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Effect of hygrothermal aging on GFRP composites in marine environment

Mohit Garg [*1], Shruti Sharma [2a], Sandeep Sharma [3b] and Rajeev Mehta [4c]

[1] *Department of Civil Engineering, University of Victoria, Victoria, British Columbia, Canada*
[2] *Department of Civil Engineering, Thapar University, Patiala, India*
[3] *Department of Mechanical Engineering, Thapar University, Patiala, India*
[4] *Department of Chemical Engineering, Thapar University, Patiala, India*

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Abstract. In the present work, the effect of hygrothermal aging on the glass fibre and epoxy matrix interface has been investigated by destructive and non-destructive techniques. The glass fiber reinforced polymer (GFRP) composite laminates were prepared using Vacuum Assisted Resin Infusion Molding (VARIM) technique and the specimens were immersed in simulated seawater, followed by quantitative measurement. Besides this, the tensile tests of GFRP specimens revealed a general decrease in the properties with increasing aging time. Also, exposed specimens were characterized by a non-destructive ultrasonic guided Lamb wave propagation technique. The experimental results demonstrate a correlation between the drop in ultrasonic voltage amplitude and fall in tensile strength with increasing time of immersion. Hence, the comparison of the transmitted guided wave signal of healthy vis-a-vis specimens subjected to different extents of hygrothermal aging facilitated performance evaluation of GFRP composites.

Keywords: GFRP; polymer composites; environmental degradation; marine environment; mechanical properties; damage mechanism; non-destructive testing

1. Introduction

Glass-fibre reinforced polymer (GFRP) composites form an important topic of research as they have replaced conventional materials like steel, aluminum etc. (Ray 2005, Arun *et al*. 2010) in infrastructural applications. They are widely used for preparing structural components in marine structures such as canoes, fishing trawlers, patrol boats and naval mine-hunting ships. They are also used for repair and rehabilitation of civil structures such as highways, bridges and buildings to improve their load carrying capacities, resistance against environmental degradations like corrosion and performance against earthquake loads. The wide use of GFRPs is due to their high strength-to-weight ratio, lower initial and maintenance costs and excellent corrosion as well as thermal resistance as compared to traditional building materials. Typically, in marine applications, the factors affecting the longevity, durability and performance of GFRP components is based on exposure to hygrothermal conditions. The rate of degradation of such composite materials when exposed to different environmental conditions (such as heat, stress, moisture, seawater etc.), depends upon the intensity, duration and type of exposure, which makes it a complex and rather unpredictable phenomenon. Moreover, the deterioration in the mechanical performance of the GFRPs composites is due to various physical and chemical processes such as plasticization, hygro-strains, hydrolysis, interface degradation, stress corrosion and swelling of polymer matrix (Smith 1990, Gellert and Turkey 1999, Ray 2005, Surathi and Karbhari 2006, Kar *et al*. 2008, Chakraverty *et al*. 2013). The water absorption mechanism at room and elevated temperature results in the degradation of GFRP laminates as the immersion time is increased. The physical/mechanical/ chemical changes due to water absorption weakens the fibre-matrix interfacial bonding initially, visualized as delamination or microcracking under the microscope, but on prolonged exposure causes failure of the composites.

The structural GFRP components used in ships, boats etc. consist of glass fibre mat strongly bonded using a thermosetting matrix, mainly epoxy resin because of its excellent properties such as low shrinkage after curing, good resistance to corrosion and stability at higher temperatures. Water absorbed by the resin at room temperature acts as a plasticizer, tends to lowers the glass transition temperature (T_g) and causes swelling of the matrix, but it's a reversible process. The effect of water absorption on the mechanical properties at room temperature is less serious as compared to higher temperatures. A study by Netravali *et al*. (1985) compared the T_g, weight gain and curing energy of aged and dry specimens. In their study, it was confirmed that the effect of water absorption in epoxy matrix was reversible, at room temperature, while at elevated temperatures, there was a chemical reaction between the water and the unreacted epoxide groups, which causes a permanent change in the physical and chemical

*Corresponding author, Ph.D.,
E-mail: mohitgarg2810@gmail.com
[a] Ph.D., E-mail: shruti.sharma@thapar.edu
[b] Ph.D., E-mail: sksharma@thapar.edu
[c] Ph.D., E-mail: rmehta@thapar.edu

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nature of epoxy. Additionally, the water content in the composite increases at an accelerating temperature, which induces swelling of the matrix that leads to faster occurrences of damages such as crack formation, stress concentration sites, fibre-matrix debonding etc. thus affecting the stability and behavior of the composite.

The performance of GFRPs is also dependent upon the diffusion mechanism of water because different water types show variation in their absorption process. In order to understand the diffusion mechanism, researchers have experimented hygrothermal aging of GFRP in sea water, distilled water, de-mineralized water etc. It is generally observed that the absorbed equilibrium moisture content for GFRPs is higher in distilled/de-mineralized water than in seawater (Kar *et al*. 2008, Surathi and Karbhari 2006, Krawczak and Pabiot 1995, Chifu and Iroh 1996, Davies *et al*. 2001, Aktas *et al*. 2002a, b, Wu *et al*. 2002, Barraza *et al*. 2003, Guo *et al*. 2004, Kootsookos and Mouritz 2004, Mula *et al*. 2006, Aldajah *et al*. 2009). This has been attributed to the formation of salt layer on the immersed surfaces which reduces the diffusion of water molecules significantly. Another possible methodology to reduce water absorption into the GFRPs has recently been reported by incorporating nanofillers such as carbon nanotubes (CNTs) in the matrix (Zulfi *et al*. 2013, Barkoula *et al*. 2009, Prolongo *et al*. 2012, Zafar *et al*. 2012). Overall, hygro-thermal studies in relation to the diffusivity of seawater in Epoxy/GF/CNT nanocomposites are very few. The outcome of such investigation would be helpful in quantitative analysis i.e., understanding the diffusion mechanism and relative weight gain of the nanocomposites, which could be implemented for preparing future naval structures entirely made up of nanocomposite materials.

