PRELIMINARY EXPERIMENTAL STUDY OF USING NANO-ENHANCED EPOXY ADHESIVE TO BOND CARBON NANOFIBERS Z-THREADED CFRP LAMINATES

Ryan A. Warren, William W. Taylor, Mohammad R. Islam, Kuang-Ting Hsiao*
University of South Alabama
Mobile, AL

ABSTRACT

Previous studies have provided evidence that reinforcement of epoxy adhesives with nanostructures such as carbon nanofibers (CNFs) produces higher strength bonded joints between carbon fiber reinforced polymer (CFRP) laminates and shifts bond-line failure modes from the adhesive into the laminate. Despite this, there has been no research dedicated to applying reinforced adhesives to the bonding of nano-reinforced CFRP such as CNF z-threaded carbon fiber reinforced polymer (ZT-CFRP) laminates, which have been proven to exhibit increased interlaminar shear strength, mode-I delamination toughness, and compressive strength over traditional CFRP. This study examined the effectiveness of using CNF reinforced epoxy adhesives for unidirectional ZT-CFRP laminate bonding through single-lap shear tests using the ASTM D5868-01 standard. Unidirectional CFRP laminate samples bonded with both epoxy adhesive and CNF reinforced epoxy adhesive were also tested for comparison. It was found that the average shear strength observed for ZT-CFRP samples bonded with CNF reinforced epoxy adhesive was approximately 44% and 26 % higher than that of CFRP samples bonded with epoxy adhesive and CNF reinforced epoxy adhesive, respectively. Microscopic image analysis was performed to examine the mode of bond failure. The roles of nanomaterials in the fracture mechanism of the adhesives and the composite laminates are also discussed.

Keywords: Bond-line, Carbon Nanofiber, Z-threaded CFRP, Nano-Enhanced Composite Bonding System
*Corresponding author: Kuang-Ting Hsiao, Email: kthsiao@southalabama.edu

1. INTRODUCTION

Carbon nanofiber (CNF) z-threads have proven to be a reliable resource in improving the mechanical properties of carbon fiber reinforced polymer (CFRP) laminates. The addition of CNF z-threads has been observed to largely strengthen properties such as mode-I delamination toughness, interlaminar shear strength and longitudinal compressive strength that are more dependent upon the matrix used within a CFRP laminate rather than the reinforcing carbon fiber. Hsiao et. al showed that mode-I delamination toughness was increased by 28.93% with the introduction of CNF z-threads when compared to a traditional CFRP laminate [1]. CNF z-threads inclusion was shown by Kirmse et. al to result in an increase in compressive strength and interlaminar shear strength when compared to regular CFRP by 14.83 and 35.13 %, respectively [2,3]. The principle behind z-threaded CFRP (ZT-CFRP) is that CNFs are threaded through the fiber array in the through-thickness direction. A depiction of the idea behind ZT-CFRP is provided in Figure 1. The fiber array (shown as blue circles in Figure 1) embedded in a polymer matrix runs longitudinally within the x-y plane. The much thinner z-threaded CNFs (shown as black lines in Figure 1) weave through this array in the z-direction.

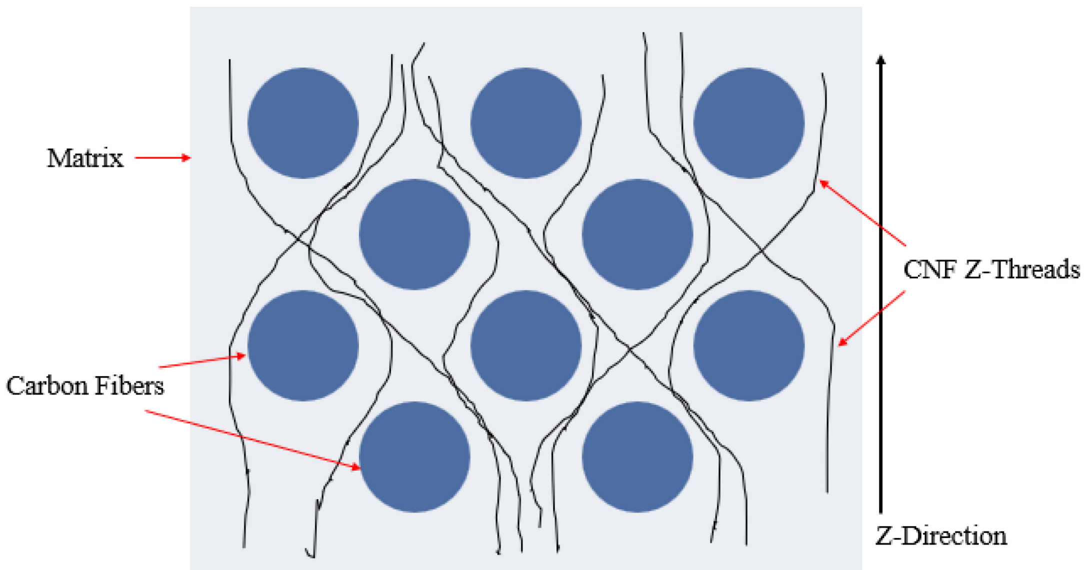

Figure 1: Depiction showing the principle behind ZT-CFRP.

It has also been observed that the addition of nanomaterials to reinforce adhesives has increased bonding performance of CFRP and other materials such as metal [4,5,6]. Vietri et. al showed that the addition of CNFs increased the shear strength of single-lap bonded joints by up to 40% and caused the failure mode to shift into the adherend [7]. The addition of 0.5 wt% carbon nanotubes (CNTs) caused the ultimate shear strength of single-lap bonded CFRP joints to increase by approximately 19% in a study by Soltannia and Taheri [8]. Hsiao et. al found even further gains in improving shear strength of bonded CFRP through use of CNTs to reinforce epoxy adhesives [9]. It was observed that the adhesive shear strength was increased by 31.2 and 45.6% when using 1 and 5 wt% CNTs, respectively. Korayem et. al used CNT reinforced epoxy adhesives to bond CFRP to steel in double-strap joint arrangements and found that the ultimate shear stress of the reinforced joints was increased by approximately 8% [10]. The effects of CNF and CNT epoxy reinforcement on mode-I delamination for CFRP double cantilever beam joints were observed by Gude et. al [11]. It was found that failure occurred within the laminates rather than the reinforced adhesive layer and mode-I fracture energy was increased by 26 and 24% for CNF and CNT reinforcement, respectively.

