

IMPROVE THE THROUGH-THICKNESS ELECTRICAL CONDUCTIVITY OF CFRP LAMINATE USING FLOW-ALIGNED CARBON NANOFIBER Z-THREADS

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ABSTRACT

Traditional Carbon Fiber Reinforced Plastics (CFRPs), carry high in-plane strength and electrical conductivity but exhibit intrinsic weaknesses in strength, toughness and conductivity in the through-thickness direction (i.e. z-direction). This paper presents a novel approach to align and thread Carbon Nanofibers (CNFs) through the porous medium (Carbon fiber fabric) using an interesting radial-flow alignment method and manufacture a novel CNFs z-threaded CFRP prepreg. This new radial-flow alignment approach is unique and has been found highly effective to z-thread the array of carbon fibers (diameter ~ 7 microns) with numerous long CNFs (length ~ 50-200 microns) under a Scanning Electronic Microscope (SEM) analysis. Experimental tests performed on a cured laminate sample prepared by this novel technique with 1 wt% aligned CNF concentration showed a significant improvement on the z-directional electrical conductivity for direct current (DC). The 1 wt% CNFs z-threaded CFRP was found about 100 times as conductive as the control CFRP; whereas the unaligned 1 wt% CNFs modified CFRP was only about 16 times as conductive as the control sample.

1. INTRODUCTION

Carbon fiber reinforced polymer composites (CFRP) are highly desired materials for aerospace, automotive, portable electronics, medical devices and marine instruments owing to their high specific strength, stiffness, lightweight, in-plane electrical conductivity and corrosion resistant features [1,2]. However, low electrical conductivity (σ), particularly in out-of-plane direction [3] (e.g. $\sigma_{\text{out-of-plane}} = 3.2 \times 10^{-3}$ S/m for unidirectional CFRPs with $V_f = 60\%$) has limited their applications, especially in aircraft, wind turbine blade, electromagnetic shielding, lightning strike protection (LSP), damage detecting, strain/stress sensing and chemical and thermal sensing [4-5]. Single and multi-wall carbon nanotubes and vapor grown carbon nanofillers (VGCNFs) have been promising candidates as the possible nano-fillers for polymer matrices. CNTs have attracted significant attraction for electrical conduction applications due to its extraordinary attributes like low density, high aspect ratio (length/diameter), tunable electrical and mechanical properties

superior than conductive metals. The cost to produce VGCNFs is 3-10 times cheaper compared to multi-wall carbon nanotubes or single-wall carbon nanotubes [6]. Moreover, VGCNFs possesses electrical conductivity about 10^3 S/cm [7], which make them suitable for application that require electrostatic potentials discharge and shielding from radio frequency interference. Through thickness electrical conductivity enhancement is possible with directional alignment of these nanofibers in a CFRP laminate, which is the major scope of work in this paper.

1.1 Literature Review and Motivation

Ajayan et al. [8] conceptually proved outstanding properties of CNTs can help improving the properties of a polymer if one aligns CNTs in host matrix. These results paved the path for creation of various approaches to attain the desired composite material properties via aligned nano-reinforcement. In recent years, CNT alignment has been achieved using various techniques including mechanical force [9,10], magnetic field [11,12], electric field [13,14], shear flows [15], electrospinning [16,17], spray coating [18] etc. However, most of the alignment techniques are for aligning CNTs in the bulk polymer matrix or in the in-plane direction of CFRP instead of in the z-direction of a CFRP, which requires more sophisticated techniques.

Pegorin et al. [19] used z-pins made of pultruded rods of unidirectional T300 carbon fiber-Bismaleimides (BMI), stainless steel (316L), titanium (grade 1; 99.5% purity) and copper (99.9% purity) with volume content 0.2% to 4% to enhance the through thickness electrical conductivity of fiber-polymer composites. Carbon fiber z-pins were inserted into uncured laminate using ultrasonically assisted pinning (UAP) [20] while cleaned and surface treated metallic z-pins were inserted manually using tweezers in a square grid pattern. The carbon fiber-BMI was recorded as the least effective which showed 1.5×10^5 % increase in z-direction electrical conductivity at 4% volume content with negligible change in density of material. The copper z-pin was the most effective with 1.1×10^8 % increase in electrical conductivity at 1.84% volume content with 9.4% change in material density. Though, the use of z-pins to increase the electrical conductivity in thickness of fiber-polymer composites showed greater improvement, it can be usually detrimental rather than beneficial due to its water absorption behavior and possible galvanic corrosion of carbon-epoxy laminate under hot and wet conditions [21].

