COMPARISON OF SEAWATER EFFECTS ON MECHANICAL AND VISCOELASTIC PROPERTIES OF EPOXY COMPOSITES WITH GLASS, CARBON AND THEIR HYBRID FABRIC REINFORCEMENTS

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ABSTRACT

Increasing demand for high performance materials with enhanced durability in marine environments has led to the developments of hybrid polymer composites consisting of different fibers as epoxy reinforcements. The goal is to harness various properties of individual constituents of the composites. In the current study, fiber reinforced polymer composite (FRPC) laminates were fabricated using SC-780 epoxy resin reinforced with E-glass (G), carbon (C) and hybrid of carbon/E-glass fabrics, and conditioned in seawater at room temperature. Hybridized fibers consisted of profiles 1: (2G-9C-2G); 2: (G-C-G - alternating sheets), and 3: (5C-3G-5C). Properties of these fibers were targeted to utilize their inherent features while reducing overall cost and absorption characteristics of their composites leading to enhanced durability. Unconditioned hybrid composites showed average enhancements of 25, 47 and 103% in flexural strength and 19, 58 and 94% in flexural modulus for Profiles 1, 2 and 3 respectively when compared to E-glass composites. Similarly, viscoelastic characterization through dynamic mechanical analysis showed -10, 8 and 21 % enhancements in storage moduli at 30°C for profile 1, 2 and 3 respectively compared to E-glass composites. When immersed in sea water, E-glass/epoxy composites and profile 3 hybrid composites had highest weight gain while the profile-1 hybrid had the least absorption. While the flexural strength decreased for all composites, there was slight increase in the flexural modulus. Storage modulus decreased for carbon/epoxy and profile 2 composites steadily. On the other hand it increased initially for other composites before reversing the trend. Glass transition temperature ($T_g$) decreased for all composites upon exposure to sea water.

1 INTRODUCTION

In recent years, there has been substantial increase in the use of fiber reinforced polymer (FRP) composites in various applications due to numerous advantages they have over traditional engineering materials [1-4]. However, polymers are viscoelastic in nature, making FRP sensitive to temperature and loading conditions. As a result, significant research efforts have been focused on improving properties of polymers to overcome some of their drawbacks. This has resulted in enhanced resistance to elevated temperatures, environmental attacks from majority of solvents and improved overall load bearing capabilities including durability during service. These enhancements have been achieved by employing techniques such as the use of different reinforcements and sometimes through polymer blending. Despite desirable properties of epoxy FRPC such as their resistance to chemical and other environmental attacks, they are sensitive to temperature and also prone to moisture absorption due to their viscoelastic nature [4-6]. Absorbed seawater due to prolonged exposure of matrix used in FRPC causes changes in the chemical composition and structure of the polymer leading to poor performance [7]. Moisture aging induces physico-chemical changes in FRPC, including swelling of the matrix by hydrolysis, and plasticization affecting dimensional stability and interfacial bonding between fibers and matrix in FRP. Plasticization relates to permanent changes in the polymer structure, and matrix dominated properties such as viscoelastic are significantly impacted particularly lowering glass transition temperature. Other properties including fracture toughness, stiffness and strength derived from fiber-matrix interfacial bonding are also deteriorated leading to poor load bearing capability.
Thus exposure of FRPC to prolonged water conditioning leads to weakened interfacial bonding strength and interlaminar shear strength in FRPC [8]. Factors such as fiber type, weave pattern and orientation, fiber volume fractions, matrix, degree of cross-linking, presence of voids and micro cracks, have all been showed to also affect rate of property deterioration in FRPC [7-9]. Alkali leaching at the interface between glass fiber and matrix has also been reported as major cause in degradation of glass FRP during moisture exposure, while carbon fiber reinforcement does not exhibit such reactions [10]. Additionally, chemical affinity of matrix to moisture, temperature and FRPC thickness have also shown to influence the rate of seawater diffusion leading to increased deterioration in material properties [11]. Diffusion of moisture into polymers is generally enhanced by density domains and segmental chain mobility of polymer due to presence of gaps between the molecules caused by irregular molecular packing, otherwise known as holes [4]. Mechanism of mass transportation of solvents in FRP composites materials can be described as two-step process, which depends on several factors including degree of cross-linking, temperature, fiber type and concentration of the solvent [7, 9].

