A PRELIMINARY INVESTIGATION OF MOISTURE EFFECT ON THE NANOFIBER Z-THREADED CFRP PREPREG AND LAMINATE

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ABSTRACT

Moisture is a known issue for carbon fiber reinforced polymer (CFRP) manufacturing. During the process, in which a CFRP prepreg is carefully thawed, cut, stacked, and cured into a laminate, any bad moisture control can cause voids, affect the curing, and degrade the laminate. Recent studies of carbon nanofiber z-threaded CFRP (i.e., ZT-CFRP) prepreg and its laminates showed significant multifunctional improvements in the mechanical strengths, toughness, thermal conductivity, and electrical conductivity. The carbon nanofibers zig-zag thread among the carbon fibers in the through-thickness direction (i.e., z-direction) and mechanically interlock the fiber system together to form an effective 3D-fiber-network reinforced laminate. This paper presents a preliminary experimental study on the ZT-CFRP prepreg when facing the moisture exposure during the prepreg handling and lamination process. Both the ZT-CFRP and traditional CFRP prepregs, subjected to different humidity conditions, will be cut, and cured into laminate samples. The samples will be tested for their interlaminar shear strengths (ILSS) and hardness. Microscope pictures of the samples' fracture patterns will be compared for explaining the combined impact of the moistures and the carbon nanofiber z-threading strategy on the laminates' interlaminar shear strength and curing state.

Keywords: carbon nanofiber, moisture, interlaminar shear strength.

1. INTRODUCTION

The void created by moisture content during the carbon reinforced polymer (CFRP) composite manufacturing has been a concern for years due to their disagreeable influence on mechanical properties [1] such as the interlaminar shear strength (ILSS). The interlaminar shear strength can be reduced from 17 Ksi to 8 Ksi if there is around 8% void in the epoxy-based CFRP with fiber volume fraction of 60%-70% [1]. Void formation in a CFRP laminate is commonly caused by the air, volatiles, and moisture entrapped in the prepreg prior to the curing process. The moisture in the fiber-epoxy system can further influence the degree of cure, void formation, and mechanical properties. Sharp et al. [2] reported that the water in an epoxy resin system can influence the cure rate; specifically, the water absorption increases the cure rate at the low degree of cure and decreases the cure rate at the high degree of cure. It is because the water-infused epoxy system has a higher cure rate initially due to the molecular self-diffusion of the epoxy molecule. However, With the increase of water content in an epoxy system, the water molecules are pushed by the cured epoxy to form water pockets that limit the full curing of the nearby epoxy eventually. They also found that low fraction of water content (0.5%) caused the plasticization of the resin and increased the fracture toughness; however, a higher water content (2%) reduced the fracture toughness by 20%. Nogueira et.al. [3] reported that, as the water content in an epoxy system increasing from 0 to 1.9%, the tensile modulus increased from 1500 MPa to 1560 MPa and the tensile strength reduced from 64 MPa to 54 MPa. Flexure mechanical properties of epoxy adhesive in the presence of different level of humidity/water have been examined by Lettieri and Frigione [4] where the epoxy adhesive was exposed to RH-55%, RH-75%, and RH-100% environments for zero day to 28 days. Their flexural strength test data maximized at either 12 days or 28 days of exposure to moisture with higher standard deviation on among the samples. Based on the aforementioned reports, one can conclude that the moisture effects in CFRP manufacturing can be quite complex from the views of resin curing enhancement, resin mechanical properties, and voids. The recent advance in nanocomposites, especially the use of carbon nanofibers in CFRP has shown the promising potential in enhancing the CFRP's mode-I delamination toughness [5], interlaminar shear strength [6], z-directional electrical conductivity [7], and z-directional thermal conductivity [8]. The carbon nanofibers zig-zag threaded through the carbon fiber bed/plies in the thickness direction (i.e., z-threading) of a CFRP prepreg (i.e., ZT-CFRP prepreg) and provided the additional

interlaminar, intralaminar reinforcement and the z-directional conductive path in a CFRP laminate. In this preliminary study, it is hypothesized that the ZT-CFRP prepreg could also improve the CFRP laminate manufacturing with respect to the moisture exposure concern. The ZT-CFRP prepreg will be exposed to moisture prior being stacked and cured into a ZT-CFRP laminate. The ILSS and the hardness of the laminate samples made of regular CFRP and ZT-CFRP prepregs, with and without humidity exposure prior to the curing process, will be tested and compared.