Cheng et al. [22] used hand layup technique to enhance the through thickness electrical conductivity of CFRP using carbon-based nanofillers/conduct polymer hybrids dispersed in divinylbenzene (DVB) matrix; but the authors did not mention about nanofillers alignment direction. Both multiwalled carbon nanotube (MWCNT) and graphene oxide (GO) were tested as the potential nanofillers. Among all samples, the CFRP made of 0.8% multiwalled carbon nanotubes (MWCNT)/polyaniline (PANI) achieved maximum alternating current (AC) conductivity of 22.4 S/m which is 3 orders of magnitude higher than Carbon fiber (CF)/divinylbenzene (DVB) CFRP and more than 2 orders of magnitude in comparison to CF/epoxy CFRP. The conductivity enhancement for carbon/PANI hybrids was mainly due to interfacial excess energy [23] and quantum tunneling effect [24]. Increased conductive fillers content (MWCNTs) into polymer matrix caused the interfacial excess energy to reach a critical point where fillers began to coagulate to prevent any further increase of energy and conductive networks are formed which eventually leads to quantum tunneling effect to enhance the electrical conductivity of CFRP composite. Declined of electrical conductivity with higher concentration is mainly due to aggregation of carbon nanoparticles that leads to bad disparity and destruction of

uniform network. Furthermore, due to the instability of PANI, the electrical conductivity drops when the frequency increases to 10^4 - 10^5 Hz.

Current lightning strike protection (LSP) solutions in aerospace are either based on the use of highly conducting metal and alloy meshes at the outermost laminate layer or mix them with carbon fiber in the prepreg [25,26]. Li et al. [18] addressed this problem with the use of synergistic effects of spray-coated hybrid carbon nanoparticles and reduced the CFRPs surface resistivity (measured with two-probes method) by four orders of magnitude. Spray coated hybridized CNT and graphene nanoplatelets (GNP) help to reduce the surface electrical resistivity (3.43×10^{-4} ohm/sq.) close to that of commercial Cu mesh (0.1 - 1.7×10^{-4} ohm/sq.) at a fraction of areal density 0.4 g/m² compared to 50 - 1000 g/m² of metallic meshes.

One of the straight forward techniques used by many researchers to align and form CNT network in a bulk polymer matrix is the application of electric field, which induces dipole moments in CNTs and caused the CNTs to rotate, orient and move towards the nearest electrode and align in the applied electric field. During in situ polymerization, Ma et al. [27] applied AC electric field of 15 kV/m at 500 Hz maintained across copper electrodes and reported an alignment of 0.1 wt% oxidized MWCNTs in Polymethylmethacrylate (PMMA) matrix with nearly four orders of enhanced conductivity compared with pure PMMA. Park et al. [28] employed electric field to optimize CNTs alignment in a polymer solution of urethane dimethacrylate (UDMA) and 1,6-hexanediol dimethacrylate (HDDMA) ($9:1$ ratio). They reported the optimal alignment could be achieved with an electric field of 43.5 kV/m at 100 Hz for 0.03 wt% SWNTs in the polymer solution. It was also reported that alignment and electrical conductivity of CNTs are functions of the magnitude, frequency and duration of the applied electric field. Scruggs et al. [29] used the novel method as described in the [30] for manufacturing of CNFs z-threaded CFRP (T700/ (Epon 862/Epikure-W)) and reported through thickness DC electrical conductivity was increased by 238% and 1393% compared with control CFRP and unaligned CNFs modified CFRP respectively at 0.1 wt% CNF concentration. However, in general, electric field approach is limited to the use of conductive nanofibers (or nanotubes), the concentration of nanofibers (or nanotubes), along with a relatively non-conductive and low viscosity matrix. Such physics limitations can narrow the selections of applicable materials using any electrical field alignment method.