Despite the increased mechanical properties of ZT-CFRP, there have been no studies dedicated to examining its effect on bond-line failure. This study examined the effectiveness of CNF reinforced epoxy adhesives in bonding ZT-CFRP laminates. This was accomplished using single-lap shear tests based on the ASTM D5868-01 standard to measure and analyze the shear strength of three different cases of bonded samples. The three different cases of bonded samples evaluated were CFRP coupons bonded with epoxy adhesive, CFRP coupons bonded with CNF reinforced epoxy adhesive, and ZT-CFRP coupons bonded with CNF reinforced epoxy adhesive. The process of manufacturing the samples along with shear strength testing data and selected microscopic images of the tested surfaces are provided within the document.

2. EXPERIMENTATION

This section details the materials and methods used to manufacture the three different cases of samples evaluated in this study. Each bonded sample was prepared and tested in compliance with the ASTM D5868-01 standard.

2.1 Materials

All sample coupons made in this study were manufactured from unidirectional T700S carbon fiber fabric with a fiber density and areal weight of 1.8 g/cm^3 and 680 g/m^2, respectively. The fabric had a tow size of 12K. The adhesives used for bonding and the matrices of the coupons were made from a resin mixture of Epon-862 and Epikure-W, both purchased from Miller-Stephenson Chemical Company. Disperbyk-191 and Disperbyk-192, both purchased from BYK USA, were used in cases where nanofiber reinforcement was used in either the adhesive or coupons. CNFs used in this study were PR-24-XT-HHT grade purchased from Pyrograph Products/ Applied Sciences Incorporated. The CNFs had an average diameter of 100 nm and were between 50 to 200 microns long. 20-gauge galvanized steel wire and large binder clips were used for the bonding process.

2.2 Sample Preparation

Two types of coupons were prepared and bonded for this study: CFRP and ZT-CFRP. CFRP coupons manufactured contained no nanomaterials and consisted only of fiber and resin. ZT-CFRP coupons contained CNF z-threads between the carbon fibers within the matrix, as shown in Figure 1. Regular and CNF reinforced epoxy adhesives were used to bond the manufactured coupons.

2.2.1 CFRP coupons

CFRP coupons were manufactured using a combination of Epon-862 and the curing agent Epikure-W, mixed to a stoichiometric ratio of 100:26.5, respectively. The resin batch was mixed manually for 5 minutes and then placed inside a vacuum oven for degassing at 80 °C and -0.09 MPa for 40 minutes. After degassing, the resin was then used in a hand wet layup process to impregnate four 38.1x38.1 cm (15x15 in) sheets of T700S fabric to create stackable prepreg. The impregnated fabric sheets were then placed inside a hot press at 120 °C for approximately 25 to 30 minutes until the prepreg was partially cured or reached “B-stage”.

The four sheets of prepreg were then stacked and placed on a release agent coated plate. The stack was then covered with an out-of-autoclave vacuum-bag-only (OOA-VBO) setup. A depiction of the OOA-VBO setup is provided in Figure 2. The stack within the OOA-VBO setup underwent 1 hour of debulking at room temperature before being subjected to 120 °C for 2 hours. The laminate was then removed from the OOA-VBO setup and placed within a hot press for 2 hours at 180 °C for post-curing. The OOA-VBO process was carried out using a vacuum pressure of -0.09 MPa. The 38.1x38.1 cm laminate was then cut into multiple 25.4x101.6 mm (1x4 in) coupons using a combination of a table saw with a continuous rim diamond grit edged blade and rotary tool. The coupons were then sanded as needed to reach a thickness of 2.5 mm (0.1 in). All coupon surfaces were abraded with 80 grit sandpaper prior to bonding. The use of 80 grit sandpaper to create a surface profile for adherence was based off a procedure followed by a previous similar study [12].

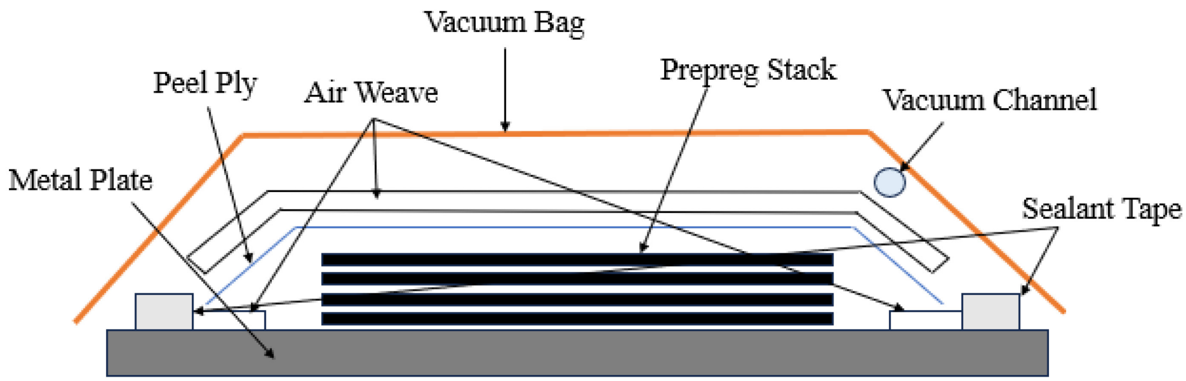

Figure 2: Depiction of the OOA-VBO setup.

2.2.2 ZT-CFRP coupons

The resin used for the ZT-CFRP was a combination of Epon-862 and 1 wt% each of CNF, Disperbyk-191, and Disperbyk-192. All components were stirred manually for 5 minutes upon being mixed with each other. The resin batch then underwent 1 hour of high-shear mixing, alternating rotational direction after 30 minutes. A quality check of the resin blend was then performed to verify whether the CNFs were adequately dispersed within the resin. This was done by taking a sample from the resin batch and viewing it under a Nikon Eclipse LV150 microscope. The resin batch was then subjected to 1 hour of sonication if it was determined that the CNFs were adequately dispersed after high-shear mixing. Another quality check was performed after sonication to confirm the CNFs were still well-dispersed and not substantially agglomerated within the resin blend. Figure 3 provides an image of CNF dispersion within the resin blend. This was again accomplished by taking a sample from the resin batch and viewing it under a microscope. If suitable, the resin blend was then placed in a vacuum oven at 120 °C and -0.09 MPa for 1 hour of degassing. A quality check was again performed to ensure adequate dispersion of CNFs was maintained. Epikure-W was then added and gently hand-mixed into the blend at a stoichiometric ratio of 26.5:100 to Epon-862. If a sample failed a quality check at any time, the previous step was repeated until the resin batch was deemed acceptable.

