

EFFECTS OF MULTIWALL CARBON NANOTUBES ON THE MECHANICAL  
PROPERTIES OF CARBON-REINFORCED CYANATE ESTER COMPOSITES

by

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## ABSTRACT

Current applications within areas such as electronics, military, and aerospace are demanding for lightweight and high-performing composite systems. More specifically, thermosetting formulations with minimal hazardous emissions that are used for high-temperature applications are in high demand. Cyanate ester resin (CE) has a high glass transition temperature ( $T_g$ , as high as 350°C), excellent flammability, thermal stability, mechanical properties, and it does not release harmful volatiles during the cure process. Multiwall carbon nanotubes (MWCNT) can offer excellent electrical and thermal conductivity, structural strength and stiffness, and thermal stability. The enhancement of the resin's properties is highly dependent on the qualitative and quantitative dispersion of MWCNT. In this research, CE was blended with MWCNT (0.5%, 1%, and 1.5% by weight) using a combination of a Planetary Centrifugal Mixer (THINKY™) and a Stand Mixer. In order to improve dispersion, MWCNTs were processed with ceramic beads using the THINKY™ mixer to break-up the entangled nanoparticles. Transmission electron microscopy (TEM) was performed to evaluate separation of MWCNT entanglements. Carbon fiber-reinforced nanomodified cyanate ester composite panels were manufactured using a wet layup process followed by compression molding. Mechanical tests were then performed to evaluate tensile strength and modulus, flexural strength and modulus, compressive strength and modulus, and short-beam shear strength. Thermogravimetric analysis (TGA) was used to study the four different formulations thermal stability in both air and nitrogen. Lastly, the flammability properties were also

analyzed with micro combustion calorimetry (MCC). Results were compared with control samples showing a positive effect of MWCNT on the final properties of carbon-reinforced cyanate ester composites.

## 1. INTRODUCTION

Cyanate ester nanocomposites are gathering attention from both the aerospace and aircraft industries due to its excellent multifunctional properties. Nevertheless, reinforced cyanate ester nanocomposites have not been extensively studied. Researches have proved that the mechanical, thermal, and electrical properties of cyanate ester resins can be improved significantly by the addition of various nanoparticles [1-27]. By improving thermal properties without deteriorating mechanical properties and  $T_g$ , CE nanocomposites could be considered as a replacement to polyimide composites in high-temperature applications such as thermal protection and heat shield.

Carbon fiber-reinforced cyanate ester nanocomposite panels were manufactured using prepregs (developed using hand layup process) and compression molding. Mechanical (tension, flexure, compression, and interlaminar shear), flammability (microscale combustion calorimeter (MCC)), and thermal stability (thermogravimetric analysis (TGA)) properties were analyzed to complete the material characterization.

### 1.1 Background

#### 1.1.1. *Cyanate Ester Resin*

Cyanate esters (CE) are a high-temperature resin family traditionally associated with space applications, because of very low dielectric properties and extremely low moisture uptake when compared to other resin systems, particularly polyimide [28]. CE has high glass transition temperature ( $T_g$ , as high as 350°C), excellent flammability properties, and doesn't release harmful volatile (m-PDA, MDA, etc.) during its curing process [1, 27]. Therefore, CE could be considering as a exceptional candidate to replace

polyimide within high-temperature applications. CE has been used in the industry for decades, but not much research has been conducted on nanomodification of the resin. Lonza Corporation offers high performance thermoset cyanate ester characterized by high  $T_g$  (up to 350°C) which also holds excellent dielectric and mechanical properties and an epoxy-like processing, for applications such as electronics and aerospace. Lonza Corporation's Primaset® PT-15 cyanate ester is selected for this study, since it is multifunctional, and has low viscosity in its molten state at elevated temperatures, which is desired to assist with obtaining a good nanoparticle dispersion in the polymer resin during the processing of nanocomposites. This resin matrix is an off-white waxy solid that possesses a 65% char yield, less than 0.5% volatiles, no decomposition by-products during curing, and yields an amber cured solid [5].

### ***1.1.2. Multiwall Carbon Nanotubes***

In early studies, cyanate ester resin has been nanomodified with nanoclay [3-12], polyhedral oligomeric silsesquioxane (POSS) [13-20], carbon nanotubes (CNT) [21-23], nanosilica [24], zirconium [25], silicon [26], and nanoalumina. Most of these studies showed improvements in particular mechanical, electrical or thermal properties, but a detrimental effect for  $T_g$  was observed. Carbon nanoparticles are inexpensive and are capable of offering excellent electrical and thermal conductivity, structural strength and stiffness, and thermal stability. That is why multiwall carbon nanotubes (MWCNT) are known for their excellent multifunctional properties [34]. A nanotube/polymer composite with unique combination of excellent mechanical, electrical, and thermal properties could be obtained if a suitable dispersion is achieved.

### ***1.1.3. Carbon Fiber***

It is well known that high specific modulus and high specific strength are the most required characteristics of the materials within aerospace and defense structural applications. Fibers that are in textile form exhibit good out-of-plane, fatigue, and impact resistant properties. Additionally, textile fabrics have better dimensional stability and conformability. The variety of textile fabric architectures includes weaves, knits, and braids. The composites that are being developed under this research are considered for structural applications.

PAN-based carbon fibers have superior mechanical properties when compared to rayon-based and pitch-based. It is readily available in large quantities on the market at affordable prices. Specifically, the fabric selected for this research is plain-woven T300-3k carbon fabric (carbon fiber produced by Toray and woven by BGF).

### ***1.1.4. Carbon Fiber-Reinforced Cyanate Ester Nanocomposites***

Due to a long series of military and aerospace research projects, an array of thermoset resins has been developed to handle moderate-to-high temperatures as well as tough conditions. Polyimide, PMR-15 (polymerization of monomer reactant), developed at NASA, is the most common of these thermosetting formulations as a result of its good thermal and mechanical properties. However, PMR-15 and similar variants contain the hazardous compound methylenedianiline (MDA), creating potential health and safety issues related with cancer. NASA encouraged researchers to develop new versions using less-toxic monomers, therefore several have emerged. In bonding applications, cyanate esters (CE) are compatible with the majority of other resin systems and can be formulated for manufacturing methods, such as prepreg, resin transfer molding (RTM), filament

winding, towpreg, syntactic core and adhesive forms [28]. Carbon fiber has been used for many years in the aerospace and aircraft industry due to its high specific modulus, high specific strength, and good resistance to both impact and fatigue. Carbon fiber reinforced cyanate ester nanocomposites systems have great potential to be used in electronics, aerospace, aircraft, automotive, and military applications.

## **1.2. Specific Objective of the Research**

During the last 30 years, the Occupational Safety and Health Administration (OSHA) has imposed strict regulations on the fabrication of PMR-15 composites, due to the fact that these formulations are made from methylenedianiline (MDA), a known carcinogen and a liver toxin. Since then, researchers have started to work on the development of new polyimide formulations with lower toxicity, but with similar processability, dimensional/thermal stability and mechanical properties. However, all of these concerns have led to the implementation of costly production measures that have increased the price of the product. Consequently, alternative resins in composites are gaining traction because they offer a broader palette of modifiable matrices from which to choose when called on to meet thermal challenges. Cyanate ester has very low dielectric properties, extremely low moisture uptake, and it doesn't release harmful volatiles during its manufacturing process. Also, CE has excellent long-term stability at elevated end-use temperatures, along with excellent flammability properties that make it suitable to be considered as an alternative to polyimide. In addition, CE's properties could be easily tailored by the addition of nanoparticles, since it has low viscosity and it is easy to process. This research investigates the effects of multiwall carbon nanotubes on the mechanical properties of carbon fiber-reinforced cyanate ester nanocomposites.

### ***1.2.1. Assumption, Limitation and Delimitation***

It is well known that the addition of MWCNT into a resin system will cause a dramatic increase to its viscosity. During this research, three loading rates of MWCNT were selected to divide the range (0–2wt%) in equal parts, assuming that a loading rate exceeding 2wt% will increase the viscosity of CE to a point where the simple processing of CE will be lost.

This research did not analyze the techniques to disperse MWCNT into CE, since Lao [37] has already studied dispersion. In fact, some techniques used in this research are based on the results obtained by him. Moreover, CE has a very low viscosity at high temperatures, but the viscosity will increase as the temperature decreases. In order to take advantage of easy processing of CE at elevated temperatures, panels of 305mm by 152 mm were manufactured. This will provide enough time to wet all layers of carbon fiber by hand before the temperatures decreased to the point that the processability of CE was lost, and the panels were big enough to cut the samples required by the ASTM for the different test.

Primaset PT-15 is suitable for several manufacturing processes, such as filament winding, resin transfer molding (RTM), and vacuum assisted RTM (VARTM). Wet hand layup followed by compression molding was used in this research to imitate a procedure that has been previously established at the Advanced Composites Lab at Texas State University, which produced excellent results. However, no closed mold was used in this experimentation, as a consequence, an even distribution of resin throughout all of the fibers cannot be guaranteed.

## **2. MANUFACTURING AND PERFORMANCE EVALUATION**

A statistical design of experiments (DOE) was implemented to properly plan the manufacturing process and performance evaluation, so that the data obtained can be analyzed to validate the research objectives. The manufacturing process of building a fiber-reinforced nanocomposite was divided into four different stages. In the first stage, aggregated dry nanoparticles were separated with zirconia grinding media through the use of planetary centrifugal mixing. A morphological analysis was performed to evaluate if the time of exposure to grinding has an effect on the final dispersion of nanoparticles in the resin. The batch with the best results was used to modify the resin in stage two. In this stage, a combination of mixing techniques was used to blend three different loadings by weight of nanoparticles with the resin. In the third stage, three formulations of nanomodified CE and one formulation of neat CE were used to manufacture carbon-reinforced panels, using wet lay-up and compression molding. Coupons for thermal and mechanical tests were then manufactured. In the fourth and final stage, the thermal and mechanical properties from these four formulations were compared after the completion of characterization test. One-way analysis of variance (ANOVA) was performed to study the effects of independent variables on the final properties of carbon-reinforced CE nanocomposites.

The figure below shows a summary of the manufacturing and performance evaluation of this project.

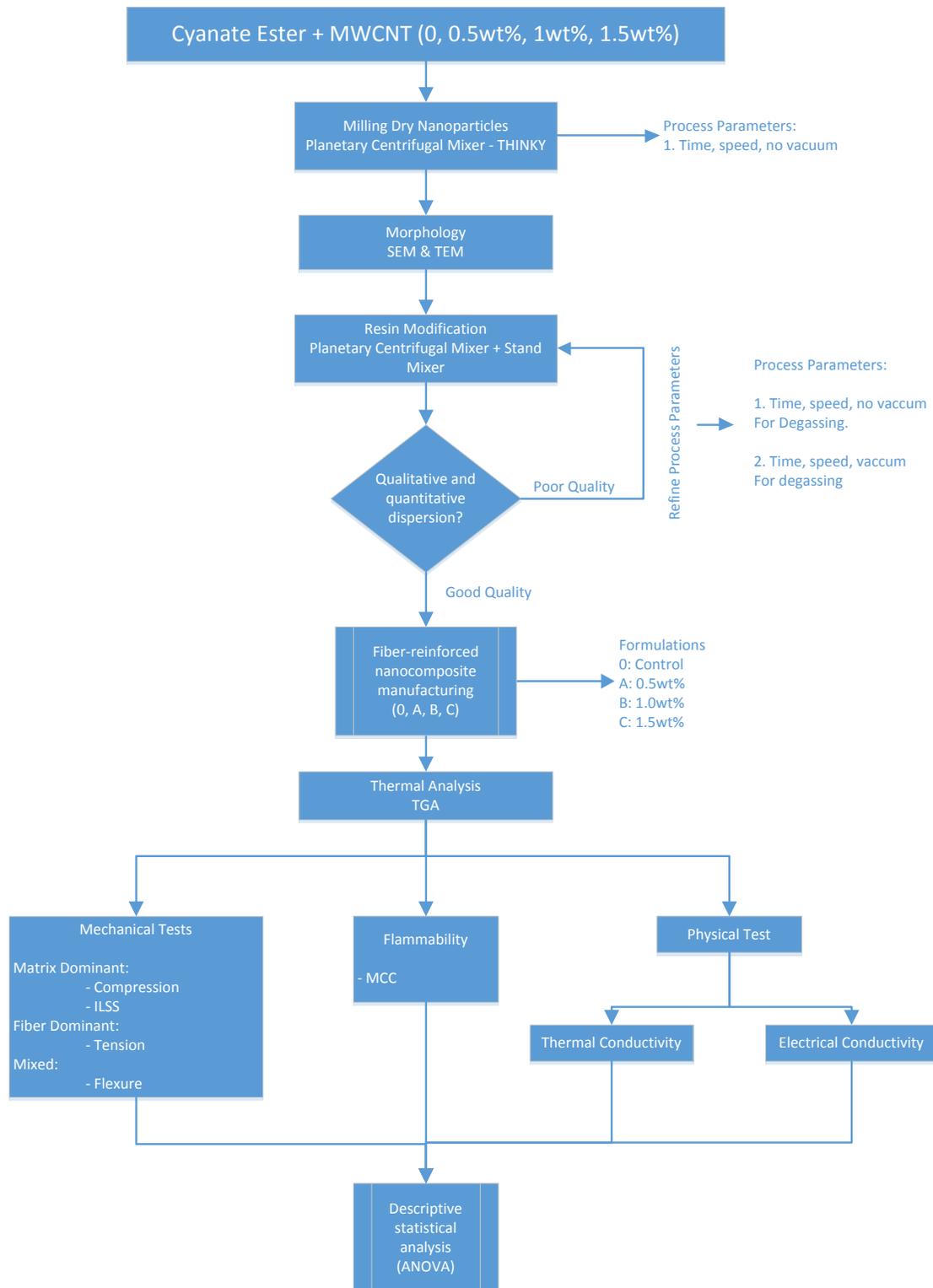


Figure 1 Manufacturing process and performance evaluation

The material system, manufacturing process, and performance evaluation are better described below.

## **2.1. Material System**

### ***2.1.1. Cyanate Ester***

Lonza Corporation, a well-known company in the composites industry, offers high performance thermoset cyanate ester characterized by high  $T_g$  (up to 350°C), excellent dielectric and mechanical properties and an epoxy-like processing parameters, for applications, such as electronics, aerospace, among others. Lonza Corporation's Primaset® PT-15 cyanate ester was selected for this study since it is multifunctional, and has low viscosity in its molten state, which is desirable to obtain a good dispersion of MWCNT in the liquid polymer resin. This resin matrix is an off-white waxy solid, has a 65% char yield, less than 0.5% volatiles, no decomposition by-products during curing, and yields an amber cured solid [33].

### ***2.1.2. Multiwall Carbon Nanotubes***

Arkema offers MWCNT for composite that are synthesized by catalytic chemical vapor deposition (CVD) processing. It has approximately 90 wt% purity without any purification. Graphistrength™ C100 are high-quality MWCNT that hold outstanding mechanical properties, as well as good electrical and thermal conductivity. This made them suitable for a variety of applications such as high-performance electrostatic dissipative plastic parts and coatings, high-strength thermosetting composites, high-strength rubbery materials, electrode materials for batteries, super-capacitors, and fuel cells [34]. Table 1 summarizes the main characteristic of MWCNTs.

Table 1. Graphistrength C100 characteristics

MWCNT Characteristics	
Carbon content	> 90 wt%
Free Amorphous Carbon	No detectable (SEM/TEM)
Mean number of walls	5 – 15
Outer mean diameter	10 - 15 nm
Length	0.1 - 10 $\mu\text{m}$

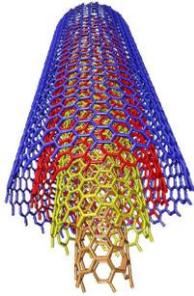


Figure 2. Multiwall carbon nanotube

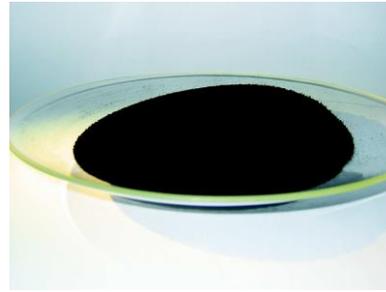


Figure 3. Powder appearance of MWCNT

### 2.1.3. Carbon Fabric

Standard carbon fibers typically exhibit a fiber modulus of 230 GPa or incrementally greater. These are the most cost-effective fibers as measured by tensile strength or modulus per unit cost. TORAYCA<sup>®</sup> carbon fibers are specifically designed to meet diverse and challenging applications, such as aerospace. Toray's T300 standard modulus carbon fibers are a recognized industry standard, having been in production for over 30 years. Toray's T300 properties are shown in the Table 2 [35].

Table 2. T300 fiber and composite properties

<b>FIBER PROPERTIES</b>	
Tensile Strength	3,530 MPa
Tensile Modulus	230 GPa
<b>COMPOSITE PROPERTIES*</b>	
Tensile Strength	1,860 MPa
Tensile Modulus	135 GPa
Flexural Strength	1,810 MPa
Flexural Modulus	125 GPa
ILSS	10 kgf/mm <sup>2</sup>
* Toray 250 F Epoxy Resin. Normalized to 60% fiber volume.	

