The Effect of Long Term Hygrothermal Aging by Immersion on Carbon/Epoxy Composites Exposed to the Heat Sources for Naval and Marine Applications

SoonKook Hong

1Department of Weapon system engineering, Republic of Korea Naval Academy, Korea.

Abstract. Fiber-Reinforced Polymer (FRP) composites have many advantages over conventional materials in terms of high strength-to-weight and stiffness-to-weight ratios, design flexibility and enhanced service life. Due to these advantages, FRP composites are used in many different fields such as Construction, Electric/power generation, Marine, Corrosion/infrastructure, transportation and so on. Most researches of FRP composites were focused on the applications used in ground field. However, in Navy, marine composite materials are increasingly being used in diverse applications: Submarine, Autonomous Underwater vehicle, Unmanned Surface vehicle and Payloads in Naval vessel. It is known that polymer composites are very sensitive and are friendly to water or moisture in any forms. Moisture in polymer composites often causes degradation by swelling and hydrolysis. Especially, if polymer composites will be immersed in water and seawater, faster degradation can be caused by water uptake than any other moisture environments. While general investigations regarding water uptake are concentrated on the composite materials cured in ambient temperature, the immersion effects of polymer composites exposed to elevated temperatures were studied because underwater applications of composite materials can be exposed to the various heat sources. For example, fires on naval vessels and underwater vehicles can be started by any number of causes such as electrical faults and ignition of flammable gases or liquids. Accordingly, immersion effects must be studied on marine composite materials exposed to various temperatures in order to evaluate service life in an underwater environment. This study investigated the water uptake, diffusion coefficient, and Short beam shear (SBS) for Interlaminar Shear Strength(ILSS), delamination between fiber and resin using test specimens exposed to the elevated temperatures. The specimens were immersed for a definite period of time (~one and a half years) in seawater and deionized water (DI water) to compare both degradation mechanisms.

1. Introduction

1.1. Background

FRP composite materials are being used in a variety of underwater applications based on their stiffness, strength, reduced weight, and corrosion-free capabilities. Until recently, the use of FRP composite materials for military applications was limited to aerospace and air force for high-performance applications. Currently, applications of FRP composite materials in the Navy are widely broaden into sonar bow domes, windows, hulls and so on. Moreover, there is a resurgence of interest
for the use of composites in military applications including naval vessels, army combat vehicles, underwater robot fish and unmanned underwater vehicles. Beside inherent advantages of FRP composites such as high strength-to-weight and stiffness-to-weight ratios, composites materials using the carbon fiber as a reinforcement are particularly useful because they exhibit better mechanical properties than other FRP composites as well as provide the ability for electromagnetic shielding for stealth purpose. The all-composite naval ships are currently operating to perform multifunctional operation with the benefits for FRP composite materials. In early, use of composite materials was constrained to the construction of small patrol boats and landing craft in displacement due to relatively poor fabrication quality and low stiffness of the hulls. However, as fabrication technique and mechanical properties were improved, FRP composite materials can be applied to larger patrol boat, minecountermeasure vessels, and corvettes.

Because the usage of FRP composite materials in underwater environments enable various applications to have good benefits in terms of stealth function on SONAR and RADAR detection, this research is focused on immersion effects of the underwater applications: submarine, underwater robot fish and unmanned underwater vehicle. These applications in immersion can cause the severe degradation compared to exposure to the moisture and moisture-immersion mixed environments. Polymer such as an epoxy can be modified into superhydrophobic surface by nano pattern. The superhydrophobic surface of the polymer can bring out the lower water uptake than any other matrices. Carbon mentioned above has good stealth function by superior electric conductivity. For this reason, carbon/epoxy composite materials were investigated to evaluate the mechanical property, water uptake, and diffusion coefficient after immersing in seawater and deionized water for one and a half years.

1.2. Seawater Effect

There are a lot of researches related to carbon- and glass-fiber composites immersed in saline conditions. In this section, the effects exposed to various environments will be introduced from summarizing of many studies toward tensile strength and modulus.