Based on the literature review, there is a need of robust and efficient method for uniform alignment of nanotubes or nanofibers in the z-direction of CFRPs to address the limitations caused due to low electrical conductivity in thickness direction. The present work aims to use a new radial-flow method [31] to directionally align and thread carbon nanofibers into a carbon fabric/epoxy CFRP and measure the through thickness DC electrical conductivity of the CNFs z-threaded CFRP. To the best knowledge of the authors, this method is a novel approach to align the nanofibers and nanotubes in the z-direction of fiber reinforced polymer composites. With straightforward physics concept and operation simplicity along with some promising features in comparison with other approach reported in literatures, this new radial-flow method could provide a scalable, cost-effective, and robust solution of aligning the CNTs or CNFs in the thickness direction (i.e., z-direction) of CFRP. This paper will focus on the DC electrical conductivity improvement and use SEM microscopy to understand the microstructure of the CNFs z-threaded CFRP laminate.

2. EXPERIMENTATION

2.1 Materials

An unmodified control CFRP, a CFRP with 1 wt% (measured as percentage of matrix weight) unaligned CNFs, and a CFRP with 1 wt% z-aligned CNFs (i.e., 1 wt% CNFs z-threaded CFRP) were prepared to study the electrical conductivity performance. The carbon fiber used to prepare the sample was HexTow™ AS4 unidirectional fabric (190 g/m² areal weight, 1.79 g/cm³ fiber density, 3k tow size). The polymer matrix to create the laminate is a mixture of Epon resin 862 and Epikure W catalyst, both received from Momentive. The reinforcement CNFs were R-24-LD-HHT carbon nanofibers acquired from Pyrograf Products, Inc., with average diameter of 100 nm and lengths ranging from 50 μm to 200 μm [32]. The surfactant Disperbyk-191 and Disperbyk-192 acquired from BYK USA Inc. were also used for helping the dispersion during the preparation of unaligned and z-aligned samples.

2.2 CFRP Preparation

During the preparation of control sample, the Epon 862 and Epikure W curing agent were mixed mechanically in the stoichiometric ratio of 100:26.5 for 5-7 minutes. Then the mixture was degassed in a vacuum chamber at 80 °C for an hour. A 0.255 m (L) × 0.012 m (W) unidirectional AS4 carbon fabric was placed on a preheated hot plate at 120 °C. Degassed resin was pour on the top of the fabric and rolled with a roller for uniform impregnation of resin. After an hour, the resin impregnated fabric reached the desired B-stage cure and was transferred to nylon bagging and stored in a -18 °C freezer for later use. Five such prepreg plies were prepared.

Dispersion and alignment of CNFs in the polymer matrix is critical for the reinforcement performance and requires additional steps. First the surfactant Disperbyk-191 and Disperbyk-192 (about 1 wt% each) were added to Epon 862 and mechanically mixed for about 5-7 minutes. Then weighed CNFs were added to the resin and mixed with a magnetic stirrer. Once the CNFs were incorporated in the matrix, the mixture were subjected to one-hour mechanical mixing at 80 °C and followed by one-hour sonication in a QSONICA Q700 sonicator. After sonication, as the agglomerations of CNFs were mostly broken apart already, the required amount of Epikure-W cure agent was added on the matrix and mechanically mixed for about 5-7 minutes. The mixture was then degassed in a vacuum chamber for an hour at 80 °C for unaligned sample and 50 min at 120 °C for aligned sample preparation. The unaligned prepreps were prepared following the same procedure for control prepreps. However, z-aligned prepreps (i.e., CNFs z-threaded CFRP prepreps) were prepared using a new radial flow alignment technique to thread CNFs into the AS4 fabric as described in [31]. A perforated hollow roller was employed to draw the heated viscous B-stage resin containing CNFs towards the center of the roller whereas the unique converging flow of the viscous resin caused the CNFs being stretched, aligned in the radial direction and forced to thread through the carbon fiber fabric conformally placed on the curved surface of the perforated roller (detailed apparatus design can vary and is not disclosed here). The CNFs z-threaded CFRP prepreps, after being removed away from the roller, were then stored as 0.255 m (L) × 0.012 m (W) plies in a -18 °C freezer for later use.