#### 2.1.4. Planetary Centrifugal Mixer

The Advanced Composites Lab's Planetary Centrifugal Vacuum Mixer

"THINKY MIXER" ARV-310 has the capability to mix, disperse, and degas materials in seconds to minutes. It can process materials with very low to very high viscosity (up to 100 million centipoises). The material container rotates at a 45° angle whilst it revolves in a set radius, which produces the "planetary" mixing action by the combination of rotation and revolution. The intensive circulation of the material within the vessel (under 400G of force) results in a quick and thorough mixture along with air being vacuumed out of the container. The maximum centrifugal power of the ARV-310 is 400G, which is produced from 2,000 rpm and the 9cm in diameter arc of the containers rotation. The revolution speed is adjustable in a range of 200-2000 rpm and the ratio of the revolution speed to the rotation speed of the cup holder is fixed at a 2:1 ratio. The ARV-310 holds up to 310g of material and the maximum material mixing volume is 250ml in the vacuum state and 300ml in the air state.

#### 2.1.4.1. Grinding Media

The THINKY technical personnel recommended that the use of grinding material for this kind of application is necessary. Different sizes of grinding material can be used according to the need. Smaller sizes of grinding media can pulverize the material. Ceramic balls of 3mm of diameter were selected to disentangle and break down clusters of MWCNT. This significantly helped in avoiding agglomeration of MWCNT within the resin and resulted in both quantitative and qualitative dispersion.



Figure 4. THINKY ARV-310 Mixer

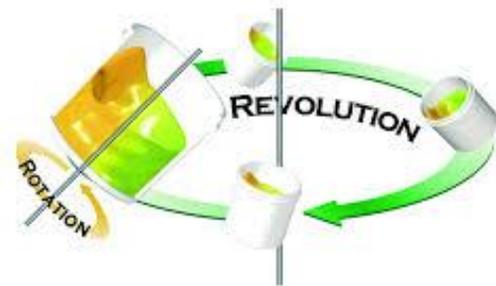


Figure 5. Planetary centrifugal mixing cycle

#### 2.1.5. Stand Mixer

Breville Scraper Mixer Pro BEM800XL Stand Mixer is a low speed mechanical mixer capable of generating enough shear force to de-bundle the nanotubes, having a small gap between the mixing blade and the container ( $<0.1\text{mm}$ ).



Figure 6. Breville Scraper Mixer Pro BEM800XL Stand Mixer

## 2.2. Milling of Dry Nanoparticles

Yuan et al. blended PA11 and MWCNT using a powder-to-powder blending method to enhance the dispersion of nanoparticles. Results showed that improved dispersion was obtained and both thermal and electrical conductivity were significantly improved [36].

MWCNT were milled using centrifugal planetary mixer with ceramic balls to eliminate the entanglement between nanoparticles.

Three different batches of MWCNT were milled with 5wt% of grinding media for 15, 30, and 45 minutes. Cycles of three minutes milling, and three minutes of cooling down were used until the desired total mixing time is achieved. Table 3 summarizes the parameters used within this process. Morphology analysis was performed to analyze which batch provided entanglement free MWCNT.

*Table 3. Cycle for milling dry MWCNT*

<b>Process</b>	<b>Parameters</b>	<b>Total Mixing Time</b>
Mixing	3 minutes 2000 rpm No Vacuum	Batch A - 15 min Batch B - 30 min Batch C - 45 min
Cooling Down	3 minutes	

## 2.3. Thermal Curing Study

Lao et al. developed two different curing cycles (adding catalyst or coupling agent) for CE resin to avoid phase separation [37-42]. Zirconate coupling agent Ken-React ® KZ-TPP was used in this research to follow the curing cycle developed by Lao. We chose to use the coupling agent rather than the catalyst, because the total curing time is shorter, it makes the mixture more stable, and the impact on the glass transition

temperature and mechanical properties is less aggressive.

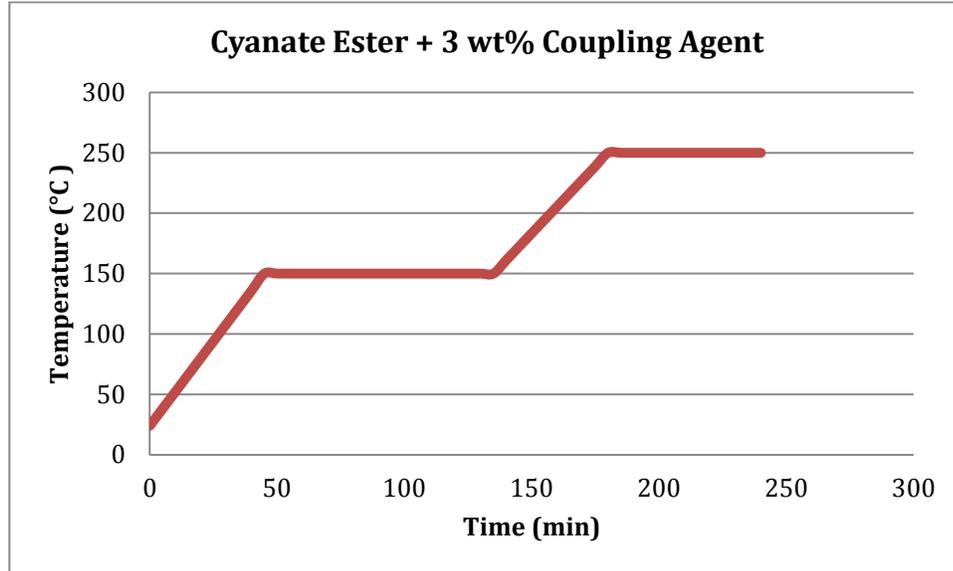


Figure 7. Curing cycle for cyanate ester + coupling agent

#### 2.4. Nanomodification of Cyanate Ester

CE resin was blended with MWCNT, in weight loading of 0.5%, 1%, and 1.5%, using a combination of planetary centrifugal mixer and stand mixer. First, the resin was heated from 24°C (room temperature) to 120°C, where the viscosity decreased to ~8cP. This temperature is ideal for the handling of the resin, because it reduces aggregates so the resin then becomes completely liquid. At this point, the CE and the coupling agent were mixed for 3 minutes at 2000 rpm. Afterwards, the mixture was taken to the nanoroom (a clean room designed and manufactured to handle dry nanoparticles) where the three different loadings of nanoparticles were then added. Lastly, the mixture was taken back to the planetary centrifugal mixer where it was subjected to a particular mixing cycle described in Table 4. Zirconia grinding media (3mm of diameter ceramics balls) was used to improve the quality of dispersion of MWCNT into the resin.

Table 4. Planetary centrifugal mixing cycle

Process	Parameters	Total Mixing Time
Mixing	3 minutes 2000 rpm No Vacuum	30 min
Cooling Down	3 minutes	

The cycle was repeated 10 times to complete a total mixing time of 30 minutes. The grinding media was then separated, and the mixture was carefully poured into the stand mixer. The stand mixer was set at the lowest speed for 1 hour. Every 15min during the mix, heat was applied for a short period of 2 minutes to raise the temperature of the mixture to help prevent the resin from partially curing to the walls of the mixer's bowl.

Figure 8 shows a resume of the process used to modify the resin.

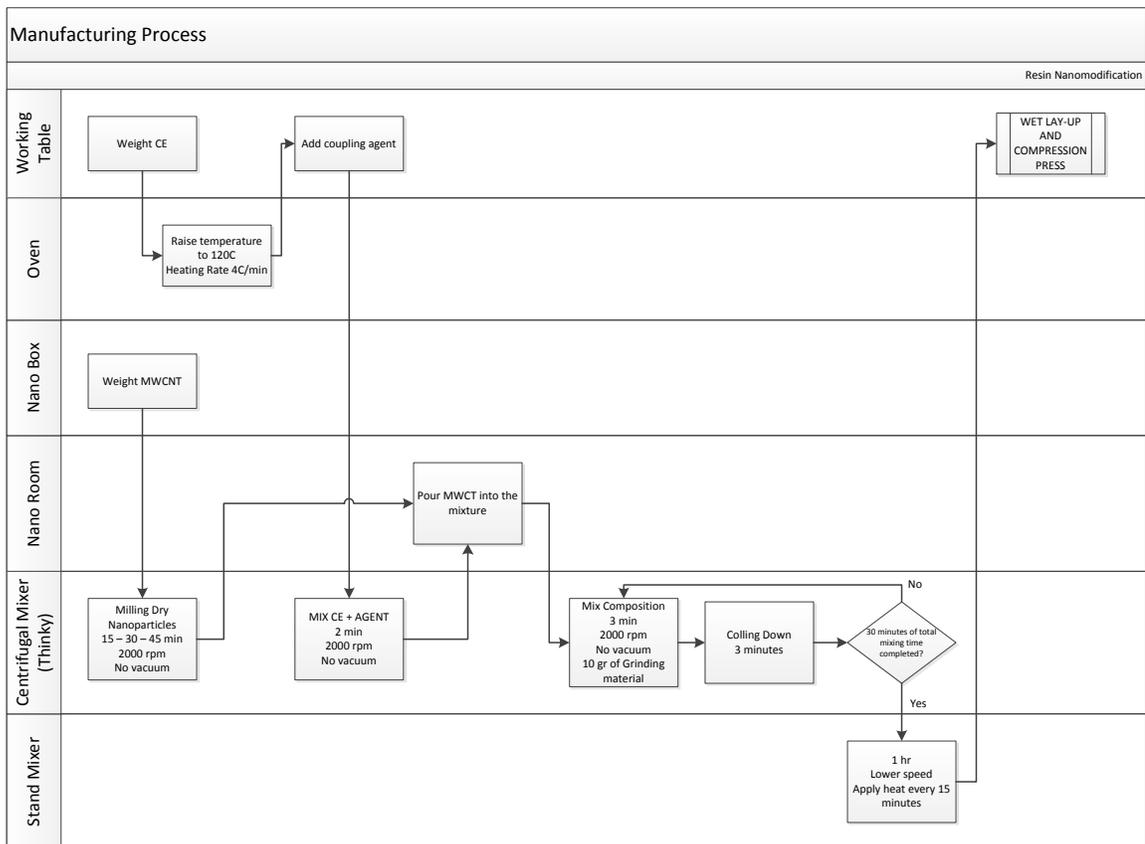


Figure 8. Process to modify CE resin

## 2.5. Manufacturing Process

The CE resin modification was completed as described above. The mixture was placed then into the oven (GRUENBERG OVEN COMPANY, B50C270), where the temperature was increased to 150°C with a heating rate of 3°C/min. Meanwhile, layers of Toray T300 carbon fabrics were cut according to table 5.

Table 5. Number of layers by panel

	Number of panels	Dimensions (mm)	Thickness (mm)	Number of layers
Mechanical tests	2	305 x 152	2	12
		178 X 152	2	12

The fibers were wet by hand using a painting brush along with a painting roller and sited one over another. After completely wetting the final layer, the panel was placed into the compression press (WABASH, G30H-18-CX) to complete the curing process.

Table 6 explains the parameters used in compression molding.

Table 6. Carbon-reinforced cyanate ester nanocomposite curing cycle for compression press

TIME (min)	TEMPERATURE (°C)	LOAD (kN)
15	150	0
15	150	45
15	150	89
15	150	134
15	150	178
15	150	223
Ramping-up temperature from 150 °C to 250 °C for 45 min		
60	250	267

## 2.6. Sample Preparation

Open mold wet lay-up followed by compression molding was used in this research, considering ease to work with CE resin at high temperatures. However, once outside of the oven the CE's viscosity starts increasing as consequence of the decrease of temperature, which tends to complicate the wetting process. The maximum dimensions for a panel were studied in the earliest stage of the research. The dimensions listed in table 5, were determined based on the size of the platens of the compression press, the number of layers needed to obtain the desired thickness, and the amount of time that CE could be easily used before its viscosity began to increase excessively. Three panels for each formulation (control, 0.5%, 1%, and 1.5%) were fabricated, therefore a total of twelve panels were produced.

Samples for tension testing, short-beam strength testing were cut from a panel with final dimensions of 305mm overall length, 152 mm in width, and 2 mm thick. Samples for both flexure and compression testing were cut from a second panel with dimension of 178 mm overall length, 152 mm wide, and 2 mm thick. Lastly, samples for MCC and TGA were cut from these panels. The dimensions of each specimen are shown in table 7.

Table 7. Specimen dimension for mechanical, thermal and flammability test

	<b>TEST</b>	<b>STANDARD</b>	<b>SPECIMEN DIMENSIONS</b>
<b>Thermal Analysis</b>	TGA		Mass: 8 - 10 mg
<b>Mechanical Test</b>	Compression	ASTM - D 6641	Length: 140 mm (5.5 in) Width: 12.7 mm (0.5 in) Thickness: 2 mm (0.08 in)
	ILSS	ASTM - D 2344	Thickness: 2 mm (0.08 in) Width: 4 mm (0.16 in) Length: 12 mm (0.47 in)
	Tension	ASTM - D 3039	Length: 250 mm (10 in) Width: 25 mm (1 in) Thickness: 2 mm (0.08 in)
	Flexure	ASTM - D 790	Thickness: 2 mm (0.08 in) Width: 12.7 mm (0.5 in) Length: 64 mm (2.5 in)
<b>Flammability</b>	MCC	ASTM - D 7309	Mass: 8 - 10 mg

## 2.7. Mechanical Characterization

The mechanical properties of the carbon fiber-reinforced CE nanocomposite were evaluated at the Advance Composites Lab at Texas State University using the Material Testing System 810 (MTS). This machinery has the capability of adapting to different fixtures to run tension, compression, flexure, and short beam strength tests, among others. Table 8 provides a very brief summary of the desired testing standards by identifying the testing fixtures and it also includes important parameters used for each mechanical testing procedure.

Table 8. Standards, fixtures and parameters for mechanical characterization

TEST	STANDARD	FIXTURE	PARAMETERS
Compression	ASTM - D 6641	WTF-WI-13	Loading Rate: 1.3 mm/min
ILSS	ASTM - D 2344	CU-SB-138	Loading Rate: 1 mm/min Loading Span: 8 mm
Tension	ASTM - D 3039	N/A	Loading Rate: 2 mm/min
Flexure	ASTM - D 790	CU-SB-138	Loading Rate: 0.9 mm/min Loading Span: 32 mm (1.26 in)

## 2.8. Thermal Stability

The thermal stability of the carbon fiber-reinforced CE nanocomposites was analyzed by Thermo gravimetric analysis-TGA (SHIMADZU, TGA-50). This equipment is capable of easily recognizing changes in the mass of a specimen in the order of several micrograms. Two samples for each formulation were heated to 900°C in air and nitrogen respectively.

## 2.9. Flammability Testing

Microscale combustion calorimetry (MCC) was used to study the flammability characteristics. The microscale combustion calorimeter MCC-2 from Govmark was developed by the Federal Aviation Administration (FAA) to improve the research on fire protection safety within aircraft grade materials. The equipment is capable of obtaining essential data from very small samples (0.5 to 50 mg). Three samples for each formulation were tested according to the standard ASTM D-7309 [43].

### 3. RESULTS AND DISCUSSIONS

Extensive thermal, flammability, and mechanical characterization were conducted. A significant number of samples were tested in each test to validate the results according to the standards used.

#### 3.1. Milling Dry MWCNT

According to TEM analysis, MWCNT that were milled for 45 minutes exhibited no entanglement. Figure 9 displays TEM images for various milling times (15 min, 30 min, and 45 min). As a result, MWCNTs that were milled for 45 minutes were chosen to manufacture the panels for mechanical, flammability, and thermal testing.

