FLAMMABILITY CHARACTERIZATION OF CARBON NANOFIBERS AND NANOTUBES Z-THREADED CFRP LAMINATES

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ABSTRACT

Carbon fiber reinforced polymer (CFRP) composites have been increasingly used in many vehicles such as airplanes, automobiles, and ships due to the advantages of high-strength, high-modulus, lightweight, and corrosion resistance. CFRP structures enhance the vehicle's performance, energy-efficiency, comfort, and safety. However, a common safety concern is how the CFRP materials perform when the vehicle is in fire and if there are enough time to safely evacuate the passengers. The elevated temperature can soften and decompose the polymer matrix, delaminate the CFRP laminate, and burn the CFRP through the contact with oxygen. As a result, the thermal and flammability response of CFRP is important for considering CFRP for vehicle applications; and some specialty high-temperature or flame/smoke/toxicity-proven resins have been investigated for CFRP parts manufacturing due to the needs. In this paper, a novel flame resistant hypothesis of utilizing the unique nano/micro- interlocked fiber reinforcing structure of the long-range carbon nanofiber z-threaded CFRP (ZT-CFRP) composite laminates for improving the flammability performance will be investigated. The carbon nanofibers (CNT) and carbon nanotubes (CNT), which have excellent thermal and mechanical properties, will be dispersed in an epoxy resin and will zig-zag thread through a carbon fiber fabric using an electrical/flow assisted impregnation process to create the unidirectional ZT-CFRP prepregs, respectively, which will be further processed into ZT-CFRP composite laminates. The UL-94 flammability test will be employed to characterize the ZT-CFRP laminates' flammability performance against the control baseline data of the regular CFRP, all without using any flame retardant chemicals. An impressive self-extinguishing flammability characteristic of the CNF based ZT-CFRP samples has been distinctly identified from all the samples. The UL-94 testing results and the effectiveness of using the long-range nanofiber z-threading strategy for enabling the novel nano/microstructure-induced flame resistant and self-extinguishing characteristics will be discussed.

Keywords: Flammability, Carbon Nanotube, Carbon Nanofiber, Z-threaded CFRP
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1. INTRODUCTION

1.1 Overview of Carbon Fiber Reinforced Polymer (CFRP) Flaming Behaviors

Carbon fiber reinforced polymer composites have been increasingly adapted to metal counterparts in many applications such as aerospace, automotive, wind blades, etc., due to the lightweight, high strength, high modulus, and corrosion resistance. However, some known concerns of using CFRP could hinder the adaption of CFRP. Flame retardance is one of the major concerns as reported in [1], which investigated the flammability characteristics of Toray Composites BMS 8-276 carbon-fiber material based on Boeing Material Specification 8-276. According to [1] the heat flux or elevated temperature, when being applied to a BMS 8-276 CFRP panel, can vaporize the resin (the onset temperature is about 300 °C), which will be then fueling the flame and burn into char. The char can serve as the surface barrier to reduce the burning rate or extinction of the flame if without continuous external heat flux. In addition, the resin vapor will create pressure and expand the BMS 8-276 CFRP panel thickness for about twice and create porosity to about 60%, and the CFRP laminate may lose its structural integrity. The expanded pore size and porosity can also increase the permeability to allow more resin vapor to escape to the surface and fueling the flame and then burned into char. In addition to flaming, the resin can also be decomposed at the onset temperature. The thermal conductivity and thickness of CFRP panel was also found affecting the burning behavior of the CFRP. The time to start a piloted ignition was found to be reduced as the incident heat flux increase. It was also found that if the BMS 8-276 CFRP laminate temperature is high enough, the auto-ignition of sufficient concentration of reactive ingredients can also occur.

While the flaming behavior of CFRP laminate is very complex and governed by many factors and interacting mechanisms, it can be attributed to the chemistry, thermodynamics, heat transfer, and the porous structure of CFRP laminate. In this paper, the investigation will be focused on a novel porous structure of CFRP only enabled by the recent nanotechnology.

1.2 Overview of Carbon Nanofibers/Nanotubes Z-Threaded CFRP (ZT-CFRP) Composites

Many next generation FRP technologies are usually seeking better performance or greener than current CFRP technologies to enable stronger, tougher, more versatile, more/better multifunctionalities, and/or better sustainability. The long carbon nanofibers z-threaded CFRP (ZT-CFRP) composite is one of the next generation technologies aiming at higher performances and high production volume possibility. The ZT-CFRP technology has been experimentally proven to notably enhance a broad range of performance characteristics (as shown in Table 1) including the mode-I delamination toughness [2], DC electrical conductivity [3, 4, 5] and thermal conductivity [6] along the z-direction (i.e., the through thickness of the ZT-CFRP laminate), the interlamination shear strength (ILSS) [7, 8], the longitudinal compressive strength [9], and is highly scalable for commercial availability [10, 11, 12, 13] . Figure 1 shows the schematic of the ZT-CFRP technology and the scanning electron microscope (SEM) picture revealing the unique and novel nano-microstructure of relative long CNFs z-threading around two or more carbon fibers inside a porous (i.e., resin-less) ZT-CFRP composite laminate sample. Note that the long CNFs zig-zag thread through multiple carbon fibers and create the desired mechanical interlocking 3D nano-/micro- fiber reinforcing network. Therefore, even with 50wt% acetone diluted epoxy formed porous ZT-CFRP, it can still retain 85% of the ILSS of a traditional solid matrix CFRP (no acetone dilution in the epoxy matrix) thanks to the CNF z-threads formed long-range zig-zag mechanical interlocking fiber network [14]. Figure 2 shows the microscope sideview of a ZT-CFRP unidirectional AS-4 prepreg; one can see the CNF z-threading between the unidirectional carbon fibers bed. The ZT-CFRP prepregs can be stacked and cured via Out of Autoclave-Vacuum Bag Only (OOA-VBO) process and manufactured into the ZT-CFRP laminates. Table 1 listed some testing data of the ZT-CFRP laminates.