For manufacturing the control, unaligned and z-threaded CFRP laminate samples, five plies of the corresponding type of prepreps were stacked and cut into the dimensions of 0.080 m (L) × 0.012 m (W) and completely cured into the corresponding type of CFRP laminate via the Out-

Of-Autoclave-Vacuum-Bag-Only (OOA-VBO) curing process. An aluminum plate, covered with mold release coating, was used as the mold with sealant tapes along all edges. The stacking sequence starting from the bottom followed as peel ply, CFRP prepreg laminas stack, peel ply, distribution media, vacuum channels on two sides and vacuum bagging on the top (see Figure 1). Vacuum was drawn from the sealed mold assembly and leakage checking was performed. Then the mold was placed in a hot press with a minimum gap between the top hot plate and the mold assembly to maintain the uniform heating on the mold assembly. The curing cycle is presented in Table 1.

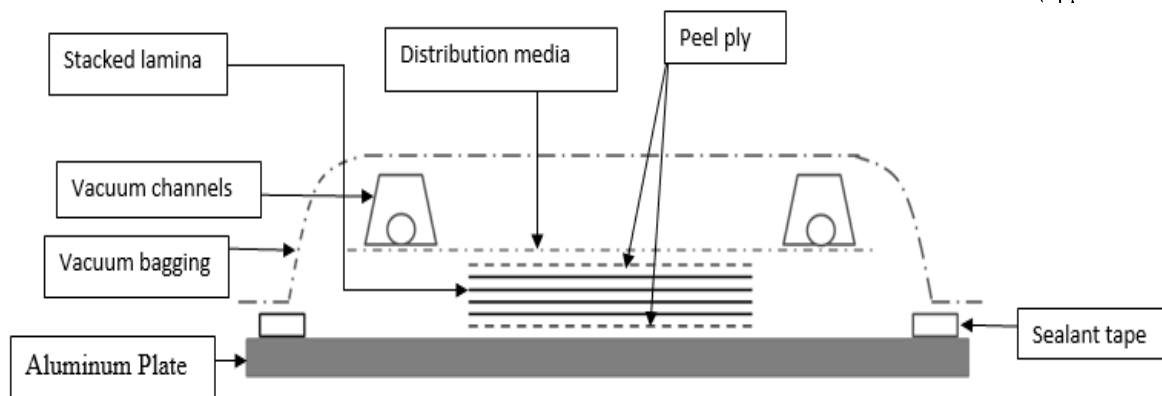


Figure 1: OOA-VBO layup scheme used for preparation of CFRP.

Table 1. OOA-VBO cure cycle used for all samples

Time (min)	Temperature (°C)	Vacuum Pump
60	Room temperature (23)	On
30	45	On
120	120	On
240	180	Off

After curing, the samples were trimmed into the final size about 0.075 m (L) × 0.010 m (W). The samples were then polished on both top and bottom surfaces for better ohmic contact and cleaned with soap water and then acetone before the electrical conductivity measurement.

2.3 Z-directional Electrical Conductivity Test

Four-probe technique [29] was implemented to measure the electrical resistance of each sample as shown in Figure 2.

