CHARACTERIZATION OF CARBON FIBER-VINYLESTER COMPOSITES EXPOSED TO COMBINED UV RADIATION AND SALT SPRAY

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Abstract

Fiber reinforced polymer resin composites are used as facings for foam core sandwich panels. When exposed to harsh environments such as salt water, temperature fluctuations, mechanical stresses, and ultraviolet (UV) radiation, composites respond deleteriously to the conditions, causing degradation and weakening. Here, accelerated aging of carbon fiber-reinforced vinylester composites is performed using multiple environmental exposure chambers (UV radiation, salt-fog spray, hygrothermal) to ascertain the effect of salt water on the composite mechanical response. Double edge notch fracture tests, three-point bending, and infrared spectroscopy (FTIR) will be presented to characterize the environmental effects. Micro-speckle of composite specimens is used to determine strain fields surrounding notches.

1 Introduction

Fiber reinforced polymer (FRP) composites provide a high strength-to-weight ratio and are used as facing materials in foam core structures. Additionally, polymer composites can provide corrosion resistance over traditional monolithic metallic materials. Infrastructure and structural applications are increasingly moving towards the use of polymer composite materials for components of structures and structural repairs. Though polymer composite materials have been successfully used in application, the long-term durability of the materials is still an open question, and effects wide-spread implementation. This is partly due to the multitude of conditions composite materials can be exposed to in application [1]. The effect of environmental exposure of vinylester resin composites has shown detrimental effects on long-term residual mechanical properties [2]. Combined effects of ultraviolet radiation and moisture at elevated temperatures have shown an increased degradation of mechanical properties for epoxy resin composites [3, 4]. An important consideration for FRPs used in off-shore and littoral applications is the effect of sea water, which creates a corrosive environment for metallic materials. Sea water immersion conditions of composites have shown deleterious effects to material properties [5-9]. Previously, the combined effects of UV radiation and moisture were shown to cause decreases in fracture strength and mechanical properties for carbon fiber / vinylester composites [10]. Combined exposures of UV radiation and sea water have not been addressed for vinylester resin composites. In this paper, the effects of the combined conditions on mechanical and chemical properties will be discussed.

2 Materials and testing methods

2.1 Materials

Carbon-fiber reinforced vinylester unidirectional composite laminates (Graphtek LLC) were used for all experiments and conditions. Composite laminate sheets with nominal thickness of 1.4 mm were machined using a diamond wet saw into two sizes: (1) 12.5 x 77 mm (width x length) for flexural testing with two fiber directions [0°] and [90°], and (2) 25 x 152 mm with [0°] fiber direction in the length for fracture testing. Two 5 mm notches were machined in specimen size (2) at the midpoint of the length with a diamond saw to create double edge notch (DEN) fracture specimens.

Figure 1. Environmental exposure performed in the laboratory with accelerated aging chambers, Top left, QUV/se ultraviolet radiation and condensation chamber, Top right, Tenney BTRS temperature and humidity chamber, Bottom, Bemco P700XL salt spray. Insets show composite samples in chambers.

2.2 Exposure Conditions

Three environmental chambers were used to create the exposure conditions. Samples were exposed to ~800 hours of combined and individual accelerated aging before characterization. The three chambers were, i) Moisture and heat in a Tenney Benchmaster BTRS temperature and humidity chamber, ii) UV Radiation/Condensation in a Q-Lab QUV/se accelerated weathering chamber, and iii) Salt spray and heat in a Bemco P700XL salt spray chamber (see Figure 1). UV radiation simulates natural sunlight using fluorescent UV bulbs at a 340 nm wavelength. Intensity is monitored by real-time UV irradiance sensors, where temperature is controlled using a blower. Condensation is provided by water evaporation which condenses on the sample surfaces. Salt spray is created by atomization of 5% NaCl and deionized water solution into a sealed chamber. Three to five specimens per condition were placed in the chambers. Sample mass is monitored every 48 hours with a precision balance by removing specimens from the temperature and humidity chamber. Samples are blotted with sterile paper tissue (kimwipe) to remove surface moisture if present and then immediately weighed.
One-half the samples are rotated between the two chambers every 24 hours to create a combined effect between controlled constant temperature and humidity, the constant salt

