (3). The unit normalized concentration was applied at the external edges of the model as depicted in Figure 3, implying a saturation state during the analysis.

The equivalent diffusivity \(D_{\text{eff}}\) was calculated by Eq. (2) according to the moisture absorption curve of the above transient diffusion FE model. Under the requirement of ensuring the same total moisture of the original model and the effective model, the equivalent solubility can be calculated to be 1294.5 mol/m\(^3\) according to Eq. (4). Meanwhile, in order to validate our concept of equivalence, an equivalent...
model was built with the same material properties and boundary conditions as the composite model, as shown in Figure 2(b).

![Figure 2. 2D transient FE model (a) composite model; (b) equivalent model](image)

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![Figure 3. Boundary conditions of the 2D composite model](image)

Figure 3. Boundary conditions of the 2D composite model

2.3. RVE model

3D RVE models of pure resin and composites were established and the steady state diffusion analysis was applied to calculate the equivalent diffusivity. As shown in Figure 4, fiber arrangements of hexagon, square and random distributions were taken into account, which all follow the periodic pattern. The material properties and geometry of the matrix and the fiber are as described in Section 2.2. Referring to the previous research results, the RVE model contains 25 fibers to guarantee the result convergence. Linear quadrilateral element (DC2D4) was chosen and the mesh element size was set as 1μm. The mesh nodes on the opposite faces should be located at the opposite position in order to simplify the applying of periodic boundary conditions (PBCs). An Python script was used to apply the PBCs. Unit concentration gradient was applied to all the three directions, and a zero normalized concentration was adopted at a corner to reach a unique solution for all models. Five replicates were conducted for each random condition.

![Figure 4. Fiber distribution of (a)Square; (b)Hexagon; (c)Random](image)

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![Figure 5. Moisture absorption curves of the transient model and effective model](image)

Figure 5. Moisture absorption curves of the transient model and effective model

3. Results and discussion

3.1. Validation of the equivalent concept

Figure 5 shows the moisture absorption curves of the 2D original composites model and the equivalent model. The diffusivity $D_{\text{eff}}$ is $0.407\mu m^2/s$ calculated by Eq. (2). The $D_{\text{eff}}$ and $C_{\text{eff}}$ was input to the equivalent model and the resulting moisture absorption curve is coincident with that of the original
composites model, which implies that the previously proposed calculation method for equivalent coefficients is correct.

3.2. Validation of the RVE model

3D RVE steady state models and 2D transient models were established respectively for the pure resin and the composites with 54.5% fiber fraction. The 3D RVE models are 90μm×90μm×90μm cubes and the 2D transient models are 90μm×990μm squares. The composites random fiber distribution of the 2D transient model was achieved by replicating that of the 3D RVE model nine times.

Table 1 shows the equivalent diffusivity of the pure resin and the composites calculated by the 3D RVE steady state model and the 2D transient model, respectively. For the pure resin, the RVE model result is equal to the input value while the 2D model result is a little smaller than it. For composites, the RVE result is about 56.8% of the input value while the 2D model result is still smaller than the RVE result. The two model results are basically the same and the RVE model may be more accurate than the 2D transient model. Figure 6 shows the moisture absorption curves of the RVE results and the 2D models for both the pure resin and the composites, in which the RVE results were calculated by the 2D equivalent model using the RVE equivalent diffusivity. The curves coincide well for both the resin and the composites, respectively.

| Materials | Input | Pure resin 3D model | 2D model | Random RVE model | 2D model |
|-----------|-------|---------------------|---------|-----------------|---------|
| Diffusivity / μm²·s⁻¹ | 0.741 | 0.741 | 0.734 | 0.417 | 0.407 |

![Figure 6](image-url)

**Figure 6.** Moisture absorption curves of the RVE model and the transient model: (a) pure resin (b) composite

3.3. Fiber fraction and arrangements

After verifying of the accuracy, the RVE model was used to analysis the influence of fiber fraction and fiber arrangements on the diffusivity of composites. Figure 7 (a) shows the relationship between the fiber fraction and the resulting relative diffusivity (D_eff / D_m). The relative diffusivity decreases along with the increasing fiber fraction. While the “Analytical” results [2, 3] and the “Whotcomb” results [7] are quite similar, the present results are much larger and the ratio increases with increasing fiber fraction. The reason of this phenomenon may be the different boundary conditions between these models. Figure 7(b) shows the RVE results of the hexagon, square and random fiber distributions. The equivalent diffusivities are quite coincident when fiber fraction are smaller than 20%. However, when fiber fraction is larger than 20%, the difference between the three models become more evident and the hexagon fiber distribution seems to be more conducive for moisture diffusing. The periodic fiber distributions, namely hexagon and square are special cases of random fiber distributions. From the above analysis we can conclude that the periodic fiber distributions may be proper substitutes for the
random one when the fiber fraction is smaller than 20%, while random fiber distribution may be more accurate with over 20% fiber fraction.

