

Moisture Sorption of a Three-Dimensional Braided Carbon Fiber–Epoxy Composite Under Different Media

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ABSTRACT: A three-dimensional braided carbon fiber–epoxy (C_{3D}/EP) composite was prepared by the vacuum-assisted resin transfer molding (VARTM) technique. Its moisture absorption behavior under different media was characterized and compared with a unidirectional composite. Similar to the unidirectional composite, diffusion in the 3D composite obeys Fick's second law of diffusion when immersed in distilled water and phosphate-buffered saline. In HCl and NaOH solutions, no Fickian behavior was observed. The similarity between the unidirectional and 3D composites suggests that fiber structure does not change diffusion pattern. However, the two composites showed different diffusion parameters (k , D , and M_e) in each medium studied. The 3D composite showed lower k , D , and M_e values because of its stronger hindrance effect to transport of

moisture molecules. Diffusion in PBS is slower than that in distilled water because of the presence of heavy ions, but the diffusion pattern remains unchanged. In HCl, the diffusion behavior of the two composites cannot be described by Fick's law. In addition, the k value calculated from the initial linear part of the moisture sorption curve is much lower than that in distilled water. Diffusion in NaOH is unusual; the uptake initially increases rather rapidly but quickly drops, which is likely caused by the extensive solubility of the polymer matrix. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 507–512, 2005

Key words: fibers; composites; three-dimensional fabrics; moisture sorption; resins

INTRODUCTION

Fiber-reinforced polymer composite materials are widely used in the fields of aerospace, marine environments, infrastructure, and sports. Many applications of the polymer composites inevitably involve exposure to moisture conditions. However, these materials are known to be sensitive to environmental conditions, such as heat and moisture. They tend to absorb moisture after exposure to humidity. The absorbed moisture often degrades their mechanical and structural integrity depending on their stability in varying environmental conditions. Moisture uptake by polymers and their composites is unavoidable and undesirable because it leads to undesirable changes in dimensions and properties, and even leads to failure of components. There is a particular need for knowledge of the effect of moisture on these materials.

The moisture sorption in water has been well documented because distilled or deionized water is more readily available and cheaper than other media. Fewer

studies have been reported regarding the sorption behavior of polymer composites in salt or saline solution.^{1–4} However, there is also potential for polymer composites to be exposed to other environmental conditions such as acidic or alkaline solutions as would be—expectedly or unexpectedly—encountered by composite pipes or containers. However, little work has been reported on diffusion in acidic or alkaline solutions.^{5,6}

As reported previously,^{7,8} three-dimensional (3D) braided composites have been developed in an attempt to replace metallic orthopedic devices such as bone fracture fixation devices. As potential materials for orthopedic application, moisture resistance is of crucial importance for these 3D braided composites. Additionally, unlike conventional structural parts, orthopedic devices are subjected to extreme exposure to moisture in the human body.

To obtain some insight into the response of the 3D composites when subjected to assault by moisture and to predict their long-term performance, this study was undertaken to investigate the moisture sorption of 3D braided carbon fiber–epoxy (C_{3D}/EP) composite samples and effects of various media. Distilled water, phosphate-buffered saline (PBS), and acidic and alkaline solutions were chosen in this study.

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EXPERIMENTAL

Materials

The fabrics used in this study were kindly provided by Tianjin Polytechnic University (Tianjin, China). As described previously,⁹ the 3D braided preform was constructed by the intertwining or orthogonal interlacing of two sets of yarns-braiders and axials to form a fully integrated structure. A home-formulated epoxy resin was used as the matrix material. The details of the fiber and matrix are listed in Table I. All fabrics were surface treated at 450°C for 1 h in air to improve fiber–matrix bonding.

Preparation of specimens

The C_{3D}/EP composite specimens were produced by a vacuum-assisted resin transfer molding (VARTM) process. Five braided fabrics with a nominal size of 160 × 12 × 2 mm were placed in a mold. The epoxy resin and curing agent were thoroughly mixed at room temperature (RT) and evacuated. The degassed mixed resin was then introduced into the mold under a pressure of 0.4–0.6 MPa and assisted by vacuum. The impregnation proceeded until bubbles were no longer observed within the resin flowing out from the exit of the mold. The preforms in the mold were then cured at 90°C for 2 h and postcured at 140°C for 3 h in an oven, and then demolded. The properties of a typical C_{3D}/EP composite prepared in this work are given in Table II.