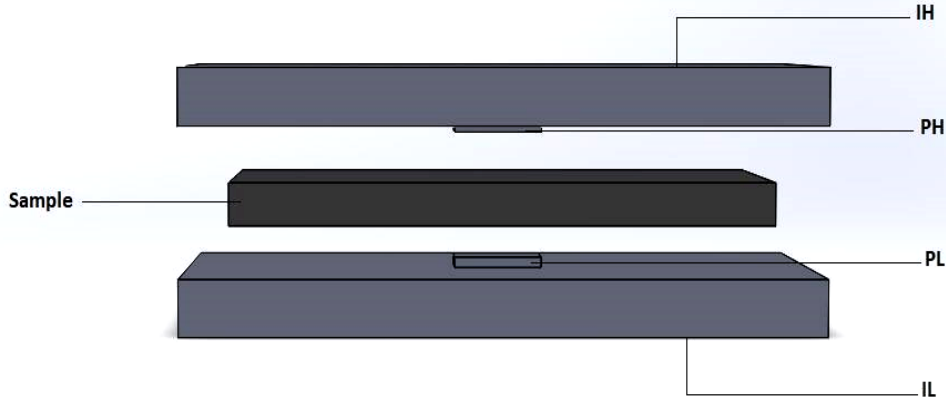


Figure 2: Four probe z-direction electrical conductivity testing apparatus. Note: IH and IL are the electrode plates to inject current through the sample and PH and PL are probes to measure the voltage drop across the sample.

The testing apparatus, which was specially designed for CFRP laminate samples, basically consisted of two flexible copper electrode plates (IH and IL in Figure 2) to inject the electrical current through the sample in the z-direction and two smaller copper probes (PH and PL in Figure 2) to measure the voltage drop across the thickness (in the direction of current) of the sample. The sample was placed between the two electrode plates (IH & IL) such that the voltage probes (PH & PL) touches the center of the CFRP sample. Once the sample position was adjusted in the apparatus, the assembly was clamped firmly to minimize the oscillation in electrical resistance signal captured in a digital multimeter (Agilent 3458A Digital Multimeter, 8.5-digit resolution). Each CFRP sample was tested 10-15 times by varying the position of the sample in the apparatus to get independent z-directional resistance measurements. Then the z-directional electrical conductivity for each CFRP laminate sample was calculated using Eq. 1:

$$\rho = \frac{L}{R * A} \quad [1]$$

Where, ρ = specific electrical conductivity of the CFRP laminate sample (S/m).

L = Z-direction thickness of CFRP laminate sample (m)

A = Area of the CFRP laminate sample (m²)

R = Electrical resistance measured (ohm)

3. RESULTS

The statistical analysis of the z-directional electrical conductivities of all samples is presented in the Table 2. Note that once the authors found the CNFs z-threaded CFRP sample has shown

impressive improvement against the control sample and the unaligned sample, additional set of measurements on the z-threaded sample have been repeated one day later to check the repeatability; and the additional set of checking tests confirmed a good repeatability.

Table 2: Statistical analysis of Z-directional DC electrical conductivities measured for control CFRP, 1 wt% unaligned CNFs modified CFRP, and 1 wt% CNFs z-threaded CFRP.

Sample	Mean Z-directional DC electrical conductivity (S/m)	Standard deviations (S/m)	Coefficient Of Variation (COV) (%)	% Increase w.r.t. Control CFRP	Normalized based on Control CFRP
Control CFRP laminate	0.161	0.0091	5.66		1 X
1 wt% unaligned CNFs modified CFRP laminate	2.70	0.302	11.20	1577	16.77 X
1 wt% CNFs z- threaded CFRP laminate	16.24	2.81	17.28	9987	100.87 X

The z-directional DC electrical conductivity observed in the 1 wt% CNFs z-threaded CFRP was 16.24 S/m, which is around +9987% increase compared to the control sample and +501% increase in comparison with the 1 wt% unaligned CNFs modified CFRP. One can also normalize all the conductivity values based on the conductivity of control sample. The 1 wt% CNFs z-threaded CFRP sample was about 100.87 times as conductive as the control CFRP sample. On the other hand, the 1 wt% unaligned CNFs modified CFRP sample was only about 16.77 times as conductive as the control CFRP sample. Significantly enhanced through thickness electrical conductivity of the 1 wt% CNFs z-threaded CFRP was obtained with this this novel radial-flow alignment method [31]. The z-directional DC electrical conductivity enhancement was possible only due to effective electrically conductive pathway formed by the alignment of carbon nanofibers in the thickness direction. To support the evidence of z-directional electrical conductivity improvement, SEM image was taken. Z-directional alignment of CNFs in the 1 wt% CNFs z-threaded CFRP sample can be seen in Figure 3. The higher COV (see Table 2) of the CNFs z-threaded sample could be due to the B-stage process of the CNFs z-threaded CFRP sample was not properly tuned against this batch of epoxy resin (i.e., each batch resin could be slightly different in curing behavior and may require fine-tuned B-stage cycle), which led the excess resin flow out of the sample and disturbing the z-aligned CNFs in the CFRP; a more precise B-stage process tuning can help resolve the B-stage resin quality issue.