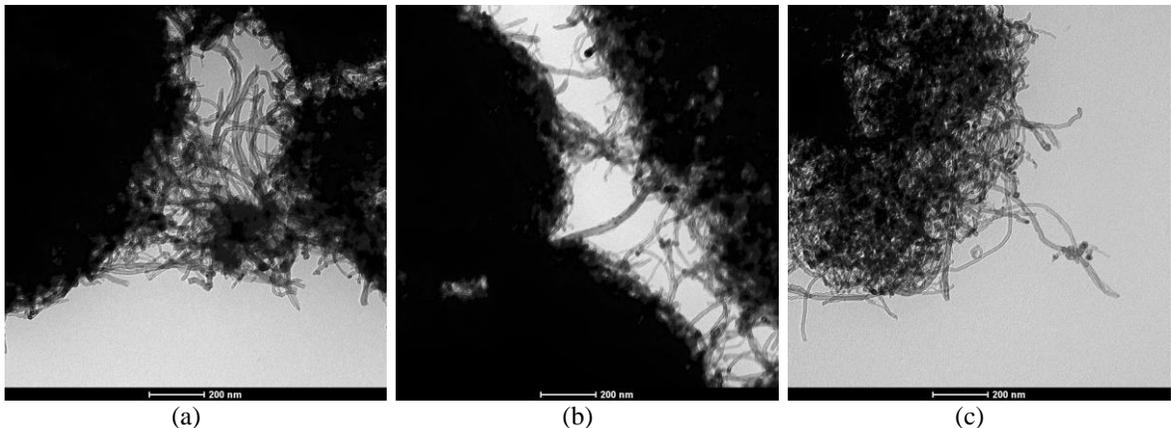


Figure 9. TEM images x200nm milling MWCNT for (a) 15 min, (b) 30 min, and (c) 45 min

#### 3.2. Qualitative Analysis of Fabricated Panels

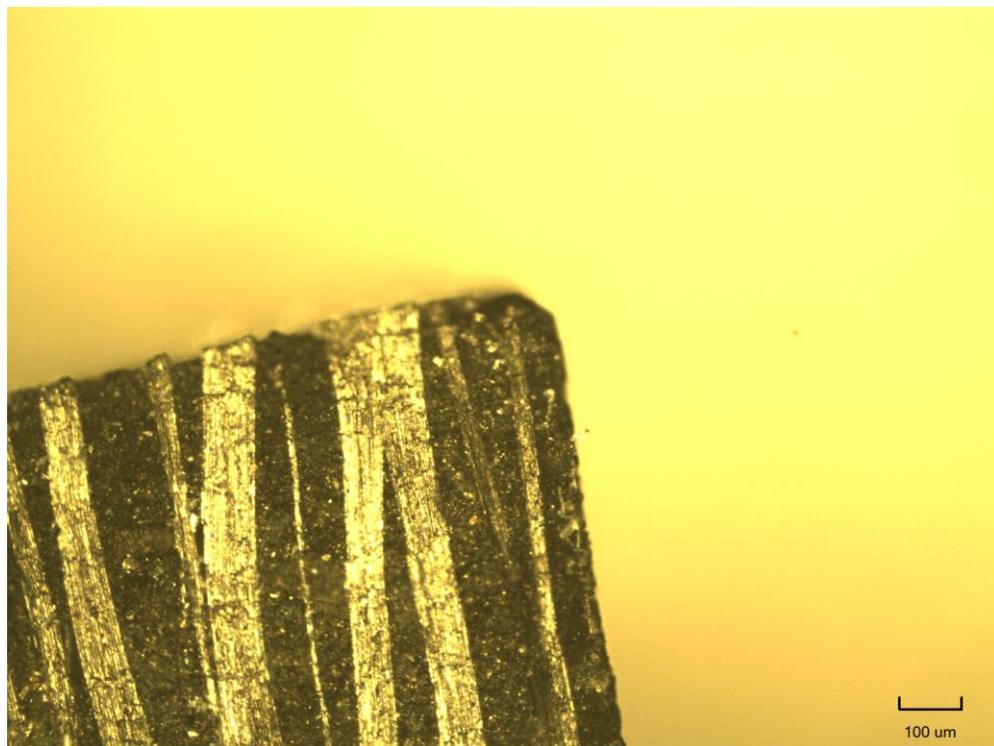
Fiber volume fraction, and optical characterization were performed to confirm the quality of the fabricated panels. The fiber volume fraction is a critical parameter in composites material, since the fiber is the main load-carrying component in this kind of materials. Thus, the overall fiber volume fraction will affect directly the behavior of the fabricated panel. The most widely used method to compute the fiber volume fraction of composites material, because its simplicity is the density method. This method based its

calculation on the density of the reinforcement (carbon fiber), the matrix (cyanate ester), and the density of the composite. Table 9 shows the fiber volume fraction for each manufactured panel. Similar results were found for all fabricated panels, which evidence that there was no variation during the manufacturing process. In general, it was found a fraction volume fiber of  $0.49 \pm 0.02$ .

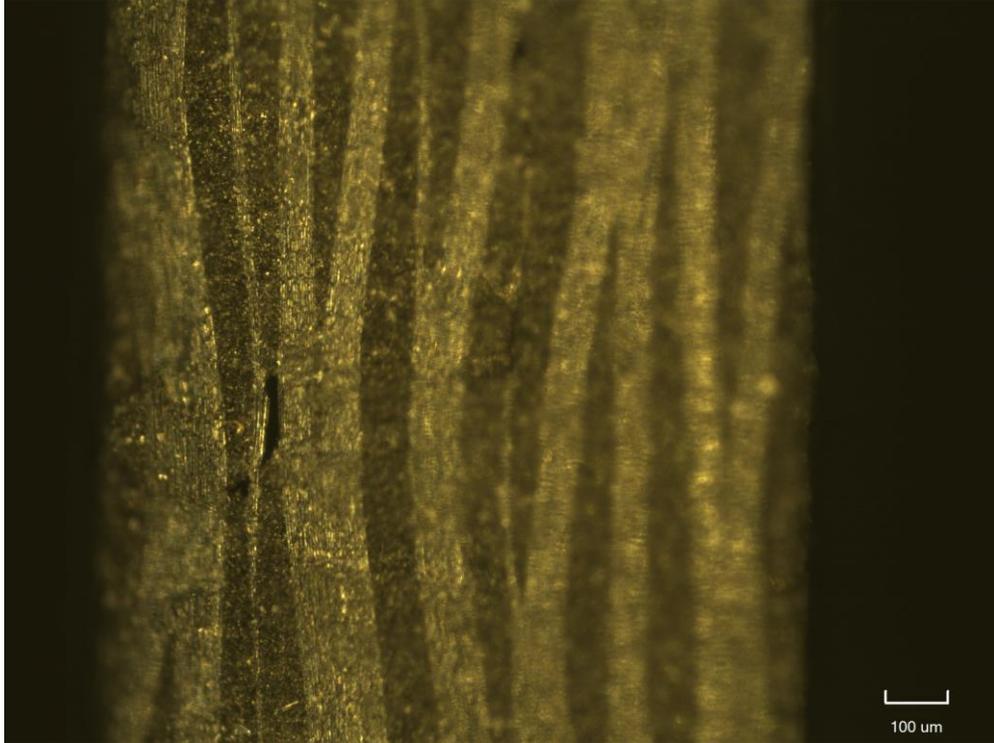
*Table 9. Fiber volume fraction*

<b>Formulation</b>	<b>Panels</b>	<b>Vf</b>	<b>Average</b>	<b>Standard Deviation</b>
Control	1	0.51	0.50	0.01
	2	0.48		
	3	0.51		
	4	0.50		
CE + 0.5% MWCNT	1	0.49	0.50	0.01
	2	0.50		
	3	0.51		
	4	0.50		
CE + 1.0% MWCNT	1	0.46	0.48	0.02
	2	0.48		
	3	0.46		
	4	0.51		
CE + 1.5% MWCNT	1	0.50	0.50	0.05
	2	0.51		
	3	0.44		
	4	0.55		

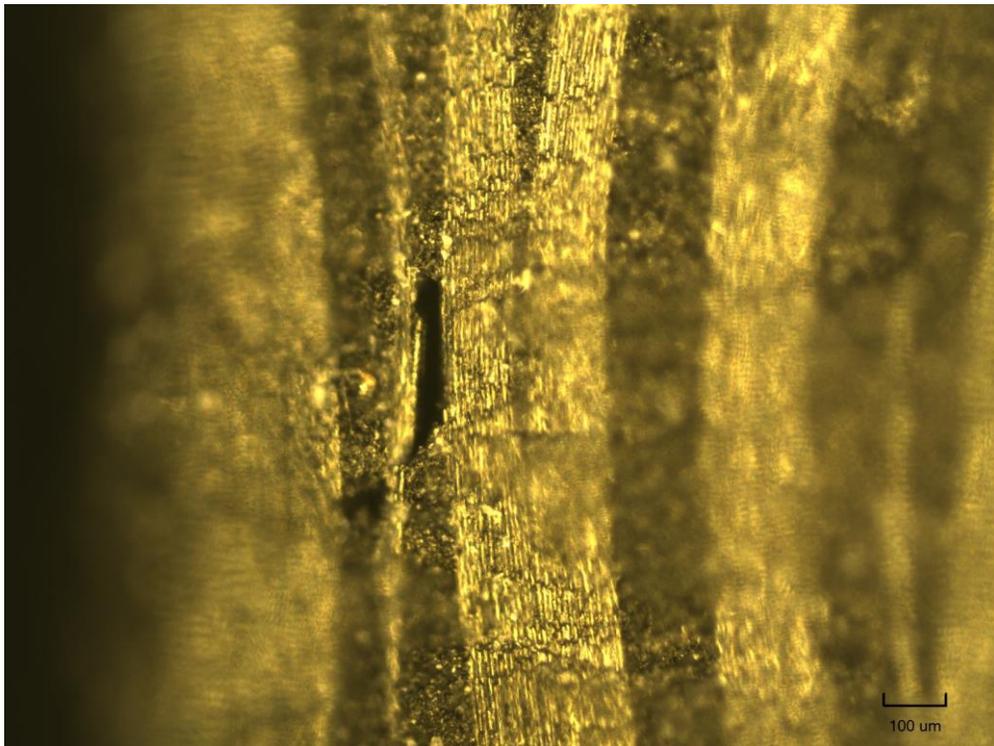
An optical characterization was executed using a measuring microscope (NIKON, MM-880). Figures 10 to 22 display that voids were observed between the fiber and resin in all the panels. Voids are the result of entrapped air into the final composite. However, no voids were observed in the resin, suggesting that these voids were formed during the wetting process. Although voids were found, these are not numerous, they are smaller than a micron, and it seems to be a constant in all panels. There is no evidence to discuss that a higher loading weight of MWCNTs promotes the formation of voids. As consequence, the formation of voids in these composites is attributed to the method used to wet the fibers during the manufacturing process. Voids can lead to delamination, high variation on the results, and a detrimental effect on the mechanical properties. Therefore, it must be evaluated if the final results are a consequence of the presence of voids in the composites.



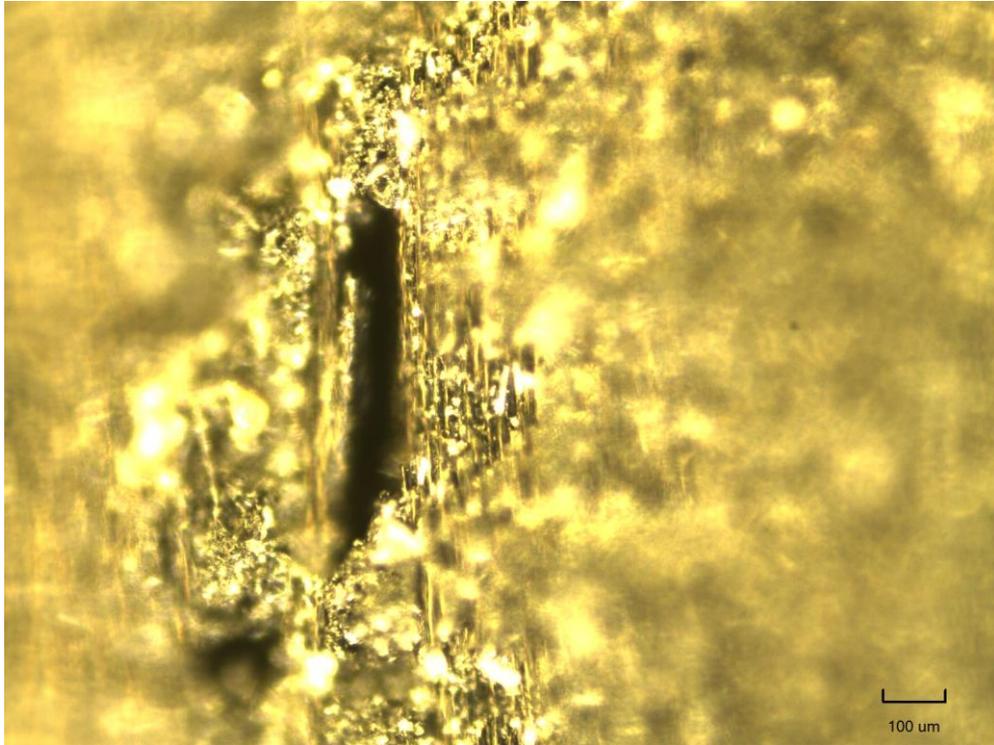
*Figure 10. Microscopic image of control sample presenting fiber and resin at a magnification of 100X*



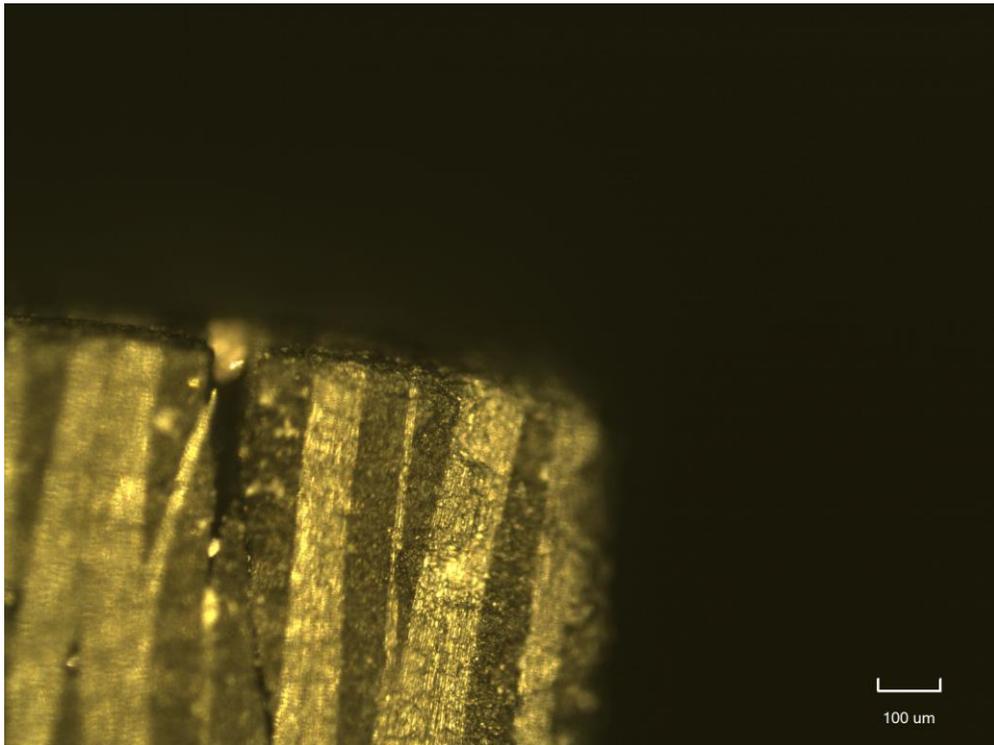
*Figure 11. Microscopic image of control sample presenting fiber and resin at a magnification of 50X*



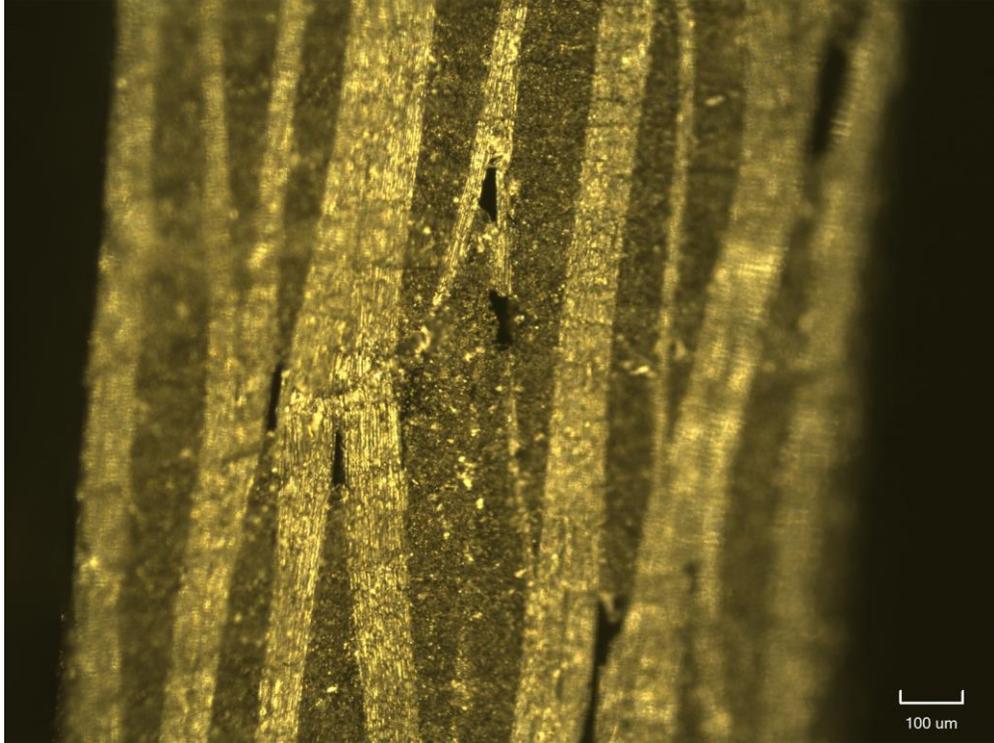
*Figure 12. Microscopic image of control sample presenting fiber and resin at a magnification of 100X*