Different types of damages and material degradations encountered during the in-service operation of the composite components in marine structures can be monitored by using various non-destructive (NDT) methods like penetrating gamma rays, X-rays, thermographic imaging, holographic interferometry, vibrothermography etc. (Pieczonka *et al*. 2013). However, implementation of these techniques requires interruption of normal service and removal of the subject structure from submerged condition. The out-of-service cost can be too high to go in for frequent inspections. Ultrasonic guided wave propagation has also established itself as a complete NDT tool for damage identification and characterization in structures due to their high sensitivity to structural damage and material in-homogeneities even when they are small in size or lie beneath the surface (Mutlib *et al*. 2016). But most of the researchers have used the guided waves in which the subject structure is dry docked and transducers are in contact with the structure, which needs the surface to be prepared and requires a coupling medium. Owing to these limitations, some researchers have designed specialized set-ups to hold local water in a container and transducers at specific angles to inspect pipes and plates in air (Guo and Kundu 2001, Ghosh and Kundu 1998). Sharma and Mukherjee (2014, 2015a, b) designed and developed a non-destructive damage monitoring technique for submerged structures using specific leaky Lamb waves which could pick up machined notches as well as corrosion in naval structures. Recently, pulsed lasers have also been used for the generation of ultrasonic stress waves in metal plates immersed in water for damage detection (Na and Kundu 2002, Rizzo *et al*. 2010, 2015, Pistone *et al*. 2013, Pistone and Rizzo 2015, Bagheri and Rizzo 2016). Several researchers have also used guided waves to characterize different types of damages in laminate composites (Hay *et al*. 2003, Chakrapani and Dayal 2014, Benammar *et al*. 2008, Badcock and Birt 2000, Diamanti *et al*. 2002, Ratnam *et al*. 2008, Kim *et al*. 2007, Kessler *et al*. 2002, Monkhouse *et al*. 2000, Lemistre and Balageas 2001, Grondel *et al*. 2002, Castaings and Hosten 2001, Yam *et al*. 2003, Toyama *et al*. 2003, Aggelis *et al*. 2013, Padiyar and Balasubramaniam 2014). The analysis has been made by studying the effect of damages on the received ultrasonic signal strength vis-à-vis the healthy signal.

Most researchers have attempted to derive the variations in mechanical properties of aged specimen by performing destructive tests (Ray 2005, Gellert and Turkey 1999, Kar *et al*. 2008, Surathi and Karbhari 2006, Davies *et al*. 2001, Aktas *et al*. 2002a, b, Wu *et al*. 2002, Mula *et al*. 2006, Aldajah *et al*. 2009, Prolongo *et al*. 2012, Zafar *et al*. 2012). Also, a correlation between weight change, mechanical behavior and immersion time has been established for GFRPs (Kar *et al*. 2008, Chakraverty *et al*. 2013, Zulfi *et al*. 2013, Prolongo *et al*. 2012, Zafar *et al*. 2012). However, in the present study, the effect of nanoreinforced GFRP i.e. by the addition of amino functionalized carbon nanotubes (ACNT) in epoxy matrix reinforced with glass fibres has been correlated to pure epoxy GFRP samples with respect to their diffusion process and weight gain in both distilled water (DW) and seawater (SW) conditions. Since, the natural degradation of GFRPs would require longer time period to show appreciable results, accelerated SW conditions have been created to analyze the mechanical behavior of GFRP composites in a shorter time span.

The present study also aims at investigating the long-term aging effect on diffusivity and material degradation of GFRP on exposure to SW conditions. The degradation effect on weakened fibre/matrix interface has been characterized and compared by performing tensile strength tests and non-destructive guided wave propagation in healthy and conditioned samples. Therefore, this study would provide an insight in the performance and durability of composite laminates under hygrothermal conditions and the results from this study could be used to investigate the performance of real time FRP components subjected to similar environmental degradation. Also, the present study proposes a damage monitoring methodology of GFRPs that is non-invasive, effective, non-contact, *in-situ* and provides real-time data of the material degradation during hygrothermal aging.

2. Non destructive monitoring using guided Lamb waves

GFRP composites are presently being used in various structural parts such as hull, decks etc. in marine structures. On exposure to water, environmental degradation and service related factors affect the fibre-matrix interfacial bonding thus causing degradation in its overall performance. The commonly seen damages under harsh service conditions include transverse micro-cracking, fibre-breakage and delamination (Sihn *et al*. 2007). Several non-destructive methods have attempted to monitor the degradation in composites by techniques such as lock-in and transient thermography (Padiyar and Balasubramaniam 2014, Chia *et al*. 2012, Bates *et al*. 2000, Inagaki *et al*. 1999, Chen *et al*. 2001, Scudder *et al*. 1996, Okafor *et al*. 2001, Hung *et al*. 2000). But for marine structures, it requires regular assessment of the components under submerged conditions which is inhibited by the above-mentioned conventional damage inspection tools. It may be due to economic constraints such as high out-of-service costs linked with frequent monitoring schedules and also time consuming process associated with the removal of structures prior to their inspection. As a result, it exposes such structures to the risk of unnoticed fatal damages with huge loss of human life and property.

Interestingly, ultrasonic guided waves have been suggested as an effective structural health monitoring tool by various researchers to detect damages such as delamination, cracks etc. in FRPs (Hay *et al*. 2003, Chakrapani and Dayal 2014, Benammar *et al*. 2008, Yeum *et al*. 2014). Guided waves travel along the geometrical boundary (like tube, cylinder or plates etc.) as a guiding surface for wave propagation and especially, the structures with plate or sheet geometry, are referred to as Lamb waves. These are complex vibrational waves that propagate parallel to the surface throughout the thickness and scan the entire thickness of the plate.

Specific Lamb wave modes in the submerged GFRP laminates can be excited by using water as a couplant medium. Lamb waves are usually generated by impinging the plate specimen obliquely with an ultrasonic signal emitted by a high frequency transducer. The wave propagation characteristics vary with the incident angle, excitation and structural geometry. In-order to monitor the degradation in GFRPs such as delamination, debonding etc., a specific Lamb wave mode sensitive to such defects needs to be excited. Desired Lamb wave mode in pitch-catch orientation can be excited by arranging the ultrasonic transducers at a specific angle with respect to the GFRP sheet. The incident angle (θ) necessary to produce a desired Lamb wave can be calculated from Snell's law as given by Eq. (1)

$$\theta = \sin^{-1}\left(\frac{V_L}{V_{Ph}}\right) \tag{1}$$

where,

V_L = longitudinal velocity of the incident wave in coupling media

V_{Ph} = phase velocity of desired Lamb wave mode

Therefore, the specific ultrasonic guided waves can be used for structural health monitoring of hygrothermally-conditioned specimens at different aging durations by utilizing a particular incident angle of the probes with respect to the GFRP laminate. This methodology has been developed and used in this study to monitor degradation of hygrothermally-exposed specimens as detailed in Section 3.4.

