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ARTICLE

Moisture Absorption and Diffusion of a Carbon Composite Structure

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ABSTRACT

Composite materials are lightweight structures and have been wildly used in marine applications. A carbon composite structure usually absorbs moisture while in-service, which can significantly affect its properties, and detriments the overall performance. We perform a detailed study on moisture absorption and diffusion of a carbon fibre reinforced vinyl ester resin composite system. Composite samples are immersed directly in four different solutions at a temperature of 37±0.5 ℃ for 1444h. The moisture diffusion is analysed through the Fickian diffusion model; the diffusion parameters are subsequently determined from the gravimetric data. The moisture absorption and interaction with the composite constituents are then discussed. These indicate the fundamentals of the moisture absorption and diffusion within the carbon composite structure.

1. Introduction

Composite materials are superior in terms of specific strength, modulus and product efficiency. There are increasing interest in their applications to aerospace, automotive, medical, as well as sustainable marine structures [1]. One disadvantage is that their properties are susceptible to aggressive environments and subjected to change while in-service [2]. Moisture absorption is one of the triggering factors that can significantly affect the material performance [3].

It is known that a carbon composite structure typically absorbs moisture in a humid environment and at elevated temperatures. This has been studied by various research groups by exposing the composites in different aggressive environments, such as water, sea water, low and high temperatures, and coupled with different loads [3-6]. The reinforcements include nature fibres, such as hemp fibre [7], jute fibre [8], sugar palm fibre [9], bamboo cellulose fibre [10], as well as synthetic fibres, e.g. graphite fibre [11], glass fibre [12,13], carbon fibre [14,15], and hybrid braided fibres [16]. Among these, the commonly used matrices are epoxy resins and unsaturated polyester resins. Vinyl ester resin (VER) is a bisphenol-drived polymer, which offers better resistance to moisture absorption and hydrolytic attack than polyester [17]; carbon fiber (CF) has a high degree of corrosion resist compatibility [2]. Thus, carbon fibre reinforced vinyl ester resin (CF/VER) composite has great potential in sustainable marine structures.

In this paper, we studied the fundamentals of moisture absorption and diffusion in a CF/VER composite system. Section 2 introduces the principles of the Fickian diffusion model; Section 3 shows the detailed experimental

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procedures; Section 4 presents the results and discussion; and Section 5 concludes the study.

2. Fickian Diffusion Model

Generally, moisture absorption and diffusion of a polymer-matrix composite can be described by Fick's second law of diffusion [18,19], where the moisture content initially increases linearly with the square root of time and then gradually slows down until it reaches the effective moisture equilibrium, see Figure 1. For a material that follows the Fick's law as in Eqn 1 is also named as a single-phase Fickian material.

$$\frac{\partial c}{\partial t} = D_z \frac{\partial^2 c}{\partial z^2} \tag{1}$$

where: c is the specimen moisture concentration, g/mm^3;

t is time, s;

$\frac{\partial c}{\partial t}$ is time rate of change in moisture concentration, g/(mm^3·s);

D_z is Fickian moisture diffusivity constant, mm^2/s;

z is through-the-thickness direction, mm.

The single-phase Fickian diffusion model as shown in Figure 1 can be established using Eqns 2-9 [20]. To predict the moisture content, the equilibrium content M_m and the Fickian moisture diffusivity constant D_z are essential [21,22]. They both can be calculated from gravimetric data, and follow:

$$D_z = \pi[h/(4M_m)]^2\left[(M_y - M_x)/(\sqrt{t_y} - \sqrt{t_x})\right]^2 \tag{2}$$

where: h is the thickness of the specimens, mm;

M_m is the equilibrium moisture content of the specimens, %;

M_x, M_y is the moisture content of any time interval t_x, t_y in the linear portion of the curve M_i versus $t^{1/2}$, %.