![Figure 7. Relative diffusivity of the composite](image)

3.4. Interface

Researchers have found that interface layer, with a thickness of 1-4μm, exists between the fiber and matrix and its diffusivity is larger than the composite matrix. In this section, an interface-embedded RVE model was established to figure out its influence on the composites diffusivity. Only square fiber distribution was modeled for simplifying.

The accuracy of the interface RVE model was firstly validated by the 2D transient model. For the composites with 54.5% fiber fraction, 1μm interface thickness and 1.556μm²·s⁻¹ interface diffusivity, its moisture absorption curves of the RVE model and the 2D transient model were shown in Figure 8 (a). The two curves coincide well and this proves a good accuracy of the interface RVE model.

The relative equivalent diffusivities under different interface diffusivity ratio and different fiber fractions are shown in Figure 8 (b), in which the ratios of 2, 5, 10, and 20 of the interface diffusivity to the resin diffusivity were taken into account. Generally, the relative equivalent diffusivities increase along with the interface diffusivity ratio. However, there may exist a critical value for interface diffusivity ration to get unit relative diffusivity. When interface diffusivity ration is smaller than the critical value, the relative diffusivity decreases along with increasing fiber volume fraction. While when interface diffusivity ration is larger than the critical value, the relative diffusivity increases along with increasing fiber volume fraction. This may because that the fiber volume fraction, which decreases the composites diffusivity, dominates the influence on the composites relative diffusivity when interface diffusivity is small. While the interface diffusivity ratio, which increases the composites diffusivity, will dominate the influence with larger interface diffusivity.

![Figure 8. Effects of interface on the relative effective moisture diffusion coefficient](image)

4. Conclusion
In this paper, total diffusion time and total moisture absorption amount were proposed as the measurement standards of equivalent coefficients for composites moisture diffusion. A steady-state RVE FE model with periodic boundary conditions was established and was validated by the 2D transient model. Based on the analysis we conclude that:

(1) The proposed standards can accurately describe the moisture absorption process for composite materials.

(2) The difference of diffusivity between the random fiber distribution and the periodic fiber distribution increases with the increasing fiber volume fraction; the hexagon fiber distribution has the largest diffusivity among the three ones.

(3) There may exist a critical value for interface diffusivity ration to get unit relative diffusivity. The opposite influences of fiber fraction and interface diffusivity ratio may be the reasons.

References
[1] Bond D A. Moisture Diffusion in a Fiber-reinforced Composite: Part I - Non-Fickian Transport and the Effect of Fiber Spatial Distribution[J]. Journal of Composite Materials, 2005, 39(23):2113-2141.
[2] Shen C H, Springer G S. Moisture Absorption and Desorption of Composite Materials:[J]. Journal of Composite Materials, 1976, 10(1):2-20.
[3] Halpin J C. Primer on composite materials : analysis[M]. Washington Univ, 1984.
[4] Whitcomb J, Tang X. Micromechanics of Moisture Diffusion in Composites with Impermeable Fibers[J]. Journal of Composite Materials, 2002, 36(9):1093-1101.
[5] Gueribiz D, Rahmani M, Jacquemin F, et al. Homogenization of Moisture Diffusing Behavior of Composite Materials with Impermeable or Permeable Fibers -- Application to Porous Composite Materials[J]. Journal of Composite Materials, 2009, 43(12):1391-1408.
[6] Rocha I B C M, Rajmaekers S, Meer F P V D, et al. Combined experimental/numerical investigation of directional moisture diffusion in glass/epoxy composites[J]. Composites Science & Technology, 2017, 151.
[7] Vaddadi P, Nakamura T, Singh R P, et al. Inverse analysis for transient moisture diffusion through fiber-reinforced composites[J]. Acta Materialia, 2003, 51(1): 177-193.
[8] Joliff Y, Belec L, Chailan J F. Modified water diffusion kinetics in an unidirectional glass/fiber composite due to the interphase area: Experimental, analytical and numerical approach[J]. Composite Structures, 2013, 97(2):296-303.
[9] M. Meng Meng M, Rizvi M J, Le H R, et al. Multi-scale modelling of moisture diffusion coupled with stress distribution in CFRP laminated composites[J]. Composite Structures, 2016, 138:295-304.
[10] Crank J. The Mathematics of Diffusion[M]. Clarendon Press, 1956.