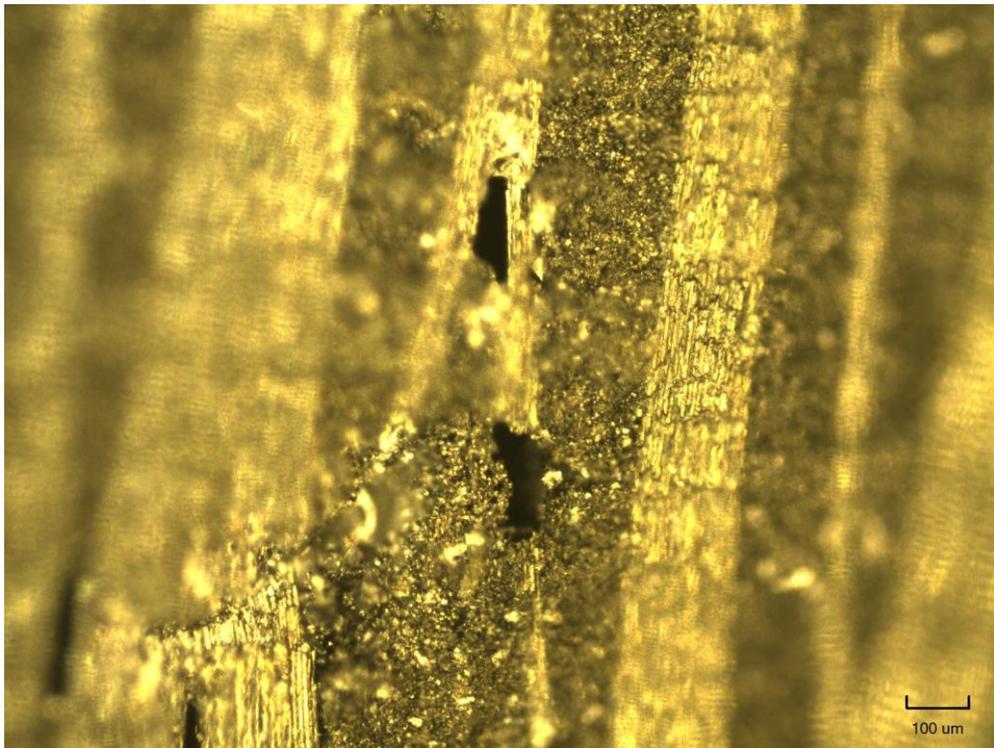
*Figure 13. Microscopic image of control sample presenting fiber and resin at a magnification of 200X*



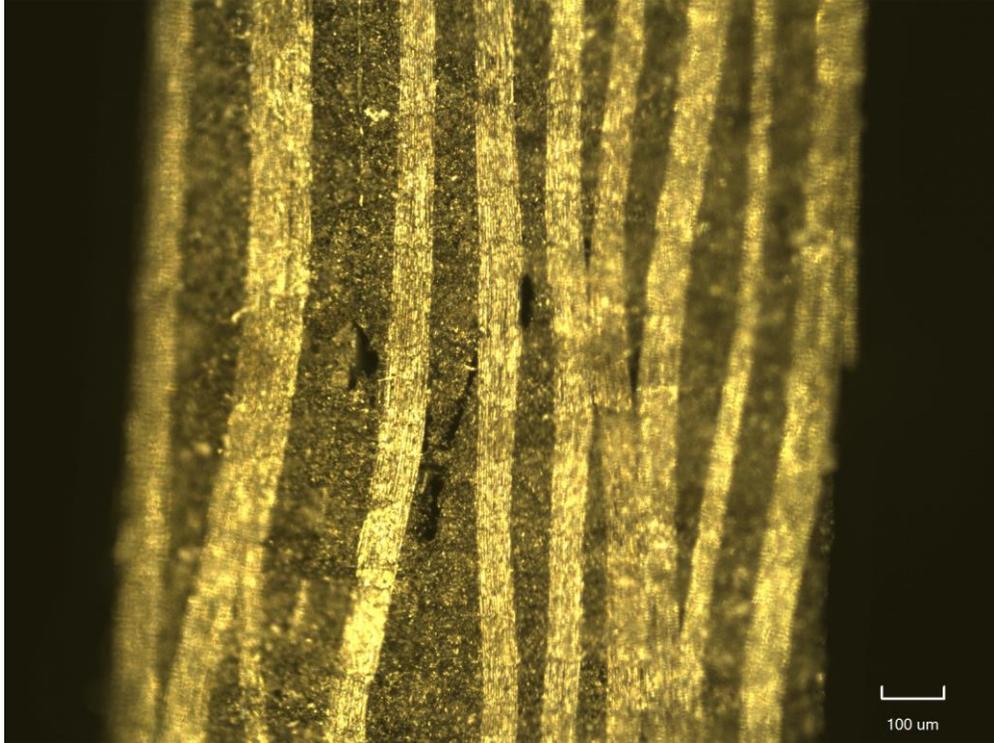
*Figure 14. Microscopic image of CE + 0.5 wt% of MWCNT sample presenting fiber and resin at a magnification of 100X*



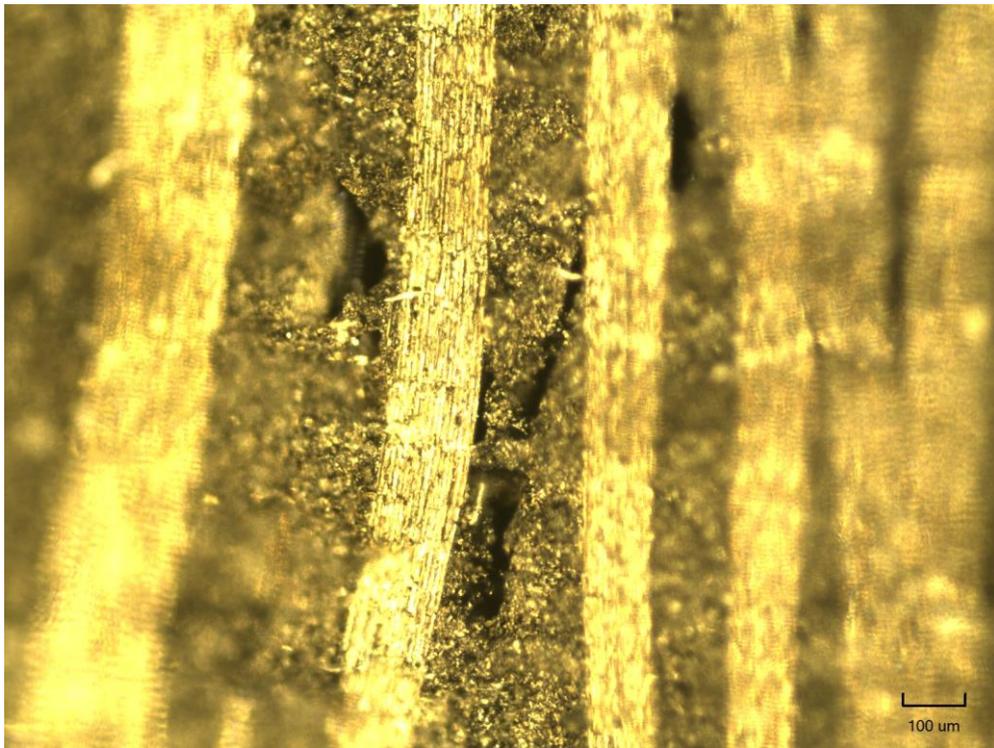
*Figure 15. Microscopic image of CE + 0.5 wt% of MWCNT sample presenting fiber and resin at a magnification of 50X*



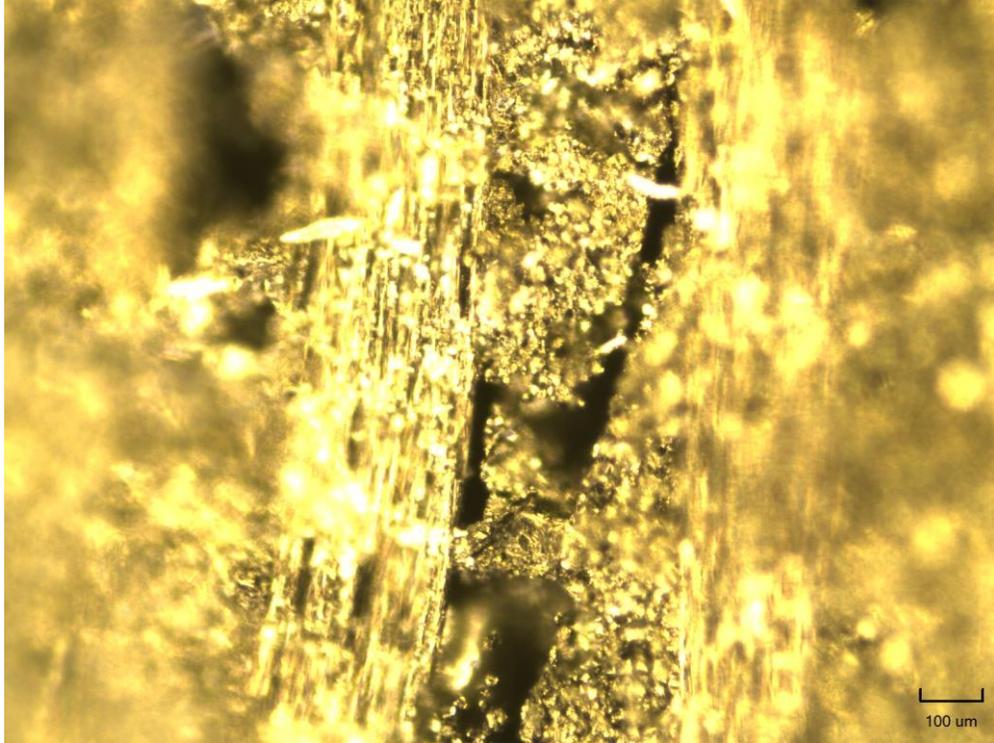
*Figure 16. Microscopic image of CE + 0.5 wt% of MWCNT sample presenting fiber and resin at a magnification of 100X*



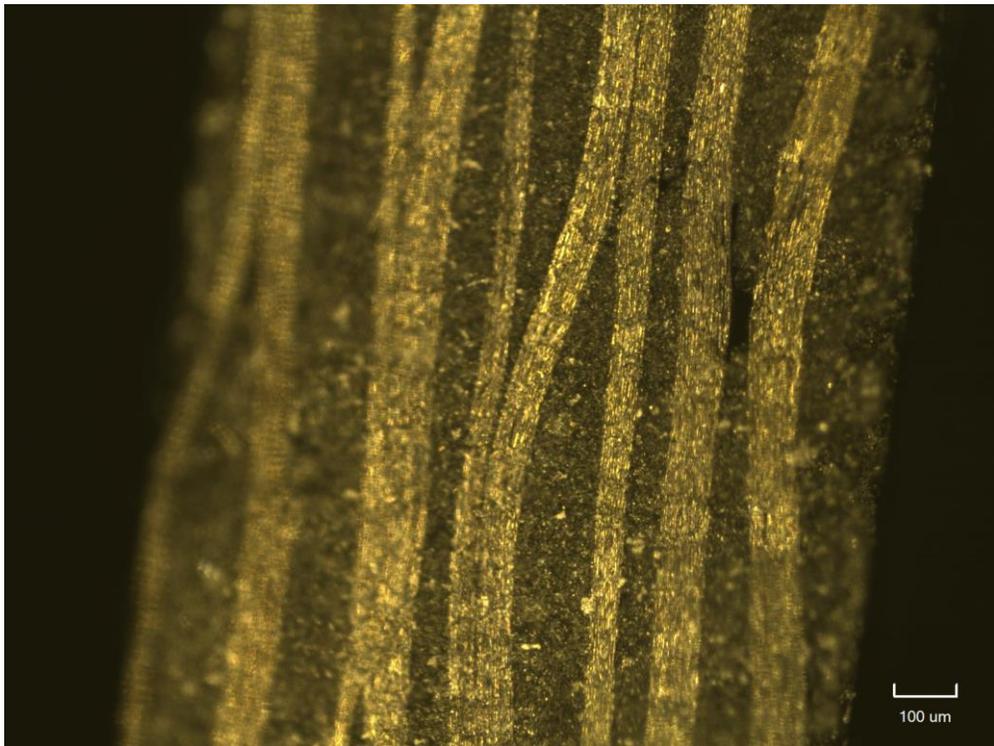
*Figure 17. Microscopic image of CE + 1.0 wt% of MWCNT sample presenting fiber and resin at a magnification of 50X*



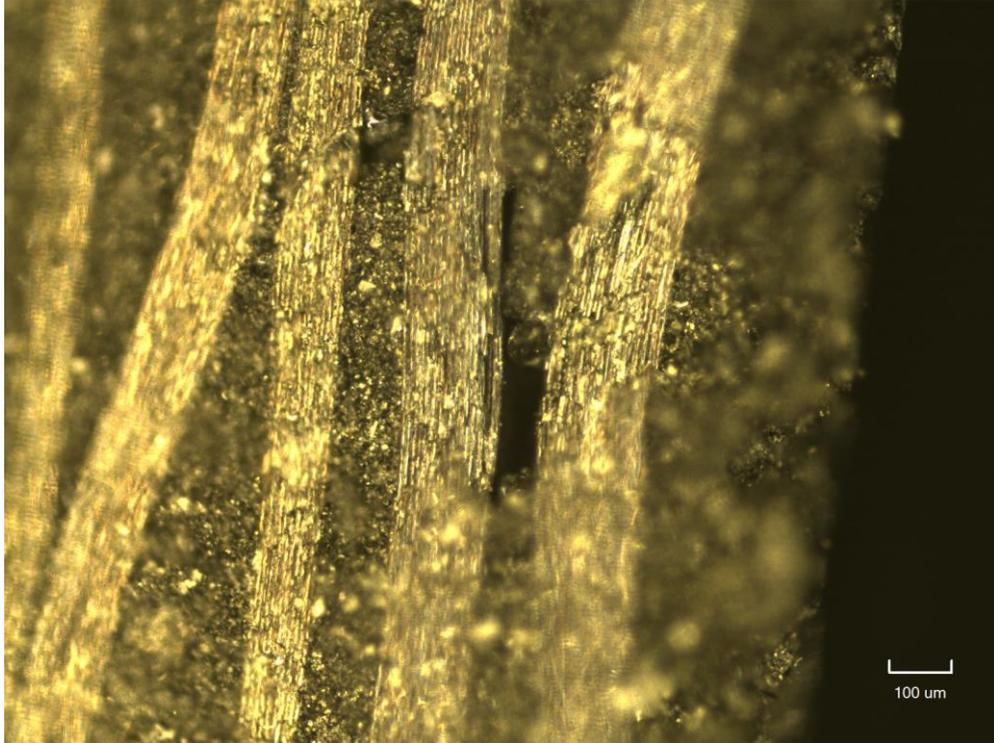
*Figure 18. Microscopic image of CE + 1.0 wt% of MWCNT sample presenting fiber and resin at a magnification of 100X*



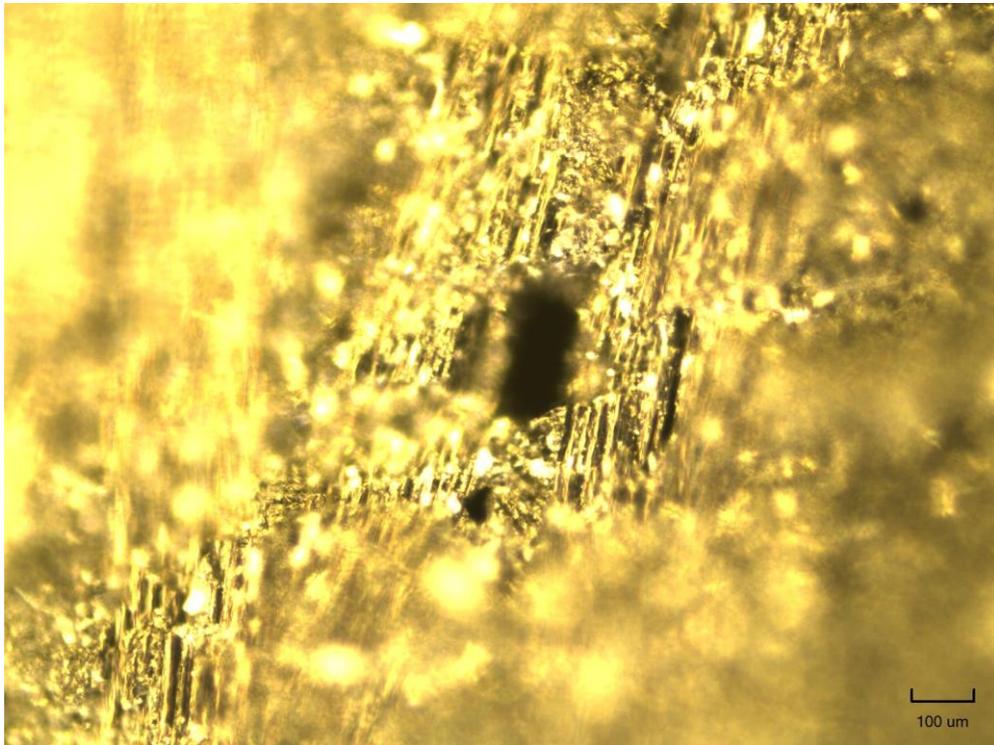
*Figure 19. Microscopic image of CE + 1.0 wt% of MWCNT sample presenting fiber and resin at a magnification of 200X*



*Figure 20. Microscopic image of CE + 1.5 wt% of MWCNT sample presenting fiber and resin at a magnification of 50X*



*Figure 21. Microscopic image of CE + 1.5 wt% of MWCNT sample presenting fiber and resin at a magnification of 100X*



*Figure 22. Microscopic image of CE + 1.5 wt% of MWCNT sample presenting fiber and resin at a magnification of 200X*

### 3.3. Mechanical Characterization

#### 3.3.1. Tension Test

Tension testing was performed according to ASTM D3039 - Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials [44]. Samples of 250 mm in length and 25 mm wide were tabbed and tested at a suggested loading rate of 2 mm/min. Additionally, A total of five specimens were tested for each formulation. Figure 23 shows the behavior of a sample of each formulation under a tensile loading.

