Carbon Nanoparticles to Monitor Moisture Damage Propagation in GFRP

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ABSTRACT: This paper presents the potential use of carbon nanofibers (CNFs) and multi-wall carbon nanotubes (MWCNTs) as sensors to monitor moisture damage propagation in glass fiber reinforced polymer composites (GFRP). GFRP coupons incorporating 2% CNFs and 2% MWCNTs by weight of epoxy were fabricated using hand layup method and examined. Water absorption tests were carried out by immersing the GFRP coupons in an artificial seawater bath at two temperatures (22 °C and 45 °C) for six months. Moisture damage propagation in GFRP coupons was monitored by continuous measurement of GFRP electrical conductivity. The effect of moisture absorption on mechanical properties of GFRP coupons were examined using Dynamic Mechanical Analyzer (DMA). The results show the ability of CNFs and MWCNTs to provide means of self-sensing that enables monitoring moisture damage propagation in GFRP coupon.

1 INTRODUCTION

The use of fiber reinforced polymer (FRP) composite in civil engineering has grown progressively over the last decades, due to their remarkable mechanical properties and light weight property (Einde et al. 2003). However, the performance and service life of FRP are greatly influenced by environmental conditions such as moisture and temperature effects. Several investigators have studied the effect of moisture degradation on the behavior of FRP composite (Boisseau et al. 2012 and Kafodya et al. 2015). It was found that the moisture degradation strongly depends on matrix properties, fiber volume fraction, fabrication method, temperature and the fiber-matrix interface. It was found that the diffusion of moisture into the matrix occupying free volumes causing matrix plasticization and the capillary penetration of moisture along fiber-matrix interfaces results in fiber debonding is the fundamental reason for moisture degradation in FRP composites.

Recently, damage self-sensing using electrical resistance has become the most promising method towards damage sensing in FRP composites providing a real-time sensing of FRP structural performance. Several studies reported that the incorporation of percolation threshold content of conductive carbonaceous nanoparticles in FRP composite transfers it from insulating state into a conductive state owing to the formation of conductive networks throughout the matrix (Gao et al. 2011 and Nanni et al. 2011). Such electrically conductive networks have significant sensitivity to intrinsic damage in FRP composites providing the means of self-sensing. Wang et al. (2002) studied the evolution of compressive damage in carbon fiber reinforced polymer (CFRP) by monitoring the change in electrical resistance. Belani et al. (1978) and Zhai et al. (2016) reported a remarkable increase in the electrical resistance of FRP composites with the square of the moisture gain. On contrary, Kotrotsos et al. (2014) and Barkoula et al. (2009) recorded significant reduction in electrical resistance of CFRP incorporating carbon nanotubes (CNTs).

In this study, 2.0 wt. % carbon nano fibers (CNFs) and 2.0 wt. % multi-walled carbon nanotubes (MWCNTs) are incorporated in the epoxy matrix prior to FRP composite fabrication by means of hand layup method. Our goal is to reduce moisture diffusion in glass fiber reinforced polymer (GFRP) composite and to enable monitoring moisture damage propagation in GFRP composites.

2 EXPERIMENTAL METHODS

2.1. Materials and fabrication

MWCNTs were provided by Cheap Tubes, Inc. with an inside diameter of 5–10 nm, an outer diameter of 20–30 nm and a length of 10–30 μm. CNFs provided by Nanostructured and Amorphous Materials Inc. They had diameter of 80–200 nm and a length of 0.5–20 μm. The epoxy system was provided by U.S. Composites, Inc. The epoxy system is EPOTUF® 37–127 epoxy and the hardener is Aliphatic Amine EPOTUF® 37–614. The bidirectional S-Glass fiber was provided by ACP Composites, Inc.

2.0 wt. % MWCNTs and 2.0 wt. % CNFs were added into the epoxy resin and ultra-sonicated for 1 hour at a temperature 40 °C. A high shear blender was then used for 1 hour at a temperature of 90 °C with a speed of 11,000 rpm to separate the agglomerates of MWCNTs and CNFs. The mixtures were then mechanically stirred for 2 hours at a temperature of 90 °C. The mixtures were then degassed to remove the bubbles for 30 min at a temperature of 50 °C. After cooling, the hardener was added into mixtures and hand-mixed for 5 min and left overnight. Carbon/epoxy nanocomposites were then cured for 60 h at a temperature of 110 °C. Hand layup method was used to prepare six layers of bidirectional glass fiber textures. The fabrics were laid in 0° direction, and then vacuum pressure (3.06 Pa) was applied for 24 h. The fabricate glass fiber composites plates (GFRP) were then cured for 60 h at a temperature of 110 °C.

