

CARBON NANOFIBER Z-THREADED CARBON FIBER REINFORCED POLYMER COMPOSITE (ZT-CFRP) LAMINATE PARTS PRODUCED USING A MAGNETIC COMPACTION FORCE ASSISTED ADDITIVE MANUFACTURING (MCFA-AM) TECHNIQUE

Bikash Ranabhat^{1,2}, Sebastian Kirmse^{1,2}, Michael Johnson¹, Kuang-Ting Hsiao^{1,*}

University of South Alabama

Department of Mechanical Engineering, 150 Jaguar Drive, Shelby Hall, Suite 3130

Mobile, AL, 36608

1.Department of Mechanical Engineering

2.Systems Engineering Program

ABSTRACT

The main challenge in AM processes of continuous fiber-reinforced polymer (FRP) composites is the lack of matured technology, advanced polymers and nanocomposites that match the performance and fabrication requirements. This research addressed the fabrication technology and materials concerns. The research presented herein developed a fast-curing porous carbon nanofiber z-threaded CFRP (P-ZT-CFRP) prepreg tape using a radial flow alignment technique (RFA) and fabricated the P-ZT-CFRP laminate using MCFA-AM. For comparison, two porous CFRP (P-CFRP) laminates cured by the Out-Of-Autoclave Vacuum-Bag-Only (OOA-VBO) method were also manufactured. The interlaminar shear strengths (ILSS) for the two P-CFRPs were 38.5 MPa (with 50 % acetone in resin to create voids) and 43.8 MPa (with 20 % acetone) respectively. The P-ZT-CFRP (with 20 % acetone) manufactured with the MCFA-AM (without vacuum) produced the ILSS of 54.5 MPa. The 0.5 wt% CNF z-threads in resin provided an effective structural integrity enhancement in the porous laminate. The specific ILSS per weight of the P-ZT-CFRP was 83% and 87% of that from the control CFRP manufactured by OOA-VBO (75.5 MPa) and the regular CFRP produced by MCFA-AM (70.5MPa), respectively; which indicated the interesting potentials to tailor lightweight and high-strength CFRPs using AM and nanomaterials. Future improvement directions were discussed.

Keywords: Additive manufacturing, Interlaminar shear strength, Z-threaded CFRP, Porous.

Corresponding author: Email: kthsiao@southalabama.edu, Phone: +1 (251) 460-7889

Copyright 2020. Used by the Society of the Advancement of Material and Process Engineering with permission.

SAMPE Virtual Conference Proceedings, 2020. Society for the Advancement of Material and Process Engineering – North America.

1. INTRODUCTION

Additive manufacturing (AM), also known as 3D printing, rapid prototyping (RP), or solid-freeform (SFF), is a "process of joining materials to make objects from the three-dimensional (3D) model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies" [1], which was first described in 1986 by Charles Hull [2]. Numerous novel AM processes have been developed over more than 20 years of AM development with its applications in aerospace (engine components), automotive (cooling systems), architectural design (exact scale models), consumer goods (eyewear), etc. [3]. Recently, AM of polymer composites has been the center of attraction for academia, industries, and national research labs due to its potential to create the lightweight and high strength structures. AM of fiber-reinforced polymer composite has been found useful to enhance the mechanical properties of the composite compared to the unreinforced polymer composite [4]. Long fiber reinforcement has offered better strength and stiffness compared to unreinforced and short fiber reinforced composites [5,6,7,8,9]. However, the parts produced by the current AM processes are still inferior to conventional composite manufacturing by a single order of magnitude [10]. The common problems observed in AM of polymer composites are voids, physical gaps at the layer/layer interface, lack proper adhesion between fibers and matrix, low fiber volume fraction, and so on [9]. Thus, the main challenge in the field of AM of polymer composite is the lack of matured technology, suitable advanced polymer materials, and compatible nanocomposites that match the performance and fabrication requirements.

From the literature, fused deposition modeling (FDM) is the most widely used AM technique. It also holds 41.5 % of the market share [21]. Some of the recent and promising results of additively manufactured fiber-reinforced polymer composite are presented in Table 1. To the authors' best knowledge, the ILSS test has been rarely performed on the additively manufactured parts.

This study uses the novel magnetic compaction force assisted additive manufacturing to print the P-ZT-CFRP laminate. The MCFA-AM feasibility[19] was demonstrated and proved useful to fast-print continuous CFRP parts with a comparable ILSS to traditional composite manufacturing method like the time-consuming Out Of Autoclave-Vacuum Bag Only (OOA-VBO). The estimated magnetic compaction pressure of 0.21 MPa was used for consolidation during printing and the compaction pressure significantly reduces the size and content of voids despite no vacuum being applied during MCFA-AM process [19].

Table 1. Summary of mechanical properties of some additively manufactured fiber-reinforced polymer composites.

Manufacturing Technique	Fiber	Matrix	Mechanical properties reported
Fused Deposition modeling [22]	U-CF	PLA	Flexural modulus 129.4 GPa
Fused filament fabrication [23]	U-CF	Nylon	- Tensile strength 600 MPa - Flexural strength 430 MPa - Flexural modulus 38.1 MPa
Fused Deposition modeling [24]	U-CF	Onyx	Flexural strength 270.63 MPa
Laser assisted AM [8]	U-GF	Polypropylene	- Tensile strength 217.6 ± 28.6 MPa - Tensile modulus 5.9 ± 0.8 GPa - Flexural strength 169.7 ± 48.6 MPa - Flexural modulus 21.4 ± 5.1 GPa
U-CF: Unidirectional Carbon Fiber U-GF: Unidirectional Glass Fiber			