Unidirectional carbon fiber–epoxy resin (C₁/EP) composite samples were also prepared in the present work to determine the effect of fiber architecture on moisture-sorption behavior in different media. The C₁/EP composite samples were also prepared by the VARTM technique. The processing parameters (except for pressure) were identical to those applied to the C_{3D}/EP composite samples. The fiber volume fractions of the C_{3D}/EP and C₁/EP composite specimens were kept at 39 ± 1 and 39 ± 2%, respectively.

Ageing condition

Specimens for moisture experiments were not cut; instead, all specimens for moisture experiments were

TABLE I
Properties of Fiber and Matrix Used

Material	Fabric	Matrix
Type	Four-directional	E-51
Tensile strength, MPa	2800	60
Tensile modulus, GPa	200	3.2
Elongation at break, %	1.5	1.8
Density, kg m ⁻³	1760	1200
Braiding angle, °	20	—
Filament number, K	6	—
Curing agent	—	Anhydride

TABLE II
Mechanical Properties of a Typical C_{3D}/EP Composite Prepared by VARTM

Property	Composite	
	C _L /EP	C _{3D} /EP
Fiber volume fraction	39 ± 1%	39 ± 2%
Average void content	~ 0.5%	0.3–0.5%
Flexural strength, MPa	868	756
Flexural modulus, GPa	53	47

as-prepared samples of dimensions of 160 × 12 × 2 mm. Before the absorption experiments, all specimens were thoroughly washed and then vacuum dried until a constant weight was attained. The medium temperature was kept at body temperature, 37 ± 0.5°C. Specimens were periodically removed from the baths, wiped, and weighed using an analytical balance with 0.1 mg precision. In the case of PBS (pH = 7.4), HCl (10 wt %), and NaOH (10 wt %) solutions, coupons were periodically removed from solutions, and rinsed with distilled water before drying and weighing. The rate of moisture sorption was measured as the rate of change in mass with respect to the initial dry mass of the specimens. The moisture uptake at any time points, M_t was calculated by

$$M_t = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

where W_t and W_0 are the mass of specimens at time t and its initial dry mass, respectively.

Desorption tests were performed only for all moisturized C_{3D}/EP specimens by placing those specimens in an oven at the same temperature as that used for moisture absorption (37 ± 0.5°C) and a relative humidity of 60%. The samples were periodically weighed until the final equilibrium. The soluble fraction was calculated in terms of the difference between the weights measured before absorption and after desorption.

Scanning electron microscopy

A Philips XL-30 environmental scanning electron microscope (ESEM; Philips, Eindhoven, The Netherlands) was used to view the morphology of the surfaces of selected specimens. The surfaces of the selected specimens were coated with a thin layer of gold before viewing to prevent charging.

RESULTS AND DISCUSSION

Moisture absorption of C_{3D}/EP and C₁/EP in distilled water

Classic Fickian diffusion model is a one-dimensional form, which gives the change in concentration C as a function of the diffusion coefficient D and time t :

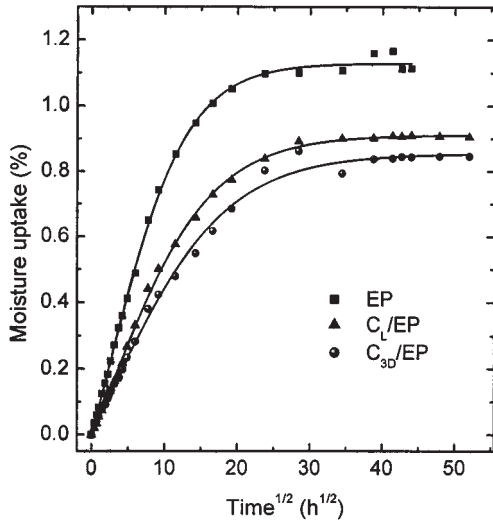


Figure 1 Mass uptake curves for different materials in distilled water.