2. EXPERIMENTATION

2.1 Materials

To understand the influence of moisture on regular CFRP and ZT-CFRP prepregs, four type of laminate samples were manufactured for the Double Notch Shear (DNS) ILSS test. Two laminate samples were manufactured from the traditional CFRP prepregs, in which one of their prepreg sets (two 10-inch x 20-inch prepregs to make a 20-ply CFRP laminate) was exposed to humidity for around 24 hours before being processed into a CFRP laminate. The two large prepregs were trimmed into 20 pieces and the 20 plies were stacked up on top of an aluminum mold. The assembly of prepreg-stack was cured into a rigid CFRP laminate using the Out of Autoclave-Vacuum Bag Only (OOA-VBO) process. Two other laminate samples were manufactured from the 1wt% CNF Z-threaded CFRP (i.e., ZT-CFRP) prepregs, and one of the two ZT-CFRP prepreg sets (two 10-inch x 20-inch prepregs as a set) was exposed to humidity identical to the traditional CFRP prepreg's humidity exposer before the OOA-VBO curing. Unidirectional HexTowTM AS4 Carbon fiber fabric (1.79g/cm³ fiber density, 3k Tow-size, and 190 g/m² areal weight) was used for all four kinds of samples. The matrix consists of EPON 862 epoxy and Epikure-W curing agent, were both purchased from Miller-Stephenson Chemical Co. Inc, The CNF PR-25-LD-HHT, purchased from Pyrograph Products/Applied Sciences, Inc., has an average diameter of 100nm and average length ranging from 50um to 100um. Disperbyk-191, and Disperbyk-192 (provided by BYK) was used for enhancing the CNF dispersion in the resin. According to [9], the CNF was reported to have a tensile strength of 2.35 ± 0.4 GPa, and a Young's modulus of 245 ± 52 GPa.

2.2 CFRP Manufacturing

The manufacturing of all four samples divided into the traditional CFRP prepreg manufacturing and the ZT-CFRP prepreg manufacturing. The control CFRP prepreg (i.e., traditional CFRP

prepreg) manufacturing process was done in few stages. At first, mechanically mixed Epon 862 and Epikure-W according to the weight ratio of 100:26.5 for 10 minutes. In the following stage, the mixed resin blend was poured in a proprietary moisture removal apparatus placed into the vacuum chamber at 110-degree Celsius temperature to remove unwanted bubbles introduced by mechanical mixing. In this final stage, four individuals 10-inch x 20-inch previously specified unidirectional carbon fiber fabrics were carefully impregnated with resin using a resin roller to ensure that carbon fiber fabric is wetted completely. Afterward, the impregnated prepregs were placed on a preheated (120 degree Celsius) hot plate for 40 minutes to get B-staged. Among all four B-stage prepregs, two of them were brought to outdoor exposure with RH-71.37% for 24 hours and other two left in the laboratory room for 24 hours in a sealed condition. The exposed two prepreg were cut into 20 pieces, stacked, and cured using OOA-VBO process. The exact same technique was used for the two CFRP prepregs stored/sealed in the lab and their CFRP laminates.