Previous studies have shown that by using carbon nanofibers (CNFs) z-threads in CFRP laminates, mechanical properties (e.g., Mode-I interlaminar fracture toughness [12], interlaminar shear strength (ILSS) [13], and longitudinal compressive strength [14]), thermal properties (e.g., through-thickness thermal conductivity [15]) and electrical properties (e.g., through-thickness DC electrical conductivity [16-18]) can be significantly improved even when using low CNF concentrations (0.3 wt% to 2.0 wt%). This paper employs a radial flow alignment technique (RFA) [20] to make CNF z-threaded CFRP prepreg tape, thus produced prepreg tape is used by MCFA-AM to print parts. However, additional new challenge is rising due to the fast curing thermoset resin in the MCFA-AM process. Conducting the RFA with the fast curing resin was challenging because that the resin's high viscosity and fast curing nature conflict with the CNF dispersion and the RFA process time requirement. Hence, in this study, the fast curing epoxy was slightly modified using acetone, which solves the two problems, i.e., dispersion of CNFs in the resin and slows the curing process allowing the extra time to work during the RFA technique. However, it was hypothesized that the acetone's complete removal from the fast curing prepreg could be difficult and the residual acetone, if any, in the matrix would reduce the mechanical strength (due to voids/porosity caused by the residual acetone); in such cases, the Porous ZT-CFRP (i.e., P-ZT-CFRP) are expected to be produced and tested in the paper. However, the P-ZT-CFRP could have lower density than traditional CFRP and could have some advantages in the weight specific properties including the specific ILSS per weight. Therefore, the goals of this paper are to:

- Produce P-ZT-CFRP prepreg using RFA technique.
- Additively manufacture P-ZT-CFRP laminate specimens employing MCFA-AM.
- Compare the specific ILSS of additively manufactured P-ZT-CFRP composite laminate with the P-CFRP composite laminate manufactured by Out-Of-Autoclave Vacuum-Bag-

Only (OOA-VBO), traditional CFRP laminate manufactured by OOA-VBO [19] and CFRP laminate manufactured by MCFA-AM [19].

- Analyze the ILSS results associated with CNF reinforcement, the fiber volume fraction, the voids content and the curing methods (either OOA-VBO or MCFA-AM).

2. EXPERIMENTAL METHODOLOGY

2.1 Materials

Three samples were prepared, i.e., sample 1: porous CFRP laminate with 50 % acetone in resin to create porosity, sample 2: porous CFRP laminate with 20 % acetone, and sample 3: 0.5 wt% CNF z-threaded porous CFRP laminate with 20 % acetone (P-ZT-CFRP). Sample 1 and sample 2 were fabricated using OOA-VBO, while sample 3 was fabricated employing MCFA-AM (without vacuum). Each laminate sample was trimmed into five specimens to conduct the ILSS test. The materials used to prepare the samples are presented in Table 2.

Table 2. Materials used and the suppliers

Materials	Suppliers
Carbon fiber: Toray T-700 unidirectional (680 g/m ² areal weight, 1.8 g/cm ³ fiber density, 12k tow size).	Toray
Polymer matrix: EPIKOTETM Epoxy Resin TRAC 06170 and EPIKURETM Curing Agent TRAC 06170 (100:16)	Hexion Inc.
Surfactants:BYK-9076 & BYK-9077	BYK USA, Inc
CNFs:PR-24-XT-HHT	Applied Science, Inc
Acetone	Fisher Scientific International, Inc

2.2 Methodology

2.2.1 Fabrication of porous CFRP laminate

The manufacturing steps for the preparation of sample 1 (50 % acetone) and sample 2 (20 % acetone) are shown in Figure 1. The resin, curing agent, and acetone x wt% (x = 50 % or 20 %) were mixed thoroughly by high shear mixing for 5-10 min until no clouding is visible. The mixture was poured on top of the fabric and spread out with a roller for uniform resin impregnation into the unidirectional carbon fabric. The prepreg was heated on top of the hot plate at 45 °C for 10-15 minutes until prepreg tackiness was reached. The prepreg was then transferred to polymer bagging and stored in the freezer at -18 °C to be later used for curing via the OOA-VBO process. The layup scheme used in the OOA-VBO process is shown in Figure 2. the curing cycle used to cure sample 1, and sample 2 is presented in Table 3.