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

By applying suitable boundary conditions, the Fickian model can be simplified to

$$\frac{M_t}{M_e} = \frac{4}{l} \sqrt{\frac{Dt}{\pi}} \quad (3)$$

or expressed as

$$D = \pi \left(\frac{l}{4M_e} \right)^2 \left(\frac{M_{t_2} - M_{t_1}}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (4)$$

where M_t is the relative mass uptake at a time t , M_e is the mass uptake at equilibrium, and l is film thickness. Therefore, moisture uptake at equilibrium (M_e) and moisture uptake rate (k) can be obtained and D can be calculated by eq. (4).

In Figure 1, moisture uptake is plotted against the square root of time for the pure epoxy and C_L/EP and C_{3D}/EP composites. Table III gives the diffusion parameters D , k , and M_e obtained in this study. Evidently, typical Fickian behavior is observed for all three materials. The substantially higher moisture uptake at any of the time points of the pure epoxy than that of the composites indicates that the incorporation of either 3D fabrics or longitudinal fibers does not change the moisture diffusion trend. Compared to those of the neat epoxy specimens, the D , k , and M_e values of the composites are much lower, which suggests that both the unidirectional fibers and 3D fabrics act to resist molecule diffusion as a result of the physical hindrance effect of fibers.

It is worth noting that the differences in D , k , and M_e are observed between the 3D and unidirectional composite specimens. This demonstrates that the fiber form exerts an effect on moisture sorption of the composites. The former exhibits lower D , k , and M_e values, suggesting that 3D fabrics have a stronger hindrance effect than that of the unidirectional fibers on the molecule diffusion. This is understandable because there are quite a few differences in their fiber structures. The 3D fabrics have a three-dimensional network structure that forces the molecules to take distorted paths. In the case of the unidirectional composite, fibers restrict molecule transport only in the radial direction. In addition, the relatively nonuniform distributions of fibers (fiber aggregation) within the 3D composites may reduce molecular transport. Furthermore, the difference in moisture diffusion can be simply elucidated by an equation for diffusion through the composite^{10,11}:

$$\frac{\partial C}{\partial t} = V_m K D_m \frac{\partial^2 C_m}{\partial x^2} = D_c \frac{\partial^2 C}{\partial x^2} \quad (5)$$

where D_m is the diffusivity of the matrix phase, V_m is the volume fraction of the matrix material in the composite, K is the structure factor for diffusion, and D is the diffusivity of the composite. It is believed that longitudinal fibers and 3D fabrics show different K values, although D_m and V_m are the same, which causes different D_c values between the two composites.

Another plausible explanation for the effect of fiber architecture is related to residual stress. It is well established that residual stresses arise when the composites cool down from preparation temperature to ambient temperature and when matrix materials cure and contract. For the longitudinal carbon-epoxy resin system, the rigid fibers restrict shrinkage in the fiber direction; most shrinkage occurs transverse to the fi-

TABLE III
Values of D , k , and M_e for Various Materials Immersed in Different Media

Medium	Material	$k \times 10^{-3}$ ($s^{-1/2}$)	$D \times 10^{-6}$ ($mm^2 s^{-1}$)	M_e (%)
Distilled water	Epoxy	1.41	1.60	1.113
	C_L/EP	0.87	0.92	0.906
	C_{3D}/EP	0.74	0.79	0.840
PBS	Epoxy	1.30	1.12	1.09
	C_L/EP	0.70	0.54	0.843
	C_{3D}/EP	0.60	0.53	0.73
HCl	Epoxy	1.1	—	—
	C_L/EP	0.85	—	—
	C_{3D}/EP	0.53	—	—
NaOH	Epoxy	1.59	—	—
	C_L/EP	0.96	—	—
	C_{3D}/EP	0.75	—	—

bers and residual tensile stress is expected in the matrix and compressive stress in the fibers. The residual stress state is considered different in a 3D braided composite. In other words, different fiber architectures cause different residual stress states in composites, which, in turn, lead to different kinetics of water diffusion, given that moisture diffusion is closely related to the stress state.¹²