Table 1. Overview of the effects of CNF z-threads on the material properties of CFRPs.

Material property	CNF wt%	CNF Type	CF Type	Fiber Areal Weight	Surfactant	Resin Type	FVF	Manufacturing Method	Control CFRP	ZT-CFRP	Improvement
Mode-I Delamination [2]	0.1-0.3wt%	PR-24-XT-PS	T300 plain weave	203 g/m^2	-	EPON 862/ Epikure-W	53%	Resin-flow transfer (sponge)	305 J/m^2	397 J/m^2	29%
Through-Thickness DC Elec. Conductivity [3]	0.1wt%	PR-24-XT-PS	T700 UD	680 g/m^2	-	EPON 862/ Epikure-W	64%	Resin-flow transfer (sponge)	1.58 S/m	5.35 S/m	238%
Through-Thickness DC Elec. Conductivity [4]	1.0wt%	PR-24-XT-HHT	AS4 UD	190 g/m^2	Disperbyk 191 & 192	EPON 862/ Epikure-W	72%	Resin-flow transfer (sponge)	0.26 S/m	4.18 S/m	1508%
Through-Thickness DC Elec. Conductivity [5]	>1.0 wt%	PR-24-XT-HHT	AS4 UD	190 g/m^2	Disperbyk 191 & 192	EPON 862/ Epikure-W	NR	Radial flow-alignment	0.16 S/m	16.24 S/m	100x
Through-Thickness Thermal Conductivity [6]	1.0wt%	PR-24-XT-HHT	AS4 UD	190 g/m^2	Disperbyk 191 & 192	EPON 862/ Epikure-W	72%	Resin-flow transfer (sponge)	1.31 W/m-K	9.85 W/m-K	653%
ILSS [7, 8]	1.0wt%	PR-24-XT-HHT	AS4 UD	190 g/m^2	Disperbyk 191 & 192	EPON 862/ Epikure-W	60%	Resin-flow transfer (resin film)	64.89 MPa	75.92 MPa	17%
Longitudinal Compressive Strength [9]	1.0wt%	PR-24-XT-HHT	AS4 UD	190 g/m^2	Disperbyk 191 & 192	EPON 862/ Epikure-W	54%	Resin-flow transfer (resin film)	673.85 MPa	773.76 MPa	14.83%

NR: not recorded; FVF: Carbon fiber volume fraction in CFRP; UD: Unidirectional; PS: Pyrolytically stripped carbon nanofibers; HHT: High-heat treated (up to 3000°C) carbon nanofibers; XT: Debulked form.

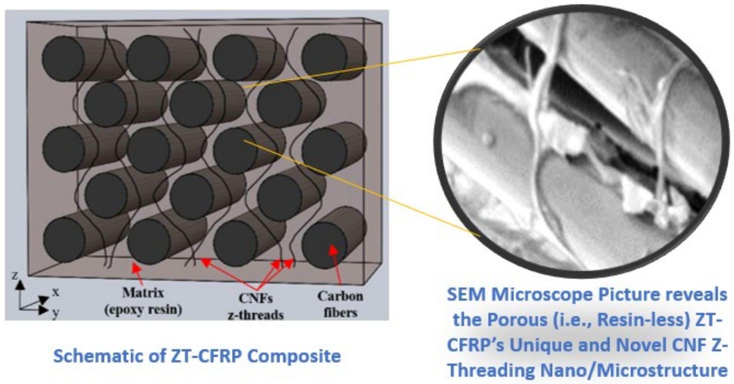

Figure 1. Schematic of ZT-CFRP composite (left). SEM microscope picture shows the unique and novel nano-microstructure of CNF Z-threading around two carbon fibers inside a porous (i.e., resin-less) ZT-CFRP composite laminate sample (right).

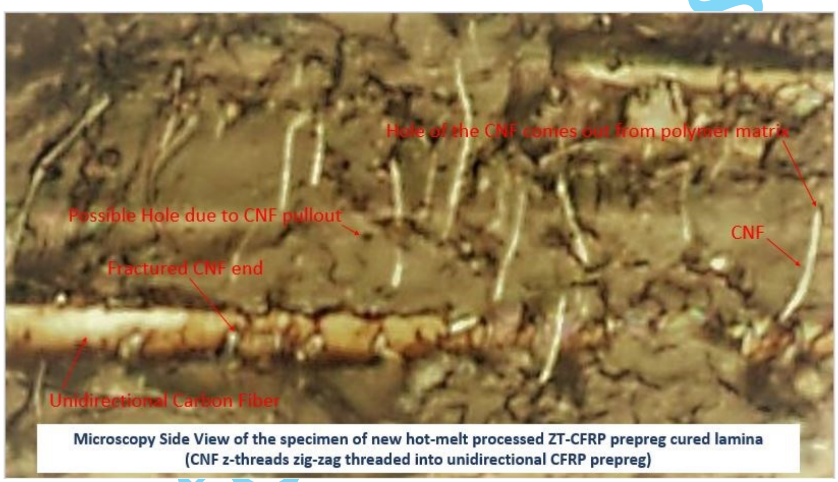

Figure 2. Microscopy sideview of a cured unidirectional ZT-CFRP prepreg shows the CNFs z-threading among the As4 carbon fibers.