The MWCNTs and CNFs content utilized for producing the glass fiber composites plates were based on our previous observations of the electrical percolation threshold of carbon/epoxy nanocomposites (Al-Sabagh et al. 2016).

2.2. Testing of the GFRP

Five specimens of Neat/GFRP, MWCNTs/GFRP and CNFs/GFRP composites plates were immersed in artificial seawater for 200 days at temperatures 22 °C and 45 °C. The artificial seawater was prepared according to ASTM D1141-98 (2005) and the moisture absorption were tested using ASTM D570-98 (2005). The mass evolution of the GFRP plates were periodically determined as a function of time by measuring the mass gain at time intervals of 20, 40, 60, 80, 100, 150 and 200 days of water immersion using an electronic balance with 0.1 mg accuracy. Before measuring mass, the specimens' surface was dried using a soft tissue. Moisture mass gain (ΔM) and diffusivity (F) of GFRP plates were calculated using following Equations after Gellert at el. (1999):

$$\Delta M = \frac{m_t - m_0}{m_0} \times 100 \tag{1}$$

m_t is the mass of specimen immersed in seawater and m_0 is the mass of dry specimen.

$$F = \left[\frac{\pi\, d^2}{t}\right]\left[\frac{M_t}{4\, M_{max}}\right]^2 \tag{2}$$

M_t is the moisture weight gain at time t, M_{max} is maximum moisture weight gain and d is the thickness of the composite plates.

To identify the significance of MWCNTs and CNFs on the degree of crosslinking of the epoxy nanocomposite, three 20 mm × 10 mm × 2 mm specimens were tested under off-axis orientation at 45° with respect to the fiber orientation using DMA, (Triton Instruments), after surface drying them using a soft tissue. The specimens were tested using tension mode at an oscillation frequency of 1 Hz with a scanning rate of 10 °C/min from room temperature to 140 °C.

According to the elasticity theory (Nielsen et al. 1969 and Hill et al. 1997), the degree of crosslinking (X_{link}) can be estimated using equation (3):

$$X_{Link} = \frac{E'}{3\,\rho\, R\, T} \tag{3}$$

E' is the storage modulus at a temperature 50 °C above glass transition temperature (T_g), ρ is the density of the polymer composite, R is the gas constant, , and T is temperature equals to ($T_g + 50$). Mechanical and electrical damage in the glass fiber composites plates was estimated in terms of the change of the complex modulus and the electrical conductivity at periodic intervals using Equations (4) and (5), respectively:

$$D_M(t) = 1 - \frac{E(t)}{E_0}\ \% \tag{4}$$

$E(t)$ is the complex modulus of GFRP specimen at time t and E_0 is the complex modulus of dry GFRP specimen.

$$D_E(t) = 1 - \frac{\sigma(t)}{\sigma_0}\ \% \tag{5}$$

$\sigma(t)$ is the electrical conductivity of GFRP specimen at time t and σ_0 is the electrical conductivity of dry GFRP specimen.

