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Performance of Composite Materials Subjected to Salt Water Environments

David Miller¹, John F. Mandell², Daniel D. Samborsky², Bernadette A. Hernandez-Sanchez³and D. Todd Griffith⁴

¹Department of Mechanical and Industrial Engineering, ²Department of Chemical and Biological Engineering, Montana State University, Bozeman, MT, 59717, USA ³ Advanced Materials Laboratory ³ Analytical Structural Dynamics Sandia National Laboratory, Albuquerque, NM, 87185, USA

Abstract

This paper presents the recent trends in the mechanical characterization of composite systems under consideration for Marine Hydro Kinetic (MHK) applications exposed to salt water environments. First, a testing protocol for environmental effects has been developed for resin infused in-house fabricated laminates. Unidirectional ([0] and [90]) mechanical test samples were submerged in synthetic sea water at 40°C and 50°C, with the weight recorded at time intervals over the entire period. Additional witness coupons were submerged to monitor effects of fiber orientation and cure temperature. Next, after conditioning to both full saturation and partial saturation, static compressive and tensile strength properties at temperatures of 0°C, 20°C and 40°C were collected. Tensile fatigue resistance was also measured at room temperature for the 0° samples. These results show trends of reduced tensile and compressive strength with increasing moisture and temperature in the 0° (longitudinal) direction. In the 90° (transverse) direction, compression strength decreases but tensile strength is little affected as temperature and moisture increase. The fatigue resistance of environmentally conditioned samples is reduced at high stress levels, but matches the un-conditioned samples at low stress levels. Finally, both mechanical and chemical analysis results are presented for samples conditioned in a Salt Fog Chamber for unidirectional, [0] and [90], samples.

I. Introduction

Early investigation of hygro-thermal effects on composites established the essential technology which guides the current approach and anticipated results. These include the works by Browning, et al.¹ and the three volume series edited by George Springer ². A preliminary survey of recent literature on sea water effects presents data on water absorption over a fairly limited class of materials, architecture and properties. These references include work that studies the effect of seawater on the static strength of glass reinforced polymers ³; ⁴; ⁵; ⁶. These references include results for multiple matrix systems including polypropylene, vinyl esters, and epoxy; however, the breadth of fiber systems and architectures is very limited and essentially no work explores the effect of testing temperature on material response. It should be noted that consistent results are seen throughout the literature showing a degradation of static strength with little change in elastic modulus with increasing moisture content.

Current literature for testing beyond static loading becomes even more limited when considering the effects of a salt water environment. Chiou and Bradley ^{7; 8} considered fatigue

loading of seawater soaked samples and identified changes in the failure mode of soaked and dry fatigue samples.

This paper outlines the process under development at MSU to expand the knowledge base of material systems and the mechanical response of those systems after treatment in seawater.

II. Experimental Methods

A. Sample Preparation and Synthetic Seawater Conditioning

Samples fabricated for testing were a unidirectional 2 ply and 6 ply composite fabricated with a vacuum assisted resin infusion process. Laminates fabricated with fabrics were vacuum infusion molded with one-sided molds following cure schedules given in ^{9; 10}. Two material systems were tested. The first laminate consisted of Momentive RIMR135/RIMH1366 epoxy resin and the unidirectional glass fiber was PPG-Devold L1200G30-E07. The second laminate consisted of Ashland 601 vinyl-ester resin and the unidirectional glass fiber was PPG-Devold L1200G30-E07. After the infusion process the composite was cured at 20°C for 24 hrs followed by a post-cure of 80°C for 12 hours. A second set of samples were post-cured at 70°C for 12 hours. The resulting fiber volume content was 56-57% calculated from density measurements. From the unidirectional composite plate, samples were cut to produce [0]₂, [0]₆ and [90]₆ samples with a geometry show in Figure 1.