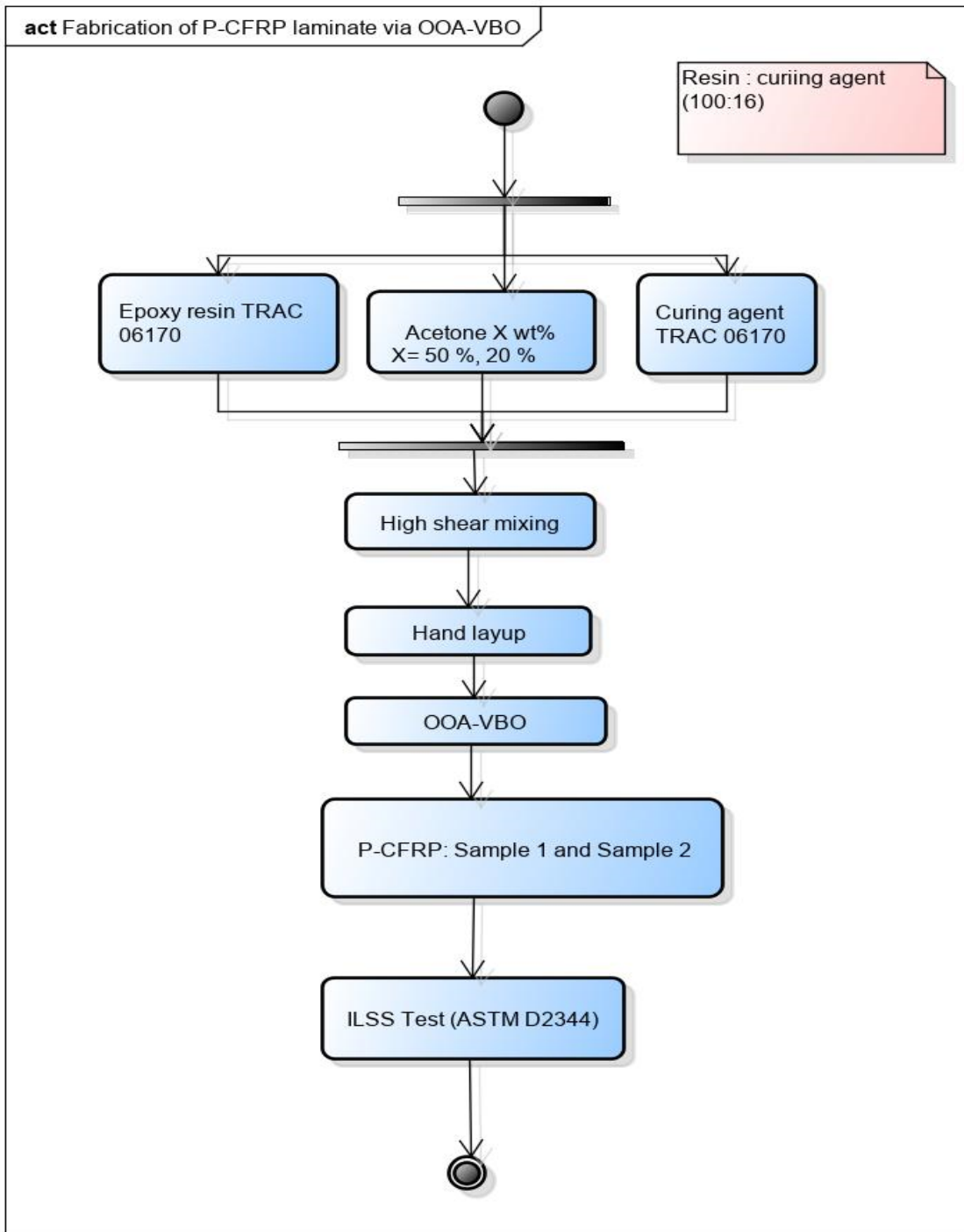


Figure 1. Fabrication of porous CFRP (samples 1 & 2)

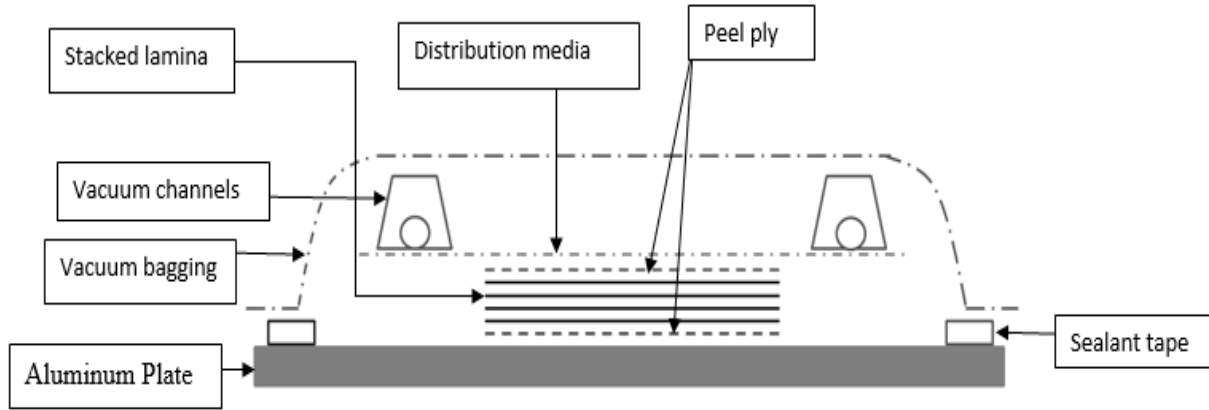


Figure 2. OOA-VBO Layup scheme used for the preparation of P-CFRP laminate [17]

Table 3. OOA-VBO cure cycle.

Time (min)	Temperature (°C)	Vacuum Pump
30	Room temperature (23)	On
30	45	On
20	55	On
60	120	On
60	140	Off

2.2.2 Fabrication of Porous CNF z-threaded CFRP Laminate

The fabrication of sample 3 (P-ZT-CFRP) laminate was achieved utilizing two novel techniques; (1) radial flow alignment (RFA) technique to z-thread CNFs into the unidirectional carbon fabric to form the P-ZT-CFRP prepreg and (2) magnetic compaction force assisted AM to fabricate P-ZT-CFRP laminate. To optimize the process, EPIKOTETM Epoxy Resin TRAC 06170 was heated at 60 °C then 1 wt% of each surfactant BYK-9076 and BYK-9077, 0.5 wt% of CNFs (PR-24-XT-HHT) was added in the resin, and the mixture was mechanically mixed by high shear mixing for an hour followed by 30 minutes of sonication. To prevent the curing reaction during RFA, 20 wt% of acetone was added in the mixture before adding the EPIKURETM Curing Agent TRAC 06170. The ratio used to mix resin to curing agent was 100:16. The mixture was then used by the radial flow alignment technique [20] to z-thread the CNFs into the carbon fiber fabric and prepared z-threaded prepreg tape. Thus, the porous CNFs z-threaded prepreg (P-ZT-CFRP) with acetone was stored in the freezer first and then transferred into the oven at 35 °C, -0.08 MPa (vacuum) for 20-25 minutes to remove some acetone without bubbling caused by acetone evaporation. Note that some residual acetone could still be in the prepreg. Then after the P-ZT-CFRP prepreg was heated at 40 °C to attain the desired B-staging, it was stored in the freezer for the future use in MCFA-AM. The MCFA-AM manufactured P-ZT-CFRP laminate sample (i.e., sample 3) was post-cured

as described in [19] with the post curing cycle, as presented in Table 4. The Radial Flow Alignment (RFA) process and the Magnetic Compaction Force Assisted AM (MCFA-AM) are further explained in the next section.