spray exposure, and the cyclic UV radiation/Condensation and cyclic UV radiation/Salt Spray condition. The conditions in the chambers remained constant for the duration of the exposure. In the temperature and humidity chamber, moisture was set at 85% relative humidity (RH) and temperature at 35 C. In the QUV chamber, the UV radiation and Condensation conditions cycled every 3 hours. For the UV cycle, the UV irradiance was set at 0.6 W/m^2 at 60 C, and the Condensation cycle was set at a temperature of 50 C. The Bemco salt spray conditions were set at 35 C and ~70 kpa air pressure. Samples were rotated within the chambers to avoid chamber location specific effects.

2.3 Surface Microscopy and Chemical Analysis

Composite coupons surfaces were examined by high resolution digital optical microscopy (Keyence VHX-500). Samples were mounted beneath the microscope objective with two orientations to image the edges and surfaces. Specimens from all exposure conditions as well as unconditioned samples were imaged. Fourier transform infrared (FTIR) photoacoustic spectroscopy was performed on 1cm x 1cm samples cut from the unconditioned and exposed specimens. Absorption spectra were obtained for wavenumbers from ~700 - 3700 cm^{-1}.

2.4 Mechanical Testing

Three point bending tests were performed on the composite samples following the ASTM D790 standard using a screw-driven mechanical loading frame (TiraTest 26005) with a 0.5 kN load cell. The tests determined flexural strength and modulus of the composites. Specimen sizes were 77 x 12.5 x 1.4 mm (L x W x H). Support geometry followed ASTM D790, with the support span set for 60 mm resulting in a span/thickness ratio of ~43. A crosshead rate of 4.25 mm/min. was used to give a strain rate of 0.01 mm/mm/min.

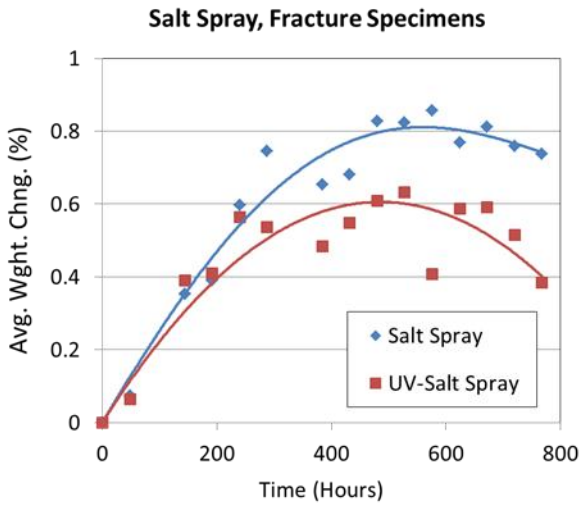

Figure 2. Average sample mass change for constant salt spray and combined UV-Salt spray exposed Carbon Fiber / Vinylester composites. Decrease in UV-Salt spray sample mass after ~500 hours due to photodegradation loss of material.

Energy release rate was determined using the DEN specimens in a hydraulic mechanical loading frame (Instron 8501). A gage length of ~102 mm was used with the edge notches in the center of the gage. Notches were measured for length and width using a high resolution digital microscope (Keyence VHX-500). A crosshead rate of 2 mm/min. was used, and load at first failure was recorded. Tensile modulus of an un-notched specimen was measured with the recorded load and instrumenting with strain gages to compute the tangent modulus.

2.5 Micro-speckle Technique

The micro-speckle technique [11-12] was used surrounding notches undergoing tensile tests to study the crack initiation and propagation through the composites. Specimens cut to 7mm x 27 mm were machined to include a single edge notch with dimensions of 1 mm x 2 mm, and loaded in tension using a Fullam micro testing stage under a digital microscope to record the deformation process. Micro-speckles made from SiC of size ~20 μm are placed on the surface. Image correlation using in-house software (CASI) [12] is used to process frames from digital image files.

