THERMAL-MECHANICAL BEHAVIOR OF ACTIVELY COOLED VASCULARIZED COMPOSITES

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1 Introduction

Fiber-reinforced polymer (FRP) composite materials have proven to be a weight saving alternative to traditional structural materials, such as metals, in the aerospace, marine, and automotive industries. A major drawback to FRPs in these applications, however, comes from the limited temperature range over which typical matrix materials such as epoxy, vinyl-ester, and polyester maintain sufficient structural properties. Depending on the glass transition temperature of the matrix, the maximum use temperature for these matrices generally falls in the range of 100 – 200 °C [1]. To use FRPs at higher temperatures active cooling can be utilized. One of the most promising methods for thermal regulation is the use of vascular networks containing an actively pumped coolant.

Vascular networks for thermal management are inspired by a similar system found in nature—the circulatory system—which is capable of maintaining constant body temperature throughout an organism. In addition to thermal stasis, the circulatory system is capable of performing other important functions, such as healing wounds, delivering nutrients, and removing cellular waste; microvascular composites provide a platform for multifunctional behavior in engineering structures [2]. Currently, functions that have been achieved using vascular networks in FRPs include thermal management [3], self-healing [4], electrical and magnetic modulation [2], and damage detection [5]. The focus of this paper is on the use of vascular networks and active cooling for improving the structural performance of a FRP in hot environments.

Several methods have been established for manufacturing vascular networks into a composite. These include wire removal through manual extraction or melting [6], hollow glass fiber integration [7], and sacrificial fiber (SF) removal [2], [8]. For this study the SF method was used to create the channels. In this method, a poly(lactic acid) (PLA) fiber is treated with tin(II) oxalate catalyst, decreasing the thermal degradation temperature of the material. This allows for integration of the SF into a fiber textile at room temperature and subsequent removal at elevated temperatures through thermal depolymerization.

The effectiveness of active cooling on maintaining mechanical properties in a composite was evaluated using a four-point bending test in an environmental chamber, which provides a convective heating environment. Flexural stiffness was used as the metric for evaluating the structural integrity of the cooled composites. Two different channel configurations were compared to non-cooling controls, including specimens containing channels through the mid-plane and specimens containing channels placed near the upper and lower surface. In both cases straight channels were used.

2 Objectives

The objectives of this work are:

- Characterize the high temperature mechanical performance of actively cooled vascular FRP composites.
- Optimize channel configuration and coolant delivery rate to maximize cooling efficiency in vascular composites.
Examine the effect of vascular channels on the flexural strength and stiffness of a 3D textile FRP in room temperature and high temperature environments.

3 Specimen Manufacturing
Vascularized composites were manufactured using the SF method, outlined in Figure 1. The first step in this method is integration of the SF in the fiber preform. This was accomplished by manually inserting the fiber using an appropriately sized sewing hand needle. Next, the epoxy matrix was infiltrated into the composite, in this case using vacuum assisted resin transfer molding (VARTM). Because of the thermal stability of the SF at temperatures below 200 °C, the SF is able to survive a high temperature cure of up to 177 °C without damage. Following matrix solidification, the SF is removed by placing the composite in a vacuum oven for 24 h at 200 °C with the ends of the fibers exposed.

3.1 Sacrificial Fiber Preparation
Sacrificial fibers were prepared using the procedure developed by Esser-Kahn et al. [2] and Dong et al. [8]. In this procedure a 500 µm diameter commercial PLA fiber (Nextrusion Inc.) is treated with tin(II) oxalate (SnOx) catalyst to lower the degradation temperature from approximately 280 °C to 200 °C. This allows for removal of the SF at sufficiently low temperatures to avoid damage to an epoxy matrix. To make the SF, the PLA fiber was wrapped on a custom reel and placed in a bath composed of 480 mL triflouroethanol (Sigma-Aldrich), 320 mL deionized water, 13 g SnOx (Sigma-Aldrich), 40 mL Disperbyk 187 (BYK Chemie), and 1g Rhodamine 6G dye (Sigma-Aldrich). The reel containing the fibers was spun at 400-450 rpm for 24 h at 37 °C to agitate the mixture and prevent settling of the catalyst. Following the treatment process the fiber was removed from the bath and allowed to dry at 37 °C for a minimum of 24 h.