Table 4. Cure cycle for P-ZT-CFRP laminate

Time (min)	Temperature (°C)
30	45
15	55
60	120
60	140

2.2.2.1 Radial flow alignment technique and Magnetic compaction force assisted AM

Radial flow alignment [20] is a proven rheological methodology to z-thread CNFs in carbon fabric [17,18]. In this paper, RFA was used to directionally stretching and radially align long carbon nanofibers (CNFs) suspended in liquid epoxy/acetone mixture through a unidirectional carbon fabric to form the P-ZT-CFRP prepreg tape. The schematic diagram of RFA is shown in Figure 3. Then the porous CNFs z-threaded CFRP prepreg tapes were used as the feedstock for the magnetic compaction force assisted additive manufacturing (MCFA-AM) [11] methodology to fabricate P-ZT-CFRP laminate by adding the prepreg tapes layer by layer on top of a moving backing-article, which was attracted by the magnetic force emitted from the printing head) and utilizing the magnetic compaction force to compact the prepreg during the prepreg consolidation/curing; therefore a CFRP laminate can be produced under desired compaction pressure and with desired 3D-shape and 3D-carbon fiber direction control without a mold nor a fixed support substrate/plate. A simplified MCFA-AM 3D printing head was developed using the basic principle described in patent-pending publications [11] and used in this study, as described in [19]. The simplified 3D printing head is shown in Figure 4. The overall P-ZT-CFRP laminate manufacturing processing steps are shown in Figure 5. The edge (i.e., side-view) of cured P-ZT-CFRP laminate observed in microscope is shown in the Figure 6.