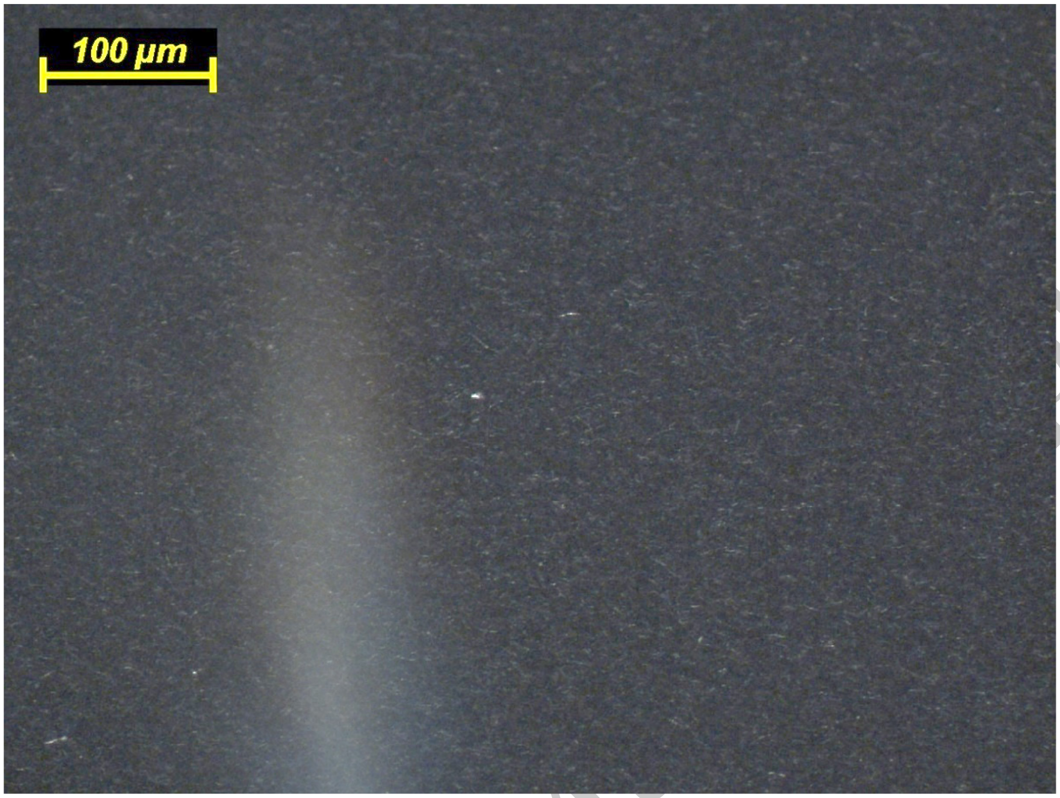

Figure 3: Microscopic image showing dispersion of CNF within the resin blend.

The resin blend was then used in a proprietary production machine for the alignment of CNFs and the subsequent manufacturing of ZT-CFRP prepreg. The proprietary production machine works by developing a film containing electrical-field-aligned CNF in the z-direction from the resin blend. The film is then used to impregnate a dry piece of carbon fiber fabric while maintaining CNF alignment. Four sheets of 22.86x12.7 cm (9x5 in) ZT-CFRP prepreg were produced and stacked for the creation of a laminate. Figure 4 provides an image of the manufactured ZT-CFRP prepreg. The CNF can be seen aligned horizontally in the image with the carbon fiber running vertically. Multiple samples from the manufactured prepreg were taken and viewed underneath a microscope to ensure the CNFs were appropriately aligned between the carbon fibers prior to stacking. The OOA-VBO setup and curing cycle used for the previously mentioned CFRP coupons was followed to cure the ZT-CFRP laminate. The ZT-CFRP laminate was cut into multiple 25.4x101.6 mm (1x4 in) coupons using a combination of a table saw with a continuous rim diamond grit edged blade and rotary tool. The coupons were then sanded as needed to reach a thickness of 2.5 mm (0.1 in). All coupon surfaces were abraded with 80 grit sandpaper prior to bonding.