After fabrication, initial sample weights were recorded for the 70°C post-cure samples before a portion of the samples were submerged in ASTM D 1141 Synthetic sea water (SSW) at 40°C. Samples were placed in a sealed bath of SSW and stored in a temperature controlled oven at 40°C \pm 1°C. Periodically, samples were removed from the SSW, patted dry, weighed and recorded. After a 1000 hour soak was attained, samples were removed from the 40°C and stored in SSW at 20°C. Several samples were left in SSW to determine a saturation weight gain. This process was repeated for the samples post-cured at 80°C; however, the soaking temperature was elevated to 50°C.

Additionally, a set of epoxy matrix samples (80°C post-cure) were conditioned in a Salt Fog Apparatus per ASTM Standard B117-03. These samples underwent a four-week soak of salt fog at 40°C. Only the final weight of the samples were collected.

B. Mechanical Characterization

Most of the experimental methods for mechanical characterization are described in more detail in the fatigue database ¹⁰. Laminate test coupons for UD geometries are shown in Figure 1. Most UD coupons followed ASTM D3039, while thickness tapering was added to avoid grip failures for some laminates. Static tests were conducted at a constant displacement rate of 0.025 mm/s, while fatigue tests were conducted under load control at 1-4 Hz, given for each test in the database ⁹. Surface cooling with forced air was used for fatigue tests. Detailed test conditions and results can be found in the current or subsequent database version. All environmentally conditioned samples were tested in a salt water immersion environment. Off ambient testing was performed in a water bath controlled environmental chamber.



Figure 1 Standard tensile coupons for UD laminates.

C. Chemical Analysis of Salt Fog Conditioned Samples

After salt fog testing, samples were dried overnight. Cross-sections were cut using a diamond blade and were dry polished using 9 μ m Al₂O₃ paper. Figure 2 illustrates the locations (end and middle) where cross-sections were cut from the coupon. The cross-sections were mounted to the holder with carbon tape and imaged using a Zeiss Supra 55VP field emitter gun scanning electron microscope (FEGSEM). A Noran EDS detector and Noran System Six software was used for the acquisition of EDS spectra. The EDS mapping area for these samples are shown in Figure 3 and dimensions of cross-sections cut can be found in Table 1. For elemental composition comparisons, EDS spectra were normalized and overlaid using results from a non-treated coupon (baseline) and spectra taken on both exposed and unexposed samples.



Figure 2 Dashed lines represent where coupon was cut to expose inside cross-section for analysis.



Figure 3 EDS mapping areas represented by black dots on (a) unexposed polished cross-section and (b) unpolished exposed surface. Cross-section dimensions are shown in (c) and sample dimensions can be found in Table 1

Sample	Length (mm)/(in)	Width (mm)/(in)	Thickness (mm)/(in)
2-1 end	27.84/1.096	3.54/0.139	2.22/0.087
2-1 middle	27.80/1.094	9.38/0.369	2.32/0.091
2-5 end	27.99/1.102	4.03/0.159	2.45/0.096
2-5 middle	27.99/1.102	8.50/0.335	2.25/0.088
6-1 end	26.22/1.032	5.87/0.231	5.49/0.216
6-1 middle	26.10/1.028	7.49/0.295	5.42/0.213
6-5 end	26.68/1.050	5.96/0.235	5.43/0.213
6-5 middle	26.65/1.049	7.16/0.281	5.33/0.209
E1 end	24.86/0.979	26.33/1.036	3.33/0.131
E1 middle	44.89/1.767	24.86/0.978	3.29/0.129

Table 1 Sample Cross-sections and their Dimensions

III. Test Results and Discussion

A. Weight Gain for Conditioned Samples

Figure 4 shows the weight gain for epoxy samples conditioned at 40°C, and indicates that the $[0]_2$ samples are approaching an equilibrium moisture content at 1000 hours. However, the thicker samples, $[0]_6$ have lower moisture absorption and have not reached saturation. Initial testing protocol was to remove sample after 1000 hrs at 40°C and store in synthetic sea water at

20°C until testing. These mechanical results are presented later as complete and partial saturation.