The patented [10] ZT-CFRP prepreg manufacturing process [6] is different from the control prepreg manufacturing process for z-threading the CNFs into the CFRP prepreg. An overview of ZT-CFRP manufacturing is illustrated in Figure 1. The prepreg manufacturing process starts with mixing of Epon 862 with surfactants (BYK-191 and BYK-192) and the CNFs using a stirrer before placing into an electrically operated high shear mixer. The surfactants BYK-191, BYK-192 to CNFs weight ratio 1:1:1 has been proven to be an ideal ratio to get homogeneous resin blend that can help to avoid entanglement of CNFs during the dispersion process. Next, the resin mixture was blended with high shear mixture for an hour, 30 minutes clockwise and 30 minutes counterclockwise. In the following stage, the mixture went through sonication process for an hour in ASONICA Q700 sonicator to break aggregations. Afterward, the Epikure-w (26.5:100 against the Epon 862 weight) was added into the sonicated resin mixture and blended with high shear mixer for 10 minutes to get a homogeneous mixture. The mixture was degassed in a vacuum oven assisted by the proprietary moisture removal apparatus for 10-15 minutes to remove any air bubble introduced by previous process. Following, the CNF-resin mixture was placed in a vacuum oven at 120 degrees Celsius temperature for around 45 minutes to get B-staged. This B-stage resin mixture have been used to manufacture CNF-resin films. In the following steps, the randomly aligned CNFs resin film was passed through an electrical field to align the CNFs in the Z-direction (through thickness direction) to form the ZT-resin film [6]. This process was done in a proprietary R2R assembly line developed by Hsiao group. This ZT-resin films were used to impregnate four

pieces of 10-inch x 20-inch unidirectional carbon fiber fabric using a one-directional non-isothermal flow transfer technique described in [6]. From this, four prepregs were produced, two of them were exposed to outdoor humidity for around 24 hours and other two prepregs were stored in the laboratory in a sealed condition. The following day the exposed prepregs and the laboratory prepregs were cut and cured into two different ZT-CFRP laminates using the OOA-VBO process.

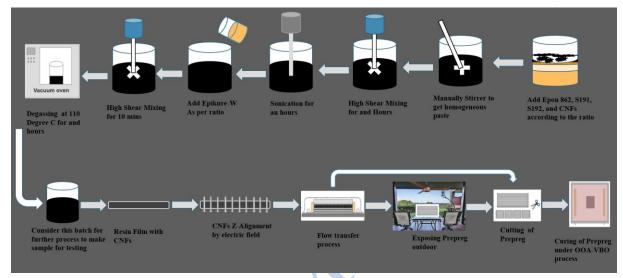


Figure 1. The flowchart of the ZT-CFRP prepreg and laminate manufacturing process.

Figure 2 shows the 4 small pieces trimmed from the ZT-CFRP prepregs for the CNF alignment observation/checking. Figure 3 shows the microscopy side-view of the ZT-CFRP prepreg. One can observe many CNFs -threading through the carbon fibers along the z-direction.

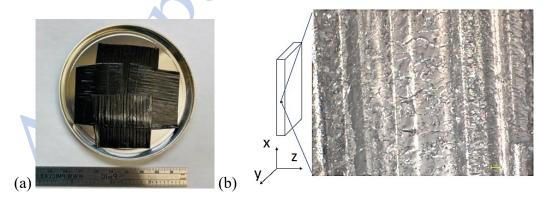


Figure 2. (a) Four small pieces of ZT-CFRP prepreg samples trimmed from the four larger 10" by 20" ZT-CFRP prepregs for alignment observation/checking. (b) The side-view microscope picture of a small ZT-CFRP prepreg shows many CNFs z-threading through the carbon fibers in the z-direction.

The OOA-VBO setup is shown in Figure 3. The peel ply was used for easily separating the cured laminate from the distribution media layer and the vacuum bag. The curing cycle for all laminates curing was done in the same three stages. First, the assembly was under full vacuum at room temperature (around 23 degrees Celsius) for 10 minutes for debulking and removing the excessive air trapped when stacking the prepreg plies; but the 10 minutes duration was kept relatively very short compared with a typical hour-long debulking/degassing in OOA-VBA since the experiments requires the moisture to be presented during the OOA-VBO curing to compare the effect of moisture. The second step, the assembly was placed between two preheated (120 degree Celsius) hot plates of a hot press (to simulate the oven effect) for 2 hours curing under full vacuum. In the third step, the composite laminate was post-cured at 180 degree C without vacuum for two hours, which was also shorter than a common four hours of post curing so the final curing could show some difference due to the moisture.