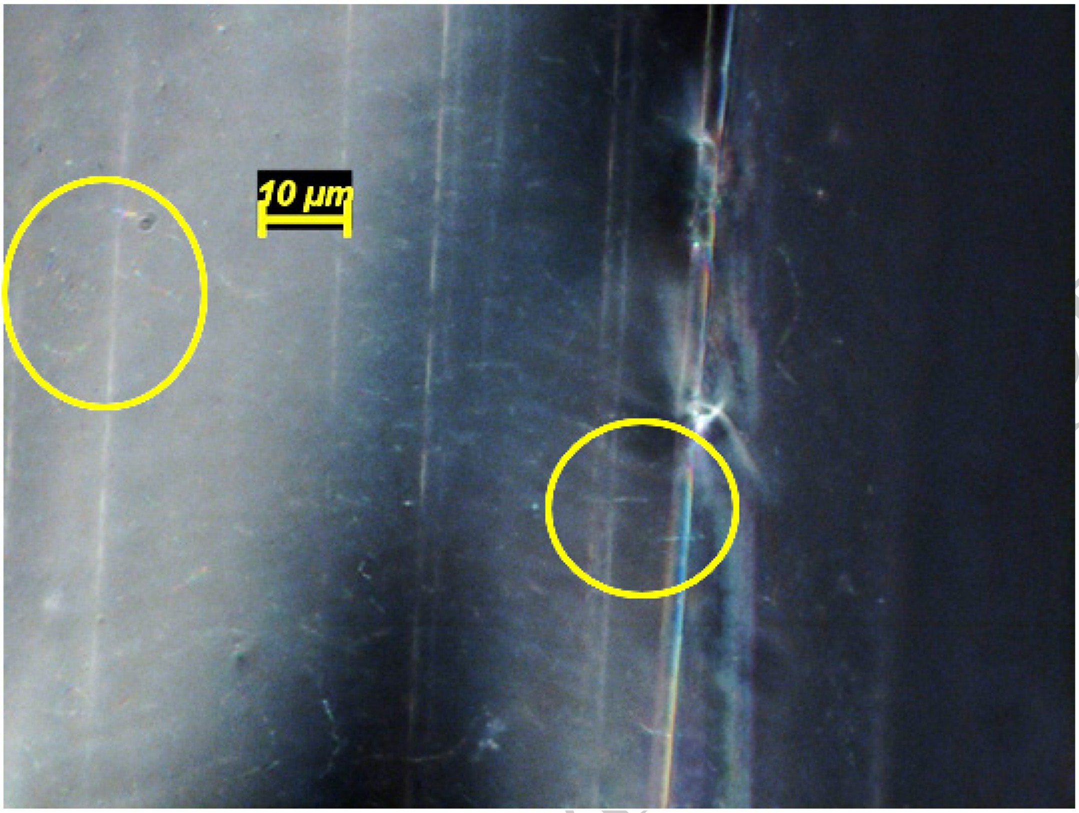

Figure 4: Microscopic image showing aligned CNF fibers between the carbon fiber array.

2.2.3 Adhesives

Two types of adhesives were prepared for this study: epoxy and CNF reinforced epoxy. Epoxy adhesive was prepared by mixing Epon-862 and Epikure-W at a ratio of 100:26.5, respectively. The mixture was hand mixed for 5 minutes and then degassed in a vacuum oven at 80 °C and -0.09 MPa for 40 minutes.

The reinforced epoxy adhesive was also prepared mixing Epon-862 and Epikure-W at a ratio of 100:26.5, respectively, but included CNF and surfactants Disperbyk-191 and Disperbyk-192. CNF and the two surfactants were added each as 1 wt% of the total mass of the resin blend. Prior to the addition of Epikure-W, the blend was high-shear mixed for 1 hour, alternating rotational direction after 30 minutes. A quality sample was then taken from the batch and viewed under a microscope to assess the dispersion of CNFs within the resin blend. If adequate, the resin blend was then sonicated for 1 hour. A quality sample was taken again to assess whether there was substantial agglomeration of CNFs within the blend. If acceptable, the blend was then placed in a vacuum oven at 120 °C and -0.09MPa for 1 hour for degassing. Another quality sample was then taken to assess the dispersion of the CNFs. If acceptable, Epikure-W was then added and gently hand-mixed into the resin blend. If a sample failed a quality check at any time, the previous step was repeated until the resin batch was deemed acceptable.

2.2.4 Bonding

The CFRP and ZT-CFRP coupons manufactured through the procedures described in the previous sections were bonded with either epoxy or CNF reinforced epoxy adhesives. Bonding of samples all followed the same procedure regardless of the case being tested. All samples were bonded in compliance with the ASTM D5868-01 standard [13]. Figure 5 provides a depiction of the dimensions required for a bonded CFRP sample by the standard.

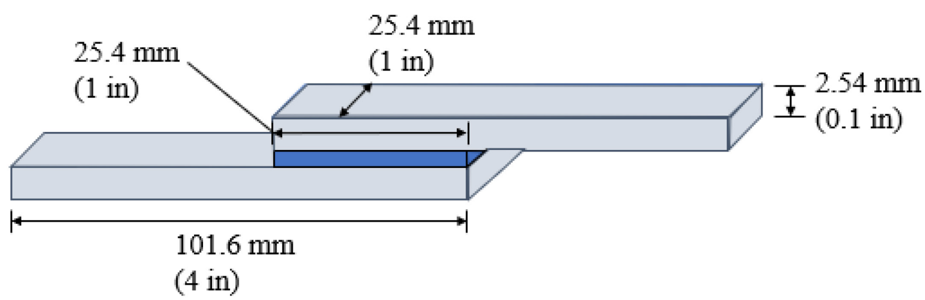

Figure 5: Sample dimensions required by the ASTM D5868-01 standard for fiber reinforced plastic bonding.

The individual coupons were cleaned prior to bonding. The cleaning process started by vacuuming the samples to remove residual debris from sanding. The coupons were then wiped down with acetone before being cleaned with water and hand dried. The coupons then set out for 24 hours to completely dry. The coupons were then marked to designate the area where adhesive would be applied and to help with positioning while bonding.

The adhesives, both unreinforced and CNF reinforced, were B-staged for approximately 40 minutes at 120 °C prior to being applied to the coupons. The B-staged adhesive was then applied to a 25.4x25.4 mm (1x1 in) area at the end of a coupon. A minimum amount of small pieces of 20-gague galvanized steel wire was then distributed within the 645.16 mm^2 (1 in^2) area of adhesive. This was done to maintain an approximate bond-line thickness of 0.76 mm (0.03 in) since 20-gague wire is approximately 0.81 mm (0.03 in). The procedure for adding a wire to control the bond-line thickness while still in compliance with the ASTM D5868-01 standard was adapted from a previous similar study [14]. The top image of Figure 6 provides an image showing how the pieces of wire were placed within the applied adhesive. A clean coupon was then aligned and pressed onto the 645.16 mm^2 area of epoxy so that it would resemble the bonded sample shown in Figure 5. The coupons were pressed down so that they were in contact with the pieces of steel wire. Medium-sized binder clips were then applied to both sides of the adhesive area to maintain an adequate pressing force during bonding. This is shown in the bottom image of Figure 6. Excessive adhesive squeezed out during pressing was wiped away.