T.S Grant et al.[1] investigated the effect of immersion in seawater on transverse tensile properties of three graphite/epoxy composite materials. The transverse tensile strength was found to be reduced by 17% in one of the systems with essentially no change in the other two systems studied. The 17% decrease in transverse tensile strength was associated with degradation of the interfacial strength. Also they found that little difference was found in the behavior of composite immersed in distilled water and in seawater at ambient pressure or seawater at 20.7 MPa pressure. Leif A. Carlsson et al.[2] accomplished tests using carbon/bismaleimide-epoxy, E-glass/epoxy, E-glass/polyphenylsulfide and carbon-epoxy for immersion more than 4000 hrs in distilled water and natural seawater at room temperature and 35℃. Transverse modulus, $E_2$ was not significantly changed after water absorption except for E-glass/polyphenylsulfide that lost about 60% of its dry modulus, despite of its low water absorption. The substantial reduction of $E_2$ was attributed to extensive fiber/matrix debonding induced by water. Also, all composites experienced large reduction in transverse tensile strength due to water absorption. The maximum reduction took placed in E-glass/polyphenylsulfide with 85% decrease of its dry strength. An E-glass/carbon/epoxy interlayer hybrid composite has been aged by immersion in simulated seawater for varying lengths of time and then tested in transverse tension by C.A Wood et al.[3].

The flexural test measures the force required to bend a beam under three point or four point loading conditions. The data is often used to select materials for parts that will support loads without flexing. Flexural modulus is used as an indication of a material’s stiffness when flexed. E.P. Gellert and D.M. Turley[4] performed flexural test using the polyester, phenolic and vinylester glass-fiber reinforced polymer materials immersed in 30℃ seawater either unloaded or loaded at 20% of the maximum strain at flexural failure ($0.2\varepsilon_f$) to examine the effects of loading on flexural property. Flexural strength continued to degrade for the unloaded polyester and vinylester GPRs as water uptake continued toward saturation, where strength losses between 15% and 21% occurred. The unloaded phenolic lost 25% of initial strength at saturation. For ageing, loading affected the strength of only
phenolic GRP with strength loss advancing from 25 to 36% loss from the initial strength. Wayne C. Tucker and Richard Brown[5] generated all data on the vinlyester/graphite composite material immersed in natural filtered seawater in tubs in the laboratory at 1 atmosphere of pressure and in natural filtered seawater pressurized to a depth of 2000 feet of seawater. The flexural strength and stiffness of the composite material were decreased by the high pressure exposure. In contrast, atmospheric seawater exposure did not produce any strength decrease. Both the enhanced moisture uptake and the strength decrease at high pressure exposure were thought to be due to mechanical damage induced by the increased pressure. In 5% and 10% salt solution, the flexural properties (strength and modulus) of pultruded glass-fiber reinforced vinylester matrix composite coupons were measured for the 90\textdegree specimens as-received and after ageing by K.Liao et al.[6].

2. Experimental Setup

2.1. Material specification

The carbon/epoxy composites were comprised of Tyfo S Epoxy and Tyfo SCH-41 reinforcing fabric supplied by FYFE Co. Composite panels comprising of two layers as shown in Figure 1 were fabricated using a manual wet layup process with cure under ambient conditions. Tests were conducted after a minimum of 7 days cure. The fiber content was approximately 60% by weight. The fabric reinforcement was consisted of a primarily unidirectional fabric of 644 g/m\textsuperscript{2} areal weight.

The fibers had a nominal tensile strength, modulus and density of 3.79 GPa, 230 GPa, 1.74 g/cm\textsuperscript{3}, respectively. The resin system was a two-component epoxy with a viscosity of 600-700 cps at 25\degree C. After curing and then after 72 hours of post cure at 60\degree C, the glass transition temperature, tensile strength, modulus and elongation are specified as 82\degree C, 72.4 MPa, 3.18 GPa, and 5.0%, respectively.

All tests were performed using unidirectional 2 layer panels. Because composite panels were fabricated in the field, they were uniformly preconditioned at 23\degree C and 30% relative humidity (RH), in a humidity chamber to set a uniform baseline.

![Figure 1 Unidirectional Panel of Carbon/Epoxy Composites](image)

2.2. Test Conditions

After cutting composites panels with a tile saw, all specimens for mechanical properties and immersion testings were stored in a humidity chamber (Figure 2(a)) to ensure an initial condition for 2 weeks. Carbon/epoxy composite specimens were exposed thermally to ambient, 66, 93, 121, 149, 177, 204, 232, and 260\degree C under ageing times of 1, 2, 4, 8, 16, 24, 48, and 72 hrs. Test specimens were kept in an oven (Figure 2(b)) until they reached a set time and temperature, and then they were removed to ambient conditions for testing.

After the simulation of exposure to high temperatures, accurate evaluations are necessary to assess whether composite materials degraded by high temperatures can operate at the required level of functionality in seawater. Therefore, the specimens aged thermally at each temperatures were immersed in seawater under ambient temperature for up to 72 weeks. Simultaneously, test specimens were immersed in deionized (DI) water in the same conditions to provide a base-line comparison.
Seawater from La Jolla shores was used and was periodically changed in the water bath. Figure 3 shows the specimens for water uptake tests and SBS tests.