Figure 4 Percentage Weight Gain for 70°C post-cure epoxy samples submerged in SSW at 40°C

Further SSW conditioning was performed at 50°C for both epoxy and vinyl-ester matrix materials. This study was performed on a variety of neat material and fiber layup orientations. Figure 5 shows the percentage weight gain as a function of the square root of time for epoxy samples with many different configurations. These include traditional flat plate configurations, as well as rectangular samples with fiber ends exposed on all edges. While this graph is difficult to discern absolute sample identification, it easily illustrates the linear nature of the moisture absorption for all samples. The rate of mass increase of each sample is dependent on the geometry of the individual sample, and sample size was not held constant for the samples shown in the figure. However, the linear nature of the graph implies that Fickian diffusion is governing the absorption of the mass increase, regardless of the size, shape, fiber orientation, and primary diffusion direction. Figure 6 shows similar data repeated for the vinyl-ester composite system soaking at 50°C. Of particular note is the difference in percent weight gain at saturation between the epoxy and vinyl-ester systems. The neat epoxy has a saturation weight gain of 2.9% while the vinyl-ester saturates near 1.3% weight gain. These values will be utilized in diffusion modeling of these composites.



Figure 5 Percentage Weight Gain for 80°C post-cure epoxy samples submerged in SSW at 50°C



Figure 6 Percentage Weight Gain for 80°C post-cure vinyl-ester samples submerged in SSW at 50°C

B. Effects of Conditioning on Material Strength and Fatigue Life

As seen in the SSW conditioning data above, samples were tested in both the fully saturated and partially saturated conditions. Due to the long times required for full saturation to occur in the thicker samples, full saturation data is not yet available for the 6-ply samples. However, testing of saturated samples has been completed both statically and cyclically for

thinner $[0]_2$ samples. Figure 7 and Figure 8 show ultimate tensile strength for $[0]_2$ samples as a function of test temperature and moisture content. These results show trends of reduced tensile strength with increasing moisture and temperature in the 0° direction.



Figure 7 Fully Saturated Epoxy Tensile sample with 0.86 % Wt. Gain, V_f = 0.56, Cured at 70 °C and soaked at 40°C



Figure 8 Fully Saturated a) epoxy Tensile sample with 0.72 % Wt. Gain, $V_f = 0.53$ b) vinyl-ester Tensile sample with 0.40 % Wt. Gain, $V_f = 0.53$, Cured at 80 °C and soaked at 50°C.

The results from a constant stress fatigue loading of fully saturated $[0]_2$ epoxy and vinyl-ester samples are shown in Figure 9. These tests were performed on samples post-cured at 80°C and used an R value of 0.1. These results show that as the applied stress decreases, the influence of

the moisture uptake is diminished. This result implies that the fatigue life of a saturated composite is only affected at areas of high stress.



Figure 9 Cycles to failure under constant stress amplitude, i.e., the S-N curve, for both the epoxy and vinylester composites post-cured at 80°C

For partially saturated composite samples, both longitudinal and transverse samples were tested in tension and compression. Figure 10 shows the results of partially saturated $[0]_6$ samples tested in compression and show a decrease in strength as a function of temperature and moisture. However, Figure 11 shows the results for the $[90]_6$ samples tested in tension and compression and show that the tensile strength is little affected by temperature or moisture, but the compressive strength is reduced by both. Samples conditioned in the Salt Fog chamber showed little uptake in moisture and little drop in material properties. The thinner $[0]_2$ samples had a 0.31% mass increase while the thicker $[0]_6$ samples had a 0.24% mass increase. The only samples which showed statistically relevant changes were in the $[0]_6$ samples tested in compression and are shown in Figure 12.



Figure 10 Partially saturated epoxy compressive sample with 0.47 % Wt. Gain, V_f = 0.56, Cured at 70 °C and soaked at 40°C



Figure 11 Partially saturated epoxy sample with 0.47 % Wt. Gain, $V_f = 0.56$, Cured at 70 °C and soaked at 40°C tested in a) tension and b) compression.



Figure 12 Partially saturated epoxy sample from Salt Fog Conditioning with 0.24 % Wt. Gain, $V_f = 0.6$, Cured at 80 °C.