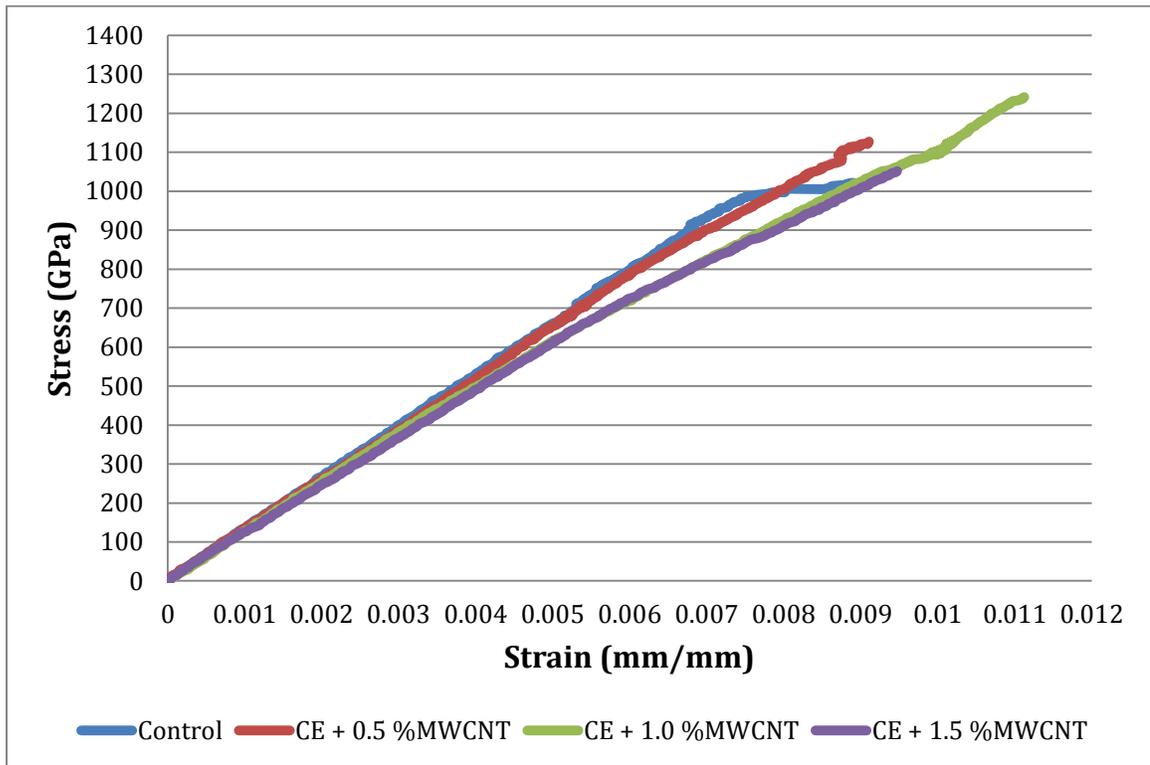


Figure 23. Stress-strain curve under tensile loading

Figure 24 shows the ultimate tensile strength (UTS) of the carbon fiber-reinforced CE nanocomposites. In general, samples of the three modified formulations showed superior UTS when weighed against the control samples. However, samples with

1.5 wt% of MWCNT showed less improvement than samples with 0.5 and 1.0 wt% of MWCNT. A positive increment of 10% in the UTS was observed for samples with 0.5 wt% of MWCNT, while 19% was observed for samples with 1.0 wt% of MWCNT. On the other hand, samples with 1.5 wt% of MWCNT% only showed a 2% of improvement.

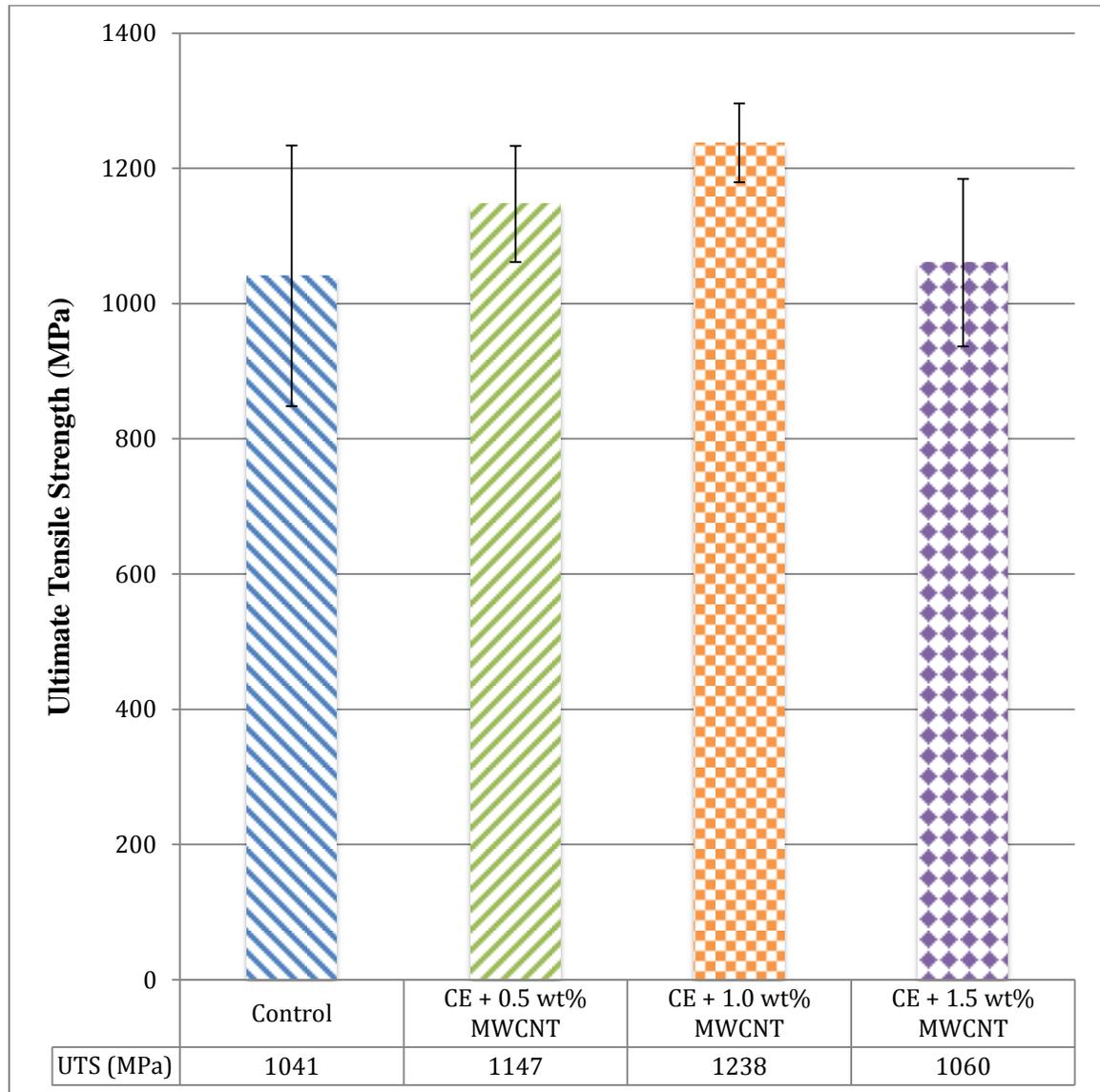


Figure 24. Ultimate tensile strength of CE composites

Figure 25 shows the tensile modulus for the four formulations. Samples modified with 1.0 and 1.5 wt% of MWCNT showed an inferior tensile modulus when compare to control samples. However, an increase of 8% was observed in samples with 0.5 wt% of MWCNT.

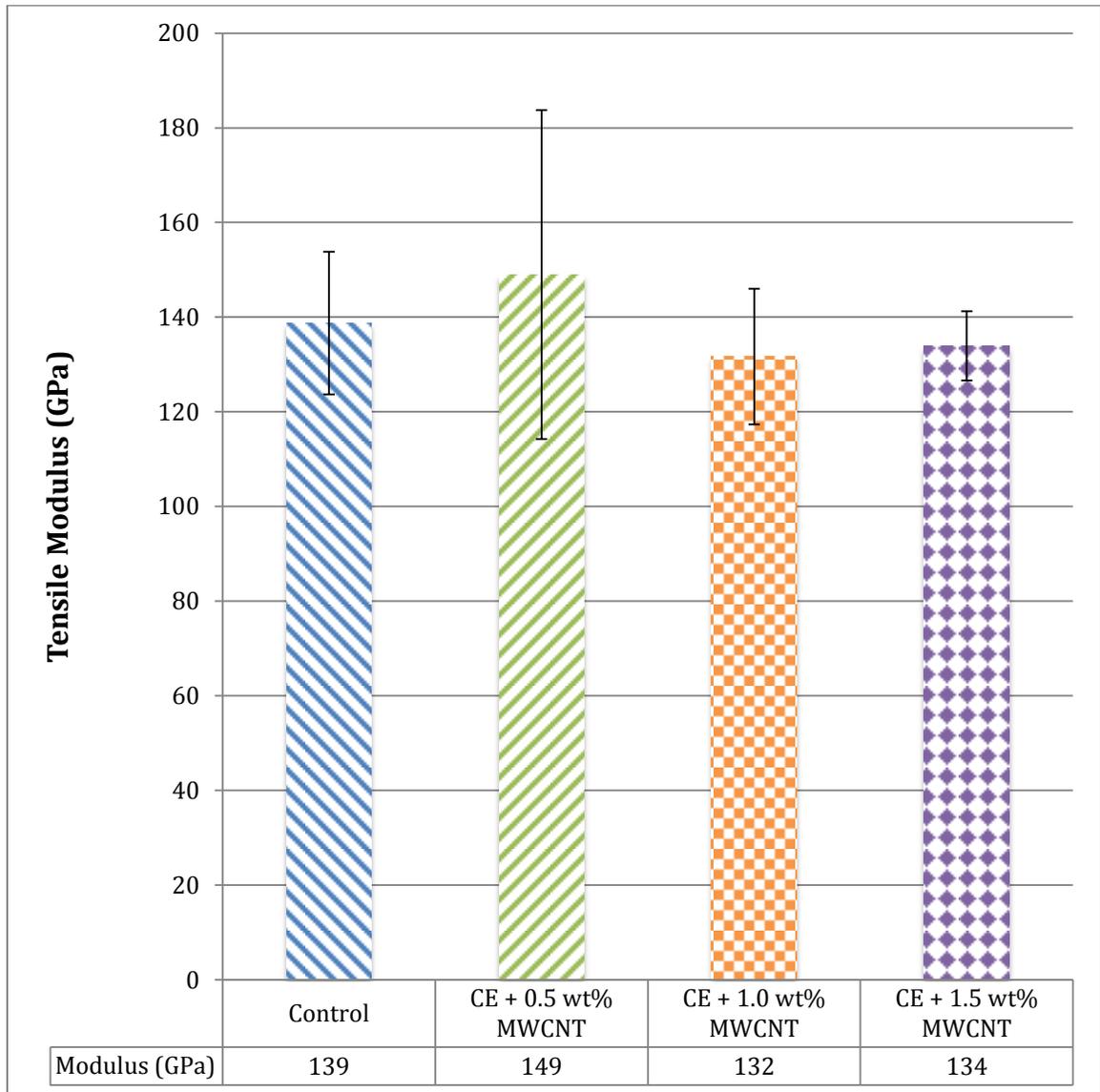


Figure 25. Tensile modulus of CE composites

### 3.3.2. Flexure Test

ASTM D790 - Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials [45], was used to perform flexural test. The dimensions of the specimens for this testing method depend on the thickness (2mm thickness in this case) of the panel from where samples will be cut. Five specimens of 64 mm in total length and 12.7 mm width were prepared according the listed standard for each formulation. Tests were performed at 0.5 mm/min for a loading span of 32 mm. The behavior of each formulation under a loading is shown Figure 26.

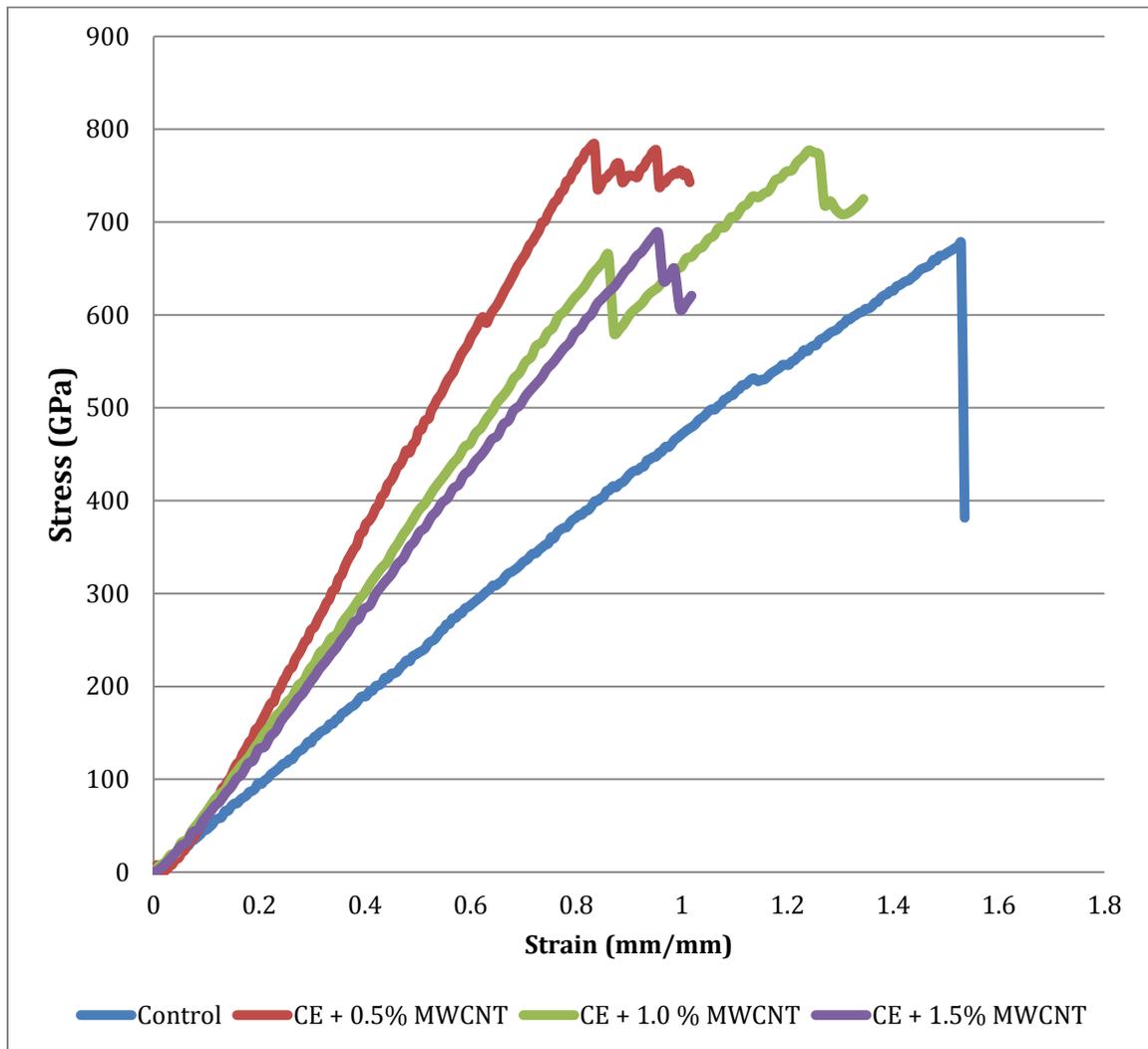


Figure 26. Stress-strain curve under flexure loading

It was observed that the modified formulations have a different behavior than control samples. This behavior is similar to what was observed in the tensile test, and it can be easily observed in figure 27. Samples with 0.5 and 1.0 wt% of MWCNT showed superior flexural strength when compared with the control samples. Samples with 1.5 wt% of MWCNT also showed a significantly higher flexural strength than control, but lower when compared with the other nanomodified formulations.