Moisture uptake tests were performed using gravimetric analysis. Test specimens were taken out from water bath to weigh the mass, periodically. In the case of short beam shear tests, tests were conducted after immersion in seawater and DI water under specified conditions (exposure to Ambient, 66, 93, 121, 149, 177, 204, 260°C for 8 hr and exposure to 232°C for 1, 2, 4, 8, 16, 24, 48 and 72 hr). Water uptake and SBS test are summarized in Table 1.

| Test          | Specimens No                                      | Size (mm)     |
|---------------|---------------------------------------------------|---------------|
| Water Uptake  | Seawater (73) + DI water (73) = 143               | 25.4×25.4×3   |
| SBS           | 16(temp)×8(ageing)×2(case)×5(Set) = 1,280         | 18×12.7×3     |

2.3. Test Methodology

Test methods available for the determination of interlaminar shear include short beam shear, four-point shear, double notch shear and v-notch beam shear. The short beam shear test was applied to determine the interlaminar shear strength in this research.

The short beam shear tests were accomplished following ASTM D2344[7] using specimens which were cut to dimension of 6 mm in width and 18 mm in length, using test fixture, and an Instron 5583 equipment (Figure 4). According to ASTM, the following geometries are recommended:

- Specimen length = thickness × 6
- Specimen width = thickness × 2

The test span in this case was 14 mm. A cross head speed of 1 mm/min was applied for all tests and the load was applied until failure of the specimens was attained.

For measuring the moisture uptake of the specimens immersed in sea water and de-ionized (DI) water, all samples exposed to elevated temperatures were removed from each immersion environment and kept at room temperature until measuring. All unidirectional specimens were cut to dimensions of 25.4 mm by 25.4 mm for gravimetric measurement. Wet samples from immersion environments were wiped for dryness with a paper towel prior to weighing. Weight measurements were undertaken using a Sartorius Analytical Balance with a resolution of $10^{-5}$ grams. Weights were recorded when the LCD
display of the balance kept a stable value for 5 seconds to ensure the consistency in test method. After measurement of weight, all samples were returned to the original environment for further exposure.

![Image](image_url)

Figure. 4 Short Beam Shear Test Fixture and Instron 5583

3. Results

3.1. Diffusion

In general definition, diffusion is the movement of molecules from a region of high concentration to a region of low concentration by means of random molecular motion. Fick's laws provide a theoretical basis for the diffusion of a fluid into a distinct sorbing medium from a higher concentration to a lower concentration. Also, Fick's second law provides a theory for non-steady-state diffusion. Fick's law refer to that the mass of absorbed water increases linearly with the square root of time and then gradually slows until an equilibrium plateau or saturation is reached. The rate of diffusion and the attainment of an equilibrium content can be affected by materials characteristics, processing factor, environmental condition, and geometry. Since Fickian diffusion assumes no chemical reaction between the diffusion solution and composite materials, composites technically do not follow Fick's law. However, in a number of researches, the diffusion of moisture in fiber reinforced composites and crosslinking resin has been shown Fickian behavior[8,9]. Fickian diffusion has following features.

- Linear in the initial stage and the linear region until at least $M_t/M_m=0.6$
  where:
  - $M_t$ = the moisture absorbed by the composites at time $t$
  - $M_m$ = the maximum moisture content absorbed by the composite
- The decrease of the rate of diffusion until an equilibrium of moisture content
- Diffusion coefficient as a function of temperature

$$D = D_0 \exp \left( \frac{-E_a}{RT} \right)$$

where:
- $D$ = diffusion coefficient
- $D_0$ = a constant
- $E_a$ = activation energy
- $R$ = the universal gas constant