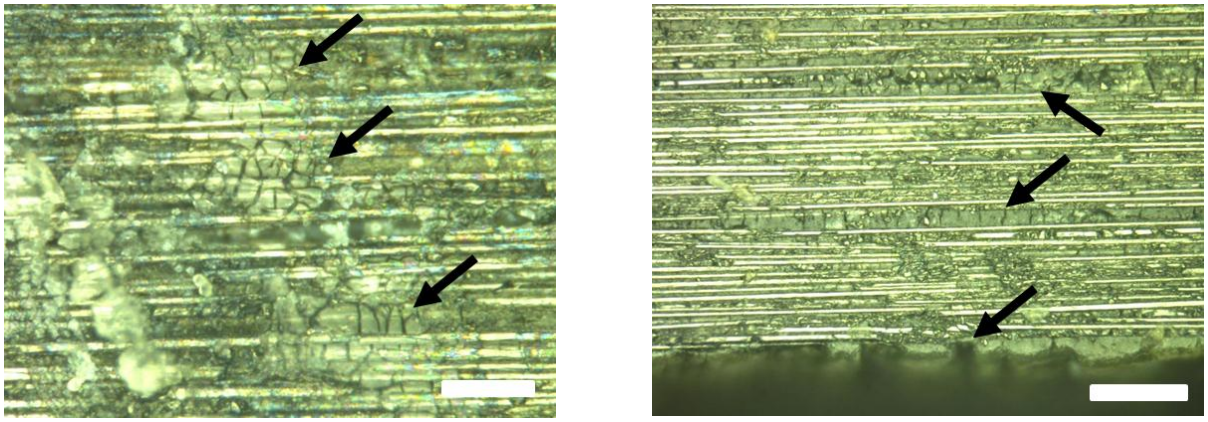

Figure 3. Optical microscopy after 768 h combined UV-Salt spray exposure of the Carbon Fiber / Vinylester composite edges; micro-cracking observed in images marked by arrows. Scale bar left 50 μm; scale bar right 100 μm.

3 Results and Discussion

3.1 Specimen Weight Changes as a Function of Duration

Changes in mass of the composite samples were tracked every 48 hours for the environmental chambers. The results indicate that samples exposed to the constant moisture and salt spray conditions all had mass gain, which is due to moisture uptake. The specimens showed a significant difference between the combined UV versus constant moisture cases most prominently for the salt spray cases (Figure 2). The fracture specimens had the largest change in mass, and are attributed to the high surface to volume ratio. The decrease in mass after a peak value of ~500 hours for the combined UV cases indicates loss of surface material due to degradation.

3.2 Surface Morphology

Surface changes due to environmental exposure of the composites were characterized by high-resolution microscopy (Keyence VHX-500), to determine the effects on the vinylester resin. Images provided evidence of micro-cracking and potential matrix erosion for samples exposed to combined UV conditions; the Salt-Spray UV condition exhibited a *high density* of microcracks on the sample edges (Figure 3). Previous results showed that immersion in salt water caused degradation of vinylester resin and a decrease in strength [1]. Combining salt spray with UV radiation, the micro-cracking due to photodegradation is more prevalent than the humidity-UV condition. Surface cracking observed on the edges was also more extensive for the Salt Spray-UV than others. There was no micro-cracking observed for specimens exposed to only constant humidity or salt spray.