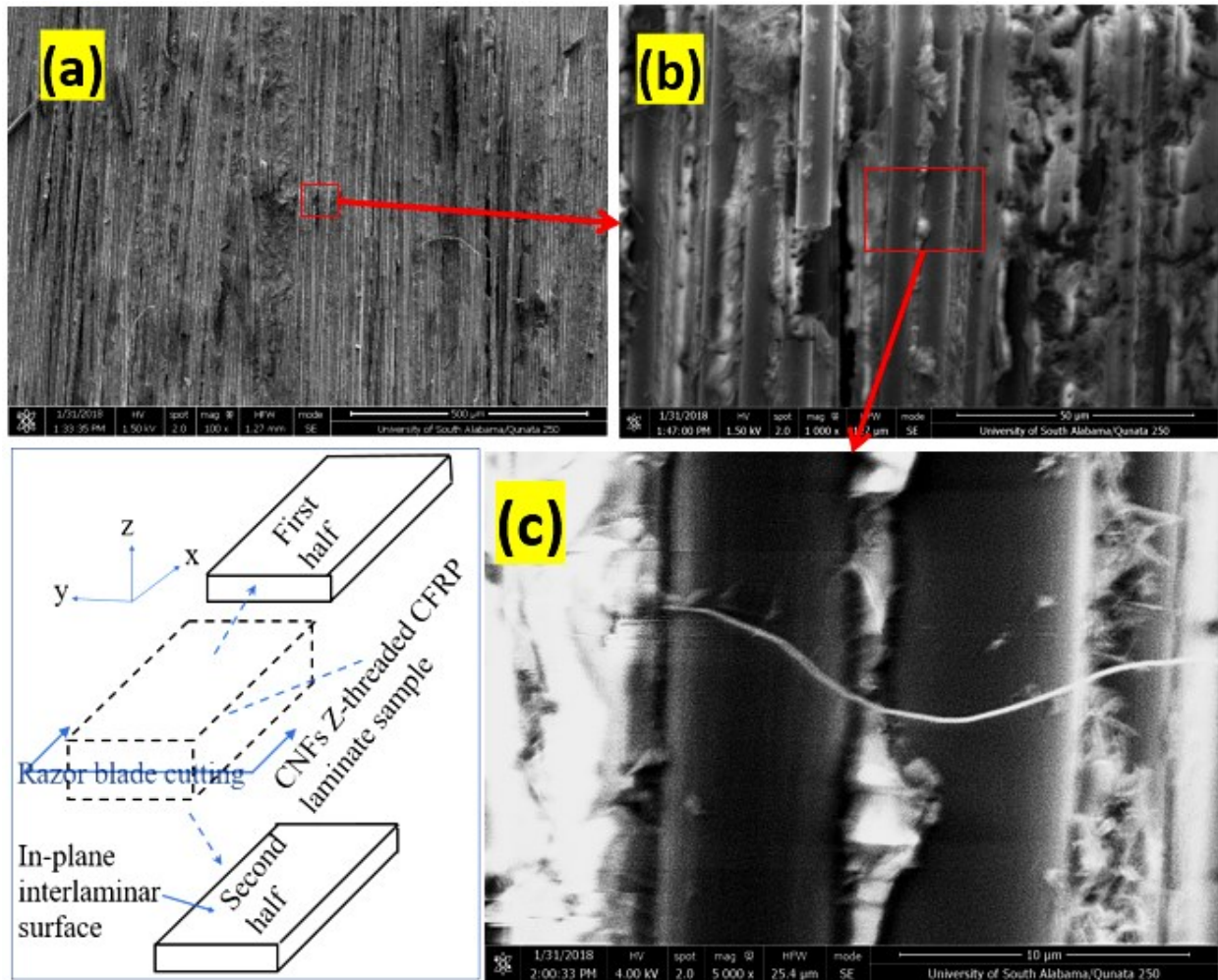


Figure 3. SEM images of the in-plane interlaminar surface of 1 wt% CNFs z-threaded CFRP laminate: (a) 100x magnification; (b) 1000x magnification; (c) 5000x magnification.