1.3 Study Focus Question

As the flammability of CFRP can be affect by many factors including heat transfer, chemistry, resin degradation, flame-collapsing CFRP microstructure integrity, resin vapor forming and transportation, it is hypothetical that the unique ZT-CFRP's nano/microstructure induced enhancement in mechanical properties and thermal conductivity could change the flammability characteristics of a CFRP. The questions one could have would be "Could the ZT-CFRP's unique nano-/micro-structure help to improve the flammability issues of CFRP without using fire retardant chemicals?" and "How much improvement the ZT-CFRP can bring in without relying on any other fire retardant additives and modifications?" These are fundamentally intriguing questions that could potentially show how the next generation composite's new nano-/micro-structure can help into improve the traditional CFRP's shortfalls such as the flammability issue. To answer the questions, a focused preliminary experiment has been designed and conducted as described in the following section.

2. EXPERIMENTATION

2.1 UL-94 Flammability Test

UL-94, the *Standard for Safety of Flammability of Plastic Materials for Parts in Devices and Appliances* testing, a commonly used industry standard to obtain preliminary flammability test results of plastic materials and their tendency to either self-extinguish or spread the flame once ignited. In the vertical UL-94 test shown in Figure 3, a 125mm x 13mm x 3mm specimen is held in the vertical position at one end as a flame is applied at its free end for two 10-second intervals, separated by the time it takes for flaming combustion to cease after the first application. The second flame is applied immediately after the afterflame from first ignition extinguishes. A Bunsen burner fueled by propane gas was tilted at 45° from its vertical position was used as flame source for the testing and the flame length was adjusted to between 20-30mm. A cotton indicator is placed 300mm directly under the specimen as an indicator of any flame dripping during the combustion. This is used to evaluate the flame propagation potentials in a real fire scenario. Five specimens were tested for each material.

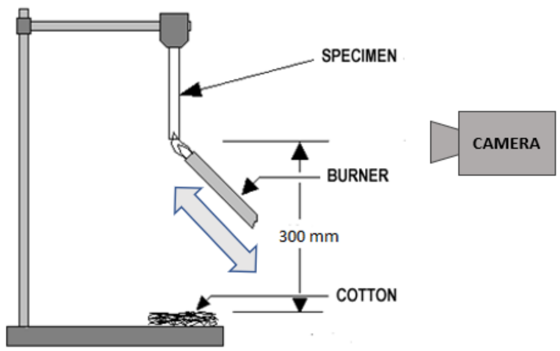

Figure 3. UL-94 vertical burn test setup

The three ratings, V-2, V-1, and V-0 (best) indicate that the material was tested in a vertical position and self-extinguished within a specified time after the ignition source was removed. These ratings also indicate whether the test specimen dripped flaming particles that ignited a cotton indicator located below the sample. In Table 2, t1 is defined as the duration of the afterflame after the first flame application, t2 is the afterflame duration after the second flame application, t3 is the afterglow duration after removal of the second flame application. Afterflame refers to flame that persists after the ignition source have been removed. Afterglow refers to persistence of glowing combustion after both removal of ignition source and extinguish of any flaming.

Table 2. UL-94 rating criteria

Criteria	V-0	V-1	V-2
Afterflame for each individual specimen (t1 and t2 individually)	$\leq$ 10s	$\leq$ 30s	$\leq$ 30s
Total afterflame for any condition set (t1 + t2 for each of the 5 specimens)	$\leq$ 50s	$\leq$ 250s	$\leq$ 250s
Afterflame plus afterglow time for each individual specimen after the second flame application	$\leq$ 30s	$\leq$ 60s	$\leq$ 60s
Afterflame or afterglow of any specimen up to the holding clamp	No	No	No
Cotton indicator ignition	No	No	Yes

2.2 Materials and Samples Manufacturing

The materials used in manufacturing the samples are: HexTow™ AS4 unidirectional carbon fiber fabric (areal weight: 190 g/m2, tow size: 3K, and fiber density: 1.79 g/m^3) provided by Hexcel Corporation, surfactants S191 and S192 from BYK, Epon 862 and Epikure-W from Miller-Stephenson Chemical Co, Inc., PR-24-XT-HHT grade carbon nanofiber (CNF) (average diameter of 100 nm, and a length ranging from 50 µm to 100 µm [15]) from Pyrograph Products/Applied Sciences, Inc, Graphistrength C S1-25 carbon nanotube (CNT) epoxy masterbatch from Arkema Group (MWCNT loading 25wt% dispersed in bisphenol A epoxy., MWCNT diameter ~ 10-15nm, length ~ 0.1-10 µm [16]). 120 grit 3M Professional Grade sandpaper and 320, 400 grit 3M Sandblaster Advanced Sanding Sheet sandpaper, wet 800 and 1500 grit 3M Wet or dry sandpaper.

Control CFRP was created through hand-layup. The appropriate ratio of 100:26.5 Epon 862 and Epikure-W was mixed manually with stirring rod for 10 minutes at room temperature. Using this resin blend 20 pieces of 130mm x 250mm AS4 unidirectional carbon fiber fabrics were impregnated using hand roller. In the following step this prepreg were placed into an industrial hot press at 120ºC for about 30 minutes for the B-stage to occur. The prepregs can then be stacked and cured via the out of autoclave-vacuum bag only (OOA-VBO) curing process as shown in Figure 4. Table 3 shows the curing cycle of the OOA-VBO process.