3. Experimental

3.1 Materials

Advantex® E-glass fibres (GF) woven roving fibre mat, WR310 (Owens Corning Inc., India) was used as FRP. The composites were manufactured using diglycidyl ether of bisphenol A (DGEBA) epoxy resin (AIRSTONE 780E) and poly (oxypropylene) diamine-based hardener (AIRSTONE 786H) (Dow Chemicals) and used as the polymer matrix with a recommended resin to hardener weight ratio of 100:31. CNTs were used as nano-reinforcements. The multi-walled carbon nanotubes functionalized with amino groups (< 0.5% w/w) (Nanocyl NC3152) with a carbon purity of > 95%, average length < 1 micron and diameter around 9.5 nm were used (Nanocyl S.A. (Sambreville, Belgium)) and referred to as ACNT in the text.

3.2 Sample preparation

In the present study, two types of laminates were prepared i.e., pure epoxy glass fibre reinforced (GFRP) and epoxy matrix modified with amino-functionalized nano-tubes glass fibre (ACNT GFRP) laminates.

The method of preparing GFRPs and nanotube modified FRP composites have previously been reported by the authors (Garg *et al*. 2015). Briefly, pure epoxy FRP composites were infused with a stoichiometric ratio of epoxy resin: hardener (100:31) by mechanical stirring (500 rpm for 5 min). Whereas for preparing nanocomposites with ACNT, a slightly different processing methodology was adopted. A weighed amount of ACNT (0.1 by wt%) was dispersed in epoxy resin and the resulting solution was mixed by high-shear homogenizer (20,000 rpm for 5 min) and then sonicated for 10 min at 40% amplitude using ultrasonicator probe. The beaker was submerged in ice-water to prevent the rise in temperature of the solution during the sonication process. The resulting ACNT/epoxy mixture was again subjected to high shear homogenization and sonication for obtaining uniform dispersion of ACNT in the epoxy matrix. The mixture was then kept in a vacuum dessicator for 1 h to remove the entrapped air bubbles in the mixture. After 1 h, the stoichiometric ratio of hardener was added to the ACNT/epoxy mixture and mechanically stirred at 500 rpm for 5 min. The glass fibre mat (2-plies) were then infused with epoxy mixture using vacuum assisted resin infusion molding (VARIM) technique and a curing schedule of 7 h at 70°C was followed. The vacuum was maintained at 1–2 mPa throughout the experiment to ensure proper vacuum conditions for the preparation of GFRP sheets with pure epoxy or ACNT modified matrix.

The pure epoxy GFRP specimens were taken from 0.7 mm sheet and considered as reference for long-term aging study. Specimens for the tensile strength and elastic modulus were prepared according to ASTM D-3039, from the aforementioned laminates with a cutter. In order to align the hygrothermal conditions with the actual usage conditions, the specimen edges were coated with a thin layer of epoxy to limit the diffusion of water from the edges in the composite. These healthy specimens might show some variation in the interface on examination under the microscope possibly due to the processing conditions and flow of resin throughout the glass fibre mat.

3.3 Aging conditions

The effect of water absorption on GFRP composites has been investigated. The simulated seawater (SW) conditions were prepared according to ASTM D1141-98 standards. The pH of sea water ranges from 7.9 to 8.1 and this was maintained in digital waterbath during the conditioning of the specimens. In order to investigate the long-term water exposure on the composite, the tensile specimens as previously mentioned were immersed in SW at an elevated temperature of 40°C for a period up to 60 days. A higher temperature was chosen because a 10°C rise in temperature causes a doubling of diffusion rate, so this would correspond to a four times acceleration as compared to 20°C aging (Davies *et al*. 2001). Three specimens each for durations of 7, 15, 30 and 60 days were coated with a thin layer of resin on the edges and their initial weight was recorded. Specimen weight was recorded by removing them from the waterbath, cleaning the edges and surface and finally weighing them on a balance. After the weight was recorded the specimens were again submerged in water. These specimens were further subjected to non-destructive guided wave testing followed by mechanical tests. Short-term conditioning was also performed in order to investigate the behavior of water uptake in GFRP and hybrid composite (ACNT/Epoxy/glass fibre) specimens. These flexural shaped specimens were submerged into SW and distilled water (DW) at room temperature, 25°C, and weighed at regular intervals i.e. after every 2 days till 121 days.

3.4 Characterization

3.4.1 Destructive tests

Tensile properties of the GFRP composites were determined using Zwick/Roell Z010 Universal Testing Machine at a crosshead speed of 2 mm/min. The specimens were prepared according to ASTM D3039 and aging conditions. An average value was determined for the three samples tested for each immersion time i.e., healthy (no aging), 7, 15, 30 and 60 days in seawater.

3.4.2 Water infusion behavior

In the experimental study specimens, a thin epoxy layer on all the edges was present during their initial weight measurement. The specimens were then immersed in water and their weight change was recorded on a balance with a precision of 0.1 mg. The percentage of water uptake after each period was determined by using the formula mentioned in Eq. (2)

$$M = \frac{W_w - W_D}{W_D} \tag{2}$$

where, M, W_w and W_D are the weight gain of the composites, the weight of the wet sample and weight of the dry sample, respectively.

Rate of water absorption in composites is defined by its diffusion coefficient. Diffusion coefficients (D) are calculated by measuring the weight of the samples on regular intervals to determine the percentage water uptake. In order to determine the diffusion coefficient, D, the M/M_∞ was plotted against the square root of time. The maximum mass water uptake in the experimental data for the samples has been considered as the point up to which the saturation occurs and reported as M, while the equilibrium weight gain is referred to as M_∞. The slope in the linear region was obtained through a linear regression. D was calculated by putting the value of slope in the Eq. (3) as per the methods adopted by Zafar *et al*. (2012) and Ishak *et al*. (2001)

$$D = \frac{\frac{M^2}{M_\infty} \times \pi \times h^2}{16 \times t} \tag{3}$$

where: h is the thickness of the specimen, t is the immersion time at which maximum water content occurs, M is the maximum weight gain and M_∞ is the equilibrium weight gain recorded.