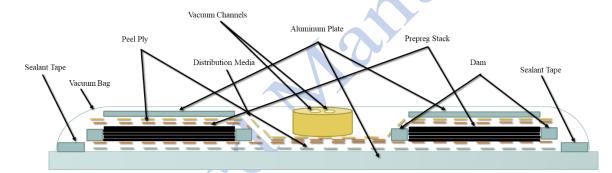


Figure 3. Schematic of OOA-VBO Setup

Table 1. Cure cycle overv	1ew of the OOA-VBO process used for	or all four CFRP Laminates.
Time (minute)	Tomporotura (oC)	Vacuum (Rar)

Time (minute)	Temperature (°C)	Vacuum (Bar)
10	23 (Room Temp.)	1
120	120	1
120	180	0

2.3 Preparation of Double Notch Shear (DNS) Test Samples

Once the laminates were cured, they were trimmed into small DNS test coupons and sanded down to the dimensions stated in the ASTM standard D-3846 at 79.5 mm x 12.7mm. The standard had some leeway on the thickness at a range of 2.54 mm to 6.60 mm. Because of this it was decided to sand down to the thickness of the thinnest sample to maintain consistency. The chosen thickness

was 3.75 mm. After preparing the dimensions the two notches were cut into place at about 6.30 mm away (the precise distance will be measured on the shear fracture surface) and 1.1 mm in channel width. The thickness ranges from 3.74 - 3.87 mm with an average of 3.792 mm. The distance between the two notches was measured from 6.09 - 7.53 mm with an average of 6.64 mm. The notch cut measured from 1.32 - 1.78 mm with an average of 1.482 mm. The width measured 12.55 - 12.79 mm with an average of 12.696 mm. Due to the nature of the test the cuts must be very uniform and at an ideally perpendicular arrangement with the surface. If not, the sample could possibly produce invalid data as the unevenness could cause an inconsistent stress concentration effect at the edge of the shearing section (between the two notches). Additionally, it is important for the samples to maintain uniform thickness all over. If the thickness isn't homogeneous, it will offset the testing vice and lead to poor results as the DNS sample could shift due to the imbalance and non-uniformness of holding.

2.4 Shear Strength Testing

Shear Strength testing can be carried out in many ways, some tests are more conclusive than others. This applies to the previously tested Short Beam Shear (SBS) test [6] and the Double Notch Shear (DNS) test to be used in this study. The test is somewhat convoluted in its description where it is actually technically closer to an interlaminar shear strength (ILSS) test rather than the name implies as an in-plane shear strength test. This discrepancy stems from the position of failure for the sample, the region between the notches. This test is more complicated than the SBS test as the sample is intentionally given damage along its thickness, too much damage would cause a stress concentration on the short end and could fail unevenly. This is to reduce the amount of compression force needed to split and break the sample. However, harking back to the previous SBS test, it seemed some of the CFRP composite's carbon fiber buckled and pushed the delamination of the laminate on the compression side before the sample was destroyed by shear damage and that could affect the effectiveness of the short beam elastic model and the SBS shear stress prediction. The DNS test is more solely based on shear damage so could avoid the disturbance on the shear strength identification due to other failure modes.

The testing apparatus for this new batch of testing is the TINIUS OLSEN Super "L" universal testing machine. This machine has a 5337N loading cell and run the test at 13 mm/min following

the standard. For each case there are 5 testing samples in case there are outliers. Before testing, the sample is inserted into modified ASTM D695 anti-buckling fixture.

2.5 Microscopic Morphology Study and Hardness Test

The failure mode of the sample owing to the DNS test were characterized and compared using a Nikon Eclipse LV150 optical microscope equipped with and extended depth of focus module. The laminate DNS samples, after being fractured, were tested for their hardness using the digital durometer hardness Tester (Model DD-4-A-W).