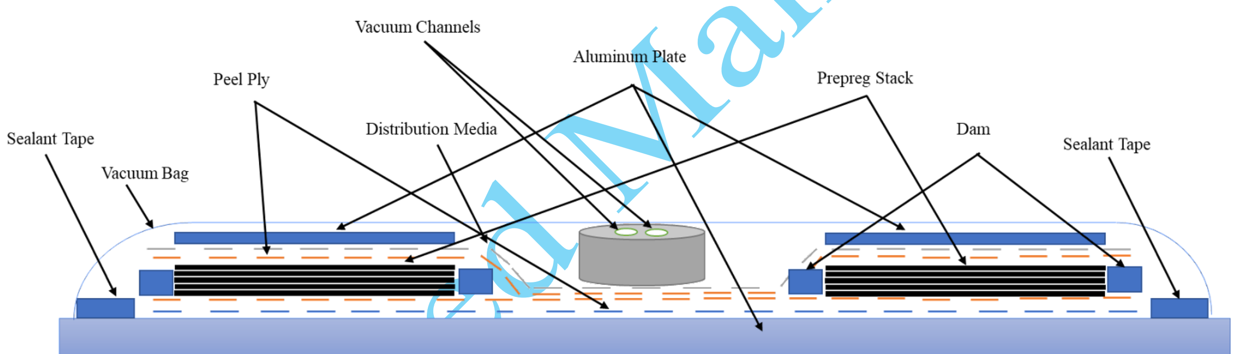

Figure 4. Out of autoclave-vacuum bag only (OOA-VBO) curing process setup.

Table 3. Out of autoclave-vacuum bag only (OOA-VBO) curing cycle used in this study

Samples Post Cure		
Time (minute)	Temperature (OC)	Vacuum (Bar)
60	23 (Room Temp.)	1
120	120	1
240	180	0

The ZT-CFRP prepregs with various CNT and CNF loadings were to manufacture as shown in Figure 5. The ZT-Film was created the same way for each combination of CNF and CNT after the first round of high shear mixing (HSM) for an hour at 90ºC. Note that the Arkema MWCNT/epoxy masterbatch came in the form of pellets and was melted and blended to liquid epoxy at about 80ºC per the manufacturer. Epon 862, CNF, CNT, and surfactants S191 and S192 were manually mixed and then mechanically mixed for 1-hour, alternating direction at 30 mins, on a hot plate at 90ºC. Then the batch was sonicated for 1 hour. After sonication concluded, a sample of the batch was taken for quality assessment. If the CNFs were well dispersed it would continue to the next step, if not it would be sonicated once more until it yields favorable results. The batch was then manually mixed with an appropriate amount of Epikure-W curing agent then HSM for 10 minutes alternating directions every 5 mins at 90°C temperature. The batch was taken to a vacuum oven at 110°C and allowed to degas with a proprietary tool used to accelerate the rate of degassing for 15 mins. B-staging came next which usually lasted from 35 to 45 mins at 120°C temperature while stirring and taking samples to monitor the rate of cure. Once B-stage was reached, the batch would be passed through an electric field during a high speed phase change on a proprietary R2R assembly line and yielded the hot-melt ZT-film containing z-aligned CNFs. A sheet of dry AS4 were impregnated with a ZT-film for 10 minutes on an industrial oven at 120°C to form a ZT-CFRP prepreg [9]. The prepreg was then trimmed and stacked together at 20 layers thick and underwent 1 hour 1 bar vacuum at room temperature (23°C) and then 2 hours of OOA-VBO at 120°C. Figure 6 summarizes the manufacturing process of the ZT-CFRP prepregs. Figures 7-9 show the optical microscopy morphology (by Nikon Eclipse LV150 optical microscope with extended focus) of the four types of laminates, and it was found that the 1wt% CNF ZT-CFRP seemed have the roughest fracture surface and large amount of CNF extending in the z-direction on the facture surface.

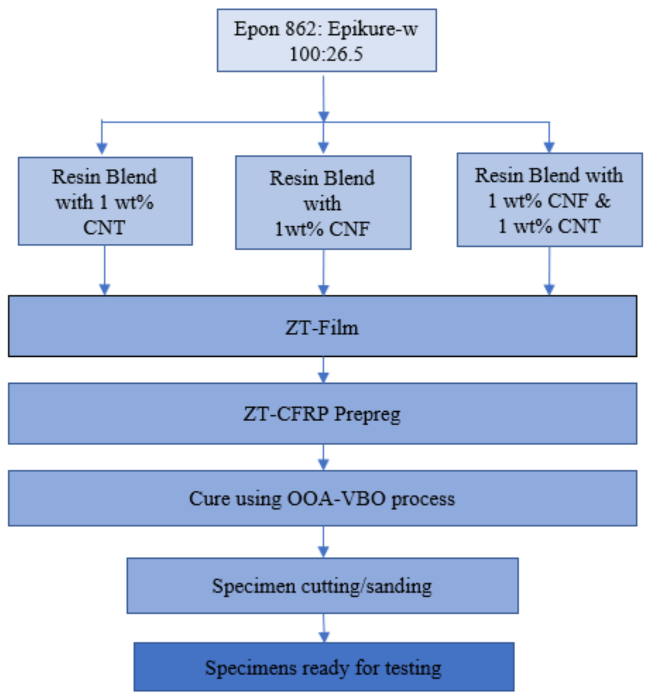

Figure 5. The entire process of manufacturing various ZT-CFRP laminates for burning test.