3.2. Water Uptake

Glass fiber laminates have low Young's modulus, which makes it difficult to build ultralight marine structures including naval vessels with adequate stiffness. Therefore, marine composite structures requiring high stiffness are often made of carbon fiber composite. However, a little of published papers are available on the effect of long-term seawater immersion on carbon fiber composite[10]. In addition, atmospheric ageing at high humidity has been reported to cause water uptake similar to that from immersion for epoxy laminates[11], while Gutierrez reported that ageing in sea air was as severe as in seawater for a range of marine composite. Especially, this study is focused on the effect of long-term seawater immersion on carbon fiber composites exposed to elevated temperatures for up to 72 hrs of ageing time using comparison with the effect of immersion in deionized water.
Figure 5 shows the maximum weight gain (%) on specimens immersed in deionized water and seawater at atmospheric temperature for 72 weeks. There is a little difference in the maximum weight gain. In particular, the maximum weight gain of all specimens which ageing time is less than 8 hrs in entire exposure temperatures was almost identical. All data of the maximum weight gain in these conditions existed between 1.2% and 2.8%. In both immersion conditions, the maximum weight gains were slightly increased in proportion to ageing time and exposure temperature. The difference among the maximum weight gains in lower (ambient, 66 and 93°C) and higher (121, 149, 177, 204, 232°C) exposure temperatures existed on specimens immersed in deionized water. However, this gap was not shown on specimens immersed in seawater. This means that the unreacted chemical species in partially cured composite were released more rapidly into deionized water. In addition, it should be pointed out that the maximum weight gains in seawater were slightly lower than those in deionized water in overall environmental conditions. Apparently, the sorption of salts into the epoxy by diffusion and along fiber-matrix interface debonds and bulk material cracks by wicking can be resulted in the higher mass retention in seawater while the organic species leached from the specimens were separated from the salty residue by solvent extraction. The organic species were even found visually in seawater container. Consequently, mass loss by leaching of organic species than mass uptake by sorption of salts largely contributed to lower maximum weight gain in seawater compared to the values of deionized water.

Figure 6 shows comparison of diffusion coefficients on specimens immersed in deionized water and seawater for 72 weeks. Overall diffusion coefficients calculated for deionized water immersion were higher than those for seawater immersion in all environmental conditions. Diffusion coefficients in deionized water were widely distributed with increase of ageing time and exposure temperatures. In other words, the degree of cure on specimens was strongly dependent on the diffusion coefficient. On the other hand, the variation of diffusion coefficients in immersion of seawater was less than that in deionized water. Lower diffusion coefficient in seawater seems to be attributed to mass loss by leaching out of organic species.

![Figure 5](Image)

**Figure. 5** The maximum weight gain (%) on specimens immersed in (a) DI water and (b) seawater for 72 weeks

![Figure 6](Image)
3.3. Short Beam Shear Testing

Comparison of short beam shear strength on specimens immersed in deionized water for 72 weeks after exposure to elevated temperatures in 8 hrs of ageing time are presented in Figure 7. Except for the specimens immersed in deionized water after exposure to 260°C for 8 hrs, all specimens showed similar characterizations which had initially decrease (~ 16 weeks), asymptotic trend or slightly increase (16 ~ 48 weeks) and rapidly decrease after 48 weeks in terms of short beam shear strengths. Initially rapid drop and asymptotic trend were corresponded to Fick's law which the mass of absorbed water increases linearly with the square root of time and then gradually slows until equilibrium. The rate of decrease in short beam shear strengths after immersion from original state to 72 weeks in deionized water was 23.0, 28.1, 35.7, 38.7, 36.0, 35.2, 35.9 and 30.7% on specimens exposed to ambient, 66, 93, 121, 149, 177, 204, 232 and 260°C, respectively. Post-cured specimens in intermediate exposure temperatures (121, 149, 177, 204, 232°C) had higher rate of decrease in short beam shear strengths compared to other conditions since specimens post-cured from the increase of ageing time and exposure temperature showed the rapid saturation and the higher maximum weight gain compared to un-cured specimens. Contrary to specimens in other conditions, specimens exposed to 260°C for 8 hrs showed initially a little of increase in short beam shear strengths. However, after 48 weeks in immersion time, rapid decrease of short beam shear strengths occurred by delamination between 2 layers due to moisture uptake.

From many researches, it is well known that epoxy has the superior durability and the lowest diffusion coefficient compared to vinyl ester, polyester and phenolic resins in water environmental conditions. In addition, it is known that glass fibers chemically react with water while carbon fibers do not absorb moisture and are resistant to any corrosive effects of water. Therefore, intrinsic properties of epoxy and carbon fiber against water resulted in a slight decrease or asymptotic trend in terms of short beam shear strengths until 48 weeks in immersion period. However, it appears that catastrophic drop of short beam shear strengths after 48 weeks of immersion was derived from irreversible degradations such as hydrolysis, microcracking, microvoids and epoxy relaxation.