3. RESULTS AND DISCUSSION

The carbon fiber volume fraction of four type of sample were calculated as Control CFRP 47.49%, Control CFRP/exposed 48.25 %, ZT-CFRP 47.39%, and ZT-CFRP/exposed 53.74% using the fabric areal weight, total ply numbers, and the laminate thickness by assuming there was no fiber expansion since the OOA-VBO process was guided by dams and caul plate. Table 2 shows the ILSS test data of all types of samples, and five specimens each. Table 3 removes the maximum and minimum ILSS values samples from the list shown in Table 2 to remove any potential outliners for the potentially more representative comparison and added the hardness values of the CFRP samples. The outliners could be due to improper fitting of the testing fixture and the sample, the cutting of the notches, or unexpected scenario involved in the testing facture process. The ILSS results of Table 3 are graphically presented in the Figure 4. From Table 3 and Figure 4, one can see the that the control CFRP samples without humidity exposure had the average ILSS of 67.08 MPa with C.O.V. of 1.79%, which show a very repeatable set of ILSS measurements. For the samples of the control CFRP with the humidity exposure, the ILSS increases to 74.06 MPa (a 10.40% increase), but the C.O.V. also increase to 4.11%. As shown in literatures [3], the small amount moisture can enhance the resin curing and increase the ILSS, this increase of ILSS mean is reasonable and the uncertainty of moisture introduction and the effect caused the C.O.V. increased. The samples of ZT-CFRP without humidity exposure also increased the ILSS mean by 10.40%, but also further increased COV to 6.04%. Note these set of CFRP had a potentially less post curing (180 C by 2 hours rather than commonly used 4 hours 180 C post cure) and the added surfactants could also slow the curing). This could be supported by the lowest hardness values of the ZT-CFRP samples (see Table 3). If with more completely post curing, it is possible the ILSS

mean and C.O.V could be improved. The ZT-CFRP prepreg with humidity exposure increased laminate samples' ILSS mean to 71.53 MPa (a 6.63% increase) and reduced the C.O.V. to 1.12%. The hardness values also increased for the ZT-CFRP/exposed samples compared with ZT-CFRP samples. However, while one expects the moisture would help the curing and CNF would also help the ILSS, it could be disappointing that the ILSS of this set of ZT-CFRP prepreg with humidity exposure didn't produce the highest ILSS values among all four types of samples. However, as one reviewed the OOA-VBO process, it was noticed that the room temperature dwelling stage (debulk/de-gas) was merely 10 minutes, which is way too short compared with regular OOA-VBO practice of hours debulk/de-gas stage. Given the CNF was hollow tube structure, the excessive moisture could be trapped in the CNF and not being removed by the short debulk/degas process. The excessive moisture, as supported by the literatures [4] can cause adversary effect to the ILSS possible due to voids and inhibit the maximum achievable degree of cure near the water pockets [2].

Table 2. Original ILSS data for all types of samples, including potential outliners

	Contol CFRP	Control CFRP	ZT-CFRP	ZT-CFRP Prepreg	
	Shear	prepreg Humidity	Shear	Humidity exposed	
	Strength	Exposed Shear	Strength	Shear Strength	
	(MPa)	Strength (MPa)	(MPa)	(MPa)	
Laminate Materials					
sample 1	66.84	70.58	79.48	70.37	
sample 2	71.87	71.51	73.99	79.32	
sample 3	68.38	77.43	78.52	72.39	
sample 4	61.11	73.24	54.36	70.82	
sample 5	66.02	83.07	69.57	71.36	
Mean	66.85	75.16	71.19	72.85	
Standerd deviation	3.91	5.14	10.20	3.69	

Table 3. Original ILSS data for all types of samples (after removing the potential outliners, i.e., the maximum and the minimum ILSS values for each type of sample) and the hardness tested results for all 20 samples

Laminate Materials	Contol CFRP Shear Strength (MPa)	Control CFRP Hardness %	Control CFRP prepreg Humidity Exposed Shear Strength (MPa)	Prepreg Exposed	ZT-CFRP Shear Strength (MPa)	ZT-CFRP Hardness %	ZT-CFRP Prepreg Humidity exposed Shear Strength (MPa)	ZT- CFRP Prepreg Exposed Hardness %
sample 1	66.84	99.70	*	99.90	*	99.60	*	99.80
sample 2	*	99.50	71.51	99.80	73.99	99.60	*	99.70
sample 3	68.38	99.70	77.43	99.80	78.52	98.60	72.39	99.70
sample 4	*	99.80	73.24	99.70	*	99.80	70.82	99.70
sample 5	66.02	99.70	*	99.90	69.57	99.30	71.36	99.80
Mean	67.08	99.68	74.06	99.82	74.03	99.38	71.53	99.74
Standerd deviation	1.20	0.11	3.05	0.08	4.47	0.47	0.80	0.05
C.O.V.	0.0179	0.0011	0.0411	0.0008	0.0604	0.0047	0.0112	0.0005
ILSS relative change due to prepreg								
humidity exposure (%)			10.40%				-3.38%	
ILSS relative change from the Control								
CFRP without humidity exposure	N.A.		10.40%		10.36%		6.63%	