Several attempts have been reported in literature to minimized impacts of moisture on properties of FRPC by using nanoparticles as matrix reinforcement to slow down the moisture ingress [12-14]. Others have also employed the use of hybrid fiber reinforced polymer composites for various applications [3,5]. In many of these FRPs, fiber lay-up and the interlocking interactions between constituents minimize environmental attacks, resulting in enhanced durability [1, 6, 8]. Synergy between service environments and loading type are also critical factors to FRPC survivability during service, and therefore requires serious attention during designing. Enhanced barrier properties of polymer composites are particularly of great importance to marine applications where most structures are exposed to prolonged seawater conditioning [15]. Other targets also include enhanced durability through minimization or delayed detrimental effects of service and environmental factors over time [8, 12].

In the current study, influence of hybridization on absorption characteristics of seawater and its effect on durability in terms of viscoelastic and mechanical properties of FRPC over duration of 120 days of exposure was investigated. FRPC laminates were fabricated using SC-780 epoxy resin reinforced with E-glass, carbon and hybrid of carbon/E-glass consisting of profiles 1: (2G-9C-2G); 2: (G-C-G - alternating sheets), and 3: (5C-3G-5C). Moisture absorption characteristics of all samples were studied using measurements in weight gain by each sample, while corresponding degradation in mechanical properties were characterized using three-point bending flexure tests as function of duration of seawater exposure time. Influence of hybridization and seawater on viscoelastic properties were studied using dynamic mechanical analysis (DMA), and results characterized as function of exposed duration.

2. EXPERIMENTATION

2.1. Materials

Materials used in this study are commercially available two part diglycidyl ether of bisphenol A (DGEBA) based SC-780 epoxy resin (Part A) with proprietary cycloaliphatic amine hardener (Part B) as matrix. The SC-780 epoxy resin was acquired from Applied Poleramic Inc. Stoichiometric mixing ratio of 100 part A to 22 part B by mass was used as recommended by the supplier. Eight harness satin weaved carbon fiber purchased from US composites, and E-glass fiber purchased from Fiberglassite (Kingsville, Maryland) were used as reinforcements.

2.2. Composite Fabrication

Pre-calculated amounts of SC-780 part A and B were mechanically mixed in a beaker at about 600rpm for approximately 5 minutes followed by desiccation. Fibers mats were cut and desiccated epoxy resin applied to completely wet each layer of fiber mat layup process. Wet fiber mats were arranged sequentially by hand and composite laminate fabricated using compression molding technique using Wabash Hot press. Targeted thickness of each FRPC sample was 5±0.5mm, requiring different number of layers for each type of fabric and density including hybrid based. Fabricated FRPC samples were E-glass, carbon and carbon/E-glass hybridized composites indicated as profiles 1, 2 and 3, with fiber arrangements previous discussed. Various test coupons were machined from each composite laminate according to ASTM standards for characterization and comparison of properties.
2.3 Characterization

2.3.1 Dynamic Mechanical Analysis (DMA)

Effect of various reinforcing fiber types on viscoelastic properties of SC-780 epoxy composites was investigated using dynamic mechanical analysis (DMA). Test was conducted using TA Instruments’ Q800 in dual cantilever mode at oscillating frequency and amplitude of 1 Hz and 50 µm, respectively. DMA samples were scanned from 30-160 °C at 5 °C/min according to ASTM D4065. Rectangular shaped samples of size 60 x 12.5 x 5mm were used. Storage modulus (G’), loss modulus (G’’) and damping coefficient (Tan Delta) were recorded as function of temperature for each sample. Glass transition temperature (Tg) was determined using the peak of loss modulus curves and reported as function of reinforcing fiber type and duration of seawater exposure.

2.3.2 Flexure Test

Flexural properties of all FRPC samples were characterized using three point bending flexure tests according to ASTM D790-10. Tests were conducted in displacement mode with crosshead speed of 2.0 mm/min using MTS servo-hydraulic system MTS 809 testing machine equipped with data acquisition software. Five sets of samples were tested from each sample set including conditioned and unconditioned, and average data reported as function reinforcing fiber type and duration of seawater exposure. Flexure strength and modulus of elasticity were determined based on the following expression;

\[
\sigma_f = \frac{3PL}{2bd^2} \quad (1)
\]
\[
E = \frac{L^3m}{4bd^3} \quad (2)
\]

Where
- \(\sigma_f\) – stress in the outer fibers at midpoint, MPa
- \(E\) – modulus of elasticity in bending, MPa
- \(P\) – maximum load observed at rupture, N
- \(L\) – support span, mm
- \(b\) – width of sample, mm
- \(h\) – thickness of sample, mm
- \(d\) – depth of sample, mm
- \(m\) – slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm