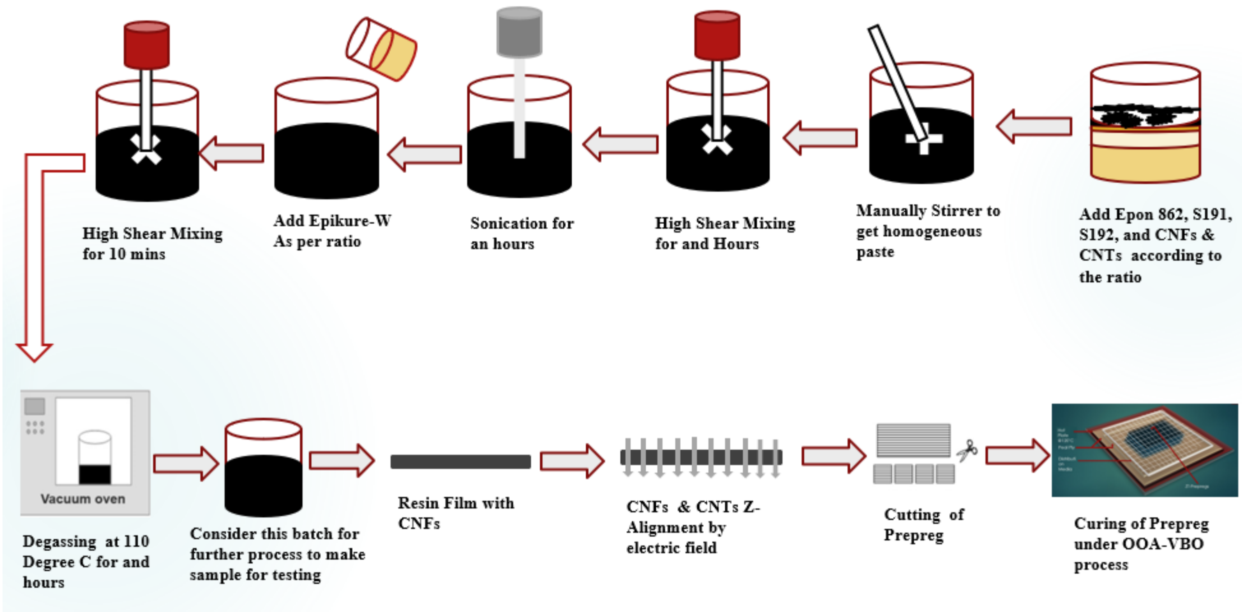

Figure 6. Manufacturing process of ZT-CFRP prepreg.

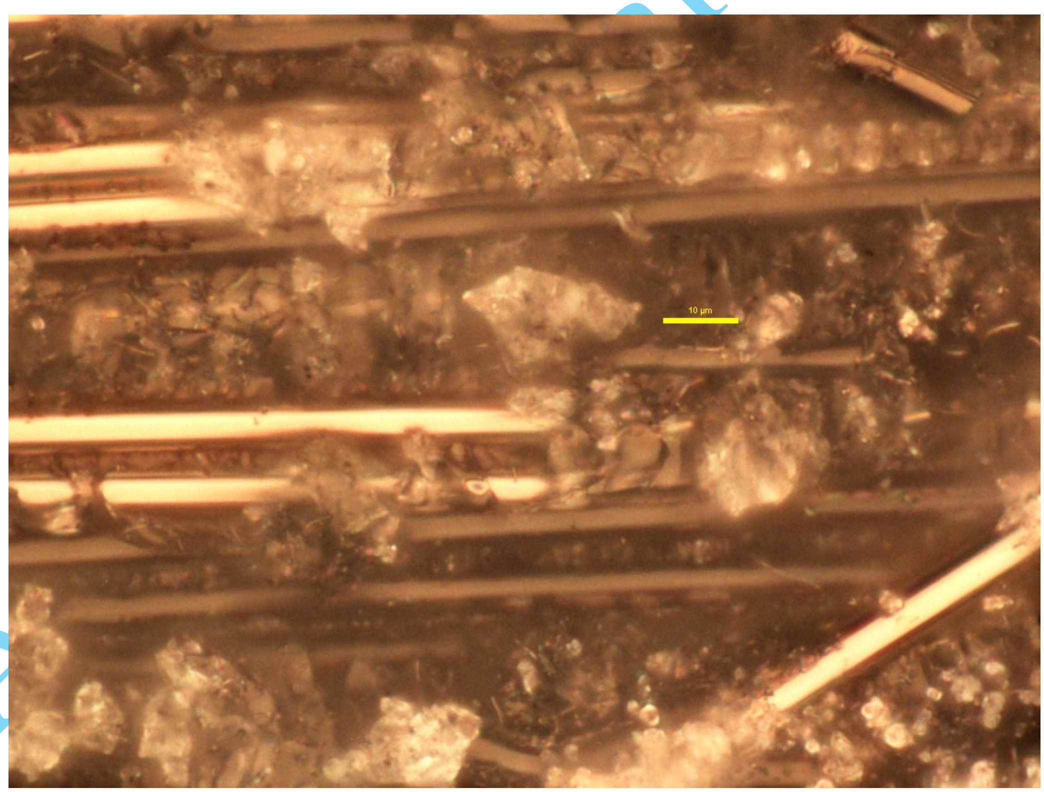

Figure 7. Microscopy picture (1000x) of shear fracture surface of 1wt% CNF ZT-CFRP shows a very rough fracture surface and many CNFs extending in the z-direciton.

Figure 8. Microscopy picture (1000x) of shear fracture surfaces of 1wt% CNF/1wt% CNT ZT-CFRP showed smooth fracture surface and few z-extending CNFs presented on the fracture site.