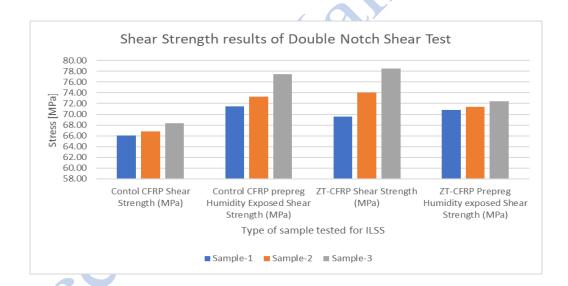


Figure 4. Double Notch Shear Test ILSS results comparison of selected three sample form each case after removing the potential outliners (i.e., the maximum and minimum).

Figure 5 shows the shear stress vs crosshead displacement curves for all type of samples, three samples each case. The sample's shear fracture moment can be easily identified in the end peak-sudden drop of the shear stress. However, some samples experienced the laminate buckling right at the notch sections and some didn't. Those experienced the notch section laminate buckling was due to the high force moment of the imbalanced compressive stress acting on the notched laminate

section. However, the bucking notch section can still provide the compressive/shear load to the sample till its shear-failure at the targeted area thanks to the guide of the testing fixture to support its further buckling induced separation/breakage; under such as scenario, the overall compressive stiffness of the DNS sample is reduced due to the buckled notch laminate section but the final shear strength seemed not affected if one compare the three curves of the control CFRP case. It is interesting that all CFRP with humidity exposure didn't have any single notch laminate bucking issue, it is likely caused by the more complete cure of the resin matrix. On the other hand, since all the ZT-CFRP have the buckling issue, as also indicated previously, it is possible the added surfactants may require the composite being post-cured longer than 2 hours.

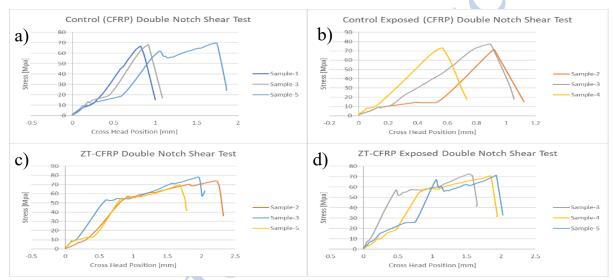


Figure 5. Shear stress vs. crosshead displacement during the DNS tests for a) Control CFRP samples, b) Control CFRP/prepreg-exposed samples, c) ZT-CFRP samples, d) ZT-CFRP/prepreg-exposed samples.

The fracture surfaces of the four types of laminate samples were examined by microscopy and are shown in Figure 6. Figure 6a shows the side-view of the control CFRP DNS sample, which has a clean and straight crack due to the shear. Figure 6b shows the top-view of a fractured DNS sample and reveals a void triggered a complex fracture surface near it. Figure 6c shows the close-up top-view of a ZT-CFRP DNS fractured sample. It shows the carbon fiber tow was broken and the snapped CNFs, which was previously embedded in the resin and carbon fiber bed, were pulled out from the other side of the broken/fractured carbon fiber tow. The majority of the CNF pullout lengths, under this fracture mode, were about 5-10 micrometers, which is close to the diameter of the AS-4 carbon fiber (7 micrometers). Figure 6d shows the side-view of the ZT-CFRP/exposed

DNS fracture sample. It shows a fiber layer fractured and the crack propagation was re-directed due to the additional fracture resistance provided by the CNF z-threads. From the microscopy analysis one can see the control CFRP has the clean and straight crack propagation, which may also explain its lowest shear strength measured in the double notch shear (DNS) tests.