C. Microstructural and Chemical Inspection

SEM and EDS mapping was performed to determine the extent of NaCl water diffusion into the uncoated coupons during salt fog exposure. Four sample types were analyzed and included: (a) an untreated coupon for baseline measurements, (b) 2 mm miscellaneous samples (2-1 & 2-5), (c) 6 mm miscellaneous samples (6-1 & 6-5), and (4) an epoxy resin. Figure 2 and Figure 3 show the end and middle locations where cross-sections were removed from and the EDS mapping areas. Table 1 summarizes the samples cross-section dimensions. The unexposed sample is not included.

The SEM images, shown in Figure 13, are representative of the 2 and 6 mm crosssections revealing unexposed and polished surfaces: (a) outer left edge, (b) center, and (c) outer right edge, along with unpolished and salt fog exposed (d) side and (e) surface. The images show the configuration of the fiberglass embedded within the epoxy resins. Flecks of NaCl crystals could be found on the (d) exposed side and (e) surface of the coupons. For our mapping analysis, the spectra obtained from these areas were compared and normalized to identify if significant NaCl diffusion was occurring during exposure. The EDS baseline measurements from the unexposed coupon and from the epoxy resin both revealed the presence of Na and Cl, Figure 14. The red EDS spectrum is from the epoxy resin and the green trace is from the exposed side with NaCl crystals. Two have been normalized against each other to determine the contents. The exposed side has a stronger signal than the epoxy resin. Trace amounts are expected since epoxy polymerization often uses chlorinated precursors and NaOH to catalyze the reaction in the presence of amine-based crosslinkers.



Figure 13 Images of the unexposed and polished: (a) outer left edge, (b) center, and (c) outer right edge, along with unpolished and salt fog exposed (d) side and (e) surface.





EDS Mapping along the unexposed surface of the epoxy resin and fiberglass regions within the coupon is shown in Figure 15. The yellow-boxed fiberglass region is represented by the orange EDS spectrum. Elements from the glass include: Si, Ca, Al, and Na. For the epoxy region (greenbox), EDS shows that there is more Cl associated with this region in comparison to the glass fibers that tend to have more Na content due to the glass chemistry.



Figure 15 SEM and EDS mapping of fiberglass region (Blue EDS), and the epoxy region (orange EDS) found within the composite.



Figure 16 EDS of 6-5 middle outer edge: (red) baseline, (blue) 6-5 outer edge, (green) exposed surface with NaCl crystals.

Analysis was performed on all the samples listed in Table 1. The thickness of each sample was measured to get an estimate of diffusion depth for the Na and Cl. Figure 16 shows the EDS of 6-5 and is similar to the areas examined. Upon examining all the different regions from coupons, it was found that the epoxy naturally contains some presence of Na and Cl. Analysis on both the end and middle sections does not indicate an increase in the Na or Cl content within the unexposed regions of the samples. However, this analysis would only see crystals on exposed edges. Based on our test, the exposure conditions did not allow for any significant NaCl diffusion within the sample as verified by the EDS analysis.

IV. Conclusions

This paper describes the influence of sythetic sea water (SSW) on the static and cyclic strength of epoxy and vinyl-ester composites. Samples were artifically aged at 40°C and 50°C while submersed in SSW and then mechanically tested at ambient and off-ambient temperatures. These results showed the both epoxy and vinyl-ester composites gained weight similar to a diffusion based mechanism. A saturation content of neat epoxy and vinyl-ester was identified. The neat epoxy has a saturation weight gain of 2.9% while the vinyl-ester saturates near 1.3% weight gain. The strength of fully and partially saturated composites was found to be a function of temperature and moisture content for both longitudinal [0] and transverse [90] samples. The only sample condition which showed a negligible effect of temperature or moisture was the [90]₆ samples tested in tension; however, these samples were tested at a partial saturation level. Additionally, a significant effort was undertaken to interrogate the chemical structure of the composite after conditioning within the Salt Fog chamber. These results showed that the salt fog conditioning did not affect the internal chemistry, namely NaCl diffusion, of the samples.

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