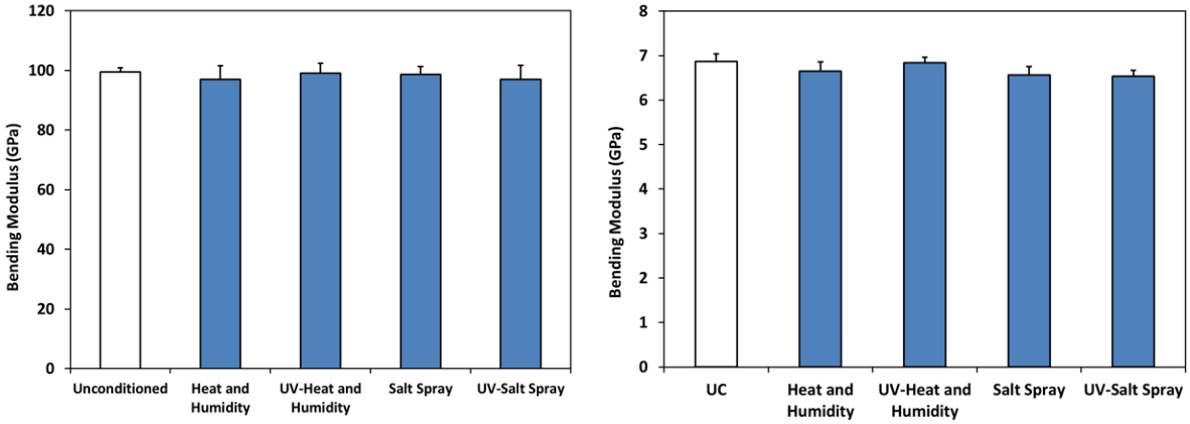

Figure 4. Bending modulus of carbon fiber/vinylester composites determined from three point bending tests; 0° specimens (left), 90° specimens (right).

3.3 Chemical Changes due to Exposure Conditions

Photoacoustic FTIR was used to determine photodegradation processes of the vinylester resin, since surface effects govern the environmental degradation of the composites. The vinylester spectrum was acquired for all specimen conditions, with several peak magnitude and spectral changes identified by FTIR (not shown). The changes were most prominent for the Salt Spray-UV condition, with peak suppression at 3040 cm-1 and 2180 cm-1, and attenuation of multiple peaks, most notably at 1730 cm-1, 1610 cm-1, 1500 cm-1, 1250 cm-1 and 1190 cm-1. Also, the O-H stretching peak (3400 cm-1) broadened for all conditions, notably for the Salt Spray-UV. The peak at 3040 cm-1 is associated with the C-H bond on the benzene ring, where side groups may be disrupted, and the peak at 1730 cm-1 is related to changes in the carbonyl content. The O-H stretching and carbonyl are indications of hydrolysis [5], and carbonyl and indicator of photodegradation. The changes in the peak at 1610 cm-1 and 1500 cm-1 are associated with aromatic structure changes and photodegradation [6]. Other peaks are still being analyzed for significance.

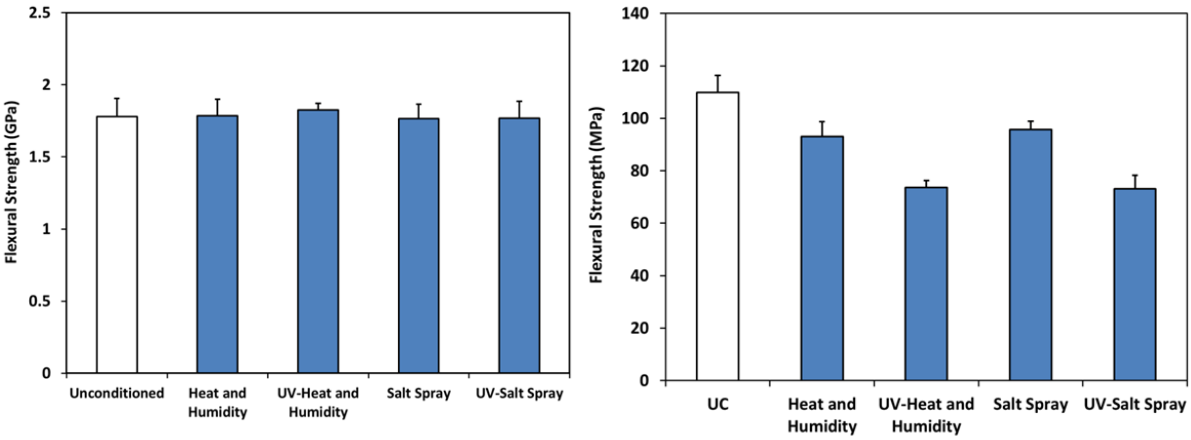

Figure 5. Flexural strength of carbon fiber/vinylester composites determined from three point bending tests; 0° specimens (left), 90° specimens (right).