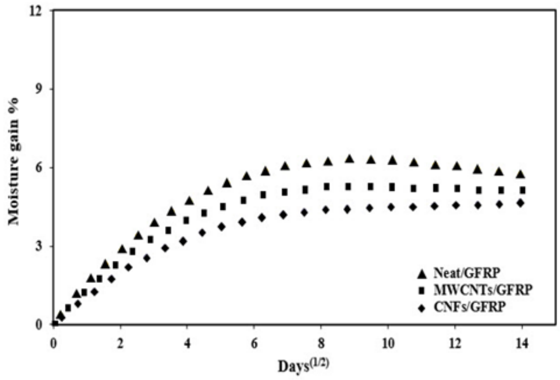
3 RESULTS AND DISCUSSIONS

3.1. Moisture Absorption

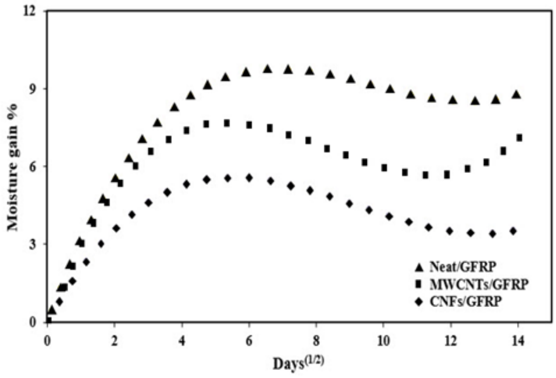
Figure 1 shows the evolution of moisture weight gains as function of square root of time for the Neat/GFRP, MWCNTs/GFRP and CNFs/GFRP composites plates immersed in seawater at temperatures 22 °C (Figure 1a) and 45 °C (Figure 1b), respectively. For GFRP plates immersed at temperature 22 °C, the moisture gain increased sharply until 20 days of time (4.4 day$^{1/2}$), representing rapid moisture penetration into the composite followed by a relatively slowing down of moisture ingress up to a period of 200 days (14 day$^{1/2}$). In this case, the moisture absorption behavior exhibited a Fickian behavior (Tsotsis at el. 1994). On the other hand, for GFRP plates immersed at temperature 45 °C, the moisture gain also increased sharply until 20 days reaching to a maximum value and the moisture gain starts to decrease slowly up to a period of 200 days showing a non-Fickian behavior. Such behavior was previously reported by Gu (2009), and arises from the interaction of two processes; moisture penetration into composite occupying free volumes resulting an increase in moisture weight gain and extraction of soluble components from the GFRP composite plates into the seawater resulting in the observed mass loss (Wei et al. 2011). Moreover, the maximum moisture gain for Neat/GFRP, MWCNTs/GFRP, and CNFs/GFRP is

6.2%, 5.3%, and 4.3% in case of temperature 22 °C and 9.7%, 7.3%, and 5.6% in case of temperature 45 °C, respectively. Our results were found to be consistent with several works published in literatures (Basri et al. 2015 and Thomason et al. 1995). Basri et al (2015) reported that maximum moisture gain for epoxy resin is approximately 8.0 % after 100 days of water exposure. Thomason et al (1995) also reported maximum moisture gains are 13.0 %, 8.0 % and 7.5 % for glass fibre-reinforced epoxy composites with difference curing systems and void contents.

Table 1 shows the diffusivity of the Neat/GFRP, MWCNTs/GFRP and CNFs/GFRP composites plates immersed at temperatures 22 °C and 45 °C that were determined using Equation 2. By considering the Neat/GFRP plates immersed at temperatures 22 °C and 45 °C as references respectively, it can be observed that the diffusivity of MWCNTs/GFRP composite plate decreases by 8.8 % at temperature 22 °C and by 6.7 % at 45 °C while it decreases in case of CNFs/GFRP plate by 27.8 % at temperature 22 °C and by 33 % at 45 °C. The MWCNTs has limited effect on controlling the diffusivity of GFRP composites on the contrary of the effect of CNFs. The significant of CNFs on the diffusivity of GFRP plates is owing to the ability of CNFs to interact with epoxy during the polymerization process increasing the crosslinking bonds and resulting in a significant reduction in the free volume inside the CNFs/epoxy composite matrix. Such reduction in the free volume limits the diffusion of seawater into the matrix.



(a)



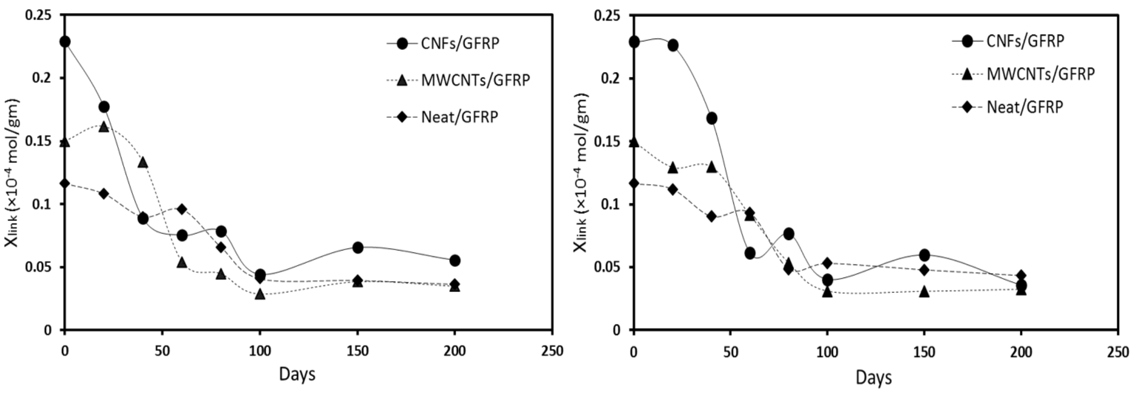
(b)