Figure 3 shows the SEM images of the in-plane interlaminar surface of CNFs z-threaded CFRP sample. The SEM images clearly show that many CNFs successfully penetrated through the gaps among carbon fibers and aligned in the z-direction. At a high magnification (5000X) (see Figure 3 (b)), one can find a long CNF coming out from beneath the resin surface near the carbon fiber and extending in the z-direction. In addition, one can also see many fuzzy structures in Figure (b) that are in fact many vertically orientated CNFs z-threading through the gap among carbon fibers as shown in more detailed in Figure (c). The intriguing SEM images shown in Figure 3 suggested the vertically aligned CNF z-threads in the CFRP laminate are responsible for the two order of magnitude electrical conductivity enhancement in the z-direction as shown in Table 2. Furthermore, the results from Figure 3 and Table 2 validated that the new radial-flow alignment method is an effective method to align and thread CNFs into the CFRP in the through-thickness direction.

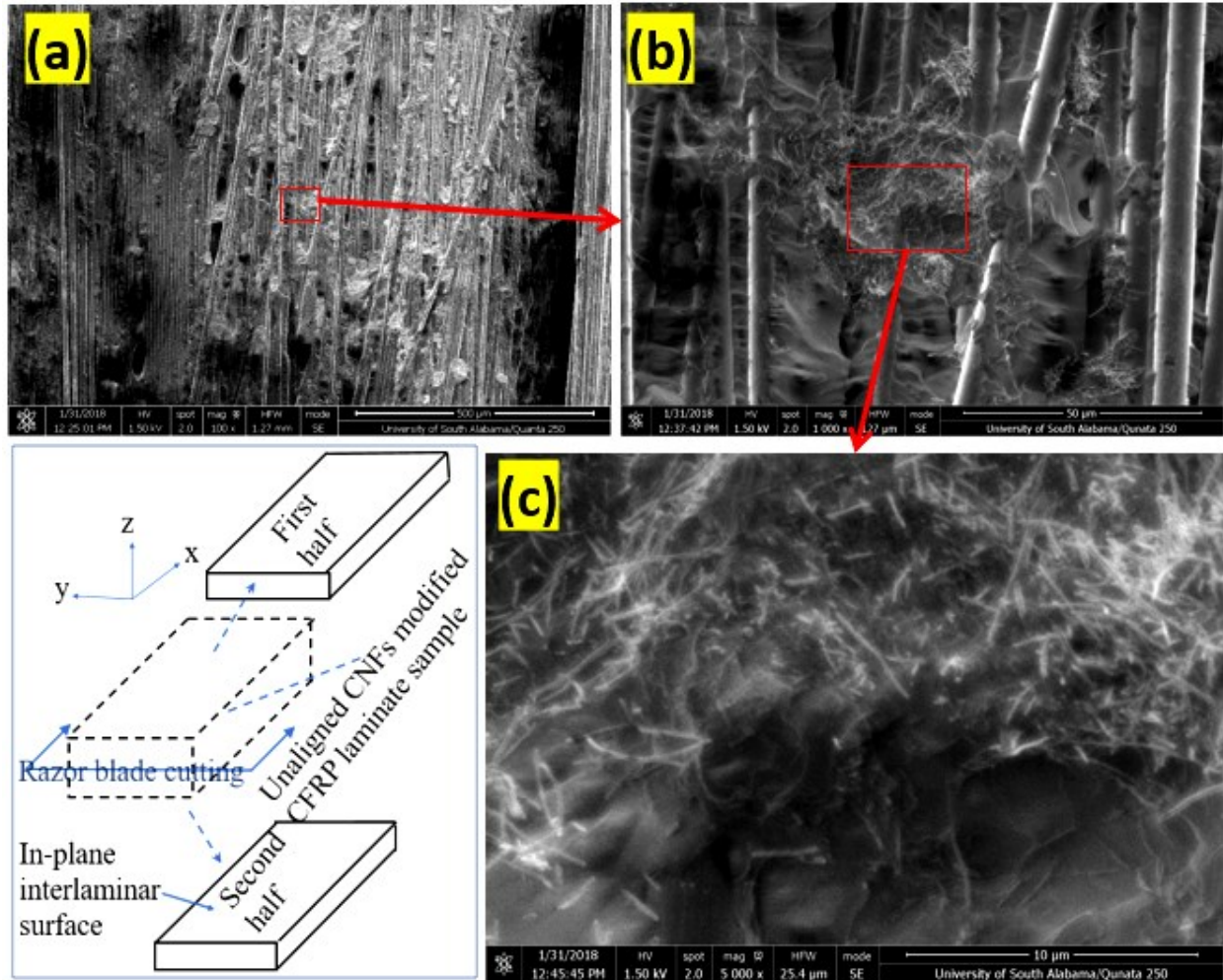


Figure 4. SEM images of the in-plane interlaminar surface of 1 wt% unaligned CNFs modified CFRP laminate: (a) 100x magnification; (b) 1000x magnification; (c) 5000x magnification

On the other hand, the z-directional electrical conductivity improvement of the 1 wt% unaligned CNFs modified CFRP compared to control CFRP, was also significant but was not on the same order of magnitude level of the CNFs z-threaded CFRP sample. In the unaligned CNFs modified CFRP, as shown in the SEM images of Figure 4, the CNFs were mostly aligned in the x-y direction (in-plane directions) with only very few aligned in the z-direction. Moreover, many CNFs were agglomerated on the carbon tow surface, which is apparently not an effective way to use the CNFs in the CFRP laminate if one is looking for the improvement in the z-directional conductivity or other properties. The SEM images in Figure 4 and Figure 3 showed great microstructure difference between the unaligned CNFs modified CFRP and the CNFs z-threaded CFRP. Such microstructure difference also helps to explain why the unaligned CNFs modified CFRP was much less conductive than the CNFs z-threaded CFRP in terms of z-directional performance. The unaligned CNFs modified CFRP apparently lacked CNFs alignment control and has been suffered with the CNFs agglomeration issue, which could be due to the unaligned CNFs being filtered out by the carbon fiber bed and forming agglomerates. These shortfalls found in the unaligned CNFs modified CFRP sample in this study could explain why many