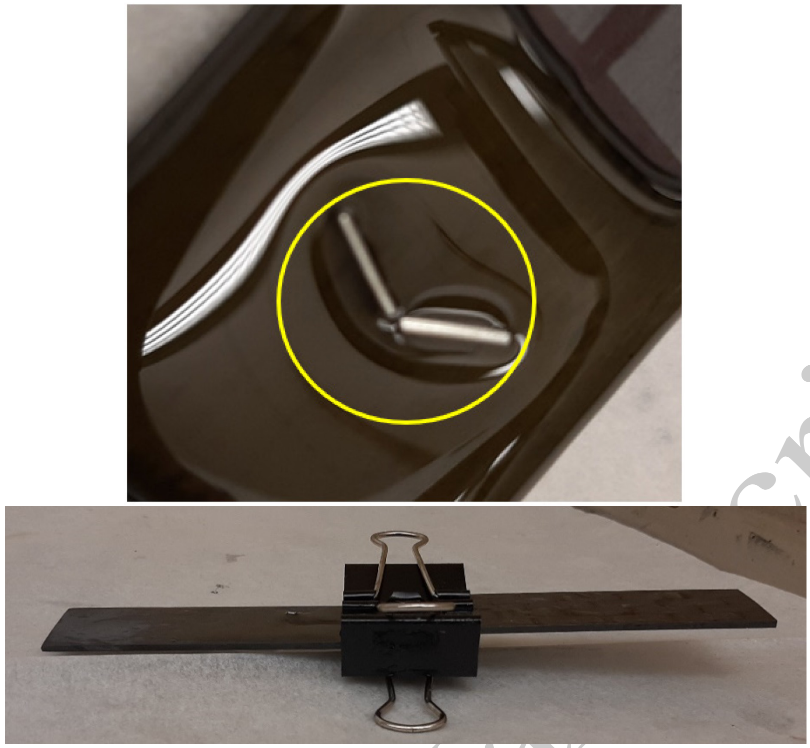

Figure 6: Placement of 20-gauge steel wire (diameter~0.81 mm) within adhesive to maintain bond line thickness (*top*); use of binder clips to maintain pressing force while curing (*bottom*).

The bonded coupons were then placed within an oven at 120 °C for 2 hours for curing. The binder clips were then removed, and the bonded samples underwent 2 hours of post-curing at 180 °C. The bonded samples were sanded and polished as needed to remove any excessive resin that leaked out of the bonding area during curing. This sanding and polishing process started with 120 grit sandpaper with increasingly finer sandpaper being used until ending with 600 grit. Five bonded samples for each of the three tested cases were prepared.

2.3 Testing

Lap shear testing of the bonded samples was accomplished using a Tinius Olsen 10ST universal testing machine. The loading rate used was 13 mm/min (0.5 in/mm) as specified by ASTM D5868-01. Initial testing fixture grip separation was 76.2 mm (3 in). Approximately 50.8 mm (2in) of the sample ends were held within the testing fixture grip, fulfilling the 25.4 mm (1in) minimum requirement specified by ASTM D5868-01. Before testing it was made sure that the fixtures were appropriately aligned to produce optimal shear strength readings of the bonded samples. This was done to minimize the influence of other stress-inducing factors such as torsion and bending.

3. RESULTS

The results from testing and selected microscopic images of the debonded surfaces of the lap-shear tested samples are provided in this section.

3.1 Testing Results

All the samples tested, regardless of case, resulted in adherend failure. This means that either one or both of the either CFRP or ZT-CFRP bonded coupons in an individual test had a portion of the surface of the top fiber layer torn off. Most of the tested specimens resulted in a clean adherend breakage/delamination of just one of the coupon surfaces. There were about five samples, three for CFRP coupons bonded with epoxy adhesive and two for ZT-CFRP coupons bonded with reinforced epoxy adhesive, that had adherend damage to both bonded coupon surfaces.

Table 1 provides the shear strength values recorded from testing the bonded samples. The average, standard deviation, and coefficient of variation for the shear strength values are also provided for each of the three cases tested. The green and red highlighted cells represent the minimum and maximum shear strength, respectively, recorded for each tested case.

Table 1: Shear strength testing results observed for each of the three cases of samples.

	Shear Strength Values (MPa)		
	CFRP w/ Epoxy	CFRP w/ Reinforced Epoxy	ZT-CFRP w/ Reinforced Epoxy
Test 1	8.2853	6.3844	13.840
Test 2	8.5806	12.569	18.276
Test 3	8.9759	12.044	13.539
Test 4	9.3103	7.3340	8.3027
Test 5	10.414	13.508	11.560
Average	9.1133	10.368	13.104
Standard Deviation	0.7375	2.9185	3.2531
Coefficient of Variation (Dimensionless)	0.0809	0.2815	0.2483

Tested ZT-CFRP coupons bonded with reinforced epoxy adhesive produced the highest average shear strength with CFRP coupons bonded with reinforced epoxy adhesive following behind. Tested CFRP coupons bonded with epoxy adhesive were observed to produce the lowest average shear strength. Despite the average shear strength for CFRP coupons bonded with reinforced epoxy adhesive being higher than those bonded with epoxy adhesive by 1.2547 MPa, the average shear strength of CFRP coupons bonded with epoxy adhesive is well within one standard deviation of the values observed testing those with reinforced epoxy adhesive. The tested ZT-CFRP coupons bonded with reinforced epoxy adhesive exhibited a higher average shear strength than the other two cases, with the average shear strength of the CFRP coupons bonded with reinforced epoxy adhesives being slightly within one standard deviation of what was observed.

Six ZT-CFRP coupons were reused due to a shortage of the necessary number required for testing five bonded samples when this paper was being written. This was also done because two of the original coupons had the surface near the bond slightly damaged during sanding and polishing to remove excessive resin left from bonding. The reused samples were sanded down to remove the bond from the surface and any previous damage. Table 2 provides the shear strength observed for all the ZT-CFRP coupons tested and identifies whether the sample was made from reused coupons.

It also identifies the previous test they were reused from. The yellow shading identifies the values that were used within Table 1. Tests 6 and 7 were not included in the values from Table 1 since they were the samples that had been damaged when removing excess resin leftover from bonding. Tests 6 and 7 coupons were reused for tests 3 and 4, respectively.

Table 2: Testing results observed for all ZT-CFRP samples bonded with reinforced epoxy along with identification of the coupons that were reused.

	Shear Strength (MPa)	Reused Sample Coupons
Test 1	13.840	N/A
Test 2	18.276	N/A
Test 3	13.539	Test 6
Test 4	8.3027	Test 7
Test 5	11.560	Test 1
Test 6 (with preparation-damage prior to testing)	9.6897	N/A
Test 7 (with preparation-damage prior to testing)	9.7177	N/A
Average	12.132	
Standard Deviation	3.1493	
Coefficient of Variation (Dimensionless)	0.2596	

Table 3 provides comparisons between the average shear strengths observed for each tested case. The average shear strength that includes the testing data from the two damaged samples for ZT-CFRP coupons bonded with reinforced epoxy adhesive is also provided. ZT-CFRP coupons bonded with reinforced epoxy adhesive were observed to have an improvement in average shear strength of approximately 44 and 26 % over samples of CFRP bonded with epoxy and reinforced epoxy adhesive, respectively.

Table 3: Comparison of the average shear strengths for each of the three cases tested.