2.3.3 Marine Environmental Conditioning

FRPC test coupons were completely submerged in industrial grade seawater acquired from LiveAquaria.com for marine environmental conditioning at room temperature. Representative samples were identified and their respective weight recorded prior to complete immersion into seawater conditioning. Weight of each representative sample was recorded using an electronic weighing balance with sensitivity of 0.001g every seven days during conditioning. Samples were removed, patted with dry paper towel to remove dripping seawater, weighed and placed back into the conditioning container. Samples were conditioned up to 120 days and various properties characterized every sixty days, to study the effects of conditioning on each sample. Weight gained by each sample was measured and correlated to other properties considered in this study. Initial samples were identified from each composite panel and respective weight recorded prior to conditioning.

3 RESULTS AND DISCUSSIONS

3.1 Seawater Absorption Characteristics

Figure 1 shows images of samples fabricated and conditioned for the study. Weight changes in each samples due to absorbed seawater was characterized as function of time \(M_{(t)} \) (%) using the following expression;
Mechanism of mass transportation of solvents in FRP composites materials can be described as two-step process, which depends on several factors including degree of cross-linking, temperature, fiber type and concentration of the solvent. Interaction between seawater and polymer molecules on the surface of FRPC can lead to the first step of dissolution of the solvent into the polymer creating concentration gradient [6]. Diffusion of seawater into FRPC ensues, which is enhanced by gaps between the fibers and molecule, density domains and segmental chain mobility of polymer leading to formation of concentration gradient. Overtime, the absorbed moisture in FRPC leads to swelling and subsequent plasticization of the matrix, severing weak van der Waal forces and hydrogen bonds within...
the polymer [10]. This results in the destruction of interfacial bonding between fibers and the matrix, and degradation of material properties. Initial spike in absorption of profiles 2 and 3 showed the highest rate of absorption compared to carbon and E-glass composites. At the end of 60 days, profile 1 seemed to absorb the least amount of seawater, with profile 3 absorbing the most. Overall average weight gained for all samples at the end of 120 days were 0.56%, 0.50%, 0.45%, 0.52% and 0.56% for carbon, E-glass and profiles 1 - 3 respectively.

![Storage Modulus vs Temperature](image1)

Figure 3: Representative storage modulus versus temperature responses.

![Storage Modulus vs Seawater Absorption](image2)

Figure 4: Effect of seawater absorption on storage modulus.

### 3.3. Dynamic Mechanical Analysis (DMA)

Viscoelastic properties of carbon, E-glass and various combination of FRPC were studied using DMA for unconditioned samples (baseline) and those conditioned to seawater up to 120 days at room temperature. Representative DMA thermograms of storage modulus curves of baseline samples obtained from the study are presented in Figure 3 and average data presented in Table 1. Parameters determined from DMA tests were storage modulus and glass transition temperature ($T_g$) using data from loss modulus curve. Viscoelastic properties of carbon/epoxy composites as expected showed superior properties compared to the other samples with storage modulus at 30 °C approximately 38% better than that of E-glass/epoxy samples. Carbon/epoxy samples also showed approximately 54, 28
and 14% enhanced storage modulus values when compared to hybrid reinforcements in Profile 1, 2 and 3 respectively. Effect of hybridization on viscoelastic properties of FRPC observed especially in profile 2 and 3 showed enhanced performances compared to E-glass. Comparison of storage modulus data at 30 °C between hybridized FRPs and E-glass showed approximately 8 and 21% improvements for profiles 2 and 3 respectively. This indicates that there was strong interlocking dynamics between carbon/E-glass hybrid fibers and epoxy molecules compared to that between E-glass/epoxy molecules. Furthermore, segmental mobility of polymer molecules during glass transition was slightly restricted by the intertwined fiber weave patterns between the two fibers, especially in Profile 3. Figure 4 shows comparison of the effect of seawater exposure on storage modulus of each FRPC after 60 and 120 days. Results from the test showed slight improvements in storage modulus for E-glass, Profile 1 and 3, while carbon and Profile 2 showed steady degradation over the duration of the study.

Summary of glass transition temperature over the same period is presented in Figure 5 for comparison. Unlike storage modulus, the effect of seawater conditioning was detected immediately after 60 days and continually declined till the end of the study in all samples. The decreased in Tg values across the board was attributed to onset of damaging effect of absorbed seawater, leading to increased mobility of segmental molecular polymer chains during DMA test. Presence of different salts in seawater has been known to degrade matrix dominated properties in FRPC through the gaps between fiber and matrix interface. Absorption of seawater into the polymer matrix occurs through capillary motion along the fiber length, consequently leading to increase storage capacity and plasticized polymer which deteriorates the fiber-matrix interfacial bonding. Diffused water molecules have also been known to interfere with van der Waals forces and hydrogen bonds within polymers.