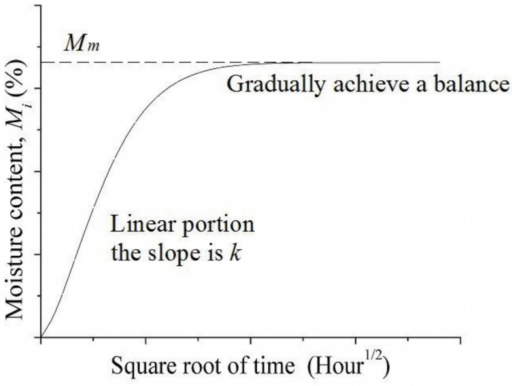


Figure 1. Single-phase Fickian diffusion model

Moisture absorption rate, k, is the slope of the linear part of the curve:

$$k = (M_y - M_x) / (\sqrt{t_y} - \sqrt{t_x}) \tag{3}$$

Thereby:

$$D_z = \pi[kh/(4M_m)]^2 \tag{4}$$

The moisture content in a material at a given moisture exposure level is:

$$M(T,t) = M_b + G(M_m - M_b) \tag{5}$$

where: T is temperature, °C;

$M(T,t)$ is moisture content as a function of time and temperature, %;

M_b is baseline moisture content, %;

M_m is moisture equilibrium content, %;

h is thickness of material, mm;

G is moisture absorption function and follows:

$$G = 1 - \frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{\exp\left[-(2j+1)^2\pi^2\left(\frac{D_z t}{h^2}\right)\right]}{(2j+1)^2} \tag{6}$$

Approximately:

$$G = 1 - \exp\left[-7.3\left(\frac{D_z t}{h^2}\right)^{0.75}\right] \tag{7}$$

To reach a given moisture content at a fixed temperature and moisture exposure level, the time can be predicted as follows:

$$t = \frac{h^2}{D_z}\left[\frac{-1}{7.3}\ln\left(1 - \frac{M(t) - M_b}{M_m - M_b}\right)\right]^{4/3} \tag{8}$$

Regardless the ambient moisture exposure level, the time necessary for a completely oven-dried specimen to get 99.9% of moisture equilibrium at a given temperature is:

$$t_{\max}(T) = \frac{0.93h^2}{D_z} \tag{9}$$

3. Experimental

3.1 Sample Preparation

The matrix used in this research is vinyl ester resin and its chemical structure is shown in Figure 2; the reinforcement is carbon fibre T300-1K purchased from TORAY, Japan.

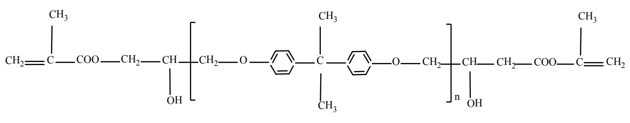


Figure 2. Chemical structure of the vinyl eater resin used in this research

To produce a composite sample, resin, hardener and crosslinker were thoroughly mixed at room temperature, the carbon fibre was then put into the mixture to ensure sufficient impregnation. The impregnated fibres were placed following $[0°/+45°/-45°/90°]_s$, and locked inside a mould. The whole mould was then subjected to a curing process of 90 ℃ /2h+110 ℃ /2h+130 ℃ /2h+150 ℃ /2h. After mould releasing, the composite specimens were cut into designated sizes and subjected to aseptic processing as detailed below.

The specimens were rinsed in distilled water under ultrasonic cleaning for 15 minutes. The naturally dried samples were exposed to ultraviolet (UV) light for 30 min, and scrubbed with anhydrous ethanol; then oven-dried and weighted separately as W_0, which was used as reference for water absorption experimenting, using an electronic balance with an accuracy of 0.1mg. The specimens were then stored in sterilized jars ready for testing.

3.2 Moisture Absorption and Degradation

The moisture absorption and degradation studies were carried out in four solutions with different pH: (i) distilled water (DTW); (ii) hydrogen peroxide solution (HPS); (iii) Fenton's reagent (FTR); (iv) phosphate buffered saline (PBS). The DTW was prepared following ISO 3696 and GB/T 16886.13; HPS was prepared using 3% H_2O_2 (in volume fraction) from LIRCON, Shandong, China; FTR contained 100 μmol/L $FeSO_4$ and 3% H_2O_2 (in volume fraction); PBS was prepared from distilled water and contains: NaCl 140 mmol/L, Na_2HPO_4 8.1 mmol/L, KH_2PO_4 1.5 mmol/L, and KCl 3 mmol/L.

Experimental procedure follows below: firstly, solutions were stored in different sterilised jars with previously processed composite samples. Here, the volume ratio of the specimens and the test solution is at least 1:10 (GB/T 16886.13), and the specimens must be completely immersed in the liquid. The jars were then placed into a constant temperature water bath which had previously reached the specified steady-state of 37±0.5℃ , and the water level must be higher than that in the jars.