Figure 1. Moisture gain for GFRP plates as function of square root of immersion time at temperatures (a) 22 °C and (b) 45 °C.

Table 1. Diffusivity of GFRP composite plates at temperatures 22 °C and 45 °C.

Diffusivity (mm^2/s) X 10^{-7}	Neat/GFRP	MWCNTs/GFRP	CNFs/GFRP
At 22 °C	1.96	1.79	1.42
At 45 °C	2.19	2.04	1.47

To further confirm significant of CNFs and MWCNTs on crosslinking of epoxy matrix, the degree of crosslinking was calculated for Neat/GFRP, CNFs/GFRP and MWCNTs/GFRP composites using equation 3. Figure 2 shows the degree of crosslinking of composites plates immersed at temperatures 22 °C (Figure 2a) and 45 °C (Figure 2b) respectively. In dry state (at 0 day), the degree of crosslinking increases by 96% and by 28.8% for CNFs/GFRP and MWCNTs/GFRP plates than that of the Neat/GFRP plates respectively. As exposure time increases, the degree of crosslinking of CNFs/GFRP and MWCNTs/GFRP decreases and became relatively close to that of Neat/GFRP. At 200 days of exposure, the degree of crosslinking is reduced by 68.7 %, 75.7 % and 76.7% at temperature 22 °C and by 62.6 %, 84.4 % and 78.4 % at temperature 45 °C, respectively (considering dry states of Neat/GFRP, CNFs/GFRP and MWCNTs/GFRP composite plates as references, respectively).



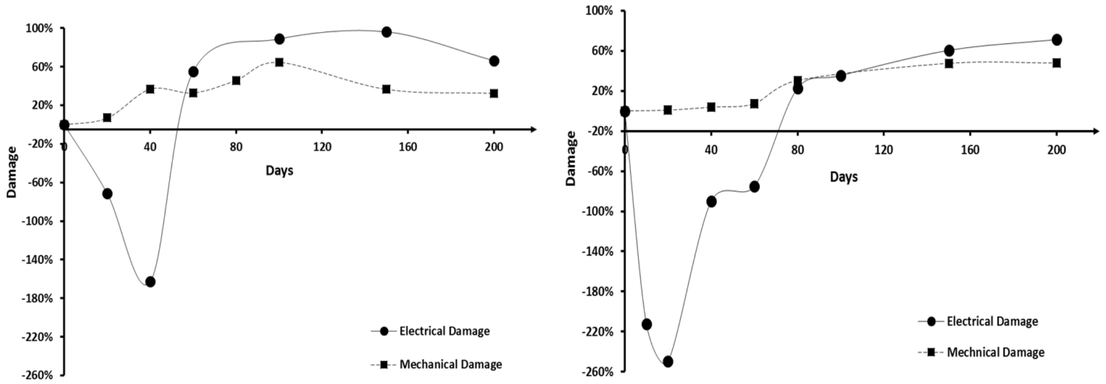
(a) (b)

Figure 2. Degree of crosslinking for GFRP plates as function of exposure time at temperatures (a) 22 °C and (b) 45 °C.