Table 1: Comparison of viscoelastic properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage Modulus, GPa</th>
<th>% change wrt E-Glass</th>
<th>% change wrt Carbon</th>
<th>Glass Transition Temperature, °C</th>
<th>% change wrt E-Glass</th>
<th>% change wrt Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-Glass</td>
<td>13.47±1.35</td>
<td>-27.6</td>
<td>-</td>
<td>100.31±0.9</td>
<td>-</td>
<td>3.1</td>
</tr>
<tr>
<td>Carbon</td>
<td>18.60±0.96</td>
<td>38.1</td>
<td>-</td>
<td>97.31±0.8</td>
<td>-3.0</td>
<td>-</td>
</tr>
<tr>
<td>Profile 1</td>
<td>12.07±0.80</td>
<td>-10.4</td>
<td>-35.1</td>
<td>103.42±0.8</td>
<td>3.1</td>
<td>6.3</td>
</tr>
<tr>
<td>Profile 2</td>
<td>14.52±0.29</td>
<td>7.8</td>
<td>-21.9</td>
<td>94.02±0.5</td>
<td>-6.3</td>
<td>-3.4</td>
</tr>
<tr>
<td>Profile 3</td>
<td>16.27±1.56</td>
<td>20.8</td>
<td>-12.5</td>
<td>102.02±1.8</td>
<td>1.7</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Figure 5: Effect of seawater absorption on glass transition temperature.
leading to damages in polymer chain network. After the first 60 days, glass transition temperature (Tg) of E-glass samples decreased by 8%, followed by Profile 1 at nearly 6%, with carbon samples recording the least changes, approximately 2%. At the end of 120 days, glass transition temperature (Tg) of E-glass, carbon and profiles 1 - 3 samples decreased by approximately 11, 6, 8, 3 and 12% respectively.

E-glass and profile 3 samples absorbed the most seawater during conditioning, approximately 0.56% and resulted in highest reduction in Tg due to damaging effect in the polymer matrix. The decrease in observed properties was attributed to FRPC exposure to seawater causing swelling and associated plasticization in the matrix. This results in segmentation in polymer chains due to bond cleavage and ease of segmental movements in the polymer network during glass transition [7]. Although Profile 1 samples absorbed the least amount of seawater, approximately 0.45%, the effect of absorbed seawater led to a reduction of almost 8% in glass transition temperature. Rate of deterioration in glass transition temperature due to seawater exposure was more aggressive in profile 3 samples, losing nearly 13% at the end of the study. Profile 1 and 2 samples had glass outer layers yet profile 1 absorbed the least amount of seawater not only among the hybrid samples but all samples. Furthermore, Profile 3 samples with carbon outer layers absorbed the most among the hybrids, and comparable to that absorbed by E-glass. It was apparent that hybridization of fibers using the configuration in Profile 3 had little effect on restrictive mobility of polymer molecules during glass transition.

### 3.4. Characterization of Flexural Properties

Baseline composite samples fabricated using carbon, glass and hybridized reinforcements were also subjected to three-point bending flexure test to characterize the effect of hybridization. Flexure properties of FRPC are ascribed through interfacial interaction between fibers and the matrix, in which additional interaction between different fibers are introduced in the case of hybrid FRPC samples. Representative flexural stress-strain curves obtained from baseline samples are presented in Figure 6 for comparison. During three-point bending stress test, applied load to each sample causes the underside of the samples to be under tension while the upper side is subjected to compression. Additionally, there is an in-plane shear stress acting around the mid-section, hence bending failure mode is generally characterized by combination of stresses. The key factors in selecting the various configurations highlighted in this study are not only cost savings with comparable properties, but also a balance in loading between tensile and compressive properties. Carbon fibers are known to have excellent stiffness and strength, but poor compressive strength due to lack of ductility, while E-glass is known for great toughness and lower stiffness compared to carbon fibers.