Moisture absorption in PBS

The moisture-absorption curves of three materials immersed in PBS are displayed in Figure 2. An obvious difference is noted between distilled water and PBS with respect to moisture uptake for all materials. However, the presence of large ions does not change the pattern of the moisture uptake versus square root of immersion time curves. As listed in Table III, values of D , k , and M_e are lower in PBS, suggesting moisture absorption in PBS is more difficult than that in distilled water. The difference observed in the moisture uptake in distilled water and PBS is ascribed to the presence of many massive ionic species, such as Na^+ , K^+ , Cl^- , HPO_4^{2-} , and H_2PO_4^- in PBS. Compared to water molecules, transport of large ions is more difficult. Large ions may block the passages to interfaces because of their large sizes or heavy weight because the quantity of a chemical species that enters into a polymeric matrix is inversely proportional to its size and/or atomic weight.^{13,14}

Although little literature is available, diffusion behavior in PBS is, to some extent, similar to that in salt or saline solution in terms of presence of ionic species such as Na^+ , Cl^- , and so forth. With respect to diffusion in salt solution, Lagrange et al.¹⁵ compared diffusion of glass/polyester composites in distilled water

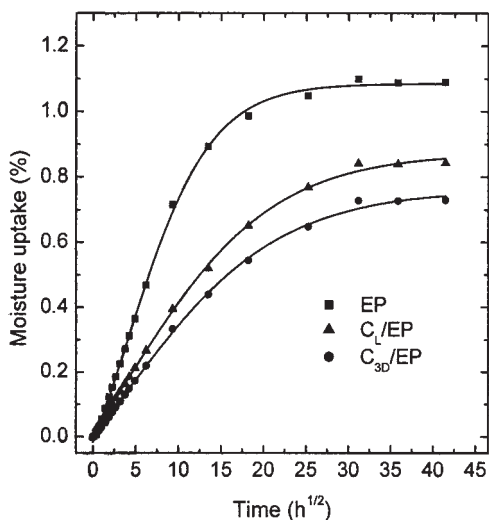


Figure 2 Moisture uptake curves for different materials in PBS.

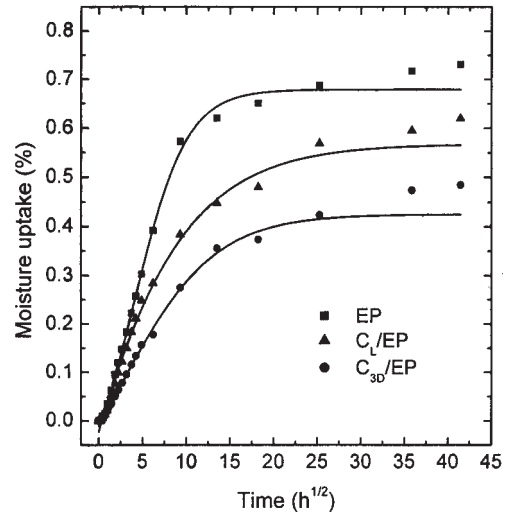


Figure 3 Mass uptake curves for different materials in HCl solution.

with salt solution and found higher mass uptake in distilled water than that in salt water. Davies et al.¹⁶ reported a considerable difference between distilled water and salt solution in terms of weight gain of glass fiber-reinforced polyester, vinyl ester, and epoxy composites. Although a difference in weight gain between RT-cured glass-epoxy composite samples immersed in distilled water and salt solution was noted, immersion in salt solution did not change the diffusion mechanism; the Fickian model was obeyed in both water and salt solution.¹⁷ The current result is in agreement with results reported in Lagrange et al.,¹⁵ Davies et al.,¹⁶ and Srihari et al.¹⁷ This suggests that diffusion in PBS is very similar to that in salt solution.