3.2. Monitoring Moisture Damage in GFRP

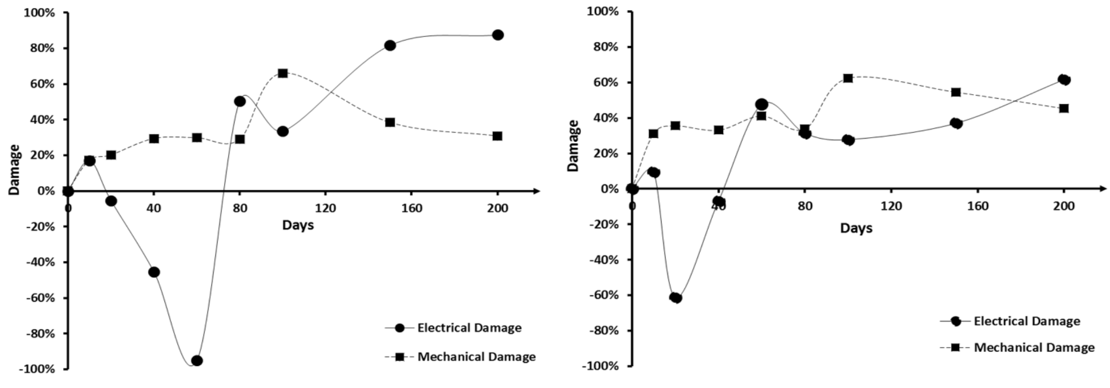
Figure 3 and 4 show damage propagation in GFRP plates incorporating MWCNTs and CNFs respectively. The Figures show a comparison between the electrical and the mechanical damage estimated using equations 4 and 5 as function of the exposure time at temperature 22 °C and 45 °C. It is apparent that while the mechanical damage of GFRP plates increases with exposure time, the electrical damage of GFRP plates exhibited V-shaped behavior. The electrical damage decreases initially reaching to a minimum owing to the penetration of seawater into the matrix occupying the free volumes. The conductivity of seawater increases the conductive paths inside the matrix resulting in an increase in the electrical conductivity causing a significant drop in the electrical damage. On the other hand, as soaking time increases, cracks start to propagate along the matrix causing noteworthy loss of conductive ways and consequently a sharp loss of electrical conductivity demonstrating an increase in the electrical damage.

It also worth noting that electrical damage evolution under high temperature (45 °C) was faster than that under ambient temperature (22 °C) where the V-shaped minimum points in case of immersion temperature 45 °C appear at immersion time lower than that in case of 22 °C. This is might be because of the fact that the high immersion temperature accelerates the crack initiation leading to fast losing in electrical paths. Moreover, the incorporation of both MWCNTs and CNFs in GFRP plates was unable to stop the evolution of mechanical damage at both temperatures (22 °C and 45 °C). As a result, moisture damage propagation can be sensed by continuous observation of the electrical conductivity of the composite. However, the electrical conductivity might not be changed by the same rate as the damage as long as electrically conductive ways can be found in the composite matrix. This means that using MWCNTs and CNFs can provide an indication of moisture damage propagation in GFRP composites. However, the electrical damage does not coordinate well with the mechanical damage evolution in the GFRP composite because of the electrical conductive nature of water. Although such method would give reasonable sensing of moisture damage evolution in GFRP plates over the long term, the method fails to give a real-time monitoring that accurately represents the mechanical damage initiation and propagation as it takes place in GFRP composite plates due to moisture absorption. Further research is warranted using methods of microstructural investigations to examine the significance of water ingress on polymer disassociation and the significance of such polymer change on the bond between polymer and glass fibers.



(a) (b)

Figure 3. Electrical and mechanical damages for MWCNTs/GFRP plates as function of exposure time at temperatures (a) 22 °C and (b) 45 °C.



(a) (b)

Figure 4. Electrical and mechanical damages for CNFs/GFRP plates as function of exposure time at temperatures (a) 22 °C and (b) 45 °C.

4 CONCLUSIONS

In this paper, 2.0 wt % MWCNTs and 2.0 wt % CNFs were well dispersed in the epoxy matrix and used to fabricate GFRP. Water diffusion and the effect of MWCNTs and CNFs on epoxy crosslinking were examined. GFRP plates incorporating CNFs exhibited a lower diffusivity owing to effect of CNFs on matrix crosslinking limiting the free volumes occupied by water molecules. Moreover, moisture damage propagation in GFRP plates was investigated by monitoring the change in its electrical conductivity. It was found that GFRP plates exhibited V-shaped damage behavior. While the mechanical damage in MWCNTs/GFRP and CNFs/GFRP was similar after 200 days of seawater exposure, the electrical damages did not match well.

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