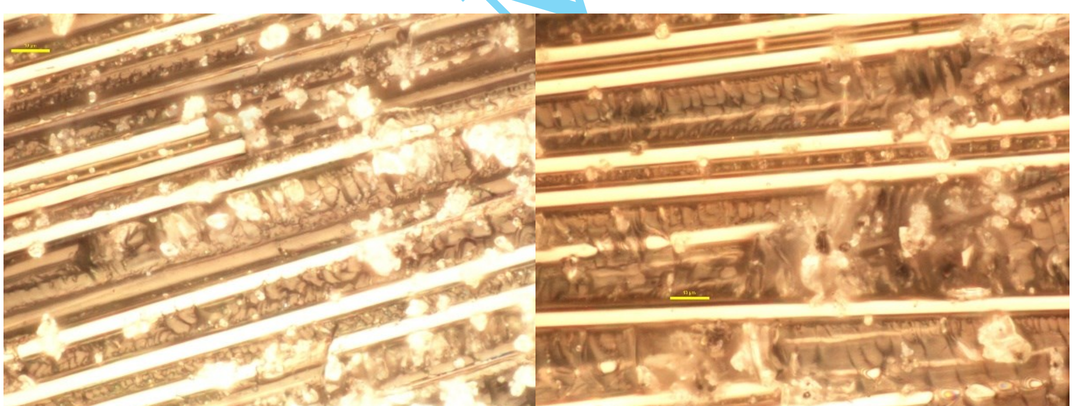

Figure 9. Microscopy pictures (1000x) of control CFRP (left) and 1wt% CNT ZT-CFRP (right). Both control CFRP and 1wt% CNT ZT-CFRP show smooth fracture surfaces.

After the curing was completed, the composite's edges were trimmed. The samples were cut from the panels with the long end running parallel to the unidirectional fibers of dimensions. The test samples were sanded to dimensions 125mm X 13mm x 3mm with 120, 320, and 400 grit sandpaper before being polished with wet 800 and 1500 grit sandpaper. After sanding, the test samples were cleaned with a soap water wash and dried in the oven for 5 mins at 90°C. The samples were taken out then left to cool for 5 mins before being cleaned with acetone and then left to dry. The specimens were then ready for the UL-94 test.

3. FAMMABILITY TEST RESULTS

The UL-94 results are summarized in Table 4. Without any flame retardant additive in the common epoxy resin used in this study, as expected, all of the test samples failed the UL-94 test due to lengthy periods of flame combustion. However, the results met the study focus and showed very clear differences among the four types of CFRP laminate materials and revealed quite intriguing insights of how the ZT-CFRP can help fighting against the flammability issue.

Table 4. UL-94 Test Results Summary

Sample	t1 (s)	t2 (s)	t3 (s)	Burn to Clamp (upward flame spreading)	Cotton Ignition (dripping flame spreading)	Sum (s) (t1+t2+t3)	Average (s) t_{avg}	Normalized Average Flame Self-Extinguishing Time based on the Control Samples' average time (%)	Burn to Clamp Chance (%)
Control									
1	39.5	0	0	N	N	39.5	86.8	100.0% (Baseline)	60% (Baseline)
2	26.5	89.8	0	Y	N	116.3			
3	0	144.3	0	Y	N	144.3			
4	0	5.5	0	N	N	5.5			
5	5.4	123.2	0	Y	N	128.6			
1wt% CNF									
1	17.2	0	0	N	N	17.2	34.9	40.2%	0%
2	0	0	0	N	N	0			
3	0	35.8	0	N	N	35.8			
4	37.2	54.7	0	N	N	91.6			
5	0	29.7	0	N	N	29.7			
1wt% CNT									
1	230.6	0	0	Y	N	230.6	184.7	212.8%	80%
2	72.2	74.3	0	N	N	146.4			
3	26.2	172.4	0	Y	N	198.7			
4	96.7	0	0	Y	N	96.7			
5	251	0	0	Y	N	251			
1wt% CNF / 1wt% CNT									
1	191.7	0	0	Y	N	191.7	142.1	163.7%	80%
2	28.8	78.3	0	N	N	107.1			
3	40.2	70	0	Y	N	110.3			
4	175.4	0	0	Y	N	175.4			
5	37.8	88.5	0	Y	N	126.3			

As a benchmark, the control sample containing no additives show average afterflame time of 86.8s and 60% of chance (i.e., 3 out of 5) of burn to the clamp (see Table 4). Timelapse pictures of afterflame t1 and t2 of representative tests are shown in Figures 10-13. Tests with the 3rd longest average afterflame time shown in Table 4 are chosen as the representative specimens to demonstrate their differences in combustion behavior. Note that all the pictures are taken after the removal of the Bunsen burner flame to show the material's ability for flame propagation, burner flame in some of the pictures are no longer in contact with the specimens.

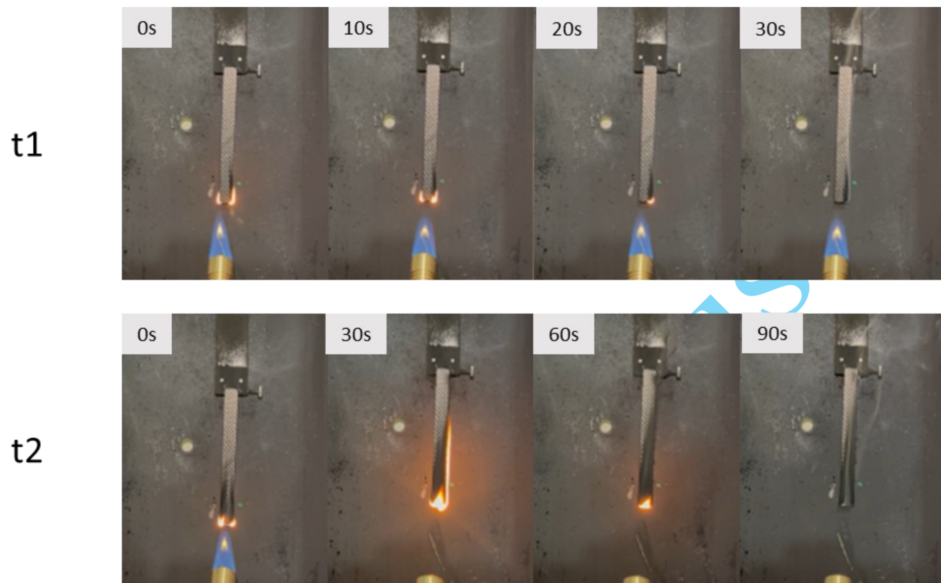

Figure 10. Afterflame of Control CFRP sample #2.