After the designated period, each specimen was taken out and rinsed with distilled water for at least three times, surface moistures were wiped out entirely with dry and clean filter paper. The specimen was weighed immediately to the required precision and recorded as W_i, along with total elapsed time and the time interval since previous measuring, then put the sample back into the jar. Each sample should not be out of the jar for more than 5 min per reading (ASTM D5229). The sample weight was monitored until effective moisture equilibrium was reached. Since H_2O_2 in HPS and FTR would become invalid after a certain time, both solutions were changed every week.

The moisture content (M_i) of specimens at different time intervals could be calculated by the weight difference from Eqn 10:

$$M_i = \frac{W_i - W_0}{W_0} \times 100\% \tag{10}$$

After been immersed in different solutions for 1444 h (two months), one specimen from each solution was cleaned following the same procedures as above, and then oven-dried until it reached the specified dry steady-state. The oven-dried weight was recorded as W_d, and the weight change (M_c) is calculated using:

$$M_c = \left| \frac{W_0 - W_d}{W_0} \right| \times 100\% \tag{11}$$

The value of pH in each solution was also monitored using a precision pH meter every week; surfaces of the immersed composite specimens were also examined using a scanning electron microscope (SEM) SU-1500 produced by HITACHI to detect any interfacial debonding.

4. Results and Discussion

4.1 Fickian Diffusion

The moisture content M_i versus the square root of time $\sqrt{t}$ is plotted together with the Fickian diffusion model in Figure 3. It is clear that the experimental data well fits the Fickian model except the one in FTR. This is because FTR has stronger oxidation effect for its well-known classical reaction between Fe^{2+} and H_2O_2 [23] than the other three mediums. The composite sample undergoes severe corrosion during the same time interval, causing more gaps and voids inside the specimens, which in turn leads to heavier moisture absorption.

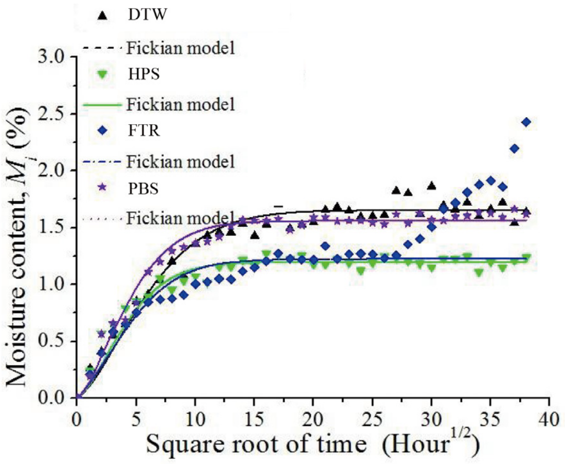


Figure 3. Moisture absorption and diffusion curve of composite specimens, curves are fitted by using the Fickian model

Three parameters of moisture absorption were computed from gravimetric data using Eqns 3, 4, and 10, resulting data are shown in Table 1. The value of D_z in TDW is the lowest, which indicts that the moisture diffusion is the slowest. This attributes to the lowest osmotic pressure in pure water which can accelerate the diffusion of moisture compared to the other three solutions. The value of M_m in both HPS and FTR are relatively low, which is caused by the corrosion of the specimens as seen from the SEM micrographs in Section 4.4.

Table 1. Parameters of moisture absorption in different solutions

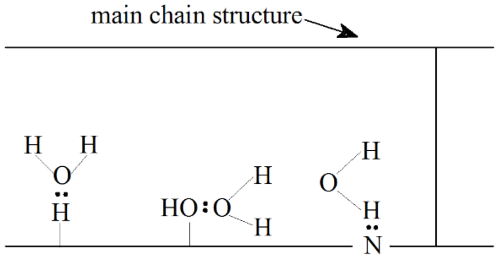
Coefficients	Solutions			
	TDW	HPS	FTR	PBS
M_m (%)	1.65	1.20	1.23	1.59
k ($s^{-1/2}$)	2.46×10^{-5}	2.50×10^{-5}	2.32×10^{-5}	3.05×10^{-5}
D_z (mm^2/s)	3.91×10^{-6}	7.69×10^{-6}	6.34×10^{-6}	6.49×10^{-6}
t_{max}(37℃) (h)	594.60	302.29	366.65	238.76
$\sqrt{t_{max}(37℃)}$ ($h^{1/2}$)	24.38	17.39	19.15	15.45

The time when M_i reached 99.9% of its moisture equilibrium is determined from Eqn 9, and shown in Table 1. The predictions show good agreement with experiments shown in Figure 3. Therefore, it is concluded that the single-phase Fickian diffusion model can properly predict the moisture diffusion of the CF/VER composite.