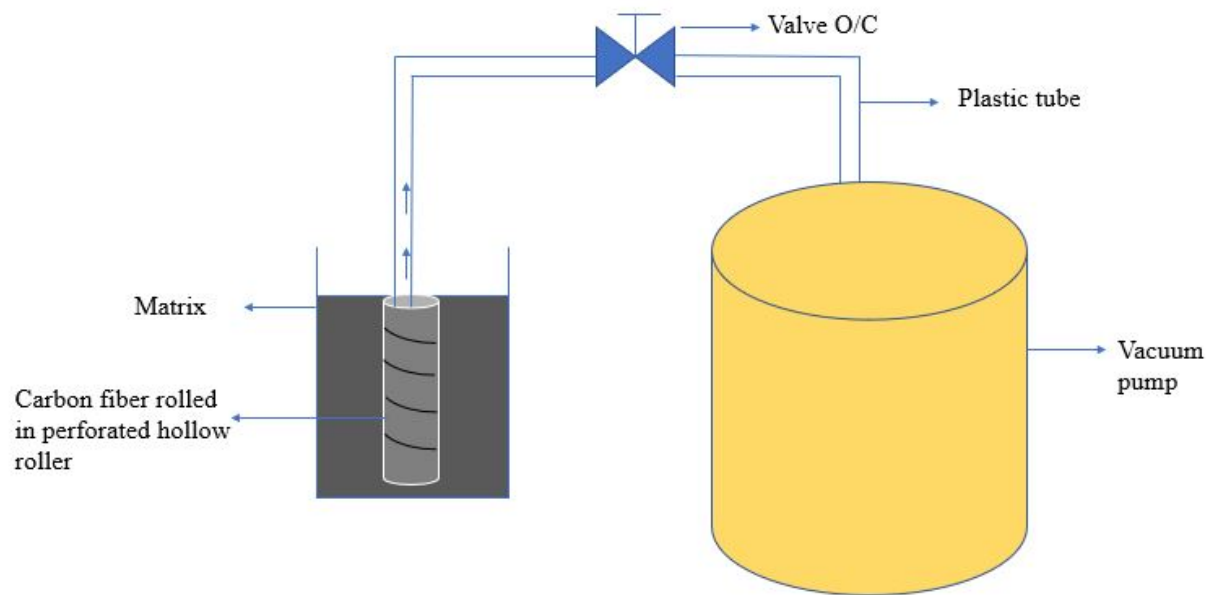


Figure 3. Schematic diagram for radial flow alignment technique

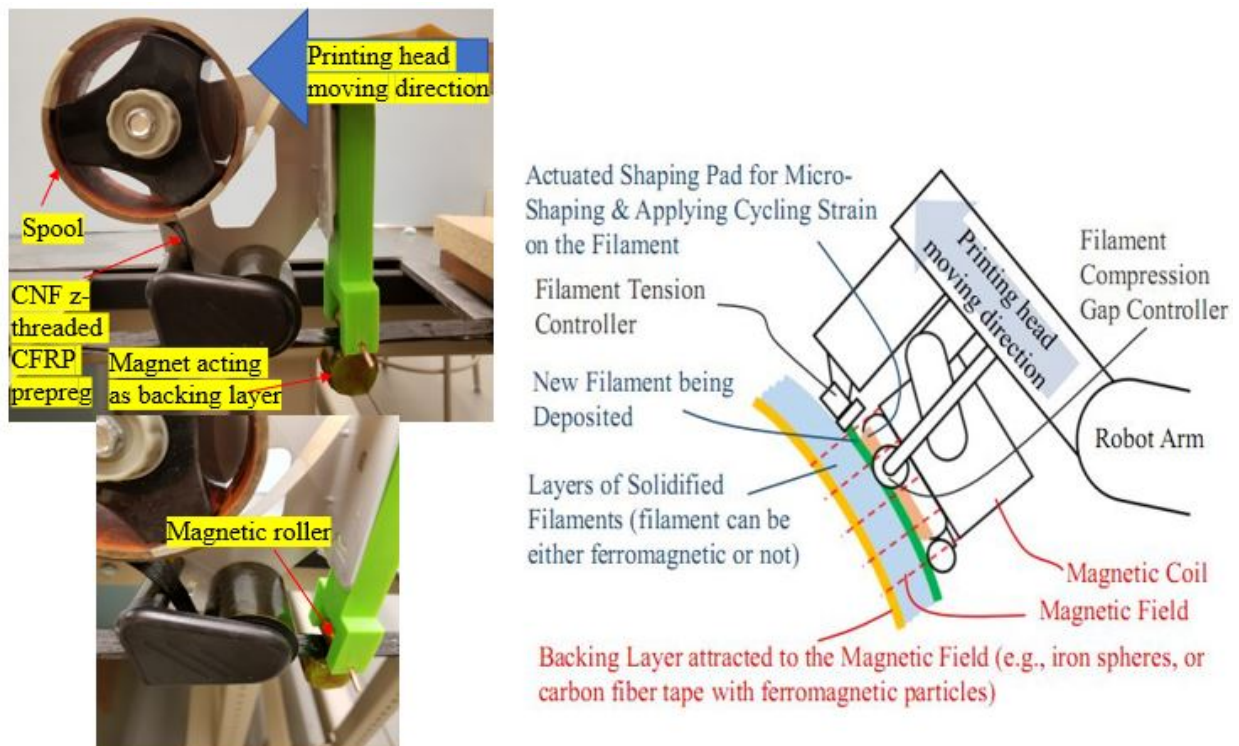


Figure 4. A simplified hand-hold printing head designed of MCFA-AM (left) and the MCFA-AM printing head schematic described in [11] (right). (modified from [19])

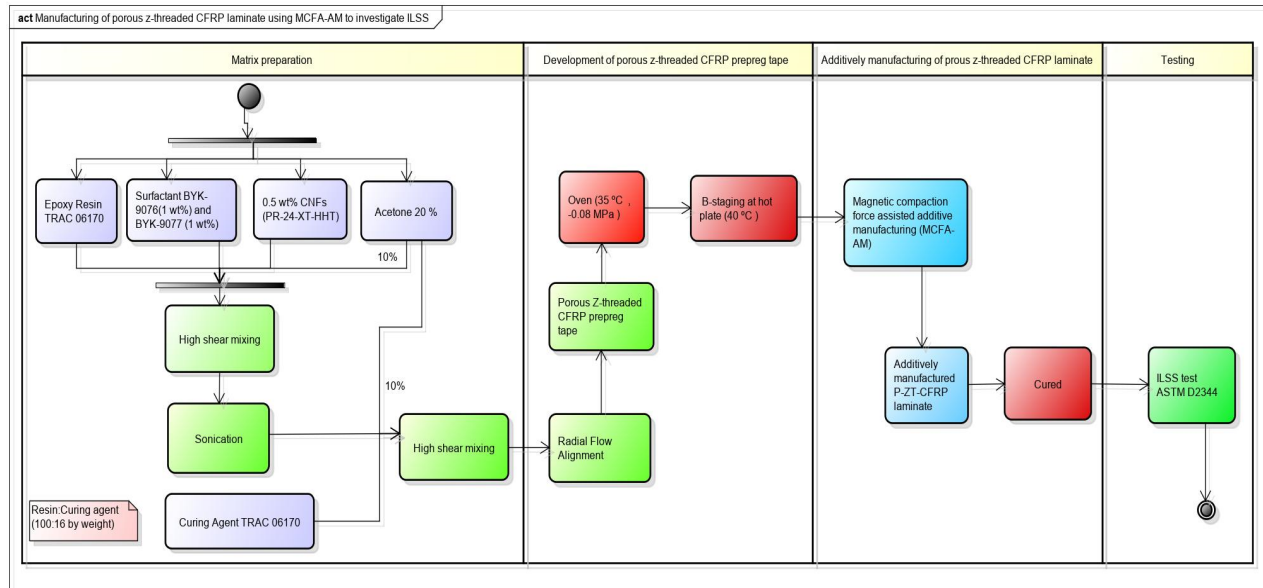


Figure 5. Overall P-ZT-CFRP laminate manufacturing.

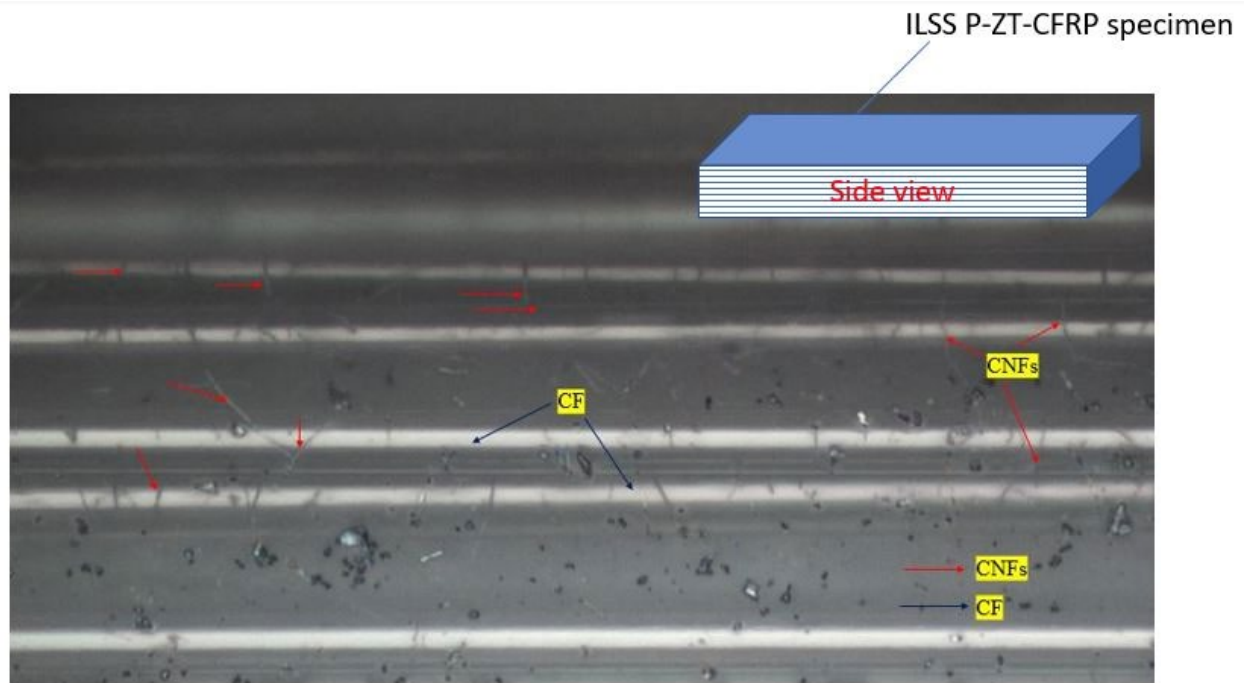


Figure 6. Microscopic image (extended-focused) taken at 1000X for the edge (i.e., side-view) of the CNC cut and hand-polished ILSS specimen from the P-ZT-CFRP laminate (sample 3).