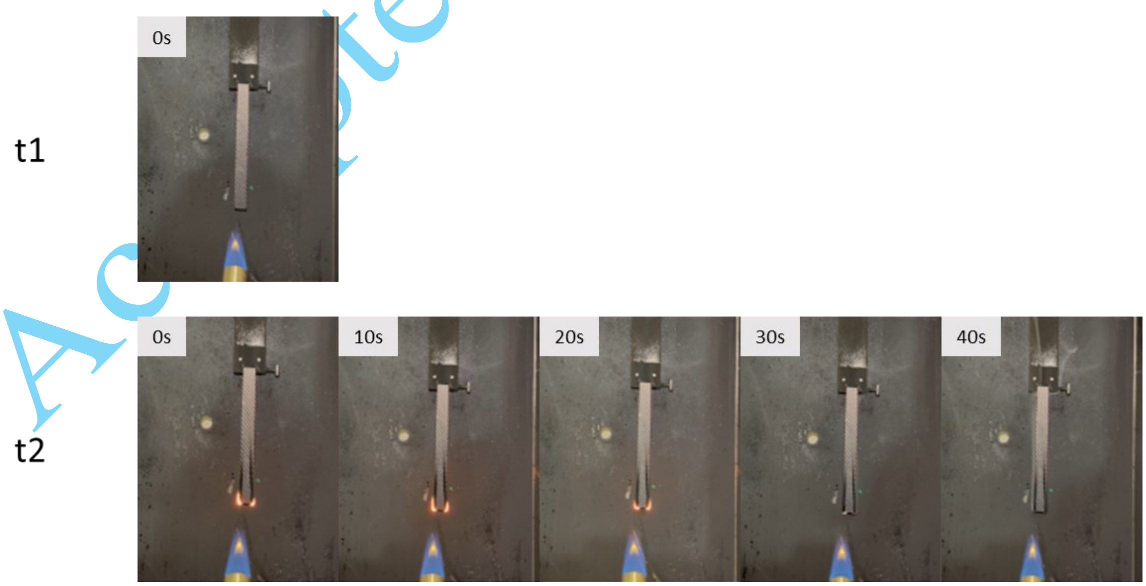

Figure 11. Afterflame of 1wt% CNF ZT-CFRP sample #5

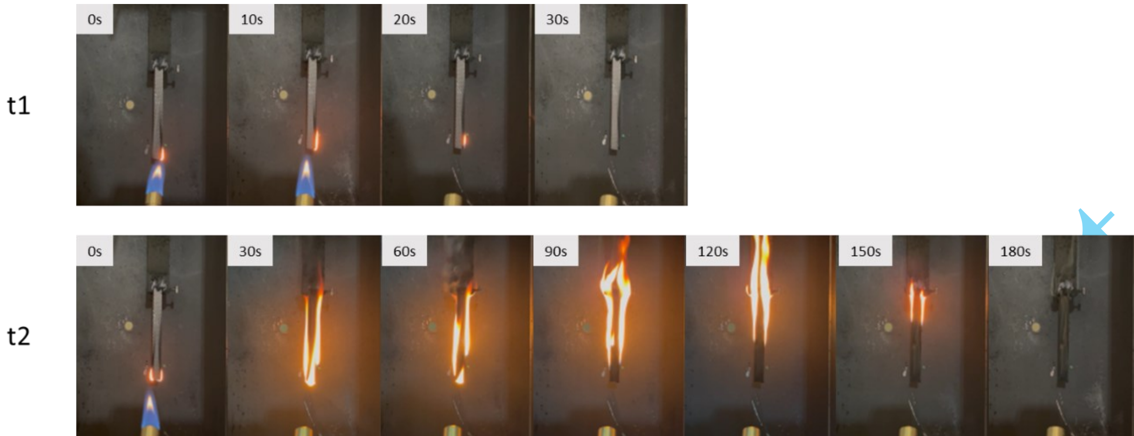

Figure 12. Afterflame of 1wt% CNT ZT-CFRP sample #3

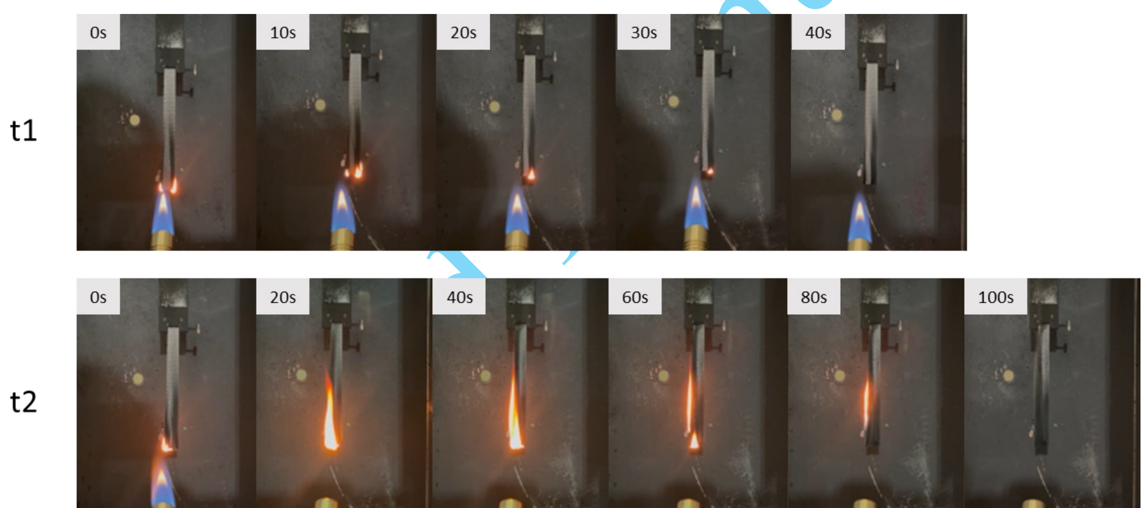

Figure 13. Afterflame of 1wt% CNF/ 1wt% CNT ZT-CFRP

Samples of 1wt% CNF ZT-CFRP showed the best results with shortest afterflame burning time. Their average afterflame duration of 34.9s is much shorter than the control's 86.8s. The 1wt% CNF ZT-CFRP samples only took 40% of the time to self-extinguish the flame compared with the control CFRP samples. The test specimen #2 even showed 0s afterflame after both the first and the second ignitions. It is also worth noticing that none of the 1wt% CNF ZT-CFRP samples experienced any afterflame burned to the clamp (i.e., spreading flame upward to the clamp), which was significantly different than the control samples' 60% chance of burn to clamp. The significantly better results indicates the addition of the CNF Z-threading structure could effectively contribute to the control of flame propagation even without any flame retardant additives/chemicals. This significant improvement in flame resistance could be caused by the by the mechanically interlocked 3D nanofibers/microfiber networks caused by the long-range CNFs threading strategy inside the CFRP. The known morphology (as shown in Figure 1 and Figure 2) of CNFs z-threading through and mechanically interlocked the packed carbon fibers network could strengthened and secured the char formation, and it could also further impede the release of combustible small molecules vapor from polymer decomposition inside the composite under elevated temperature. In addition, the high thermal conductivity of CNF ZT-CFRP (according [6], it was about 753% of regular CFRP's thermal conductivity) could also contribute to more rapid heat dissipations. The synergic effects of the 1wt% CNF ZT-CFRP could potentially contribute to the unique nano/microstructure-induced flame resistant behavior against and to confine the localized ignitions that could occur in many applications.

In contrast, both types of samples containing CNTs (i.e., 1wt% CNT ZT-CFRP and 1wt% CNF/1wt% CNT ZT-CFRP laminate samples), even with the identical ZT-CFRP prepreg process as the 1wt% CNF ZT-CFRP, showed much longer duration of afterflame (about 212.8% and 163.7% for the 1wt% CNT samples and 1wt%CNF/1wt%CNT samples, respectively) and higher risk of burn to clamp (80% for both compared with the control samples' 60% and 1wt% CNF samples' 0%). The results comparison indicated that adding the CNTs could have a reverse effect on flammability. The reason behind this phenomenon is not yet fully understood, further investigations including SEM on the posttest char structures will help to better understand the effect of CNT and CNF on the flame propagation process.

4. CONCLUSIONS