Literature reveals the diffusion of water in the polymer matrix by both Fickian (Tsenoglou *et al*. 2006, Abhilash *et al*. 2011, Roy *et al*. 2000) and non-Fickian (Yang *et al*. 2008a, Jiang *et al*. 2012, 2014) behavior. However, in most of the FRP studies, Fickian behavior has been observed during the initial stages of water absorption. Literature supports the Langmuir-type model as best fit for non-Fickian diffusion in polymer matrix composites especially, glass fibre epoxy composites (Ellyin and Rohrbacher 2000, Adams and Singh 1995). A possible reason for such behavior is due to the development of cracks, delamination, debonding etc. caused due to swelling of the epoxy matrix. Hence, in the present study it is expected that GFRP composites should follow Fick's Law.

3.4.3 Non-destructive guided Lamb wave investigation

Leaky Lamb waves have been used for non-destructive monitoring of GFRP specimens at different hygrothermal aging levels. Lamb waves were generated by using ultrasonic testing (UT) system consisting of Pulser-Receiver (PR) (JSR make, Model DPR 300), immersion ultrasonic transducers and a data acquisition system (Fig. 1). Leaky Lamb waves were generated in the GFRP specimens by using pitch-catch arrangement (Fig. 1). A pair of ultrasonic immersion probes (Model No. A301S, Olympus Panametrics NDT) with a central frequency of 0.5 MHz were used for the generation of leaky Lamb waves using water as a coupling medium.

Literature reveals that Lamb waves exhibit multimode behavior in GFRP composites. It is therefore essential to obtain desired Lamb wave propagation through the specimens with corresponding strong ultrasonic signal. Choosing an optimum mode for testing depends upon the angle of the probes with the vertical (θ), distance travelled by the wave in water prior to its interaction with water (D_s) and Lamb wave propagation span through the specimen (P_s) (Fig. 1). Specific Lamb waves in GFRP composites have

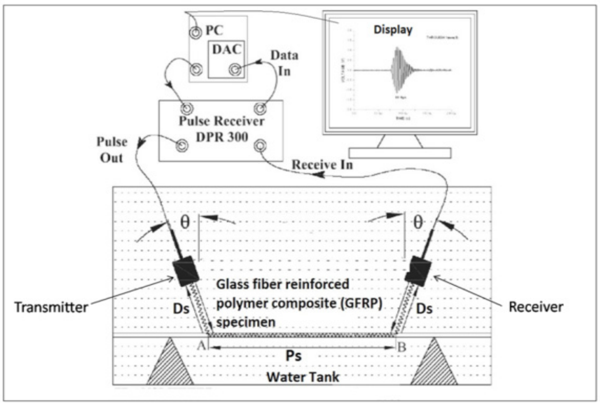


Fig. 1 Schematic arrangement of the ultrasonic test set-up

been identified in the previous study by the authors (Garg *et al*. 2016). The leaky guided wave was generated by keeping the transmitter and receiver probes at $\theta = 24°$, $t_s = 30\ \mu s$ and keeping the receiver probe at an appropriate distance of P_s = 110 mm in pitch-catch orientation.

Ultrasonic signatures are recorded initially for all the tensile hygrothermal specimens prior to their conditioning in seawater. The peak-to-peak voltage amplitude (V_p) of the healthy samples before hygrothermal aging was recorded. The effect of hygrothermal aging of the specimens was studied with comparing healthy voltage amplitudes with specimens undergoing aging.

4. Results and discussion

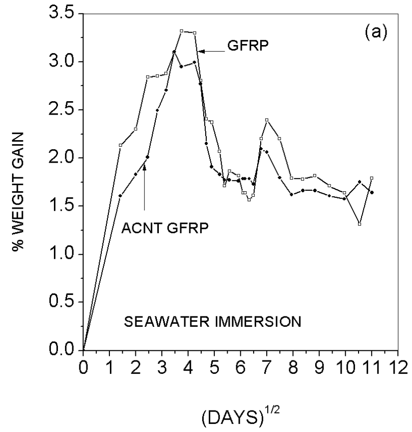
4.1 Kinetics of water absorption

In order to investigate the water absorption mechanism of pure epoxy and amino-functionalized CNT modified glass fibre composite specimens, percentage weight gain was plotted against square root of time for specimens immersed in SW and DW, respectively as shown in Fig. 2.

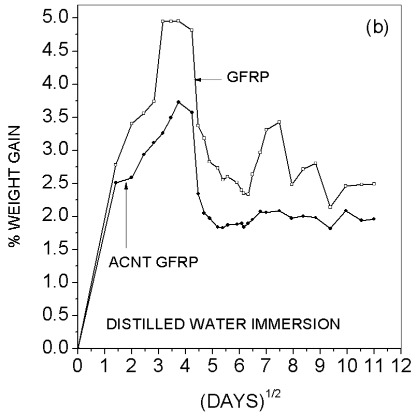
The curves obtained for both types of specimens in the simulated SW and DW follow Fickian diffusion behavior as illustrated by the initial linear slope of water uptake with the square root of time. The present study results are in agreement with those reported in literature (Adams and Singh 1995, Ellyin and Rohrbacher 2000, Mourad *et al*. 2010, Prolongo *et al*. 2012, Zafar *et al*. 2012, Zulfi *et al*. 2013, Kar *et al*. 2008, Iglesias *et al*. 2002). It can be seen from Fig. 2 that water absorption increases with the immersion time and shows a maxima for both SW and DW within 15 days. However after 15 days, the weight gained by the composites showed a decreasing trend, non-Fickian behavior, and similar behavior has previously been documented (Roy *et al*. 2000, Ellyin and Rohrbacher 2000). This is likely due to chemical interaction of glass fibres with the surrounding water molecules and possible reaction mechanisms are shown in Eqs. (4) and (5).

$$\mathrm{Si} - \mathrm{O}^- + \mathrm{H_2O} \longrightarrow \mathrm{Si}-\mathrm{OH} + \mathrm{OH}^- \quad (4)$$

$$\mathrm{Si}-\mathrm{O}-\mathrm{Si} + \mathrm{OH}^- \longrightarrow \mathrm{Si}-\mathrm{OH} + \mathrm{Si}-\mathrm{O}^- \quad (5)$$