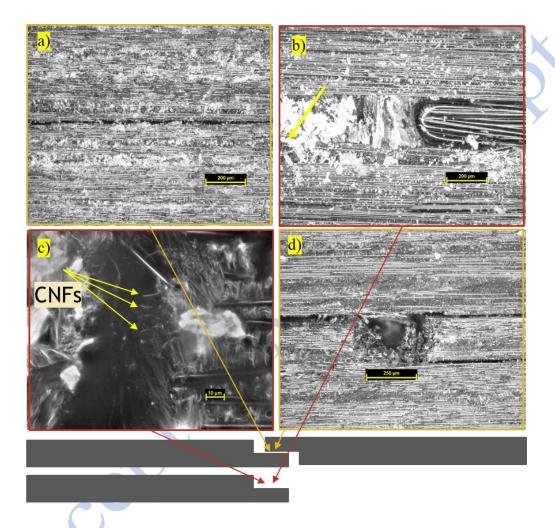


Figure 6. Microscope pictures of the fracture surfaces of the four types of DNS shear-tested composite laminate samples. a) The control CFRP sample has a clean shear crack, b) The control CFRP/exposed sample has a void in the crack zone and a complex fracture surface nearby. c) The carbon fiber tow fractured in crack zone and on the shear-fracture surface, whereas the CNFs were fractured and pullout (pullout lengths were about 5-10 micrometers) from the other side of resin matrix and carbon fiber bed. d) The ZT-CFRP/exposed DNS sample showed a fiber layer fractured and the crack propagation was re-directed due to the additional fracture resistance provided by the CNF z-threads.

4. Conclusions

In this preliminary experimental study, the effect of CFRP and CNF z-threaded CFRP (i.e., ZT-CFRP) prepregs' moisture exposure prior the curing process was investigated by evaluated the cured composite laminate samples through the double notch shear (DNS) test, hardness test, and microscopy analysis. The prepreg's moisture exposure was done with RH-71.37% for 24 hours. The OOA-VBO curing cycle used in this study had a relative short debulking/degas duration of 10 minutes to only remove the excess air but not all the moisture in the prepreg stack prior curing. And the post-cure was done at 180 degree C without vacuum for two hours rather than four hours so the final curing could show some difference due to the moisture. The mild moisture exposure helped the curing of the resin and yielded 10.40% improvement of ILSS and had the highest hardness. It is likely due to the small amount of water enhanced the curing rate and also plasticized/toughened the resin. The ZT-CFRP without moisture exposure also showed 10.36% increase in the ILSS due to the CNF z-threads provided the resistance/reinforcement against shear failure. However, it was found the ZT-CFRP composite samples had the lowest hardness values; it is possible that the added surfactants slightly slowed down the epoxy curing reaction and could require a longer post curing duration to be fully cured. The ZT-CFRP with moisture exposure samples showed 6.3% ILSS improvement against the control CFRP without moisture exposure. While one expects the moisture would help the curing and CNF z-threads would also help the ILSS, it could be disappointing that the ILSS of this set of ZT-CFRP prepreg with humidity exposure didn't produce the highest ILSS values among all four types of samples. It is possible that the room temperature dwelling stage (debulk/de-gas) was merely 10 minutes, which is way too short compared with regular OOA-VBO practice of hours debulk/de-gas stage. Given the CNF was hollow tube structure, the excessive moisture could be trapped in the CNF and not being removed by the short debulk/degas process. The excessive moisture, as supported by the literatures can cause adversary effect to the ILSS possible due to voids and also inhibit the maximum achievable degree of cure near the water pockets. The moisture effect and the nanotechnology, especially given the hollow tube structure of many nanofillers, could have complex interaction for composite manufacturing as indicated in this study. To optimize the combined synergetic effects, one will need to find the balanced OOA-VBO processing parameters and prepreg humidity control conditions.

5. ACKNOWLEDGEMENT

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