The flammability is a known significant shortfall of the light-weight and high strength CFRP composites. The CFRP flammability affected by many factors such as resin chemistry, thermodynamics of resin vapor, heat transfer, and the porous structure of CFRP laminate. In this paper, the focus was placed on exploring the potential improvement of utilizing the novel long range CNF z-threading strategy to create a mechanically interlocked 3D nanofiber/microfiber network that can help the self-extinguishing the flame and stop spreading flame during the UL-94 flammability tests. To keep the study scope well-focused, no other flame retardant chemical additives were used in all samples. Compared with the control CFRP consisting of unidirectional AS-4 carbon fibers and epon-862/curing agent-W epoxy matrix, the 1wt% CNF ZT-CFRP clearly achieved a better UL-94 performance as evidenced by the shorter self-extinguish time (40% vs 100% of the control samples' time) and the minimum chance of burn to the clamp (i.e., spreading flame upward) (0% vs 60% of the control samples' burn to the clamp chance). No case experienced dripping to ignite the bottom cotton pad scenario. One of the five CNF ZT-CFRP samples even showed 0s afterflame (i.e., immediate self-extinguishing) after both the first and the second ignitions, which indicated the promising potential of this new type of flame-resistant material and the intriguing approach. It is possible the unique nano/microstructure of the 1wt% ZT-CFRP strengthened and secured the char formation. In addition, the 3D integrity of the nanofiber/microfiber interlocked network could also further impede the release of combustible small molecules vapor from polymer decomposition. Furthermore, the high thermal conductivity of CNF ZT-CFRP (according [6], was about 753% of regular CFRP's thermal conductivity) could also contribute to more rapid heat dissipations and self-extinguish the flame. These synergic effects of the 1wt% CNF ZT-CFRP could potentially contribute to the unique ZT-CFRP composite's nano/microstructure-induced flame resistant behavior against and to confine the localized ignitions that could occur in many applications. However, the samples with much shorter but much finer and more conductive CNTs, even with the same ZT-CFRP prepreg process, despite of adding CNFs or not, performed much more susceptible to the flame and less capable of self-extinguishing during the UL-94 flammability tests. The reason behind this phenomenon is not yet fully understood, further investigation will be conducted in the future to help exploit the full potential of the nano-/micro-structure induced flame resistant CFRP. It is worth of noting that one of 1wt% CNF ZT-CFRP samples showed immediate self-extinguishing (i.e., 0 s afterflame) after both the first and the second ignitions. This indicate the potential through appreciate materials design and manufacturing quality control based on understanding the phenomenon, such immediate self-extinguishing could be achieved for CFRP laminates with regular epoxy resin matrix without fire retardant chemicals.

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