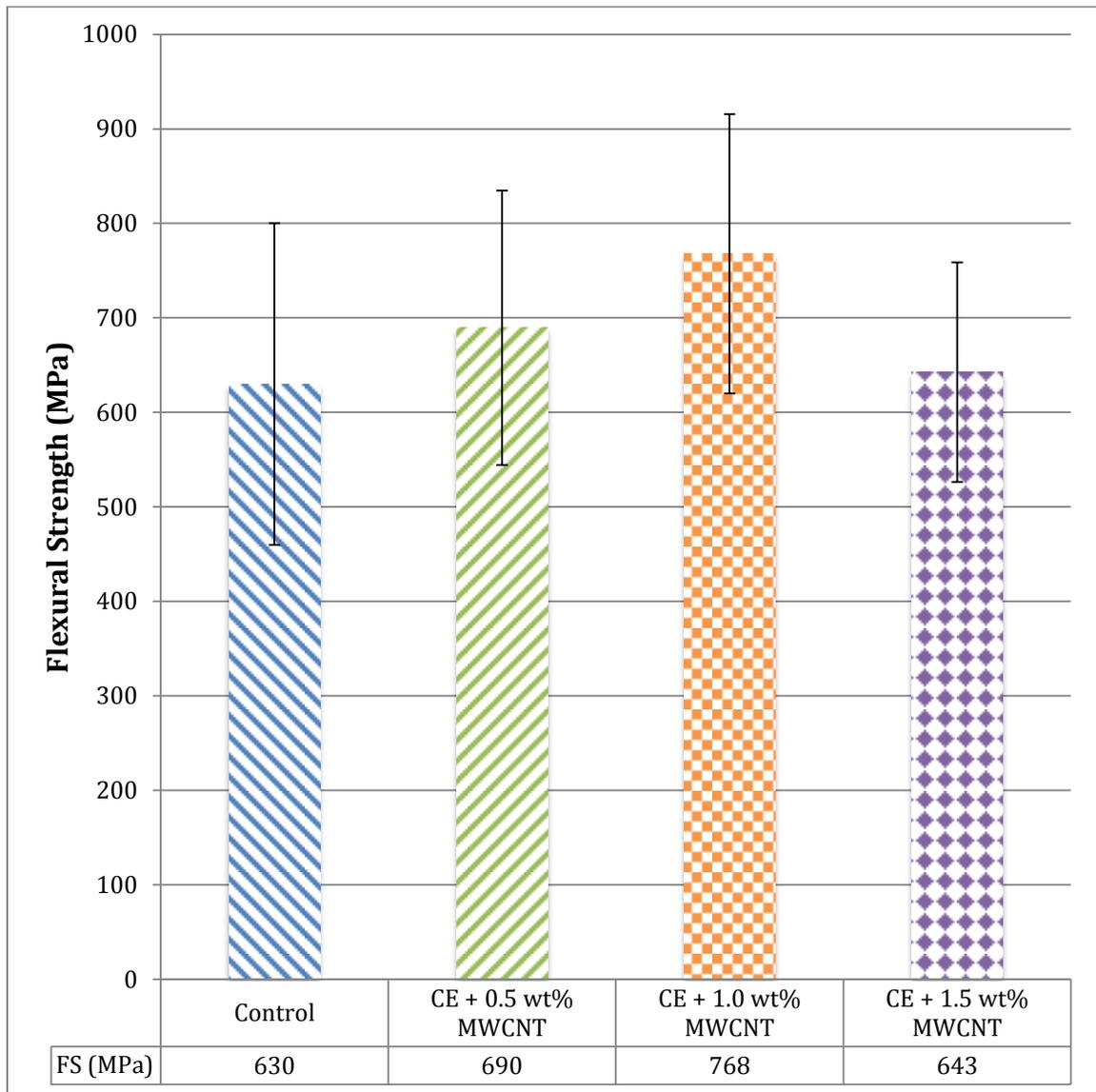


Figure 27. Flexural strength of CE composites

Figure 28 shows the flexural modulus for the four formulations. Samples with 1wt% MWCNT showed considerable improvement in flexural modulus compared to control.

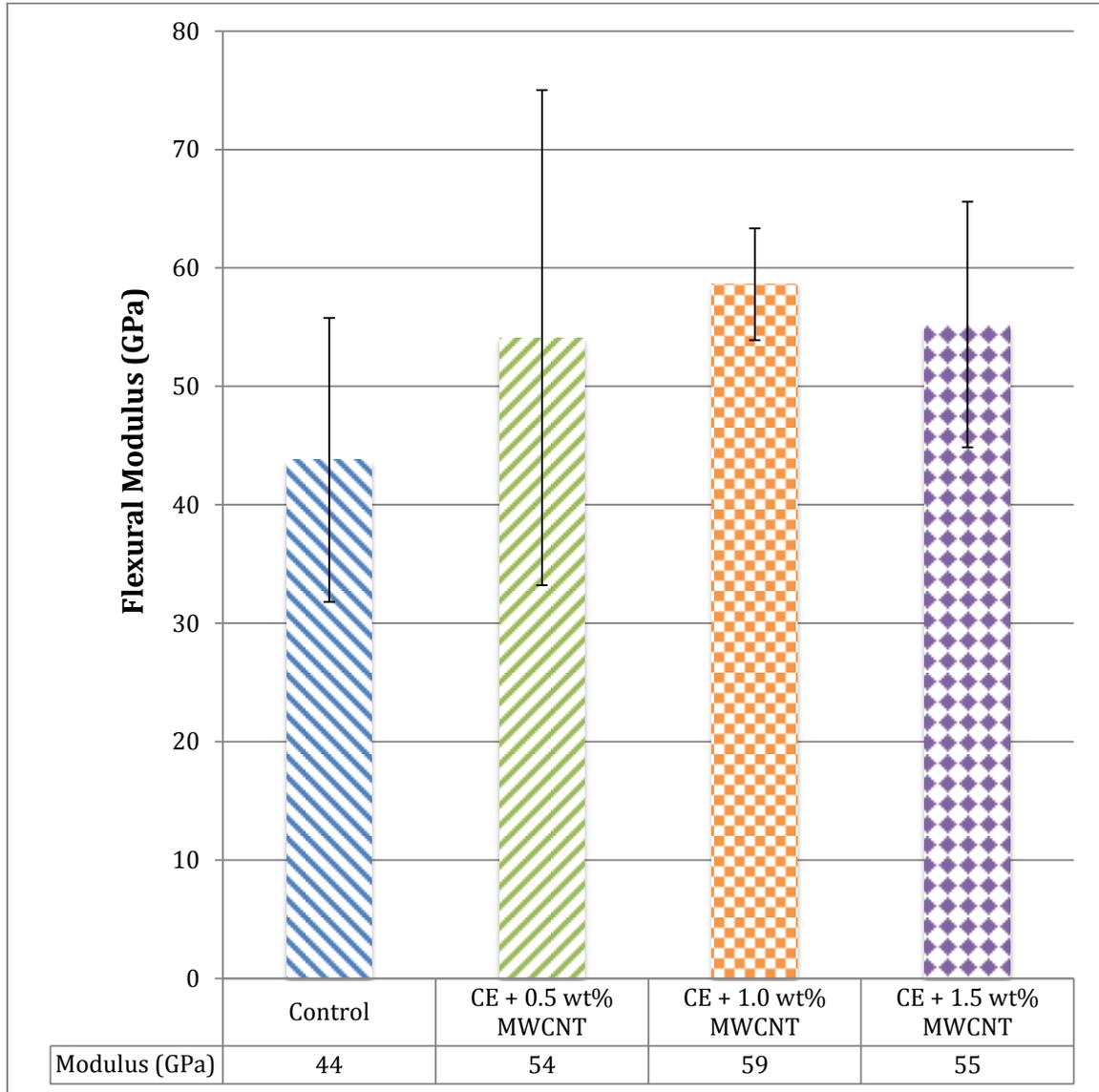


Figure 28. Flexural modulus of CE composites

### 3.3.3. Compression Test

Compression test was performed according with ASTM D6641 - Standard Test Method for Compressive Properties of Polymer Matrix Composite Materials Using a Combined Loading Compression (CLC) Test Fixture [46]. Five specimens of 140 in length by 12.7 mm in width were prepared for each formulation, and then tested at an optimal loading rate of 1.3 mm/min. The behavior of each formulation under loading is shown in figure 29.

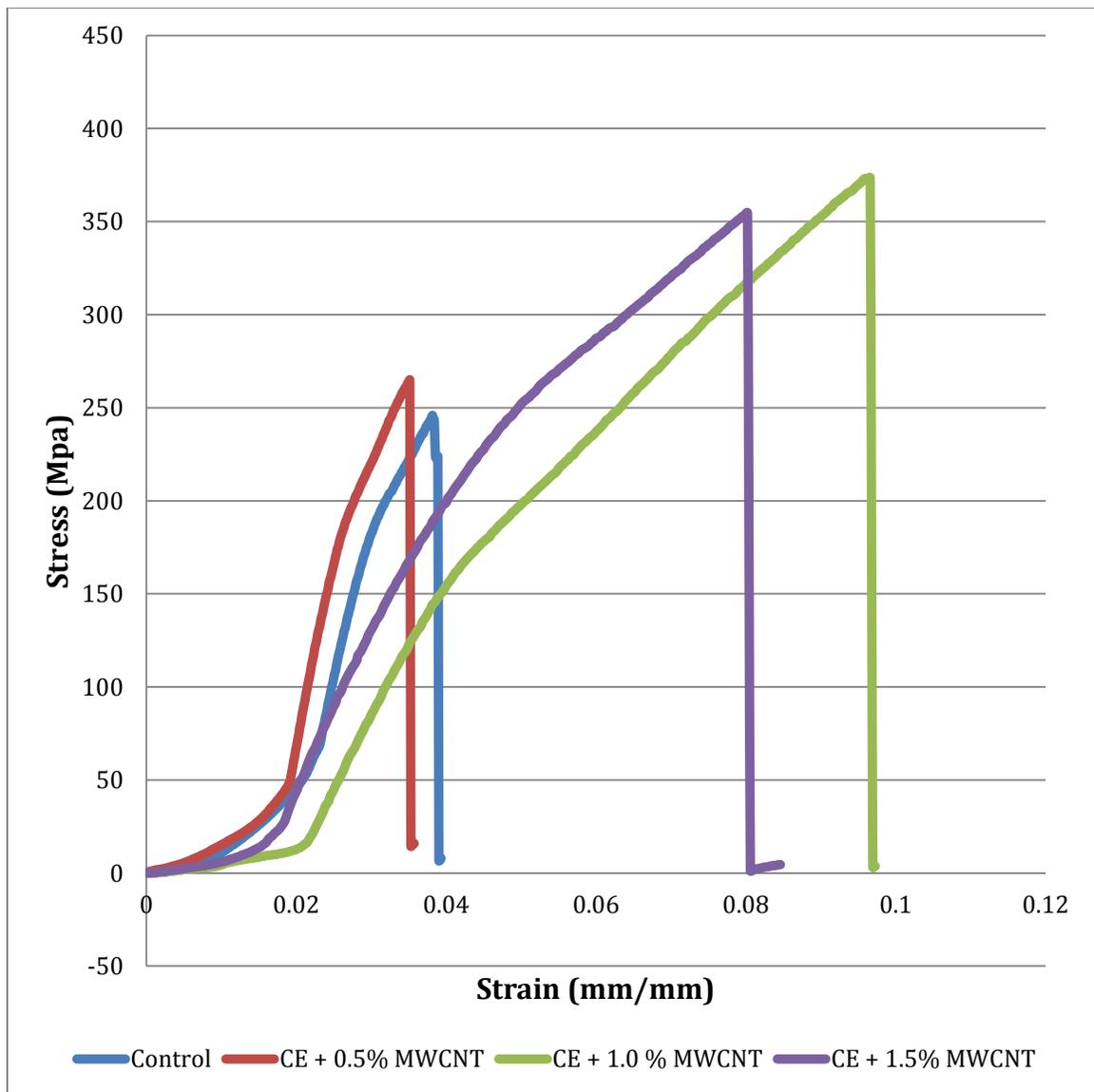


Figure 29. Stress-strain curve under compressive strength

The standard recommends tabbing the samples when thickness of the specimens is less than 3mm. The tabs for both the control samples and the samples modified with 0.5 wt% MWCNT were 0.5 inches shorter than the tabs used for samples modified with 1.0 and 1.5 wt% of MWCNT. The behavior of the samples seems to be affected by the dimensions of the tabs, especially in the percentage elongation. However, the ultimate compressive strength (UCS) results showed improvement for modified samples when compared to control, as shown in figure 30.

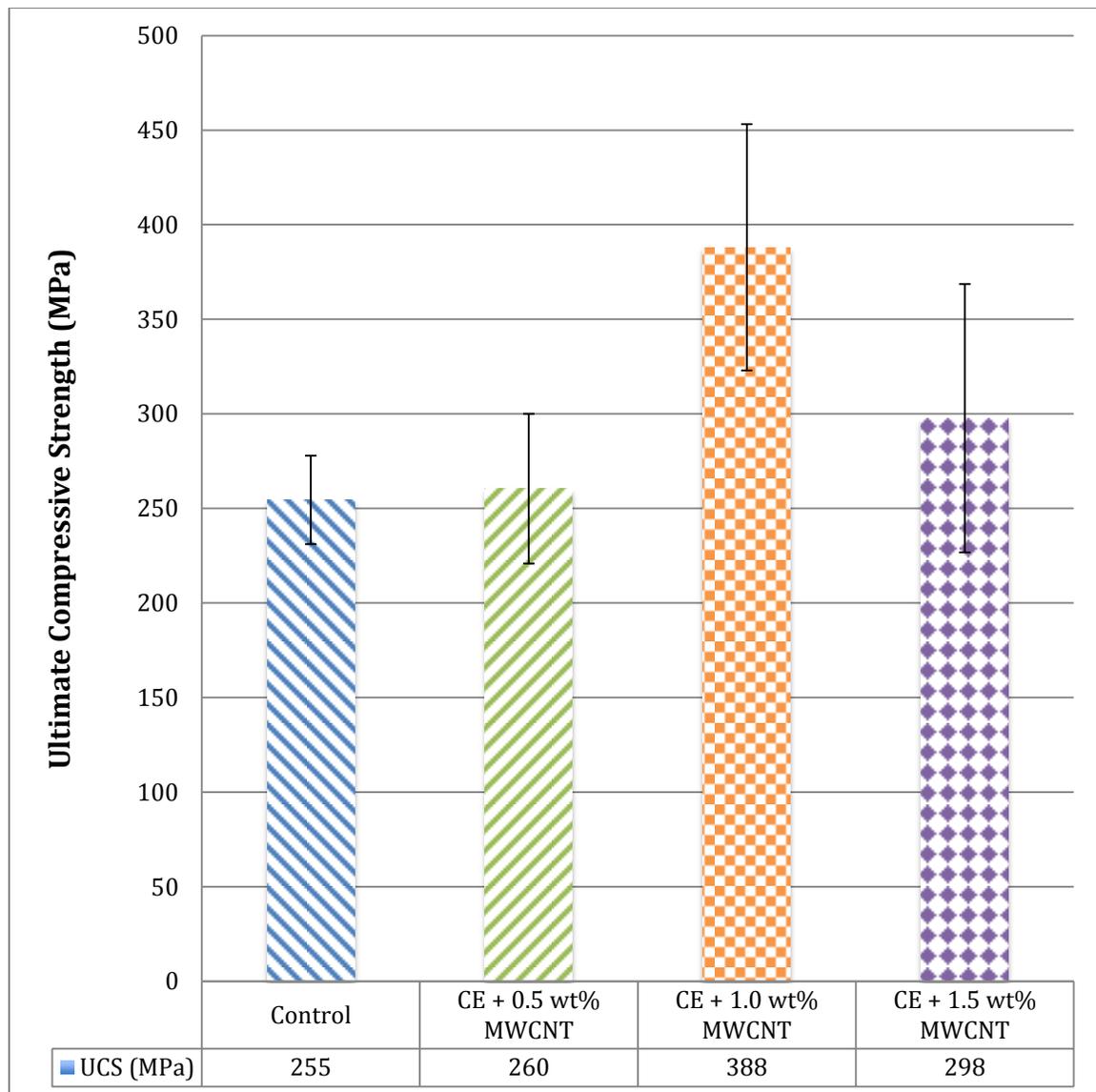


Figure 30. Ultimate compressive strength of CE composites

It is observed that modified samples produce better results than control samples. From the modified samples, those with 1.0 wt% MWCNT show highest UCS than the rest, and those with 0.5 wt% MWCNT showed minimal improvement. The compressive modulus has shown a similar behavior, showing superior results for samples modified with 1.0 wt%. Figure 31 illustrates the compressive moduli for the four different formulations.