Sample Case	Average Shear Strength (MPa)	Improvement over CFRP w/ Epoxy (%)	Improvement over CFRP w/ Reinforced Epoxy (%)
CFRP w/ Epoxy	9.1133	N/A	-12.101
CFRP w/ Reinforced Epoxy	10.368	13.767	N/A
ZT-CFRP w/ Reinforced Epoxy	13.104	43.786	26.386
ZT-CFRP Including Preparation-Damaged Samples	12.132	33.126	17.017

3.2 Microscopic Images

Microscopic image analysis was performed on the damaged coupon surfaces after testing. Figure 7 provides example images from each tested case showing the amount of fiber pulled off from the adherend. It was found that CFRP bonded with epoxy adhesive resulted in the most fiber being removed from the adherend (approximately 500 μm from each test), however, there was also more variability in the amount of fiber pulled off when compared to the other sample cases. ZT-CFRP bonded with reinforced epoxy adhesive had the second highest amount of fiber removed with approximately 160 μm of adherend removed for each test. CFRP bonded with CNF-reinforced epoxy adhesive had the least amount of fiber removed with approximately 100 μm of adherend removed for each test. When comparing the CNF-reinforced epoxy adhesive bonded ZT-CFRP and CFRP samples, assuming the CNF-reinforced adhesive contributed to a similar stress distribution and concentration effect to the adherend, the CNF z-threads seemed to hold the ZT-CFRP laminate better during the single lap shear test. It is not clear why the CFRP bonded with epoxy adhesive had thicker layer of adherend being removed and more variability in the amount of fiber pulled off; a hypothetical explanation is that the epoxy adhesive could contribute to higher stress concentration triggering such failure, however, this could not be validated in this preliminary study.

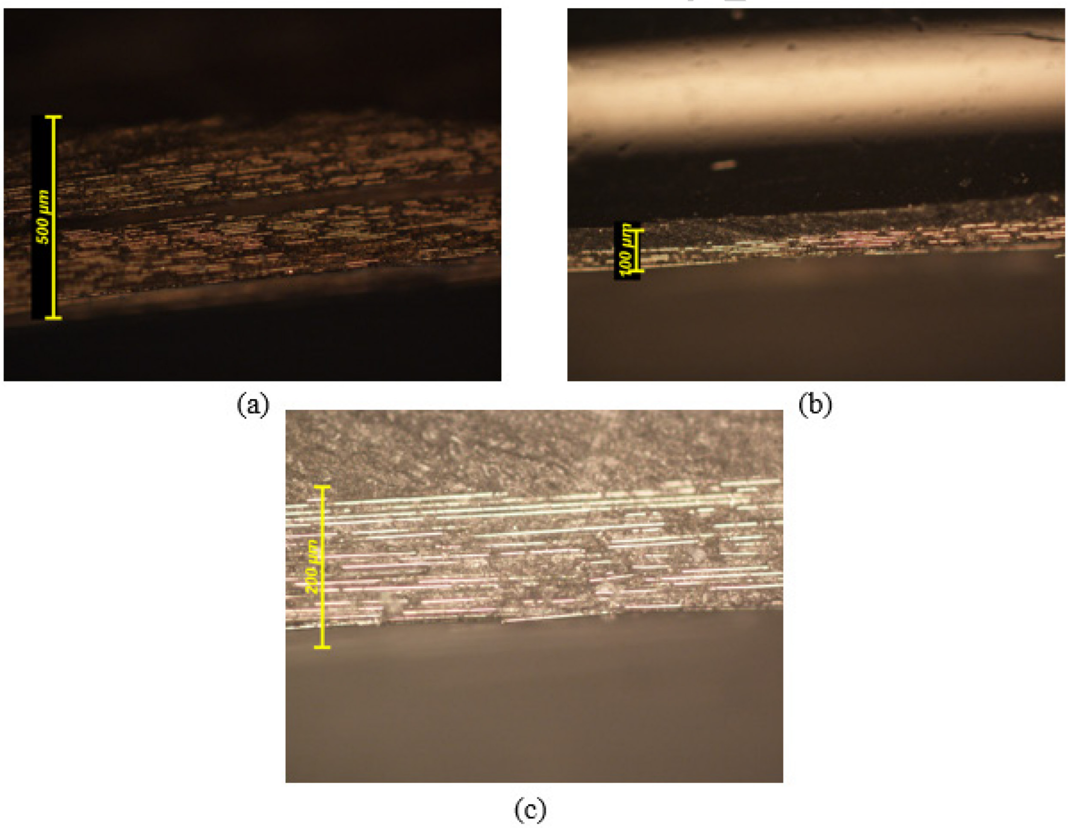

Figure 7: Carbon fiber pulled off from testing for: CFRP bonded with epoxy adhesive (Test 2) (*a*), CFRP bonded with reinforced epoxy adhesive (Test 5) (*b*), and ZT-CFRP bonded with reinforced epoxy adhesive (Test 4) (*c*).

Figure 8 provides two images showing CNF alignment within the ZT-CFRP samples near the fractured surface of the adherend. The top image provides a good depiction of how CNFs are threaded through the fiber array. Areas with CNF alignments are circled. The bottom image shows more CNF alignment than the top image but does not benefit from the inclusion of carbon fibers within the image.