3.2 Vascularized Composite Manufacturing
The fiber preform used for this study was a three-dimensional (3D) orthogonally woven S2 glass fiber textile (TEAM Inc.). A schematic of the unit cell of this textile is shown in Figure 2. The textile has an areal density of 4.07 kg/m² (120 oz/yd²) and is composed of seven total layers, with three in the warp direction and four in the weft direction. These layers are then held together using the z-fibers to create a single textile. To balance the fabric, the spacing between the tows is different in the two directions with 3.0 tows/mm in the warp layers and 2.7 in the weft layers. This results in the fabric having approximately equivalent fiber content in each direction.

Two channel architectures were used for this study, one containing four channels and one containing eight per unit cell (Figure 1). In the four channel specimens the channels were placed at the midplane, adjacent to the warp tows. For the eight channel specimens, four channels were placed on each side of the specimen near the surfaces. Control specimens containing no channels were also manufactured for comparison to vascularized specimens.

Specimens were manufactured by first manually inserting the SF fiber into the textile using a sewing hand needle. Matrix infiltration was then accomplished using the VARTM process. The matrix was composed of EPON 862 epoxy (Miller-Stephenson) mixed with EPIKURE W curing agent (Miller-Stephenson) at a ratio of 100 to 26.4 by weight. Prior to the infusion the epoxy was degassed at 60 °C for approximately 2 h. The preform was placed on a flat aluminum tool and a double bag procedure was used to prevent air leakage into the infusion. While the epoxy was degassing, the textile was heated to 80 °C to reduce the viscosity of the epoxy and speed up the infusion. Following infusion, the vacuum port to the inner bag was sealed to prevent excess removal of epoxy while the outer bag continued to exert pressure on the composite. The epoxy was cured at 121 °C for 8 hours with a 3 °C/min ramp up and 1 °C/min ramp down.

After solidification of the epoxy, the composite was removed from the bag and the four-point bend specimens were cut to size, making sure to expose the ends of the SFs. Final specimens were 100 mm long, 16 mm wide, and approximately 3.75 mm thick. The thickness of the composite did vary slightly but was kept between 3.60-3.90 mm. For all
samples, the loading axis of the beam was along the warp direction in order to orient the channels along the loading axis. The 16 mm width represents slightly more than the width of one unit cell of the textile. Care was taken when cutting the samples to ensure that the channels were centered in the specimen. For specimens containing no channels, the unit cell was positioned to match its location in specimens containing channels. Vascularization was achieved by placing the specimens in a vacuum oven for 24 h at 200 °C. Control specimens were also placed in the oven for this thermal treatment. Following the treatment slightly browning of the epoxy matrix was observed.

3.3 Epoxy Samples

Epoxy samples were manufactured for evaluation of glass transition temperature ($T_g$) and degradation temperature. These samples were made using EPON 862 epoxy (Miller-Stephenson) mixed with EPIKURE W curing agent (Miller-Stephenson) at a ratio of 100 to 26.4 by weight. The epoxy was first degassed in a vacuum oven at 60 °C for approximately 2 h, to remove bubbles. The epoxy was then poured into a closed mold composed of two glass plates separated at a distance of 2 mm by a silicone rubber gasket. The epoxy was cured in a convection oven at 121 °C for 8 hours then removed from the mold. The solid epoxy was post-cured in the same vacuum oven used for removal of the sacrificial fibers at 200 °C for 24 h. Samples were cut from the resulting epoxy plate using a diamond blade wet saw to the appropriate size required for the test.

4 Testing Procedures

4.1 High Temperature Flexure Testing Of Composites

Composite samples were evaluated using a four-point bending procedure according to ASTM D7264 on an electromechanical testing machine (Instron Model 5982). To control temperature, tests were run in an environmental chamber (Instron Model 3119-410), which provided convective heating to the sample. Load was measured using a 150 kN load cell, which was included on the frame. Center point deflection was measured using a video extensometer (Instron Model 2663-821) with a 60 mm field of view lens. Flexural modulus was used to compare structural integrity of the composites under different cooling conditions. The maximum flexural stress was calculated as

$$\sigma_f = \frac{3PL}{4bh^2}$$

where $P$ is the load, $L$ is the length, $b$ is the width, and $h$ is the height of the beam. The maximum flexural strain is

$$\varepsilon_f = \frac{4.36\delta h}{L^2},$$

where $\delta$ is the center point deflection of the beam. The modulus is then calculated as the change in flexural stress over change in strain between two defined strain limits,

$$E_f^{chord} = \frac{\Delta \sigma_f}{\Delta \varepsilon_f}. \quad (3)$$

Figure 3 shows a schematic of the testing setup. Load was applied at a constant crosshead displacement rate of 1 mm/min. The test was conducted to 0.21% strain in order to prevent damage to the composites and allow for multiple tests on each specimen. Modulus was measured between 0.1-0.2% strain. For both 4 channel and 8 channel specimens the channels were oriented along the length of the beam. In control samples, the orientation of the unit cell matched the orientation in cooling specimen. Tests were run at five environmental temperatures: 25 °C, 175 °C, 225 °C, 275 °C, and 325 °C. At each temperature the specimen was tested twice in succession to confirm that modulus remained constant and steady state was reached.