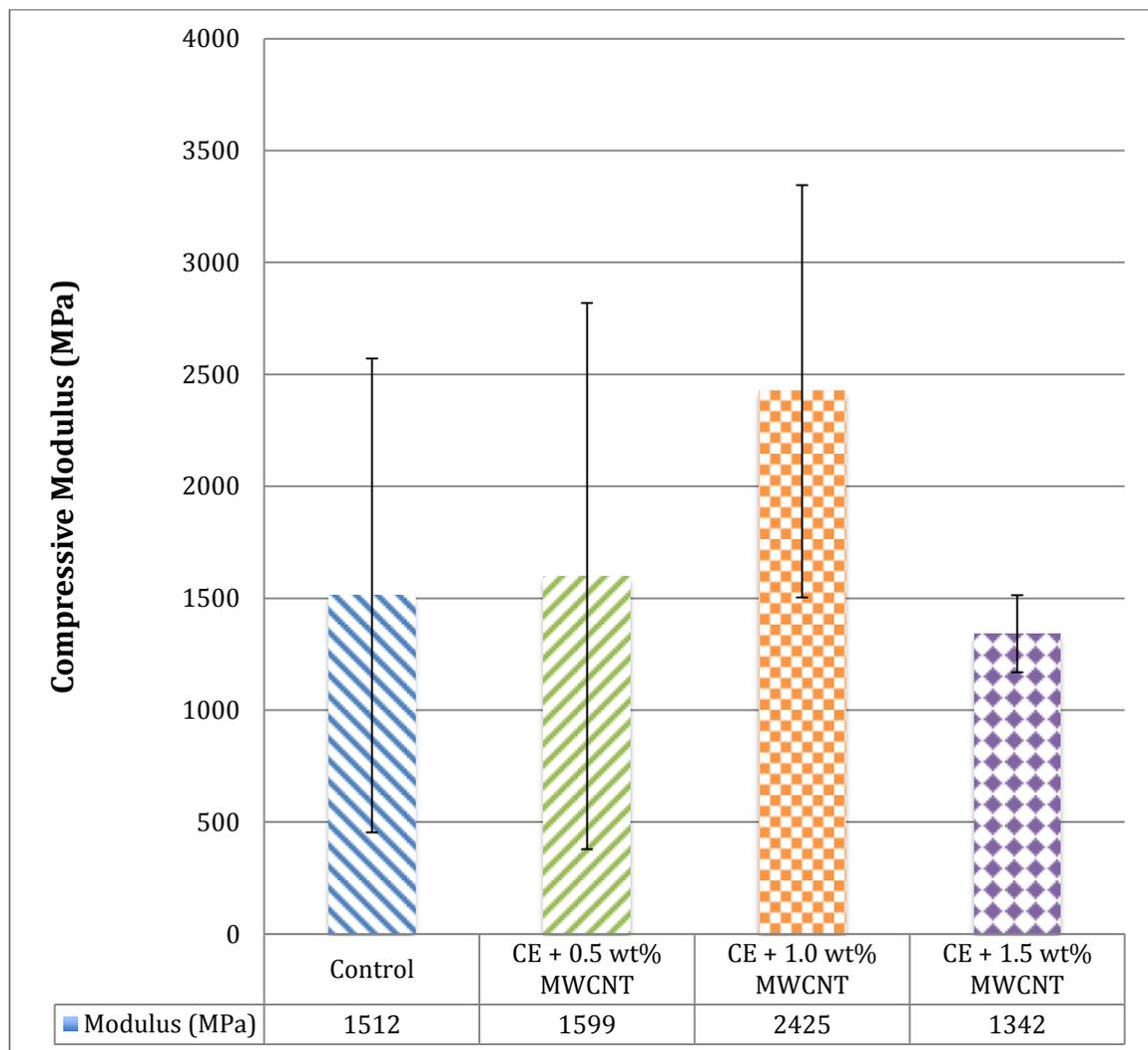


Figure 31. Compressive modulus of CE composites

### 3.3.4. Short Beam Strength Test

Short-Beam test was performed according to ASTM D2344 - Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and their Laminates [47]. Samples of 12 mm length, 4 mm in width, and 2 mm in thickness were tested at a loading rate of 1 mm/min. Figure 32 shows the behavior of each formulation under loading.

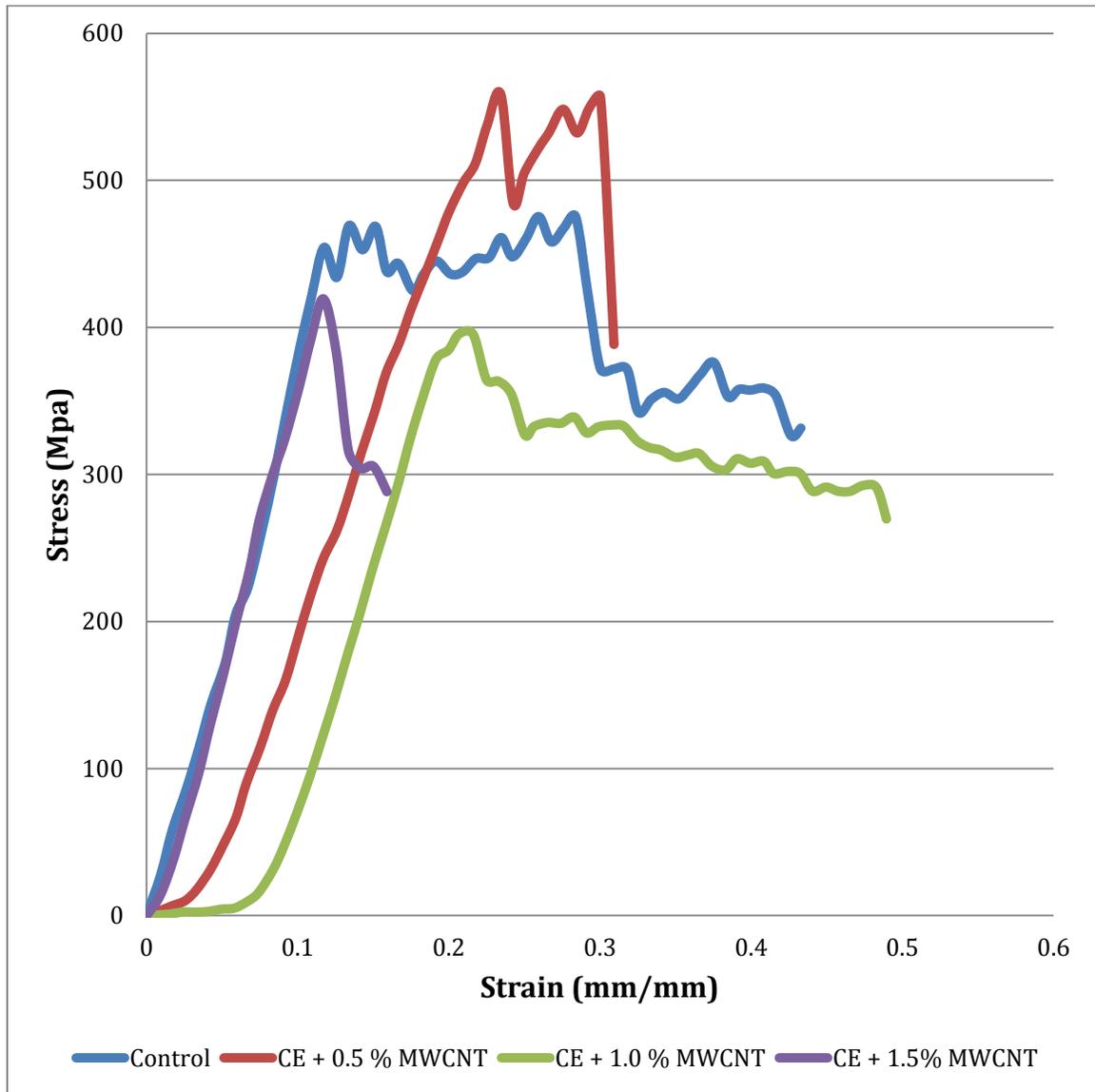


Figure 32. Strain-stress curve under loading

Samples modified with a 0.5 wt% MWCNT showed a slight improvement in the interlaminar shear strength (ILSS) when compared with control samples, whereas samples for 1.0 and 1.5 wt% MWCNT showed a significant decrease ILSS. The short-beam strength for the four formulations is exhibited in figure 33.

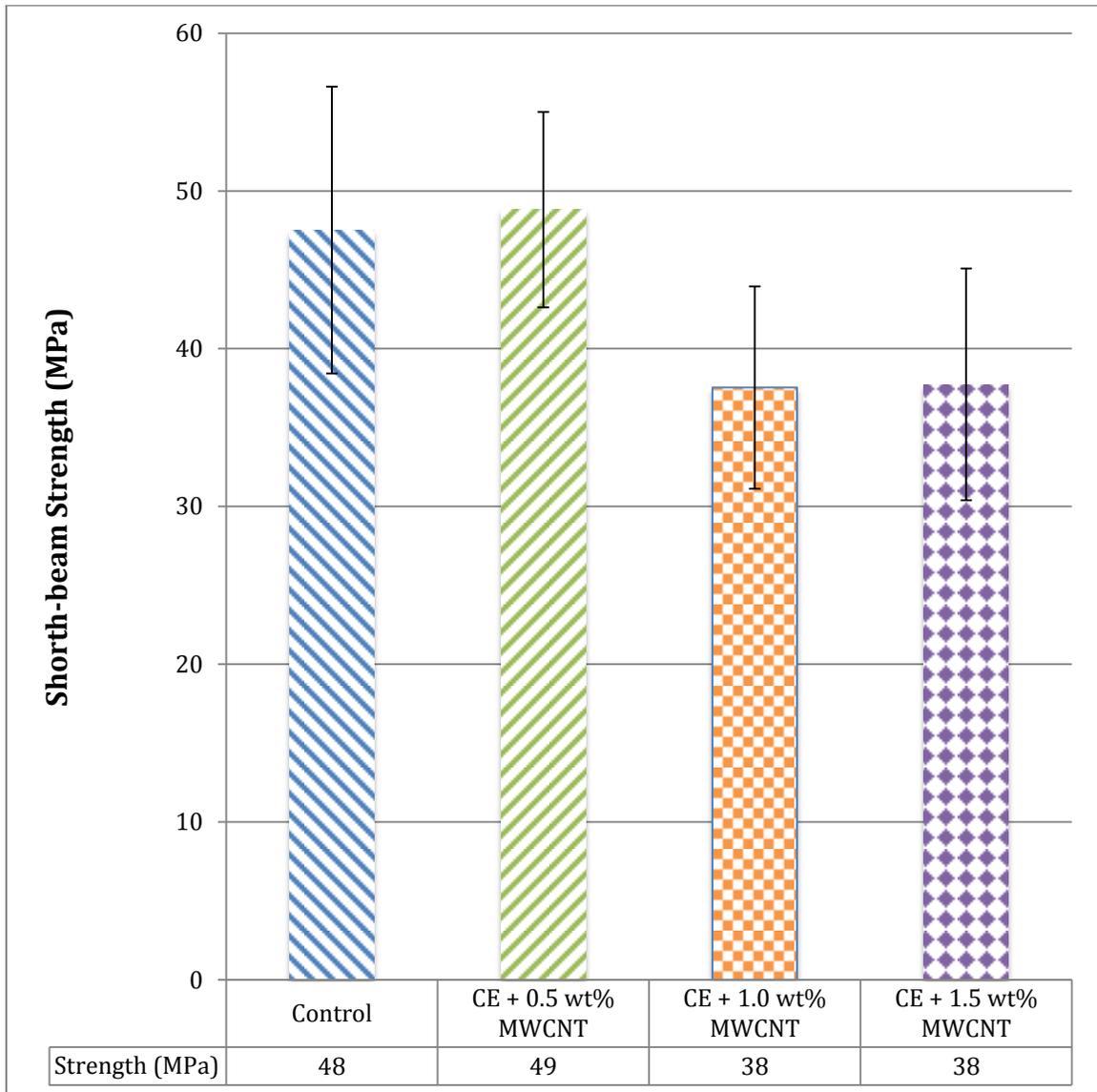


Figure 33. Short-beam strength of CE composites

### 3.4. Flammability Characterization

#### 3.4.1. Microscale Combustion Calorimetry

Three samples of each formulation were prepared according the ASTM D7309 - Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials using Microscale Combustion Calorimetry. The samples were pyrolyzed in nitrogen from 75 to 900°C. The resulting gaseous particles were combusted in air (20% oxygen) at 950°C. The heat release rates (HRR) for the four formulations are shown in figure 34.

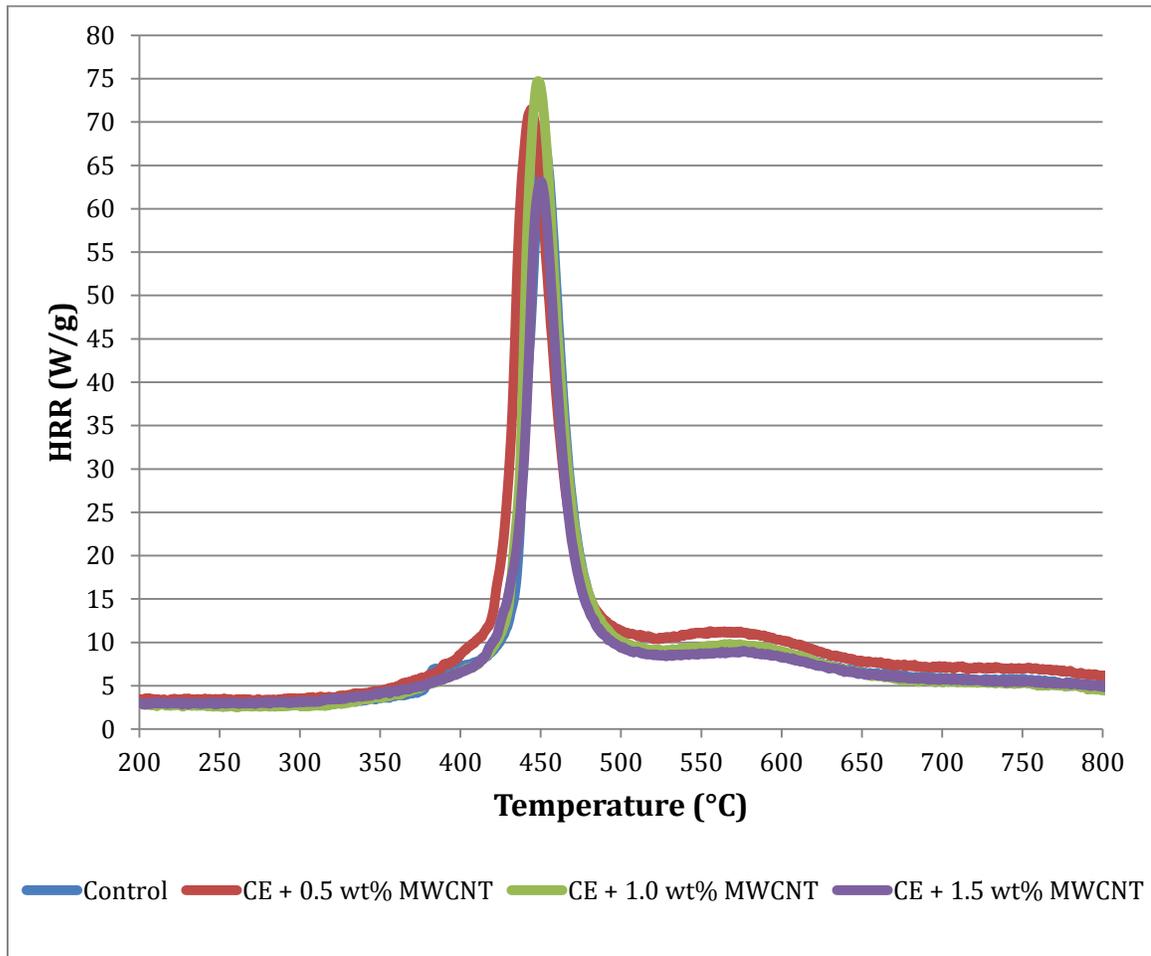


Figure 34. Heat release rates for four formulations of CE composites

Samples modified with 0.5 and 1.0 wt% of MWCNT showed a higher HRR than the control specimens. On the other hand, samples with 1.5 wt% MWCNT presented a lower HRR when compared to the control. Although there is a difference between the HRR results, the temperature at which this phenomenon is occurring doesn't change.

Table 10 shows a summary of the results obtained for MCC test.

*Table 10. Heat release capacity, peak heat release rates, and total heat release for four formulations of CE composites*

FORMULATION	HR CAPACITY (J/g-K)	PEAK HRR (W/g)	TOTAL HR (KJ/g)	TEMPERATURE (C)
Control	43.67	63.8	2.27	450.17
CE + 0.5% MWCNT	47.00	69.36	2.43	446.67
CE + 1.0% MWCNT	49.33	72.73	2.53	447.43
CE + 1.5% MWCNT	40.67	59.56	2.17	448.33

### 3.5. Thermal Characterization

#### 3.5.1. Thermal Gravimetric Analysis

Thermal Gravimetric Analysis (TGA) was performed to analyze the thermal stability properties of the four formulations. The samples were heated to 900°C at 10°C/min in both air and nitrogen. Figure 35 shows the behavior of the samples tested on air, and Table 10 displays their decomposition temperatures. The decomposition temperatures at 10% and 50% of mass loss showed a variation between one and two percent for all samples.