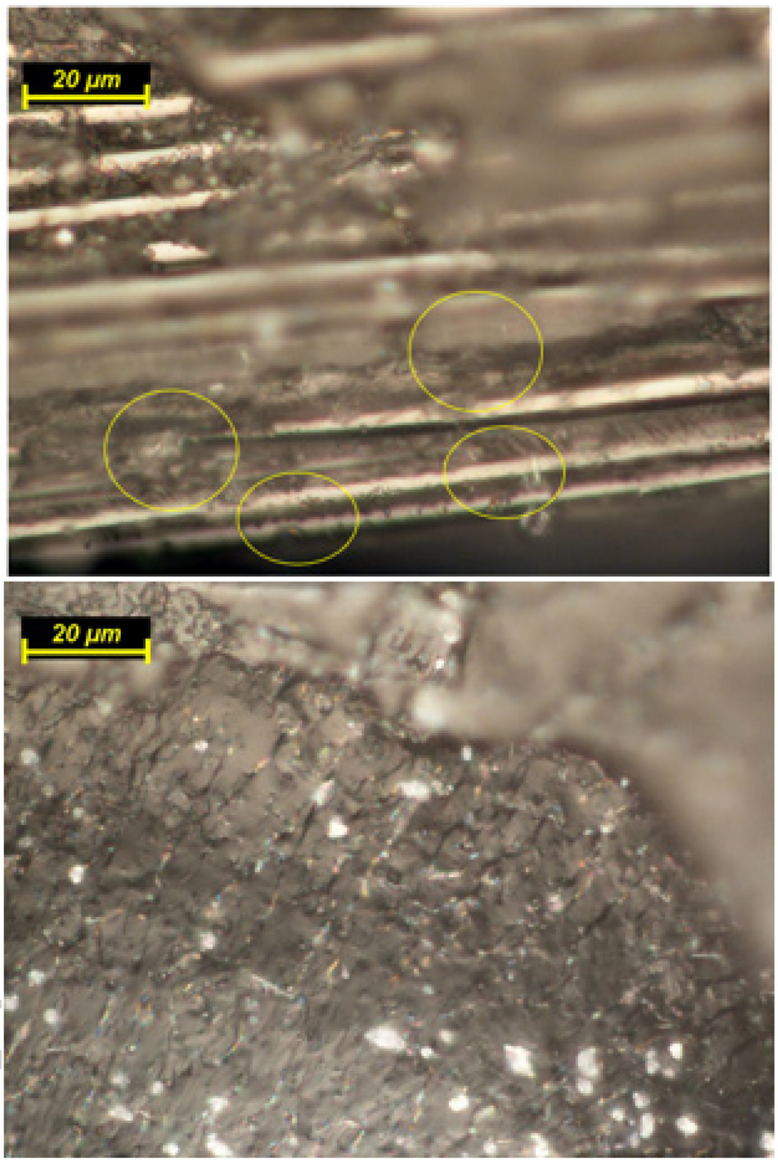

Figure 8: Images showing CNF alignment in ZT-CFRP samples from Test 4 (*top*) and Test 5 (*bottom*) near the fracture surface (images came from the thickness profile of the sample).

Fractured surfaces from a few selected samples are provided in Figure 9. Unlike Figure 7, where the images came from the thickness profile of the adherend, the images in Figure 9 are taken from the surface of the bonded area of the damaged adherend. The smaller figures with circles to the left of microscope images show the location on the coupon that was being imaged. As can be seen there is residual adhesive in both the CFRP bonded with epoxy adhesive and ZT-CFRP bonded with reinforced epoxy adhesive examples. This is shown in the right region of Image (a) and the tips of the exposed fibers in the middle of Image (c). The example image from CFRP bonded with reinforced epoxy adhesive shows no residual adhesive. All images in Figure 9 exhibit broken carbon fiber arrays.

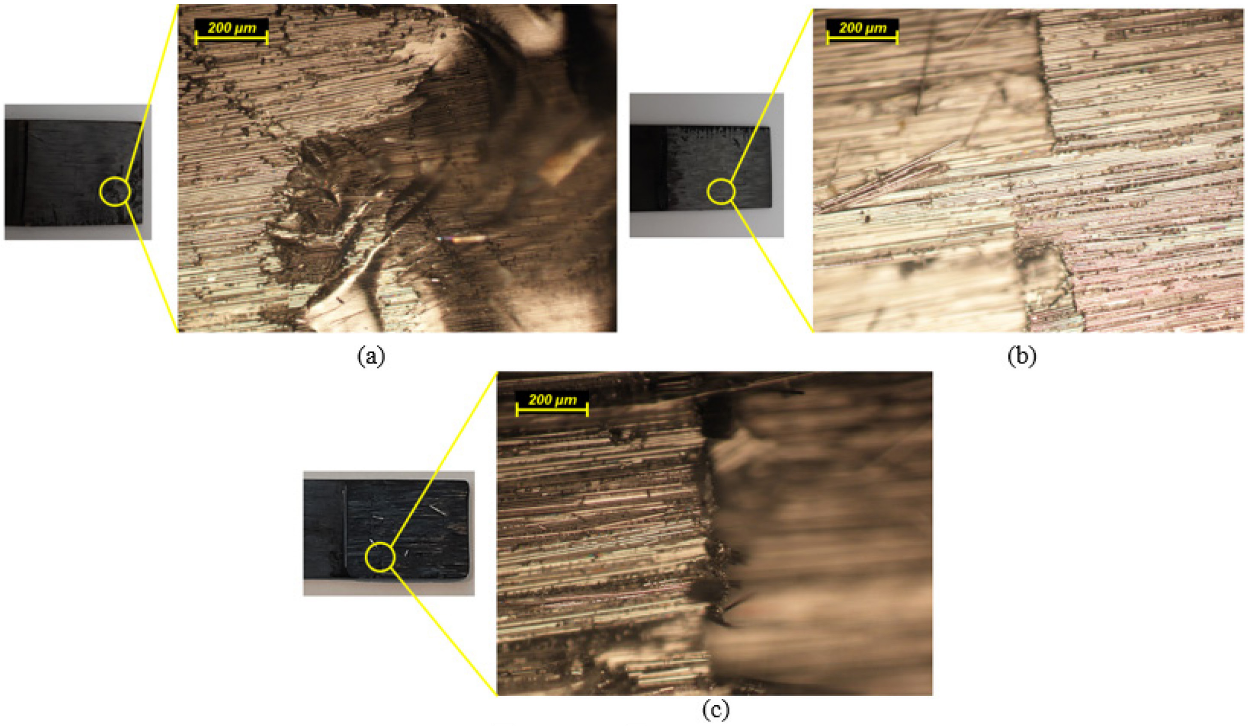

Figure 9: Images taken from the fractured bonding area of a few selected coupons: CFRP bonded with epoxy adhesive (Test 4) (*a*), CFRP bonded with reinforced epoxy adhesive (Test 1) (*b*), and ZT-CFRP bonded with reinforced epoxy adhesive (Test 4) (*c*).

4. CONCLUSIONS

This study examined the effectiveness of CNF reinforced epoxy adhesive in the bonding of ZT-CFRP coupons compared to CFRP coupons bonded with both epoxy and reinforced epoxy adhesives. Bonded testing samples were manufactured for each of the three cases in compliance with the dimensions and requirements specified by the ASTM D5868-01 standard. Single lap shear testing was also carried out using this standard to observe the shear strength of each of the bonded unidirectional CFRP and ZT-CFRP samples. It was found that all samples failed within the adherend (or the carbon fiber reinforced coupon) rather than the adhesive. The ZT-CFRP samples bonded with CNF-reinforced epoxy adhesive did exhibit a higher average shear strength when compared to the CFRP samples tested with both epoxy and CNF-reinforced epoxy adhesives.