(a)

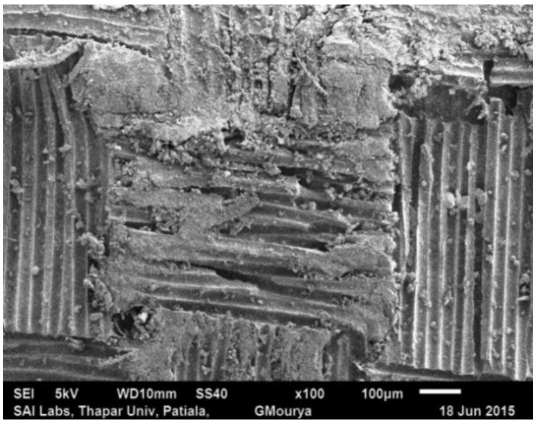


(b)

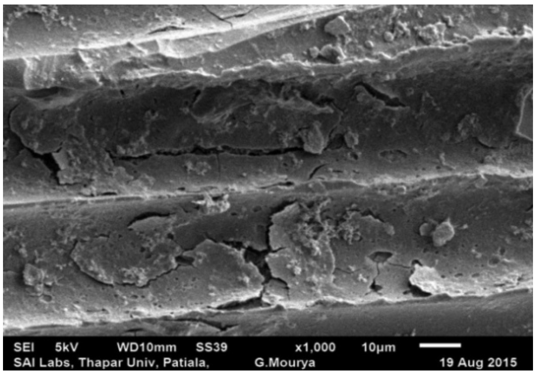
Fig. 2 (a) Diffusion curves of pure epoxy (GFRP) and ACNT epoxy glass fibre composite specimens immersed in simulated seawater; (b) Diffusion curves of pure epoxy (GFRP) and ACNT epoxy glass fibre composite specimens immersed in distilled water

The reaction mechanism reveals the presence of Si-OH and SiO_2 elements in the composites that possibly leached out from the glass fibre surface into the water during their conditioning, thus causing a decrease in weight of the samples. In case of GFRP specimens, the weight gain was linear and recorded a maximum increase of 3.32% and 4.96% after 14 days of immersion in SW and DW, respectively.

The percentage weight gain is significantly higher for DW as compared to SW. This may be due to the scale formation on the specimens immersed in SW, which restricts the capillary movement of salt molecules from the surrounding water into the composite as shown in Fig. 3. In Figs. 3(a) and (b) the surface morphology of GFRP specimens can be visualized after exposure in seawater and distilled water environment for 30 days. Fig. 3(a) depicts the scale formation on the glass fiber surface due to the diffusion of sea water moiety whereas it's missing in Fig. 3b. Moreover, it has been seen that the salt molecules are less readily absorbed than water molecules thus increasing their concentration in the water. Since, the salt concentration inside the specimen is less as compared to the



(a)



(b)

Fig. 3 (a) Microscopic analysis of GFRP specimens after exposure for 30 days in simulated seawater; (b) Microscopic analysis of GFRP specimens after exposure for 30 days in distilled water

surrounding SW, it would create an osmotic pressure which further inhibits water absorption mechanism and results in lower equilibrium water content for specimens exposed in SW as compared to those in DW (Ochoa 2006, Yang *et al.* 2008b, Zafar *et al.* 2012). The quantitative results obtained in the present study agree well with those reported in literature related to higher diffusion of water molecules as compared to SW in GFRP composites.

Additionally, the water uptake by pure epoxy GFRP composites again shows an increasing trend after 45 days of immersion in both SW and DW. The slight weight gain is clearly due to the infusion of water through the damaged fibre surface observed as pits under microscope. Another possibility is the reaction between hydrophilic cured epoxy resin and water molecules which exist as weak hydrogen bonds thus, facilitates further diffusion of water into the fibre-matrix interface (Zafar *et al.* 2012, Guadagnoa *et al.* 2009, Brondsted *et al.* 2005).

4.1.1 ACNT GFRP composites

GFRP composite reinforced with amino-functionalized carbon nanotubes (ACNT), showed a similar trend as seen in the case of GFRP conditioned specimens. However, the water uptake decreased by 12% and 25% in SW and DW, respectively vis-à-vis GFRP specimens after 14 days of immersion period (Figs. 2(a) and (b)). A recent study

Table 1 Maximum and equilibrium weight gain and diffusion coefficients for different composites during seawater immersion

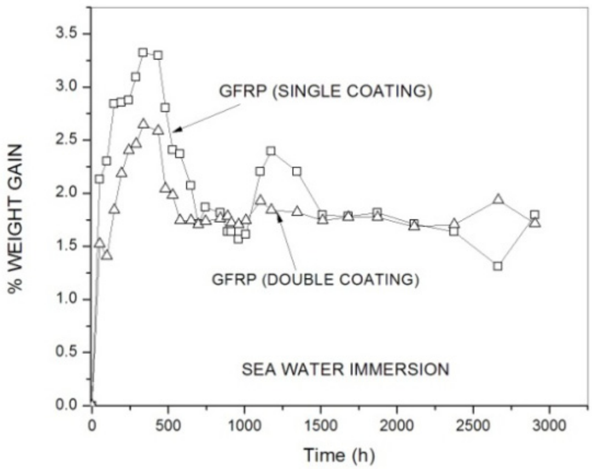
Composites under SW immersion	Maximum weight gain (%)	Equilibrium weight gain (%)	Diffusion Coefficient (*D*), mm^2/sec
GFRP – single edge coating	3.32	1.64	4.276E-07
GFRP – double edge coating	2.64	1.78	2.286E-07
ACNT GFRP – single edge coating	2.95	1.78	2.834E-07