2.3 Characterization techniques

Once samples 1, 2, and 3 were produced, a computer numerical control (CNC) router, CNC Shark Pro HD from the Next Wave Automation was used to cut five ILSS specimens (5 mm wide and 15 mm long) from each laminate sample. The specimens were sanded to the thickness of 2.5 mm.

The ILSS specimens obtained was characterized in terms of fiber content, void content, and interlaminar shear strength (ILSS). The fiber content and void content was estimated from the acetone fraction and the density measurement of the specimens as detailed in the Appendix. The ILSS was measured using the ASTM D2344 [25]. The test was conducted on TINIUS OLSEN Super “L” Universal Testing Machine, as shown in Figure 6. Short-beam strength was calculated using Equation 1.

$$F^{sbs} = 0.75 * \frac{P_m}{b * h} \quad (1)$$

Where F^{sbs} = short-beam (shear) strength (which represents ILSS), MPa

P_m = maximum load observed during the test, N

b = measured specimen width, mm

h = measured specimen thickness, mm

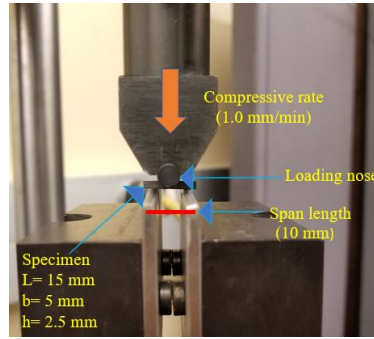


Figure 6. Short beam test setup [19]

3. RESULTS AND DISCUSSION

The results of the short beam shear tests for the OOA-VBO cured P-CFRP laminate and the MCFA-AM fabricated P-ZT-CFRP laminate are shown in Table 5, together with the OOA-VBO cured traditional CFRP and the MCFA-AM produced traditional CFRP laminate from a previous study [19].

Table 5. Mean ILSS tested by short beam strength test.

	Regular CFRP [19]		P-CFRP		P-ZT-CFRP
	Control CFRP	AM-CFRP	Sample 1	Sample 2	Sample 3
Manufacturing method	OOA-VBO	MCFA-AM	OOA-VBO	OOA-VBO	MCFA-AM
CNF (wt%)	0%	0%	0%	0%	0.50%
Acetone (wt%)	0%	0%	50%	20%	20%
Averaged Composite Density (g/cm ³)	1.49	1.46	1.52	1.21	1.3
Averaged void content (vol%)	NA	NA	6%	12%	10%
Averaged Carbon Fiber Volume Fraction (vol%)	50%	45%	70%	32%	44%
ILSS (MPa) tested by SBS test (average)	75.4	70.5	38.5	43.8	54.5
ILSS Normalized against Control Traditional CFRP		94%	51%	58%	72%
Specific ILSS per weight (10 ³ m)	5.16	4.92	2.58	3.69	4.27
Specific ILSS per weight Normalized against Control Traditional CFRP		95%	50%	72%	83%
Estimated Specific Carbon Fiber Directional Tensile Strength per weight Normalized against Control Traditional CFRP (consider only CF volume fraction and density)		92%	137%	79%	101%

Fabrication of P-ZT-CFRP utilizing the RFA and MCFA was challenging due to the fast curing nature of the resin and dispersion of CNFs in the fast curing resin. This challenge was overcome by adding acetone to the mixture. The acetone helped to disperse the CNFs in the resin as well as slow the curing process allowing additional time to work on the P-ZT-CFRP prepreg tape fabrication during the RFA. The addition of acetone solved the main challenge but created another issue i.e., difficulty in the removal of acetone during the curing process. The amount of acetone used was a critical factor in this study. Therefore, this study was started with two different concentrations of acetone in the mixture (Sample 1 (50% acetone in resin) and Sample 2 (20%

acetone in resin) both cured by OOA-VBO). The results showed the ILSS for sample 1, and sample 2 was 38.5 MPa and 43.8 MPa, respectively; compared to the traditional control CFRP sample by OOA-VBO (ILSS= 75.4 MPa), the ILSS decreased by 49 % and 42 %, respectively. The decrease in the ILSS was mainly due to the voids created by the trapped acetone during the curing process. By reducing the amount of acetone in sample 2 to 20 %, the ILSS was increased by around 14 % compared to sample 1. However, it was also interesting to note that Sample 1 had higher density , higher carbon fiber volume fraction, and lower void content compared with Sample 2; this could be due to the lower viscosity and the acetone removal by vacuum caused the carbon fibers being packed more tightly. Due to the complexity in the RFA process when utilizing fast curing resin, sample 3 (P-ZT-CFRP) was fabricated by using 20 % acetone and 0.5 wt% CNF in the matrix mixture and cured with MCFA-AM technique. The ILSS value for sample 3 was improved by 42% and 24 % compared to sample 1 and sample 2, respectively. The increase in the ILSS value of sample 3 was due to the CNF z-threads showed in Figure 6. The sample 3 ILSS value is equivalent to 72 %, and 77 % of the control CFRP laminate (ILSS = 75.4 MPa) by OOA-VBO curing and the MCFA-AM cured CFRP laminate (ILSS = 70.5 MPa) reported in [19]. The sample 3 was lighter than the control CFRP and AM-CFRP. The specific ILSS per weight of sample 3 was recorded 4.27 while control CFRP and MCFA-AM CFRP have 5.16 and 4.92, respectively. In other words. The specific ILSS per weight of sample 3 is equivalent to 83 % and 87 % of control CFRP manufactured by OOA-VBO and the regular MCFA-AM CFRP, respectively. The fiber volume fraction for sample 1, sample 2, and sample 3 were reported 70%, 32 %, and 44 %, respectively while void content reported was 6 %, 12 % and 10 % respectively. Although the carbon fiber direction tensile strength was not tested in this paper, the tensile strength for unidirectional CFRP are typically predicted by rule of mixture and can be mainly proportional to carbon fiber volume fraction if one neglect the matrix's small contribution; therefore, one could roughly estimate the specific tensile strength per weight against the control CFRP cured by OOA-VBO. It is not a surprise some porous CFRP could have higher specific tensile strength per weight thanks to the lower density. However, it is intriguing to note that the P-ZT-CFRP laminate with 83% and 101% of the specific ILSS and specific tensile strength per weight, normalized against the control CFRP cured by OOA-VBO, indicated a lighter and stronger CFRP could be tailored by tailor a good balance of porosity and CNF contents in the future.