CFRP samples bonded with both epoxy and reinforced epoxy adhesive exhibited similar average shear strengths due to all samples tested failing within the adherend rather than the adhesive. Because of this, CNF adhesive reinforcement did not have a chance to provide the full strengthening effects as the increasing loading from the lap-shear tests was exerted onto the samples. The increased shear strength of the ZT-CFRP bonded samples was likely due to the extra reinforcement provided by the CNF z-threads. The CNF z-threads have already been proven to increase the through-thickness mechanical properties of CFRPs that are more dependent on the resin matrix such as mode-I delamination toughness, interlaminar shear strength, and compressive strength [1,2,3]. The CNFs were likely able to resist and distribute the load exerted onto the coupons perpendicular to the carbon fiber direction better when compared to unidirectional CFRP without nanostructure reinforcement.

This is further supported by the observation that more adherend was removed from the ZT-CFRP bonded samples when compared to the CFRP samples bonded with reinforced epoxy adhesive. The intralaminar strength of the CFRP samples is lower than that of the ZT-CFRP samples due to the lack of CNF z-threads that would increase the through-thickness strength of the composite. That would cause the CFRP samples to break at a shorter depth more readily than the ZT-CFRP which would be more capable of distributing the through-thickness loading further into itself. This argument is not as supported when comparing the ZT-CFRP samples with the CFRP samples bonded with epoxy adhesive since it was observed that they had higher adherend peel off/fracture thicknesses. However, there was a significant amount of variability when examining the pull off adherend thicknesses of the CFRP samples bonded with epoxy adhesive, even along a single fracture line.

This study showed that the inclusion of CNF z-threads into CFRPs can improve the overall bond strength of laminates. The average shear strength observed for the ZT-CFRP bonded samples was approximately 44% and 26% higher than that observed for the CFRP bonded samples with epoxy and reinforced epoxy adhesives, respectively. Future efforts to study the effectiveness of ZT-CFRP in the bonding of laminates need to be directed towards decreasing the amount of variance within the data. This can be done by both improving upon the method for bonding the coupons together and manufacturing more ZT-CFRP testing samples. Future studies should also be dedicated to further examining the amount of adherend removed during debonding and if there is a correlation to the amount of CNF z-threads used within the CFRP laminate. It could be observed that a higher wt% of CNF contributes to a higher bond strength and subsequently either a deeper adherend failure or only adhesive failure. This would also help characterize the trend between increased wt% of CFRP z-threads and bond strength performance.

5. ACKNOWLEDGMENTS

The authors acknowledged the financial support by the National Science Foundation (Award number: 2044513), Alabama Department of Commerce through the Alabama Innovation Fund (Award number: 150436), and NASA Alabama Space Grant Consortium Fellowship award (NASA Training Grant 80NSSC20M0044). The authors are grateful for the T700S carbon fiber materials provided by Toray and the surfactants provided by BYK USA, Inc.

6. REFERENCES

1. Hsiao, K-T., et. al. "Effect of carbon nanofiber z-threads on mode-I delamination toughness of carbon fiber reinforced plastic laminates." *Composites: Part A* 91 (2016): 324-335
2. Kirmse, S., Kim, K., Ranabhat, B., Hsiao, K-T. "Effects of Carbon Nanofiber Z-Threads in the Longitudinal Compressive Strength of Unidirectional CFRP Laminates*". Proceedings of International SAMPE Tech. Conf.* Charlotte, NC, May 20, 2019. *SAMPE- Society for the Advancement of Material and Process Engineering*

3. Kirmse, S. and Hsiao, K-T. "Enhancing the Interlaminar Shear Strength of Unidirectional Carbon Fiber Reinforced Plastic (CFRP) Laminate Using a Nanofiber Z-Threading Strategy". *CAMX Conference Proceedings.* Dallas, TX, October 15-18, 2018. *CAMX- The Composites and Advanced Materials Expo.*

4. Jojibabu, P., Zhang, Y.X., Prusty, B.G. "A review of research advances in epoxy-based nanocomposites as adhesive materials". *International Journal of Adhesion and Adhesives* 96 (2020)

5. Guchait, A., Saxena, A., Chattopadhyay, S., Mondal, T. "Influence of Nanofillers on Adhesion Properties of Polymeric Composites". *ACS Omega* 7 (2022): 3844-3859

6. Ahmadi, Z. "Nanostructured epoxy adhesives: A review". *Progress in Organic Coatings* 135 (2019): 449-453

7. Vietri, U., et. al. "Nanofilled epoxy adhesive for structural aeronautic materials". *Composites: Part B* 61 (2014): 73-83

8. Soltannia, B., Taheri, F. "Influence of nano-reinforcement on the mechanical behavior of adhesively bonded single-lap joints subjected to static, quasi-static, and impact loading". *Journal of Adhesion Science and Technology* 29 (2014): 424-442

9. Hsiao, K-T., et. al. "Use of Epoxy/multiwalled carbon nanotubes as adhesives to join graphite fibre reinforced polymer composites". *Nanotechnology* 14 (2003): 791-793

10. Korayem, A. "Effect of carbon nanotube modified epoxy adhesive on CFRP-to-steel interface". *Composites: Part B* 79 (2015): 95-104

11. Gude, M., Prolongo, S., Urena, A. "Toughening effect of carbon nanotubes and carbon nanofibres in epoxy adhesives for joining carbon fibre laminates". *International Journal of Adhesion & Adhesives* 62 (2015): 139-145

12. Kaline, T., et. al. "Determination of the influence of adherent surface on the adhesive bond strength". *MATEC Web of Conferences 157* (2018) https://doi.org/10.1051/matecconf/201815705012

13. ASTM Standard D5868-01, 2023, "Standard Test Method for Lap Shear Adhesion for Fiber Reinforced Plastic (FRP) Bonding". ASTM International, West Conshohocken, PA, 2023

14. Chen, Y., et, al. "Mechanical behavior and progressive failure analysis of riveted, bonded, and hybrid joints with CFRP-aluminum dissimilar materials". *Thin-Walled Structures* 139 (2019): 271-280