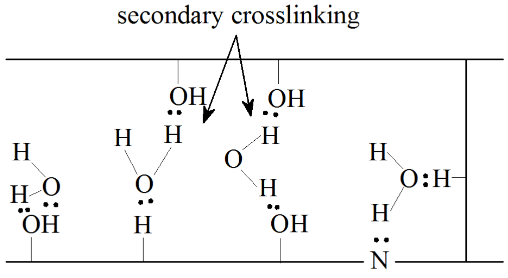
4.2 Moisture Absorption and Interaction

When composite specimens are immersed in a liquid medium, there are two main actions between water molecules and composite microstructures: (1) physical diffusion; (2) chemical degradation.

Physically, the moisture absorption of composite is mainly the diffusion of water molecules. Water go through the defects in the matrix and interface such as holes, cracks to penetrate into the composite at first. This leads to the swelling of matrix and molecular chain relaxations, causing changes in residual stresses within the composite which may further result in the formation of micro-cracks [24]. All these can speed up the moisture absorptions. In a polymer matrix, there is a distribution of micro-porous at molecular level, and water molecules can easily get into the internal of cross-linked resin. These absorptions can destruct the hydrogen bonds between original macromolecular chains, weaken the cross-linking strength and decrease the wear resistances. Thus, the existence of micro-porous facilitates the convection which also accelerates the absorption of water. The water molecules continue to spread into the composite interfaces, and initiate serious effects such as further swelling of the matrix and the generation of internal stresses. These can cause significant damage such as interface debonding and delamination, crack propagation, and so on, further increase the moisture content within a composite. Meanwhile, carbon fibre is a hydrophilic material, water molecules can easily form hydrogen bonds with the carbon fibre. Thereby, they undermine the combinations of the fibre and matrix, which decreases the interfacial strength and gradually lead to the failure of the interfaces. Furthermore, the dissolution and penetration of water soluble substances can generate the osmotic pressure within the composite which also can accelerate the diffusion of water molecules.



(a) Formation of hydrogen bonds



(b) Formation of secondary crosslinking

Figure 4. Model of potential secondary crosslinking between water molecules and a polymeric matrix material

The chemical degradation effect is mainly through the chemical reactions between water molecules interior the composite and some elements within the matrix. Water molecules connect with macromolecular chains can react with the hydrophilic groups to undermine the original composition of the composite, further lead to the irreversible changes in material properties. Thus, if there are chemical groups such as ester which can easily degraded under the action of water molecules, the material would lose weight in the humid environment. Also, water

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molecules are polar molecules, which may be combined with hydrophilic groups within the matrix or fibres to form hydrogen bonds or other new bonds, or even lead to secondary cross-linking between molecular chains. Zhou and Lucas [25] established a model to describe this new bonding between water and epoxy network as illustrated in Figure 4, which has similarity with the moisture absorption within our CF/VER composite structure.

4.3 Degradation Analysis

The varieties of pH over two months are plotted in Figure 5. There is a rapid change of pH in the TDW in the first week, and then becomes stabilised. The pH varieties are all very small in other three solutions, and there is almost the same trend of pH between HPS and FTR. The overall changes of pH in different solutions are shown in Table 2, with a maximum value of 1.42. It is noted that the secure pH value change for medical material leaching solution is no more than 1.5 [26], thus the CF/VER composite can be preliminarily determined to be safe.