(Prolongo *et al.* 2012) also reported a 25% drop in moisture uptake for CNT/epoxy nanocomposites on aging in an environmental chamber at 55°C and 95% relative humidity. The physical properties of CNT i.e., high-aspect ratio of CNTs has shown remarkable improvement in mechanical properties of GFRP composites (Garg *et al.* 2015). Subsequently, the presence of nanofillers in the hygrothermal GFRP specimens has also proven to be an advantage, due to their high barrier characteristics in a polymer matrix. The barrier properties of nanofillers in epoxy matrix (Guadagnoa *et al.* 2009) results in the formation of a tortuous path, which hinders the flow of water and thus, lowers the water content inside the specimen. Additionally, it also affects the rate of diffusion of water into the fibre-matrix interface. Secondly, the strong chemical bonding between the epoxy resin and amino-functionalized CNTs would also tend to hinder the excessive water sorption through the interface. For the present study, modification of GFRPs with amino-functionalized nanotubes proved to be beneficial since there was a fall of 37% in *D* values as shown in Table 1. To further reduce the diffusivity rate into the nanocomposites, the amount of CNT content in the polymer matrix can be further increased and a recent study (Prolongo *et al.* 2012) has reported this effect with respect to lower values of *D*. It is essential to control the ingress of water into the composites interface, as slower diffusion of water will result in lesser degradation of the material, would be able to sustain hygrothermal environment for longer time, shall enhance the durability of the composite, incur lower maintenance costs and higher service life thus, benefitting the naval industry at large.

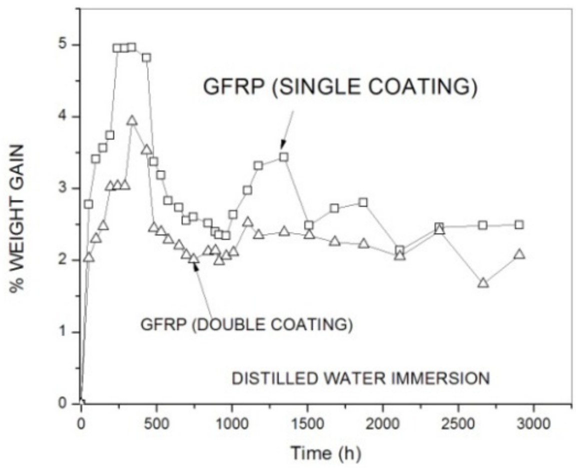
4.1.2 Effect of coating on GFRP specimens

With regard to the water diffusion an innovative idea was also experimented by double coating on all the edges of GFRP specimens, referred to as model composites in the present study. It is hypothesized that these specimens would show even further lower water sorption under both SW and DW environments. This would possibly make the GFRP composites more efficient and durable while in-service conditions. Figs. 4(a) and (b) shows the comparison of diffusion curves between single and double epoxy coating of edges of GFRP samples.

For the model composite, a linear increase in diffusion



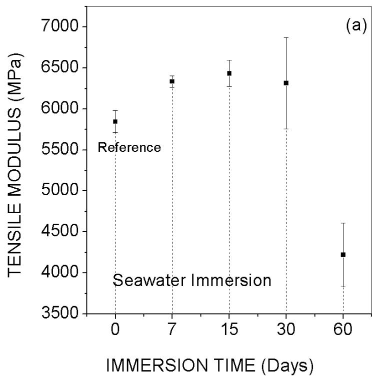
(a)



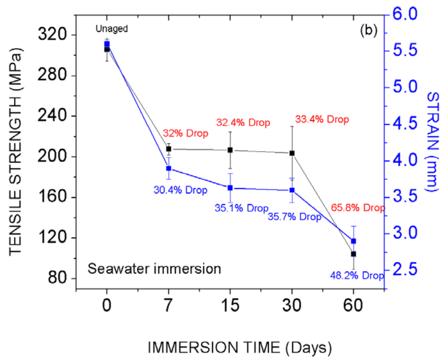
(b)

Fig. 4 (a) Diffusion curves of GFRP composite (single and double epoxy coated) specimens immersed in simulated seawater; (b) Diffusion curves of GFRP composite (single and double epoxy coated) specimens immersed in distilled water

values was observed. The maximum weight gained by model composite specimens was 2.64% and 3.93% after 14 days of immersion in SW and DW, respectively. The diffusion coefficients (D) were also calculated for these samples and compared to single coated GFRP specimens. The value of D for the double and single coated GFRP specimens were 2.286×10^{-7} mm^2/s and 4.276×10^{-7} mm^2/s, respectively as mentioned in Table 1. Thus, in case of model composite, the percent weight gain (M) and D values were lowered by 20% and 46%, respectively vis-à-vis single coated GFRP specimens. This indicates that the rate of diffusion of water into the single epoxy coating specimens is much faster due to possible openings on the edges of the composite, which is further minimized for model composite. Therefore, the ingress of water inside the composites would directly affect the materials life-span, strength and stiffness. Therefore, after analyzing the experimental results it is recommended to use double coating on the edges of the specimens for the future hygrothermal studies.



(a)



(b)

Fig. 5 (a) Tensile properties of GFRP specimens both unaged (reference) and immersed in seawater for over 60 days: modulus; (b) Tensile properties of GFRP specimens both unaged (reference) and immersed in seawater for over 60 days: strength and strain at break

4.2 Destructive tests

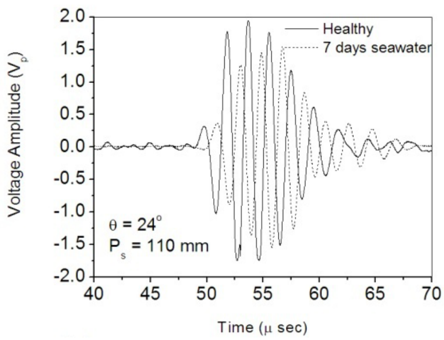
The purpose of this section is to investigate the effects of hygrothermal aging on tensile properties of the GFRP composites. The average mechanical properties of the conditioned and unconditioned samples obtained by the destructive tensile tests are shown in Figs. 5(a) and (b).

Fig. 5(a) clearly illustrates an increase in tensile modulus of the GFRP composites upto 15 days immersion and maximum decrease after 60 days of aging in seawater. The reduction in the mechanical properties of GFRP composites due to moisture, immersion in water etc. has previously been observed (Aldajah *et al*. 2009, Segovia *et al*. 2007, Brondsted *et al*. 2005, Chin *et al*. 1997). The observed deterioration was mostly seen at the fibre-matrix interface. In the present study, the drop in tensile strength and strain values showed an increasing trend as the immersion time increased (Fig. 5(b)).