Control samples were tested at only two temperatures, once at room temperature then again at one of the four high temperature conditions. For high temperature tests, the oven was preheated to steady state, then the sample was placed in the oven and given 20 min. to reach steady state before testing.
For cooling samples, a coolant delivery system was designed to pump water through the channels. Water was delivered using a peristaltic pump (Cole Parmer Masterflex Model EW-07551-00), which was able to deliver water through up to 8 channels individually. Water was delivered to the specimen through silicone rubber tubing, insulated with high temperature glass fiber wool insulation wrapped in aluminum foil. This minimized increases in coolant temperature prior to entering the specimen. Connection of the delivery system to the specimen was made using two 21 gage stainless steel syringes at each end of a channel. One syringe was connected to the silicone tubing, while the other was inserted 2-3 mm directly into the channel and sealed with epoxy adhesive (J-B Weld epoxy). To allow for insertion of these syringes into the sample, the end of the channels was drilled 2-3 mm deep. The two syringes were connected using a high temperature, low contraction heat shrink tubing (fluorinated ethylene propylene, McMaster-Carr). The purpose of the heat shrink tubing is to provide a flexible connection to the sample and avoid any mechanical constraint at the ends of the sample. The syringes were also insulated to prevent heating of the coolant outside of the specimen.

Cooled specimens were tested at all four elevated temperature conditions in succession (175 °C, 225 °C, 275 °C, and 325 °C). Prior to increasing the environmental temperature the specimens were tested at room temperature. The cooling system was then turned on, pumping water through the channels. The chamber was first set at 175 °C and allowed to come to steady state for 45 min before testing. After the test, the environmental temperature was increased to 225 °C, allowed to stabilize for 20 min., and the test was run. The process was repeated at 275 °C and 325 °C. Prior to the test at each environmental temperature the load cell was calibrated to compensated for increased temperature. For each specimen a full cycle of tests were run at a given flow rate before allowing the system to cool back to room temperature. Each specimen was tested through two cycles at different flow rates, which is summarized in Table 1. No change in room temperature stiffness was observed for the samples between cycles. For the 8 channel, 160 ml/min test, a second specimen was tested, which yielded results that differed by less than 1% at all test temperatures compared to the first sample. As part of the future work, all tests will be run with a minimum of three specimens in order to confirm consistency of results.

4.2 Epoxy testing procedure
Two different tests were run on the epoxy samples, including dynamic mechanical analysis (DMA) to measure T<sub>g</sub> and thermogravimetric analysis (TGA) to measure the degradation temperature. For the DMA test, the epoxy was cut to form a 35 mm long, 6 mm wide, and 2 mm thick specimen. A three-point bending test procedure was used with oscillations at a frequency of 1 Hz and maximum strain of 0.2% with an outer span of 25 mm. The temperature was ramped at a constant rate of 5 °C/min from 25-250 °C. The test was run twice to confirm results. For the TGA test, the epoxy was cut to form a 5-10 mg specimen with approximately cubic geometry. The test was run under a nitrogen atmosphere at a rate of 10 °C/min from 25-600 °C. Again, the test was run twice to confirm results.

5 Results and Discussion

5.1 Glass Transition and Thermal Degradation Temperature of Epoxy
Results for the DMA and TGA tests of the neat epoxy are shown in Figure 4 and Figure 5, respectively. The DMA test shows that the epoxy has a T<sub>g</sub> of 145 °C. Prior to the T<sub>g</sub> we see relatively gradual softening of the epoxy as its modulus reduces from 2.8 GPa at room temperature to approximately 1.8 GPa just prior to T<sub>g</sub>. As expected, at T<sub>g</sub> there is a rapid drop in modulus of approximately two orders of magnitude. Past T<sub>g</sub> we observe a gradual increase in modulus, which is likely due to plastic deformation and sagging of the specimen and does not accurately reflect the modulus of the material.

The TGA test shows a degradation temperature of 330 °C. Prior to degradation the mass of the epoxy is constant, with a steep drop-off at 330 °C. At this temperature the epoxy thermally degrades and irreversible damage is done to its molecular structure.