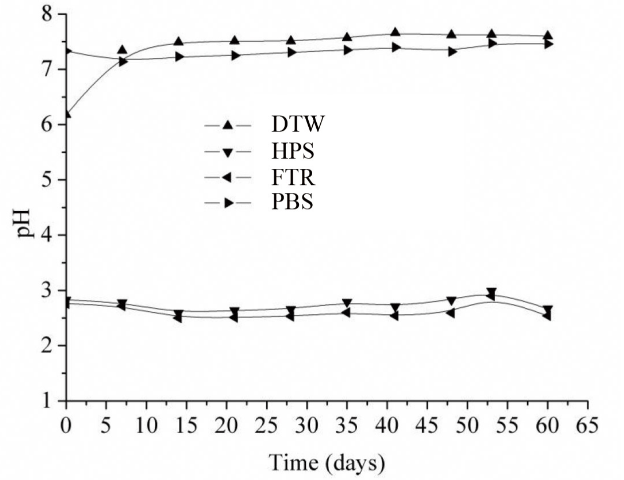


Figure 5. The value of pH in different solutions over two months

Table 2. The changes of pH in different solutions in two months

The value of pH	TDW	HPS	FTR	PBS
minimum	6.18	2.59	2.50	7.14
maximum	7.60	2.99	2.90	7.47
changed	1.42	0.40	0.40	0.33

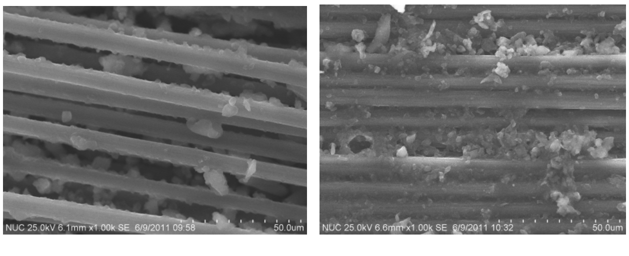
The weight changes after immersed for 1444 h (i.e. two months) are determined from Eqn 11 and show in Table 3. The M_c has increased by 0.35% in pure water, indicating that water molecules are combined with hydrophilic groups to form the hydrogen bonds, or the secondary crosslinking occurred between molecular chains as discussed in Section 4.2. For HPS and FTR, the composite samples loss weight giving negative M_c, and FTR has the strongest corrosive effect to the CF/VER composite. The weight of the specimens that immersed in PBS are almost unchanged.

Table 3. Weight changes after immersed in different solutions for 1444 h

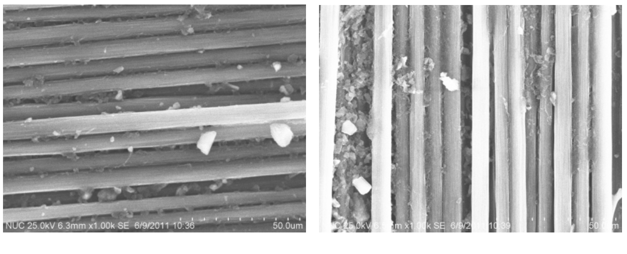
	TDW	HPS	FTR	PBS
M_c (%)	+0.35%	— 0.61%	— 2.69%	+0.03%

4.4 Surface Debonding

Micrographics of the composite sample surfaces before and after immersed in different solutions are shown in Figure 6. As it can be seen from the original composite, the adhesion of the matrix and fibres are good, fibres were tightly wrapped by the matrix. After immersed for five weeks, the composite interface remains to be good in TDW and PBS, which indicates that the degradation of CF/VER composite in such solutions are very small. This correlates with the few changes of pH as in Figure 5. However, corrosions of composite interfaces in HPS and FTR are quite obvious, leaving smooth fibre surfaces exposed to the acidic solutions, which is detrimental to the composite properties.



(a) Original sample (b) in TDW bath



(c) in HPS bath (d) in FTR bath

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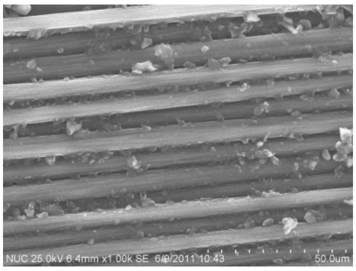

(e) in PBS bath

Figure 6. SEM micrographs of composite samples before and after immersed in different solutions for five weeks

5. Conclusions

We performed detailed experimental and analytical studies on moisture absorption and diffusion of a carbon fibre reinforced vinyl ester resin composite system. Composite samples were immersed in four different solutions at a temperature of 37±0.5 ℃ for 1444h. Moisture absorption curves of CF/VER composite in different solutions are obtained and the diffusion processes basically follow the single-phase Fickian diffusion model. The diffusion coefficients are then determined from the gravimetric data. The moisture diffusion in pure water is the lowest due to its low osmotic pressure; the changes in pH falls within a safe rang; and CF/VER system has very good corrosion resistance in salted water. These infer the fundamentals of the moisture diffusion within the carbon composite structures, and facilitate their applications in marine engineering.

Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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