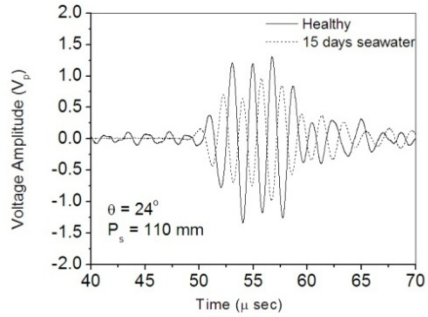
Ultimate Tensile strength (UTS) and strain were initially, after 7 days, reduced sharply by approximately 30% as compared to the reference (unaged) specimens. It can also be interpreted from Fig. 5(b) that a decreasing trend follows as immersion time increases. The drop in elongation of the conditioned specimen suggests plastici- zation effect of matrix causing material degradation (possibly breaking of bonds in the cured epoxy network) induced by the absorption of non-homogenous flow of water into the epoxy matrix, as also reported by other researchers (Zafar *et al*. 2012, Nogueira *et al*. 2001). Additionally, the significant decrease in properties indicates that there was a fast absorption mechanism between the surrounding seawater environment and surface of GFRP composite as previously determined (Figs. 2(a) and 3). However, the fall in mechanical properties after 30 days of immersion, lies within the error bars of experimental data recorded after 15 days of SW immersion, thus indicating no significant change and stabilization of properties as the samples approach towards equilibrium moisture content. After this plateau region, the GFRP specimens immersed for a prolonged aging duration, 60 days, showed a substantial drop in the mechanical properties i.e., 48% reduction in strain and 66% in the UTS (Fig. 5(b)). The reduction in UTS shows the effect of plasticization, which tends to soften the polymer when it is exposed to SW for longer span. Therefore, it is assumed that the poor interfacial bonding between the matrix and the glass fibres is the predominant factor causing the degradation of the tensile properties of GFRP specimens when immersed in simulated SW conditions for longer periods of time.

4.3 Guided wave investigations

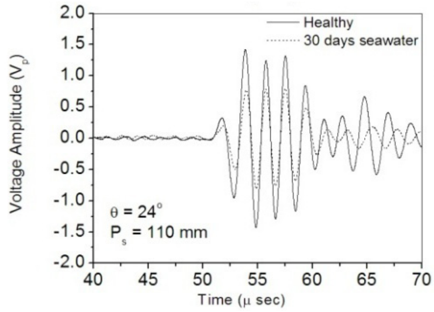
Effect of hygrothermal aging on composites has been observed in the form of effect on diffusion rate or tensile strength of the specimen. An attempt has been made in this study to relate the effect of aging on non-destructive testing parameter of guided wave signal amplitude. The study would go a long way in relating the in-situ voltage amplitudes of the signal with the deterioration due to hygrothermal aging. Specific leaky Lamb wave mode with good signal strength was recorded in healthy GFRP laminate specimens by choosing the appropriate experimental parameters such as θ, D_s *and* P_s (described previously in this article) along with other pulser receiver settings. This experimentally determined ultrasonic guided wave mode was further used for investigating the effect of SW environment on signal strength as the immersion period increases. The ultrasonic transmission signatures in Fig. 6 show the effect on signal strength with respect to their respective healthy signals (prior to the immersion of samples in SW) over varying periods of hygrothermal aging. Since each composite specimen is unique hence, a healthy signature was taken for each specimen prior to SW immersion for different periods.



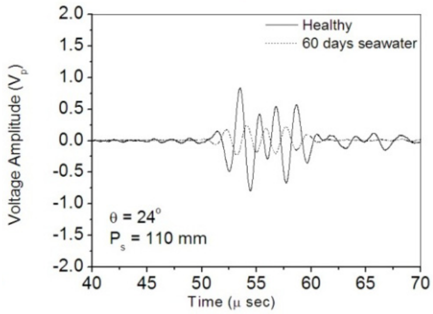
(a)



(b)



(c)



(d)

Fig. 6 (a) Ultrasonic signatures in specimens exposed to SW after 7 days of immersion; (b) Ultrasonic signatures in specimens exposed to SW after 15 days of immersion; (c) Ultrasonic signatures in specimens exposed to SW after 30 days of immersion; (d) Ultrasonic signatures in specimens exposed to SW after 60 days of immersion

The ultrasonic signatures recorded in pitch-catch mode for specimens subjected to SW for 7, 15, 30 and 60 days (Figs. 6(a)-(d)) shows a reduction in signal amplitude, V_p, as compared to their respective healthy signals. From the signatures obtained at varying ages of hygrothermal loads, it is observed that signal attenuates rapidly with increasing exposure time. During the first 7 days of exposure, signal drops less in comparison to hygrothermal loading at 30 and 60 days where the drop observed is high. This indicates towards an increase in internal imperfections because of degradation in the specimens due to water infusion. The matrix degradation could possibly be due to plasticization of the resin in the initial stages followed by swelling of the matrix which deteriorates the fibre-matrix interface. Fig. 7 represents the percentage drop in signal strength for three

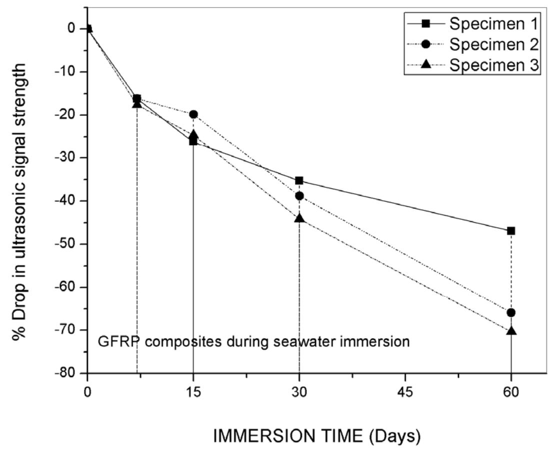


Fig. 7 Percentage drop in ultrasonic signal strength of GFRP with increasing seawater immersion time

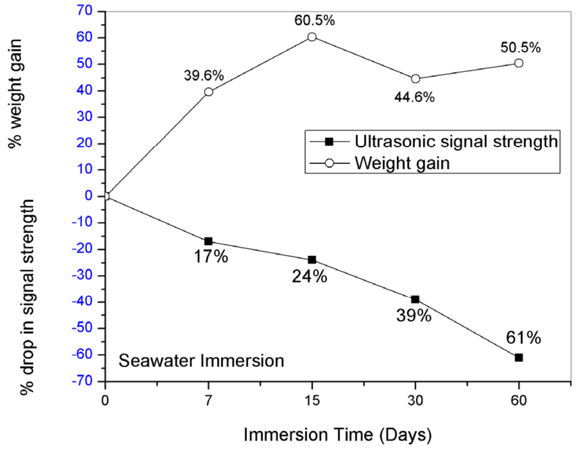


Fig. 8 Comparison of ultrasonic signal strength with % weight gain in GFRP specimens up to 60 days of immersion

different specimens conditioned for varying periods of immersion of 7, 15, 30 and 60 days.