4. CONCLUSIONS

The P-ZT-CFRP laminate was fabricated for the first time utilizing the radial flow alignment, and magnetic compaction force assisted AM. The P-ZT-CFRP laminate (sample 3) fabricated by MCFA-AM showed an improved ILSS value compared to the P-CFRP samples cured by OOA-VBO (samples 1 and 2). The fiber volume fraction for sample 1, sample 2, and sample 3 were found to be 70%, 32 %, and 44 %, respectively. The voids contents in samples 1, sample 2, and sample 3 were 6%, 12% and 10% respectively. The sample 1 with higher fiber volume fraction was heavier than the sample 2 with low fiber volume fraction . This may be due to the high void content and lower carbon fiber volume fraction in sample 2. The improvement in the ILSS was achieved due to the use of CNFs z-threads in the CFRP prepreg. The CNFs z-threaded in the thickness direction helps to improve the ILSS of the P-ZT-CFRP laminate. The improvement was found to be 42 % and 24 % compared to sample 1 and sample 2. The porous nanocomposite (P-ZT-CFRP) showed great potential to overcome the effects of void on the mechanical properties of CFRPs. The voids, which are a common problem in AM, could be overcome through the use of CNF z-threaded CFRP prepreg. The CNF z-threads provides structural integrity in the composite

laminate. The specific ILSS per weight of the P-ZT-CFRP sample manufactured by MCFA-AM technique was 0.83 times that of the control CFRP manufactured by the OOA-VBO method and 0.87 times that of the CFRP produced by MCFA-AM. The ILSS value could be improved by improving the techniques to prepare P-ZT-CFRP prepreg tape (e.g., full removal of acetone during the curing process) and application of high magnetic compaction pressure in the MCFA-AM process.

5. FUTURE WORKS

The future work of this study could be (i) finding the alternative chemical to replace acetone that does the same curing inhibiting and viscosity reduction functions as acetone in the matrix as discussed above, (ii) if acetone is still used, one could find the effective way to remove the acetone without creating much voids, (iii) finding the optimal concentration of CNFs and acetone/chemical to be used in the fast curing resin during RFA (iv) use considerable magnetic compaction pressure during fabrication and study the effects of magnetic compaction pressure on ILSS and tension test, (v) apply vacuum during the MCFA-AM process.

6. ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support from the Alabama Department of Commerce through the Alabama Innovation Fund (Award number: 150436), and the Graduate Assistantship from the Systems Engineering Program at the University of South Alabama. The authors are grateful for the carbon fiber materials provided by Troy, Resins supplied from Hexion Inc.

7. REFERENCES

1. ASTM Standard ISO / ASTM52900-15, Standard Terminology for Additive Manufacturing – General Principles – Terminology, ASTM International, West Conshohocken, PA, 2015, www.astm.org
2. Hull, C.W., Apparatus for production of three-dimensional objects by stereolithography. 1986, Google Patents.
3. Attaran, Mohsen. "The rise of 3-D printing: The advantages of additive manufacturing over traditional manufacturing." *Business Horizons* 60, no. 5 (2017): 677-688. <https://doi.org/10.1016/j.bushor.2017.05.011>
4. Blok, L. G., Longana, M. L., Yu, H., & Woods, B. K. S. (2018). An investigation into 3D printing of fibre reinforced thermoplastic composites. *Additive Manufacturing*, 22, 176-186. <https://doi.org/10.1016/j.addma.2018.04.039>
5. Parandoush, P., & Lin, D. (2017). A review on additive manufacturing of polymer-fiber composites. *Composite Structures*, 182(2017), 36-53. <https://doi.org/10.1016/j.compstruct.2017.08.088>
6. Klosterman, D., Chartoff, R., Graves, G., Osborne, N., & Priore, B. (1998). Interfacial characteristics of composites fabricated by laminated object manufacturing. *Composites Part A: Applied Science and Manufacturing*, 29(9-10), 1165-1174. [https://doi.org/10.1016/S1359-835X\(98\)00088-8](https://doi.org/10.1016/S1359-835X(98)00088-8)