3.4 Mechanical Flexural Response

Samples exposed to 768 hours of combined environments have been characterized by three point bending to determine flexural modulus and residual strength (ASTM D790) [13]. Samples with [0°] and [90°] fiber orientations were characterized after exposure. All exposure conditions showed an insignificant difference in the flexural modulus when compared to the unconditioned specimens, and within experimental error (Figure 4). Modulus results in the [0°] fiber direction were an order of magnitude larger than the [90°]

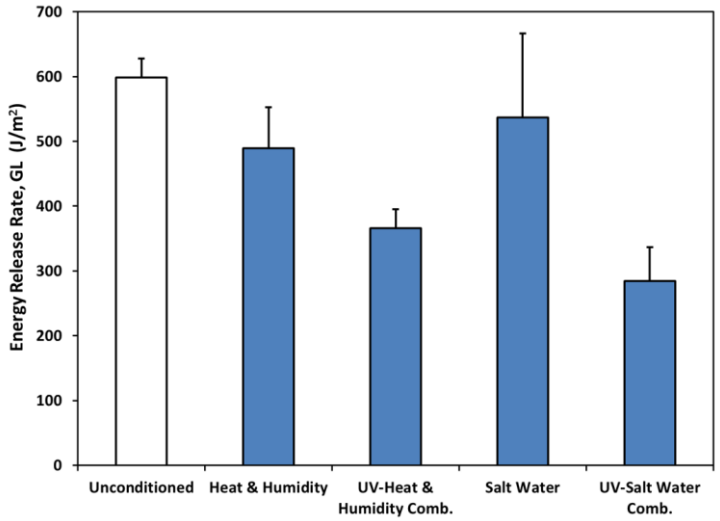

Figure 6. Energy release rate of carbon fiber/vinylester composites determined from double edge notched tensile specimens.

fiber samples, due to the fiber driven versus matrix driven mechanical response, respectively. Results showed the residual flexure strength to have minimal change within the experimental error for the [0°] fiber direction samples when compared with the unconditioned samples (Figure 5). The result is consistent with previous data on carbon fiber/epoxy composites [3]. Residual strength in the [90°] fiber direction demonstrated sensitivity to the exposure conditions, with all conditions decreasing compared to the unconditioned control (Figure 5). The conditions involving the UV radiation exhibited the most significant reduction in the residual strength, decreasing by 21% and 24% for the Humidity-UV and Salt Spray-UV cases, respectively, though statistically the results for the combined UV conditions were the same. The exposure to the UV radiation demonstrates a synergistic degradation effect which leads to a decrease in the composite mechanical strength. The strength loss is attributed to surface micro-cracking observed from optical microscopy.

3.5 Fracture Strength

Energy release rate of longitudinal fractures for samples exposed to 768 hours of combined environments were characterized with a shear-lag model using the method developed by Nairn [14]. Samples were all 0° composites with double-edge notches (DEN) machined across the fibers with a diamond saw. All exposure conditions showed a decrease in the energy release rate compared with the unconditioned specimens (Figure 6). To compute the energy release rate, the tensile modulus of an un-notched specimen was measured by instrumenting with strain gages then computing the tangent modulus, which was found to be 152 GPa. The combined exposures showed a decrease in the energy release rate of ~25% for the UV-Humidity condition, and ~50% decrease for the UV-Salt Spray condition. This difference is attributed to the increased surface micro-cracking observed on the edges of the UV-Salt Spray condition samples, which lead to a more efficient path for crack initiation.

3.6 Micro-speckle Analysis

In an effort to investigate the mechanism of crack initiation and propagation that lead to fracture failure, the micro-speckle technique is applied to mapping the evolving deformation field surrounding the tip of a notch in a single edge notch tension specimen. Random particles of ~20 μm in size are deposited in the area surrounding the notch. Tensile load was applied to the specimen quasi-statically and the speckle patterns are recorded digitally at the rate of 15 frames per second. Different frames are selected judiciously for analysis using the CASI algorithm [12]. The results are shown in Figure 7 at the crack propagation stage of the

loading. Each set of 3 pictures depicts the u and v displacement contours and together with the total displacement vector map. While the crack was not visible by the naked eye, its path is clearly demonstrated by the deformation field.