Moisture absorption in HCl solution

The weight gain versus the square root of time curves for the three different materials immersed in HCl solution are displayed in Figure 3. Overall, the absorption data for the specimens aged in HCl nearly coincide with Fick's law of diffusion initially, but followed by a positive deviation from Fickian law. The weight gain is still increasing after 1500 h in HCl. Several other features can be observed concerning the moisture-absorption behavior in this figure. First, M_t at any time points is much lower than that in distilled water for each material. Second, the sorption rate during the initial stage is significantly lower compared to that of specimens in distilled water and PBS as shown in Table III. Finally, C_{3D}/EP composite specimens still show the lowest M_t among the three materials. The lower moisture content in HCl than that in distilled water is likely explained by the incapability of acid to penetrate into the polymer network and thus acid can reach the fibers only through microcracks, voids, or

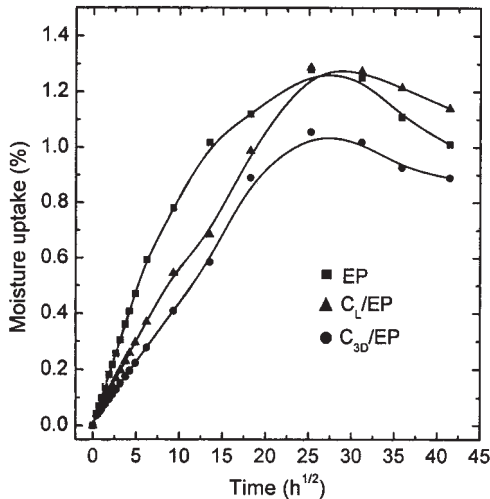


Figure 4 Mass uptake curves for different materials in NaOH solution.

crazes in the matrix.⁶ Furthermore, hydrated hydrogen and chloride ions have a higher affinity for water than for the resin and therefore no acid is expected until sufficient water is present.⁶ This may also be responsible for the disequilibrium by the end of the experiments up to around 1600 h. The lack of moisture equilibrium content makes any estimate of D impossible. However, the linearity at initial stages allows us to estimate the k value, which is listed in Table III.

It should be mentioned that the diffusion process of acid in HCl is undoubtedly complex and the mechanisms involved in this type of behavior are not well understood.

Moisture absorption in NaOH solution

Figure 4 presents the moisture absorption curves of the three different materials immersed in NaOH solution. Interestingly, C_{3D}/EP composite specimens display a lower M_t than that of C_1/EP as occurred in distilled water, PBS, and HCl, suggesting that the complex structure of 3D fabrics can restrict diffusion of moisture more effectively than parallel aligned longitudinal fibers regardless of medium. This figure clearly shows that the moisture uptake in NaOH is higher (approaching 1.0 to 1.3% after about 3 months) than that in distilled water, PBS, and HCl before a sharp drop in moisture uptake is noted. An approximate linear relation during the initial stages is observed for each specimen. The k value obtained for each material is also given in Table III. It is interesting to point out that each material shows a higher k value in NaOH than in other media.

The decrease of moisture uptake is often an indication of extensive reaction between the medium and the matrix and/or fibers. Similar results were reported

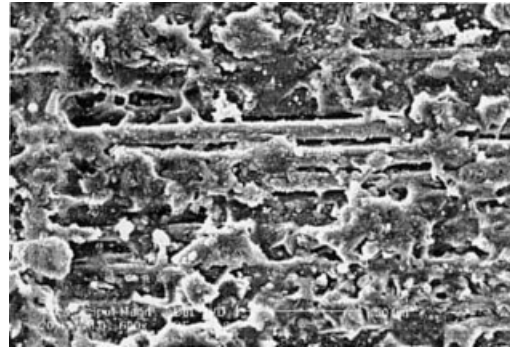


Figure 5 Surface of a typical C_{3D}/EP composite specimen after exposure to NaOH solution for 1200 h.

by other researchers that were ascribed to irreversible degradation such as dissolution, ester hydrolysis, or leaching of lower molecular weight materials such as uncured monomers.^{1,18-20} SEM observations (see Fig. 5) may indicate erosion took place during moisture absorption in NaOH solution. The erosion is believed to be caused by a reaction between NaOH and the uncured material in the matrix because the anhydride curing agent was used. Other evidence of extensive dissolution is the presence of a feculent substance after 1200 h.