previous attempts of using CNFs in CFRP without considering CNF alignment control typically yielded with marginal improvements or sometimes worse performance compared to control CFRP samples [33, 34].

4. CONCLUSIONS

The through thickness electrical conductivity could be enhanced by the alignment of conductive nanofillers in the z-direction of a CFRP. A novel radial-flow alignment approach [31] for z-directionally aligning and threading CNFs into a CFRP fabric, which was B-stage cured into a CNFs z-threaded CFRP prepreg, was examined with SEM microscopy and z-directional electrical conductivity testing and was found very effective. This novel and unique approach helped to enhance the z-directional DC electrical conductivity from 0.161 S/m to 16.24 S/m for the control CFRP laminate and the CNFs z-threaded CFRP laminate, respectively. Such a through-thickness electrical conductivity obtained from this new method makes it potentially suitable for electromagnetic shielding applications; which requires higher than 10 S/m [35].

In addition to the promising z-directional electrical conductivity enhancement, the other significance point of this paper is that directional alignment of nanofillers in the porous media is possible with the new radial-flow alignment approach, which has been proved as a powerful and straightforward alternative to the other existing complex methods reported in literatures.

The uniform directional alignment of CNFs in CFRP along with the B-stage resin processing cycle are both important for the CNFs z-threaded CFRP prepreg, which is a subject for future work in this research area. Moreover, additional mechanical, thermal, and electrical tests on larger samples will be performed to obtain more comprehensive data in the near future. Increasing the CNF concentrations and trying more viscous resin system (such as thermoplastics) to understand the process' limitation and broader potential will also be of interest for studying this new radial-flow based nanofibers alignment approach.

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