5.2 Effect of Vasculature at Room Temperature
Results for specimens tested at room temperature are shown in Figure 6, with a statistic analysis summarized in Table 2. An ANOVA test was run with a Tukey’s range post hoc test to determine if the categories were statistically different at a 5% significance level. Results show a 1.3% reduction of properties due to the inclusion of the 4 channels at the mid-plane, and a 3.3% reduction due to the inclusion of 8 channels near the surface. Only the 8 channel specimens were found to be significantly different than the controls. These results reflect that in the 4 channel specimens, channels are placed at the neutral axis yielding minimal effect on flexural stiffness. In the 8 channel specimens on the other hand, channels are placed near the surfaces where they have the potential to be more detrimental to flexural stiffness.

5.3 Actively Cooled Composites

Figure 7 shows the results for the 8 channel specimen cooled at a total flow rate of 320 ml/min compared to non-cooled specimens at elevated temperature. Results are shown in terms of stiffness retention, which is a ratio of the high temperature stiffness to the room temperature stiffness. Non-cooling results show 45% stiffness retention at 175 °C, decreasing to 40% at 275 °C. At 325 °C, the matrix of the non-cooled composites thermally degraded and showed no structural capability. In comparison, the cooled composite showed damage retention of 97% at 175 °C, steadily decreasing to 89% at 325 °C. These results represent nearly full retention of flexural properties in an environment that would otherwise destroy the composite.

A comparison of stiffness retention at high temperature for all test cases is shown in Figure 8. Composites containing 8 channels show better cooling capability at all temperatures, particularly at 275 °C and 325 °C, even with the same total flow rate. This demonstrates that placing channels near the boundaries provided better cooling than placing channels near the mid-plane. For both the 4 channel and 8 channel composites, doubling the flow rate did not provide significantly improved cooling.

6 Conclusions and Future Work

Active cooling allows composites to retain structural capability in high temperature environments. Active cooling tests were conducted using a four-point flexure procedure in an environmental chamber to evaluate stiffness retention in a high temperature environment. Two channel architectures were considered, including one with channels placed only at the neutral axis and one with channels placed near the surfaces of the composite. Tests for both architectures were run at two different flow rates. Results were compared to non-cooling control samples containing no channels. At room temperature, composites containing channels showed minimal drops in stiffness. At elevated temperatures, cooled specimens demonstrated the ability to maintain structural properties well above the glass transition temperature of the matrix. At 325 °C, a temperature that degraded the matrix of non-cooled specimens, up to 89% of stiffness was retained.

Future work will include tests of additional channel architectures and flow rates. In addition, further confirmation of results of stiffness tests will be conducted by repeating tests.

Figures
Fig. 2: The 3D orthogonally woven textile showing textile composition and placement of the channels in vascular specimens. Two vascular architectures were tested, including one with 4 channels and one with 8 channels.

Fig. 3: A schematic of the high temperature testing setup used to characterize the stiffness of actively cooled composites at high temperature.

Fig. 4: Results from the DMA test of neat epoxy showing a $T_g$ of 145 °C.

Fig. 5: Results from the TGA test of neat epoxy showing a degradation temperature of 330 °C.

Fig. 6: Flexural stiffness of specimens containing no channels, 4 channels, and 8 channels at room temperature. Error bars represent one standard deviation.
Fig. 7: A comparison between stiffness retention with and without cooling. Cooling results are for the 8 channel specimen with a total flow rate of 320 ml/min. Non-cooled composites at 325 °C thermally degraded and therefore showed no stiffness retention. Error bars on the non-cooling data represent one standard deviation. No error bars are provided on the cooling data because it only represents results from one test.

Table 1: Active cooling test conditions, including number of channels and flow rate. \( Q_t \) is the total flow rate through the specimen and \( Q_c \) is the flow rate through each channel in the specimen.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>4 Channel</th>
<th>8 Channel</th>
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<tbody>
<tr>
<td></td>
<td>( Q_t ) (ml/min)</td>
<td>( Q_c ) (ml/min)</td>
</tr>
<tr>
<td>1</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>40</td>
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Table 2: Statistical analysis of the effect of channels on flexural stiffness.

<table>
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<tr>
<th>Channels</th>
<th>Reduction</th>
<th>ANOVA ((\alpha = 0.05))</th>
<th>Significant Difference?</th>
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<tr>
<td>4</td>
<td>1.3%</td>
<td>0.314</td>
<td>No</td>
</tr>
<tr>
<td>8</td>
<td>3.3%</td>
<td>0.006</td>
<td>Yes</td>
</tr>
</tbody>
</table>

References