Desorption behavior in different media

The desorption behaviors at 37°C for the C_{3D}/EP specimens moisturized in different media at 37°C are presented in Figure 6. Kinetics of the desorption process of the C_{3D}/EP specimens previously immersed in all four media demonstrates behavior consistent with Fickian diffusion regardless of their absorption his-

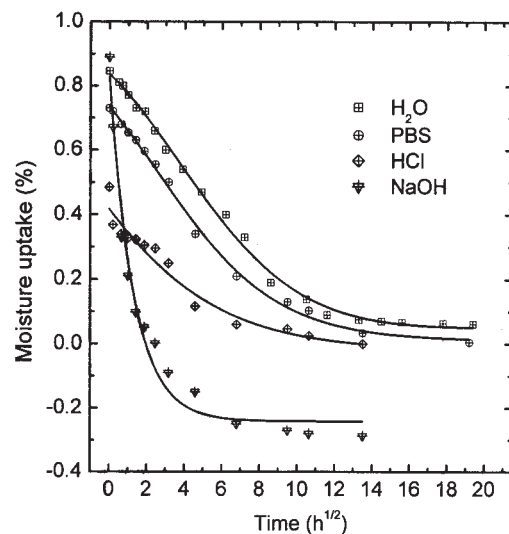


Figure 6 Moisture desorption curves for C_{3D}/EP composite.

TABLE IV
Values of k and D During Desorption

Medium	$k \times 10^{-3} \text{ (s}^{-1/2}\text{)}$	$D \times 10^{-6} \text{ (mm}^2 \text{ s}^{-1}\text{)}$
Distilled water	1.25	1.73
PBS	1.32	2.60
HCl	0.91	2.77
NaOH	5.77	70.20

tory. The D and k values obtained by eq. (4) are listed in Table IV. Interestingly, D and k values are higher than those during absorption process. These higher k and D values are believed to be attributed to the existing diffusion paths such as microvoids and debonded interfaces, created during the absorption process. These paths were still open during desorption, allowing for an efficient removal of water molecules. After drying to an equilibrium state (up to ~ 400 h), the two C_{3D}/EP specimens previously aged in distilled water and PBS still retain a small amount of moisture, 0.05 and 0.02%, respectively. A similar phenomenon was also reported by other investigators.^{18,21} Moy et al. noted that a small amount of absorbed water could not be desorbed. The retained moisture was believed to be caused by the existence of chemisorbed water.¹⁸ The details regarding this issue will be addressed in a future article.

Unlike moisture absorption behaviors in PBS and water, the moisture absorption of the C_{3D}/EP composite specimens aged in HCl is nearly reversible. As expected, specimens aged in NaOH solution experience a significant weight loss, about 0.24% after equilibrium, confirming that extensive matrix solution took place during absorption. Another likely evidence of extensive matrix solution in NaOH during absorption is the much higher k and D values during desorption compared with those in distilled water, PBS, and HCl (see Table IV). It is still unclear why the C_{3D}/EP specimens previously immersed in PBS show a higher k value during desorption than that of specimens aged in distilled water, which is a striking contrast to the trend during absorption.

CONCLUSIONS

1. In distilled water and PBS, the diffusion behavior of both 3D and unidirectional composites follows Fick's law. However, diffusion parameters k , D , and M_e are smaller in PBS than they are in distilled water.
2. Compared to distilled water, diffusion in HCl is more difficult, and thus a much lower k value is observed. In addition, a deviation from a Fickian

trend is noted in late stages of immersion and no saturation has been reached at the end of the experiment.

3. The data in NaOH diverge from Fickian prediction in late stages arising from gross moisture-induced degradation in the matrix.
4. The unidirectional and 3D composites demonstrate the same diffusion pattern, but show differences in diffusion parameters in all of the four media studied. As a result of integrated fiber structure of the 3D fabrics, diffusion in the 3D composite is slower than that in the longitudinal composite, suggesting an effect of fiber architecture on diffusion behavior.

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