7. Yang, C., Tian, X., Liu, T., Cao, Y., & Li, D. (2017). 3D printing for continuous fiber reinforced thermoplastic composites: mechanism and performance. *Rapid Prototyping Journal*, 23(1), 209-215. <https://doi.org/10.1108/RPJ-08-2015-0098>
8. Parandoush, P., Tucker, L., Zhou, C., & Lin, D. (2017). Laser assisted additive manufacturing of continuous fiber reinforced thermoplastic composites. *Materials & Design*, 131, 186-195. <https://doi.org/10.1016/j.matdes.2017.06.013>
9. Ning, F., Cong, W., Qiu, J., Wei, J., & Wang, S. (2015). Additive manufacturing of carbon fiber reinforced thermoplastic composites using fused deposition modeling. *Composites Part B: Engineering*, 80, 369-378. <https://doi.org/10.1016/j.compositesb.2015.06.013>
10. Comer, A. J., D. Ray, W. O. Obande, D. Jones, J. Lyons, I. Rosca, R. M. O'higgins, and M. A. McCarthy. "Mechanical characterisation of carbon fibre-PEEK manufactured by laser-assisted automated-tape-placement and autoclave." *Composites Part A: Applied Science and Manufacturing* 69 (2015): 10-20. <https://doi.org/10.1016/j.compositesa.2014.10.003>
11. Hsiao, K-T., Method and apparatus for 3d printing, patent-pending WO/2018/057784. (<https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2018057784>)
12. Hsiao, Kuang-Ting, Alexander M. Scruggs, John S. Brewer Jr, Gregory JS Hickman, Erin E. McDonald, and Kendrick Henderson. "Effect of carbon nanofiber z-threads on mode-I delamination toughness of carbon fiber reinforced plastic laminates." *Composites Part A: Applied Science and Manufacturing* 91 (2016): 324-335. doi:10.1016/j.compositesa.2016.10.022.
13. Kirmse, Sebastian, and Kuang-Ting Hsiao. "Enhancing the interlaminar shear strength of unidirectional carbon fiber reinforced plastic (CFRP) laminate using a nanofiber z-threading strategy." *Proceedings of CAMX 2018 (The Composites and Advanced Materials Expo)*, Dallas, TX, Oct. 15 18 (2018): 2018.
14. Kirmse S, Kim K, Ranabhat B, Hsiao K-T. Effects of Carbon Nanofiber Z-Threads on the Longitudinal Compressive Strength of Unidirectional CFRP Laminates. *SAMPE 2019 - Charlotte, NC, Charlotte, NC: SAMPE (Society for the Advancement of Material and Process Engineering)*; 2019, p. TP19--1531. doi:10.33599/nasampe/s.19.1531.
15. Scruggs, Alexander M., Sebastian Kirmse, and Kuang-Ting Hsiao. "Enhancement of Through-Thickness Thermal Transport in Unidirectional Carbon Fiber Reinforced Plastic Laminates due to the Synergetic Role of Carbon Nanofiber Z-Threads." *Journal of Nanomaterials* 2019 (2019). doi:10.1155/2019/8928917.
16. Scruggs, Alexander M., Kendrick Henderson, and Kuang-Ting Hsiao. "Characterization of electrical conductivity of a carbon fiber reinforced plastic laminate reinforced with z-aligned carbon nanofibers." *Proceedings of CAMX* (2016): 26-29.
17. Ranabhat, B., and Hsiao, K. "Improve the Through-Thickness Electrical Conductivity of CFRP Improve the Through-Thickness Electrical Conductivity of CFRP Laminate Using Flow-Aligned Carbon Nanofiber Z-Threads," in *Proceedings of SAMPE 2018 (Society for the Advancement of Material and Process Engineering)*, Long Beach, CA, May, 21-24, 2018, SE18--1100.
18. Ranabhat, Bikash, Sebastian Kirmse, and Kuang-Ting Hsiao. "Roles of carbon nanofiber alignment and concentration for the improvement of z-directional DC electrical conductivity

of CNF z-threaded CFRP laminates manufactured using radial flow alignment technique,” in Proceedings of CAMX 2019, Anaheim, CA, 2019.

19. Ranabhat, B., Kirmse, S., and Hsiao, K. “Feasibility Study of Novel Magnetic Compaction Force Assisted Additive Manufacturing (MCFA-AM) Methodology for Continuous Carbon Fiber Reinforced Polymer (C-CFRP) Composites,” in SAMPE 2019 - Charlotte, NC, 2019.
20. Hsiao, Kuang-Ting.” Apparatus and method for directional alignment of nanofibers in a porous medium” US Provisional Serial NO. 62/003,982; PCT/US2015/033000; Pub.No.: WO/2015/184151 A1 (2015).
21. Wohlers, Terry. "3D printing and additive manufacturing state of the industry." Annual Worldwide Progress Report. Wohlers Associates(2014).
22. Damodaran, V., A. G. Castellanos, M. Milostan, and P. Prabhakar. "Improving the Mode-II interlaminar fracture toughness of polymeric matrix composites through additive manufacturing." *Materials & Design* 157 (2018): 60-73. <https://doi.org/10.1016/j.matdes.2018.07.006>
23. Zindani, Divya, and Kaushik Kumar. "An Insight into Additive Manufacturing of Fiber Reinforced Polymer Composite." *International Journal of Lightweight Materials and Manufacture* (2019). <https://doi.org/10.1016/j.ijlmm.2019.08.004>
24. Yu, Tianyu, Ziyang Zhang, Shutao Song, Yuanli Bai, and Dazhong Wu. "Tensile and flexural behaviors of additively manufactured continuous carbon fiber-reinforced polymer composites." *Composite Structures* 225 (2019): 111147. <https://doi.org/10.1016/j.compstruct.2019.111147>
25. ASTM D2344 / D2344M-16, Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates, ASTM International, West Conshohocken, PA, 2016, www.astm.org

8. APPENDIX

8.1 Fiber Volume fraction (FVF)

$$V_f = \frac{\rho_c - \rho_m}{\rho_f - \rho_m} \quad (A)$$

Where, ρ_c , ρ_f , ρ_m are the density of composite, fiber and matrix respectively.

$$\rho_m = v_{fr} * \rho_r + v_{act} * \rho_{act}$$

Where v_{fr} , ρ_r are volume fraction and density of resin respectively and v_{act} , ρ_{act} are volume fraction and density of acetone respectively.

8.2 Void content

$$V_{void} = \frac{\rho_t - \rho_c}{\rho_t} \quad (B)$$

Where, ρ_t , ρ_c are the theoretical and measured density.

$$\rho_c = \frac{mass}{volume}, \quad \rho_t = V_f * \rho_f + (1 - V_f) * \rho_{matrix}$$