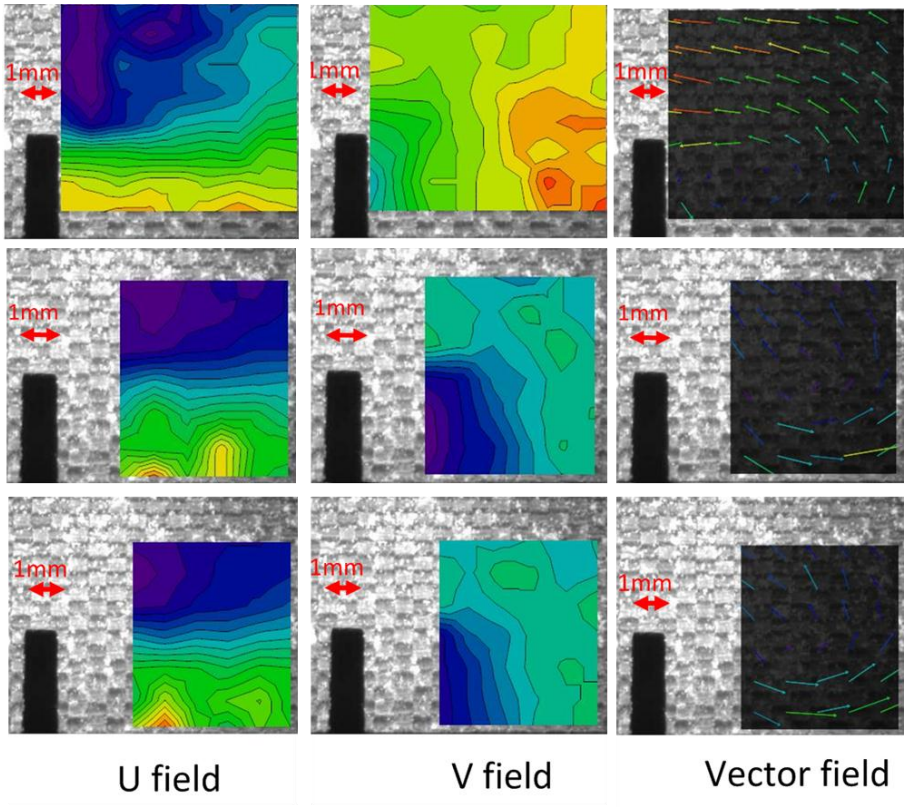

Figure 7. Micro-deformation analysis of crack initiation and propagation in a carbon fiber/vinylester composite using the micro-speckle technique; crack tip is at the left edge of contour plots, which show strain concentration at tip.

4 Conclusions

Composite laminates made from unidirectional carbon fiber-reinforced vinyleseter were characterized for their time-dependent mechanical behavior as a function of exposure to simulated environmental conditions of UV radiation, salt spray, and temperature-humidity conditions. Samples were exposed to four sets of conditions, one which exposed samples to continuous temperature and humidity, a second where samples were exposed to cyclic UV radiation and temperature-humidity conditions, a third which exposed samples to salt spray and temperature, and fourth where samples were exposed to cyclic UV radiation and salt spray. Exposure to the conditions containing UV radiation which mimics naturally occurring sunlight was found to cause micro-cracking in the composite surfaces and edges, and chemical changes in the vinylester matrix. The cracking and chemical changes were most significant when UV radiation and salt spray were combined. Mechanically, samples were tested by three point bending in two fiber orientations, 0° and 90°, where bending modulus was found unchanged, though flexural strength was found to decrease for the 90° fiber orientation, the largest change occurring for the condition containing cyclic UV. The energy release rate was computed for 0° DEN samples in tension, where the decrease in energy release rate was found to occur for the samples exposed to the environmental chambers, with the UV radiation and salt spray case causing the most significant decrease. The results demonstrate that the known synergistic effects between UV radiation and condensation are

exacerbated by the introduction of salt water, and is an important consideration in the design of structures with composites where exposure to sea water is common.

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