![Flexural Stress-Strain Curves](image)

**Figure 6: Representative flexural stress-strain curves.**

Baseline data showed superior performance by carbon fiber composite samples, highest in flexural strength samples, while E-glass showed the least properties amongst all FRPC. Properties of various combinations of carbon and E-glass hybrid composites were between that of carbon and E-glass, with profile 1 samples showing the least and profile 3 samples exhibiting the most properties respectively.
amongst the hybrid FRPC. Comparison between hybrids and E-glass FRPC showed an increase in flexural strength by approximately 25, 47 and 103% for profile 1, 2 and 3 samples respectively. Similarly, there was also an observed increase in flexural modulus by approximately 19, 58 and 94% for profile 1, 2 and 3 samples respectively. Thus, hybridization resulted in significant enhancements in flexural properties of FRPC when compared to E-glass samples [15]. On the other hand, flexural properties of carbon FRPC samples out-performed that of all hybridized FRPC including E-glass samples. Compared to carbon samples, flexure strength decreased by 54, 42, 31 and 6% E-glass and profile 1-3 hybrid samples respectively. By comparison profile 3 samples showed the minimum variation in flexure properties among the hybrids with respect to carbon, while exhibiting the highest properties among the hybrids and E-glass. The carbon fibers used in the out layers enhanced the flexural stiffness while glass fibers in the core enhanced ductility, hence improved toughness of Profile 3 samples compared to rest of the samples.

Effect of seawater conditioning on flexure property retention of all samples was characterized and results presented as function of duration of exposure and presented comparison. The goal was to observe potential defects that may affect the rate of deterioration in material’s property as duration of exposure increases. Such defect includes interlaminar delamination due to plasticization of the matrix in each FRPC, and the effectiveness of hybridized fibers in minimizing such effect as noted by Mourad et. al. [8]. Studies on the exposure of glass/epoxy composites to seawater have been reported to increase the ductility in such materials due to plasticized matrix, hence it is expected that hybridized fibers to minimize such effect [16]. Figures 7 and 8 show comparison of experimental data obtained from three-point flexure bending flexure depicting the effect of seawater aging on flexural strength and modulus properties in all samples. Results of the tests indicated an overall decrease in flexure

![Figure 6: Representative flexural stress-strain curves.](image1)

![Figure 7: Effect of Seawater absorption on flexural strength.](image2)
strength in all samples compared to their respective unconditioned counterpart. Rate of deterioration significantly varied among different samples, with E-glass and Profile 2 deteriorating the most by approximately 27 and 18% respectively after the first 60 days of exposure. At the end of the study, flexural strength of the same slightly increased after 60 days, which constitutes a decline by approximately 26 and 23% respectively compared to respective baseline data. Among all the samples, these two exhibited a slight increase in flexure properties after 120 days of exposure, while the rest showed steady decline. Outer layers of Profile 2 were E-glass fibers; however the present of carbon in the core enhanced the ability to resist bending during flexure testing leading to slight improvement in the observed results.

![Graph showing flexural modulus for different samples](image)

Figure 8: Effect of Seawater absorption on flexural modulus.

### 3.5. SEM Analysis of Failed Samples

Representative SEM micrographs on surfaces of failed samples were obtained for qualitative analysis on the effect of seawater conditioning and mode of failure during flexure testing. Figure 9 (a-e) show representative micrographs of unconditioned and samples conditioned to 120 days of seawater for E-glass, carbon and profile 1-3 samples, respectively. Failure mode of samples prior to conditioning seemed to be fairly consistent throughout, thus fiber breakage, kinking and fiber buckling. Thus, failure was caused by fibers/matrix under compression on one side and tension on the other of the composite laminate. Delamination were also occurred in some samples as seen in profile 2 sample, however it was not the principal mode of failure in tested unconditioned samples as can be seen in Fig 9 for E-glass, carbon and profiles 1-3 samples, respectively. On the other hand, fiber debonding, interlaminar delamination and matrix cracking were observed as primary mode of failure in post-conditioned samples.

![SEM micrographs of failed samples](image)
CONCLUSIONS

A study on the seawater conditioning on flexural and viscoelastic properties of E-glass and carbon fiber reinforced epoxy composites and three hybrid composites of the two are presented in this study. E-glass, carbon and various configurations of hybrid fiber composites were subjected to seawater for 120 days and properties characterized. E-glass and carbon composites absorbed the most and least amount of seawater respectively over the duration of the study. Dynamics of seawater absorption in hybrids samples were independent of the type of fiber on the outer layer, hence no particular order was observed. Glass transition temperatures decreased steadily as duration of exposure increased due to seawater ingress. Upon exposure to sea water, storage modulus values decreased slightly though steadily for carbon/epoxy and profile 2 samples. For other samples, it increased initially at 60 days before decreasing at 120 days. There was a decrease in flexural strength and slight increase in flexural modulus in case of samples exposed to sea water.
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