To compare results of short beam shear test immersed in deionized water, short beam shear tests were conducted using specimens immersed in seawater under same environmental conditions. Comparison of short beam shear strength on specimens immersed in seawater for 72 weeks after exposure to elevated temperatures in 8 hrs of ageing time are shown in Figure 8. Although a little difference between specimens immersed in deionized water and seawater existed with regard to diffusion coefficient and the maximum water uptake, the results of short beam shear strengths on specimens immersed in seawater were in good agreement with the data immersed in deionized water as shown in Figure 7 and Figure 8. In addition, it seems that salt or salinity involving in seawater did not influence deterioration and degradation in short beam shear property.

The rate of decrease in short beam shear strengths after immersion from original state to 72 weeks in seawater was 22.7, 25.2, 32.8, 36.3, 40.7, 33.4, 31.0, 35.3 and 22.7% on specimens exposed to ambient, 66, 93, 121, 149, 177, 204, 232 and 260°C, respectively. These rates of decrease in short beam shear strengths were slightly lower than the values after immersion in deionized water. However, the difference of rate of decrease was negligible.
Figure 7. Short Beam Shear Strengths on specimens immersed in DI water for 72 weeks after exposure to elevated temperatures in 8 hrs of ageing time.

Figure 8. Short Beam Shear Strengths on specimens immersed in seawater for 72 weeks after exposure to elevated temperatures in 8 hrs of ageing time.

4. Conclusion
Experimental results can be summarized as follows,
- The results of the gravimetric measurements on specimens immersed in deionized water and seawater showed a Fickian response in all conditions.
- Specimens post-cured from the increase of ageing time and exposure temperature showed the rapid saturation and the higher maximum weight gain compared to un-cured specimens.
- The partially cured composite could be expected to have a greater concentration of unreacted chemical species with the epoxy resin and it appears that these species were released more rapidly into water resulting in a slower net mass gain.
- Mass loss by leaching of organic species than mass uptake by sorption of salts largely contributed to lower maximum weight gain in seawater compared to the values of deionized water.
- Overall diffusion coefficients calculated for deionized water immersion were higher than those for seawater immersion in all environmental conditions. Diffusion coefficients in deionized water were widely distributed with increase of ageing time and exposure temperatures.

5. Acknowledgments
This research is part of the result carried out by support of LIG nex1.

References
[1] Grant, T.S. and W.L. Bradley, In-Situ Observations in SEM of Degradation of Graphite/Epoxy Composite Materials due to Seawater Immersion. Journal of Composite Materials, 1995. 29(7): p. 852-867.
[2] Leif A. Carlsson, F.P., Influence of sea water on transverse tensile properties of PMC, NIST Special Publication 887. National Institute of Standards and Technology, 1995: p. 203-221.
[3] Wood, C.A. and W.L. Bradley, Determination of the effect of seawater on the interfacial strength of an interlayer E-glass/graphite/epoxy composite by in situ observation of transverse cracking in an environmental SEM. Composites Science and Technology, 1997. 57(8): p. 1033-1043.
[4] Gellert, E.P. and D.M. Turley, Seawater immersion ageing of glass-fibre reinforced polymer laminates for marine applications. Composites Part A: Applied Science and Manufacturing, 1999. 30(11): p. 1259-1265.
[5] Tucker, W.C. and R. Brown, Moisture Absorption of Graphite/Polymer Composites Under 2000 Feet of Seawater. Journal of Composite Materials, 1989. 23(8): p. 787-797.
[6] Liao, K., C.R. Schultheisz, and D.L. Hunston, Effects of environmental aging on the properties of pultruded GFRP. Composites Part B: Engineering, 1999. 30(5): p. 485-493.
[7] ASTM D2344/D2344M-00, Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates. American Society of Testing Materials, 2006. Vol.15.03.

[8] Tsotsis, T.K. and S.M. Lee, Long-Term Durability of Carbon and Glass-Epoxy Composite Materials in Wet Environments. Journal of Reinforced Plastics and Composites, 1997. 16(17): p. 1609-1621.

[9] Liao, K., Schultesiz, C. R., Hunston, D. L., Brinson, L. C, Long-Term Durability of Fiber-Reinforced Polymer-Matrix Composite Materials for Infrastructure Applications: A Review. Journal of Advanced materials, 1998. 30, No.4: p. 3-40.

[10] Mouritz, A.P., A. Kootsookos, and G. Mathys, Stability of polyester- and vinyl ester-based composites in seawater. Journal of Materials Science, 2004. 39(19): p. 6073-6077.

[11] Bonniau, P. and A.R. Bunsell, A Comparative Study of Water Absorption Theories Applied to Glass Epoxy Composites. Journal of Composite Materials, 1981. 15(3): p. 272-293.