The results in Fig. 7 clearly indicate an increasing trend of percentage drop in signal strength as the duration of specimens in the SW increased. The trend is found to be similar for all three different conditioned specimens with varying immersion periods, thus illustrating reproducibility of the ultrasonic set-up.

Furthermore, a comparison of the effect of hygrothermal aging on ultrasonic signal drop and percentage weight gain is attempted in Fig. 8. The weight gain by GFRP composite increases by more than 60% in the first 15 days likely due to capillary action, but as the water inside the matrix tends to reach an equilibrium state the weight gain dips slightly (after 30 days of immersion). However, the diffusion of water into the fibre-matrix interface results in further sorption of water molecules and thus resulting in weight gain as shown in Fig. 8. On the contrary, the percentage drop in ultrasonic signal strength is inversely proportional to the weight gain and immersion time i.e. signal strength drops when more amount of water is infused into the composites interface which itself is a function of time.

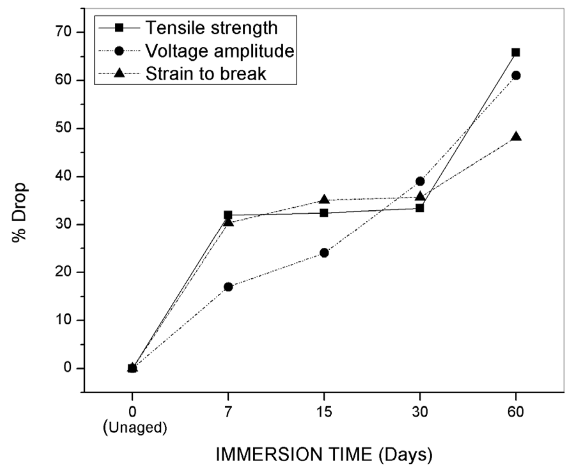


Fig. 9 Comparison of tensile strength, strain and V_p with increasing SW immersion

A possible explanation of this behavior is that: the weight gain by GFRP composites involves several concepts such as capillary action, diffusion through surface or broken edges, osmotic pressure. This implies that the water diffusion is not a controlled process. However, the absorbed water as it enters the system tends to penetrate through the matrix into the fibers via the interface. As the pressure inside increases it results in more deterioration of the composite and drop in strength. Therefore, when the ultrasonic transducers are placed over the aged specimen due to higher energy absorption by the specimen, less energy is reflected back which is reported as higher drop in ultrasonic signal strength. In brief, as the damage to fiber-matrix increases with moisture diffusion there is an increase in signal attenuation and drop in signal amplitude.

Therefore, it may be concluded that non destructive ultrasonic tests can provide an adequate means for evaluating the effects of hygrothermal environment on prolong exposure of the fibre reinforced polymer epoxy composites.

Also, the effect of drop of signal in terms of signal amplitudes (V_p) has been correlated with the drop in tensile strength when subjected to hygrothermal environment for different periods (Fig. 9).

During the initial 7 days of immersion, the tensile strength reduced by 32% which further dropped to 66% after 60 days. Similar trend has been seen in strain to break which reduces to 50% after 60 days of immersion time. Percentage drop in transmission signal strength is also observed to be 17% after 7 days that increased to 61% after 60 days of exposure in SW, as in tensile strength. It is interesting that the loss in amplitude correlates with decreasing tensile strength & strain to break quantitatively. The possible reasons for decrease in tensile strength and strain to break seem to be the continuous degradation caused by the plasticization of the matrix and weak interfacial bonding between the fibre and the matrix. Also, the decrease in peak to peak voltage amplitude is likely due to loss of adhesion or de-bonding at the fibre-matrix interface, moisture absorption, matrix swelling and chemical attack on matrix and fibre which results in greater attenuation of signal.

Hence, drop in ultrasonic signal strength can be used to non-destructively relate to the loss in mechanical properties of the GFRP laminates under hygrothermal loading. Non-destructive ultrasonic measurements can serve as an indicator of corresponding loss in tensile strength with aging and will facilitate non-destructive evaluation of GFRP laminates under SW immersion.

5. Conclusions

The aim of the present study was to quantify the influence of water uptake on the diffusion behavior, mechanical properties and non-destructive ultrasonic signal strength due to material degradation as a result of hygrothermal aging in the GFRP composites. The specimens of GFRP, hybrid and model composites submerged in seawater or distilled water conformed to Fick's law during the initial aging period. Interestingly, maximum water content of hybrid (-12%) and double coated (-20%) GFRP composites were significantly lower than single edge coated GFRP composites. In addition, the percent weight gain values are also larger for specimens immersed in DW water than in the SW. Only the effect of ACNT versus GFRP has been observed on water infusion, neither mechanical properties nor non-destructive results have been carried out.

Mechanical performance of the GFRP composites confirms that mechanical properties in general tend to decrease as water infusion increases. A reduction of 48% in strain and 66% in the tensile strength were observed after a period of 60 days immersion in SW conditions. The overall degradation in the properties are mainly due to plasticization effect, swelling of the matrix and loss of good interfacial bonding between the glass fibres and the matrix when conditioned for long time.

An attempt has been made to investigate the effect of hygrothermal aging on ultrasonic voltage amplitude signals. The experimental results clearly show that ultrasonic voltage amplitude drop correlates well with fall in tensile strength with increasing time of immersion. These findings can go a long way in non-destructive evaluation of GFRP laminates subjected to hygrothermal loading. The proposed technique can serve as an effective method to diagnose the service life of marine vessels while they are in operational mode. The modification of epoxy matrix with different nanotube contents and their corresponding effect on mechanical properties and ultrasonic signal strength during hygrothermal loading conditions shall be reported in future.

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