*Table 11. Decomposition temperature of CE composites in air*

FORMULATION	T10% at 10% Mass Loss		T50% at 50% Mass Loss	
	T10% (°C)	Δ (%)	T50% (°C)	Δ (%)
Control	571.03		816.59	
CE + 0.5% MWCNT	564.64	-1.12	805.94	-1.30
CE + 1.0% MWCNT	563.35	-1.35	812.64	-0.48
CE + 1.5% MWCNT	586.55	2.72	819.20	0.32

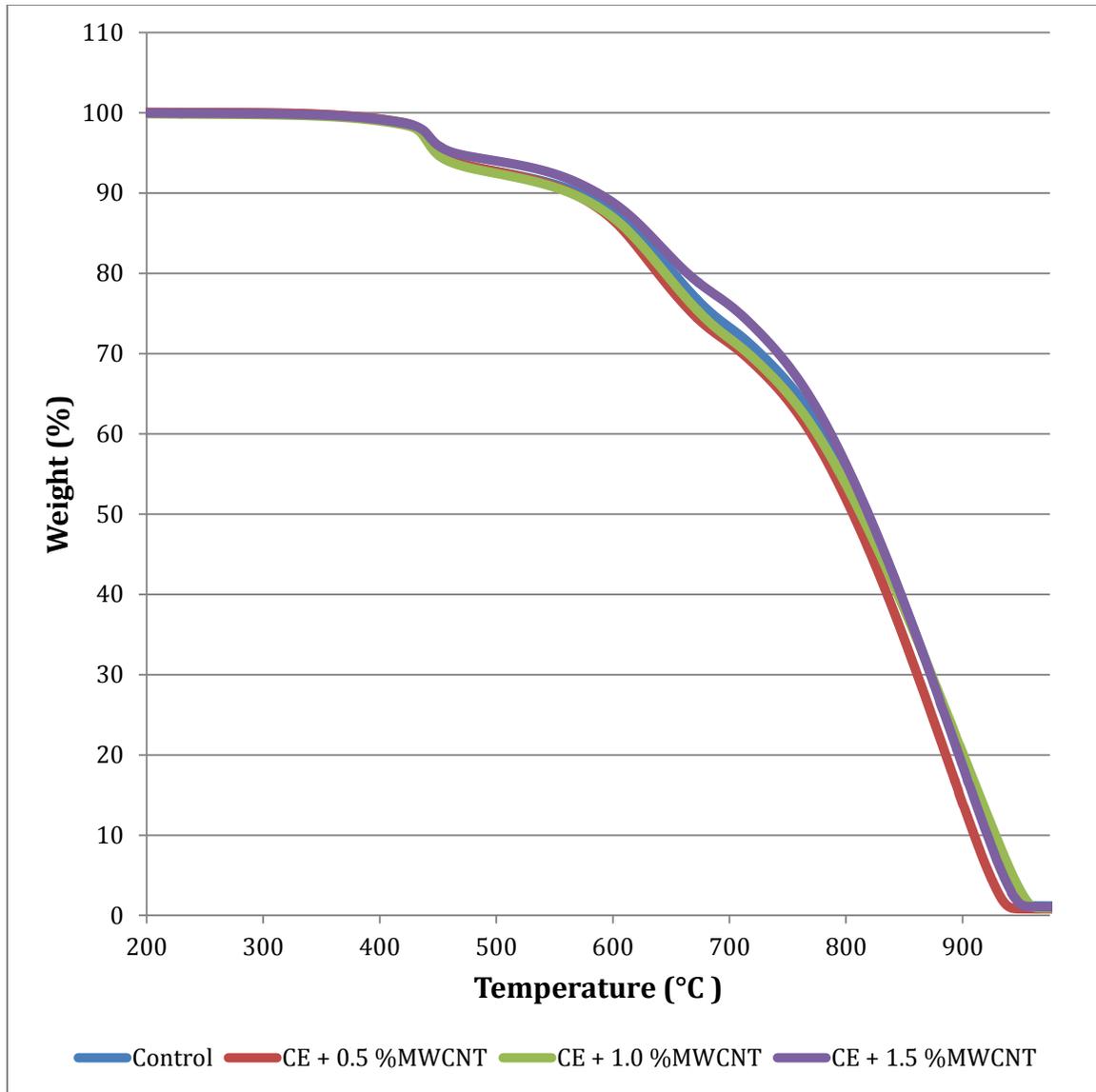


Figure 35. TGA curves for four formulations of CE composites tested in air

Figure 36 shows the TGA curve for samples tested in nitrogen. The decomposition temperatures at 10% of mass loss shown in figure 25 shows a small variation (<5%), except for the samples that contains 1.5 wt% of MWCNT that showed a variation of 12%. Table 12 shows the decomposition temperatures for samples tested on nitrogen.

Table 12. Decomposition temperature of CE composites in nitrogen

FORMULATION	T10% at 10% Mass Loss	
	T10% (°C)	Δ (%)
Control	609.98	
CE + 0.5% MWCNT	629.10	3.13
CE + 1.0% MWCNT	610.31	0.05
CE + 1.5% MWCNT	534.43	-12.39

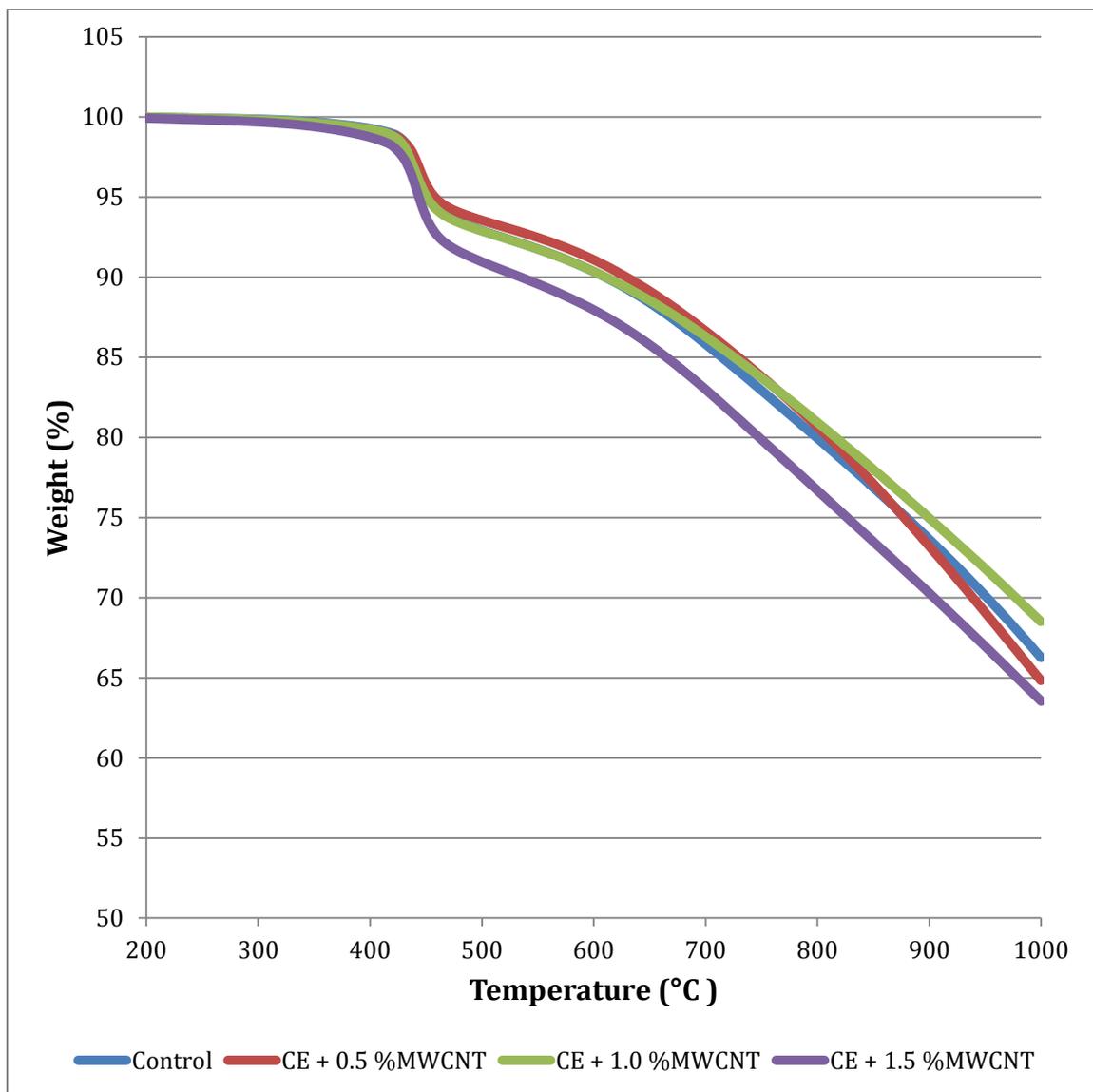


Figure 36. TGA curves for four formulations of CE composites tested in nitrogen

### 3.6. Analysis of Variance

One-way ANOVA was used to evaluate if the variation observed in the results is statistically significant. ANOVA results for the mechanical characterization are shown in table 13. The results of the mechanical characterization showed a superior results could be achieved by adding MWCNTs, especially for 1 wt% of MWCNT. However, ANOVA shows that statistically the difference between formulations is not significant, suggesting that the addition of MWCNTs has no effect on the mechanical properties.

*Table 13. One-way analysis of variance of the mechanical characterization of CE nanocomposites*

	<b>F</b>	<b>F crit</b>	<b>p-value</b>	<b>Recommendation</b>
<b>Ultimate Tensile Strength</b>	2.59972	3.15991	0.08393	Fail to reject
<b>Tensile Modulus</b>	0.73075	3.15991	0.54701	Fail to reject
<b>Flexural Strength</b>	0.96572	3.19678	0.43163	Fail to reject
<b>Flexural Modulus</b>	1.25870	3.19678	0.31995	Fail to reject
<b>Ultimate Compressive Strength</b>	7.48475	3.34389	0.00315	Reject
<b>Compressive Modulus</b>	0.22695	3.34389	0.87607	Fail to reject
<b>Short-Beam Strength</b>	3.09929	3.41053	0.06396	Fail to reject

Results for MCC were also analyzed using one-way ANOVA, as shown in table 14. Even though, a small difference was observed in the HRR between the four formulations, this difference is statistically significant. However, the probability to obtain a significant difference by modifying CE with various loads of MWCNT is low (<5%). In consequence, it can be considered that there is no enough evidence to affirm an effect of the MWCNTs in the composite.

*Table 14. One-way analysis of variance of the flammability properties of CE nanocomposites*

<b>TEST</b>	<b>F</b>	<b>F crit</b>	<b>p-value</b>	<b>Recommendation</b>
<b>Heat Release Rate</b>	9.29538	4.06618	0.00551	Reject
<b>Heat Release Capacity</b>	3.98077	3.86255	0.04652	Reject

#### 4. CONCLUSIONS

An extensive characterization of carbon fiber reinforced cyanate ester nanocomposites was successfully performed. CE was modified using three different loading rates of MWCNT. MWCNT were received in the powder form, which lead to high entanglement between nanoparticles. In order to mitigate the entanglements, dry MWCNT were exposed to a milling technique for 15, 30, and 45 minutes respectively. Zirconia balls of 3mm diameter were introduced as grinding media within the mixer's capsule. According to the results, MWCNT that were exposed to 45 minutes of milling experienced the least amount of entanglements, flowing easily, and gave the sensation of being a lighter powder. Consequently, this batch of MWCNT was selected to produce nanomodified CE resin.

The nanomodification of the resin was achieved after applying a combination of THINKY mixer and an everyday stand mixer. THINKY mixer has great potential to disperse nanoparticles due to its centrifugal planetary movement at high speeds, which is also improved by the use of the Zirconia grinding media. Stand mixer has the capacity to generate enough shearing to break up any clusters that remain prior to planetary mixing. Thus, both a qualitative and quantitative dispersion of MWCNT into CE was obtained.

Three panels of four different formulations were successfully manufactured by hand wet lay-up that was followed by compression molding. The quality of the panels was then analyzed by fiber volume fraction, and optical characterization techniques. A fiber volume fraction of  $49\pm 0.02$  was found for all panels, which reveals great precision within the manufacturing process. Several images were taken using an optical microscope to analyze the internal structure of the nanocomposite. The images evidenced the

presence of voids in all panels. The voids were always located between the carbon fibers and the CE resin, which suggests that they are the result of the wetting process. However, voids are not numerous, they are smaller than one micron, and they were equally distributed for all formulations. Therefore, there is no evidence to conclude that the voids are disrupting the nanomodification of the resin, nor that the increased loading weight of MWCNT promotes the presence of voids in the final composite. The voids are considered as defects due to the processing.

Tension, flexure, compression, and short-beam tests were performed to evaluate the behavior of carbon fiber reinforced cyanate ester nanocomposites under mechanical loading. Overall, an improvement of the mechanical properties was observed for the nanomodified formulations when compared with the control samples. It was also observed that the nanomodified formulation with 1.0 wt% of MWCNT possessed superior mechanical properties when compared to formulations containing 0.5 and 1.5 wt% of MWCNT. For tensile strength an improvement of 10, 19, and 2% was achieved for formulations with 0.5, 1.0, and 1.5 wt% of MWCNT, respectively. Likewise, for flexural strength an enhancement of 10, 22, and 2% was observed for the samples with 0.5, 1.0, and 1.5 wt% of MWCNT, respectively. Similar behavior was detected for the compressive strength, in which improvement of 3, 53, and 17% was observed for weight loading rates of 0.5, 1.0 and 1.5% , respectively. Interestingly, the results for the short-beam test displayed different behavior. When compared to control, the formulation with 0.5 wt% of MWCNT showed a slight improvement of 3%, but decline of 20% was observed for the other two formulations. This test is measure of fiber-matrix adhesion. Higher the ILSS better are mechanical properties. A deterioration of the short-beam

strength for formulations containing 1.0 and 1.5 wt% indicates that the agglomerated presence of MWCNT in between the layers that is reducing the bonding between matrix and reinforcement. This negative effect could be amplified by the presence of the voids that were observed during the optical characterization. The detrimental effect reveals that the voids originated during the impregnation of the carbon fiber is creating high variance in the results; therefore a statistical analysis of the gathered data is needed. One-way ANOVA was performed for all the tests, in order to identify if the behavior observed during the mechanical tests is an effect of the variation in the data. The results of ANOVA suggest that there is no effect of the MWCNT, except for the ultimate compression strength. Otherwise, it is evident that there is a positive effect of the MWCNT in the final composite, and that 1.0 wt% of MWCNT is the best loading by weight to modify CE resin. However, the variation within the data advises to consider that there may be no effect of the nanomodification on the final properties of the carbon fiber-reinforced cyanate ester composites.

The thermal stability was evaluated by running TGA in an atmosphere of air, and nitrogen. The results for TGA in air showed a variation of  $\pm 3\%$  in the decomposition temperatures when the 10 and 50% of the mass was lost. A similar behavior was observed when the TGA was performed in nitrogen. The results showed a variation of  $\pm 3\%$  on the decomposition temperature when 10% of the total mass was lost. By the end of the test, only 35% of the mass was loss. In conclusion, modifying CE resin with MWCNT has no effect on the decomposition temperatures of the composite.

The flammability of the carbon fiber-reinforced cyanate ester composite was evaluated with MCC analysis. The fact that CE composites held excellent flammability

properties was already understood. The results for HR capacity, and peak HRR showed a negative effect for formulations with 0.5 and 1.0 wt% of MWCNT, but a incremental improvement for formulation with 1.5 wt% of MWCNT. On the contrary, HR capacity and peak HRR decreased by 8 and 9%, respectively for samples with 0.5 wt% of MWCNT. Samples with 1.0 wt% of MWCNT showed a reduction of 13 and 14% in HR capacity and peak HRR, respectively. On the other hand, an improvement of 7% was observed in both the HR capacity as well as the peak HRR for samples with 1.5 wt% of MWCNT. One-way ANOVA showed that the variation in the results are significant, therefore the weight load of MWCNT has an effect on the flammability properties. Although the affect seems to be negative for low loadings of MWCNT, the final composite still holds excellent and superior flammability properties.

In conclusion, a positive behavior was observed on the mechanical properties, but ANOVA analysis showed that this behavior is not statistically significant. In contrast, the results of TGA strongly suggest that there is no effect of MWCNT on the thermal stability of this composite material. A negative effect of low loading by weights of MWCNT was observed for the flammable properties, however this deterioration is not significant.

## APPENDIX SECTION

### Appendix A

#### Safe Handling of Nanoparticles

New materials used in manufacturing processes can be developed constantly thanks to the continuous improvement in technology, but every new technology comes with some ethical questions related to the health and safety. These concerns should be clarified before these materials begin to be used in the industry. It is necessary to develop enough knowledge about the technology that people are dealing with and how it could impact the society. This could open the door for a big argument between those who support the development of a new technologies based on the benefits that they bring with them, and those that consider that the consequences of using a new technology must be understood before its release.

Nanotechnology is the manipulation of matter on the atomic scale to create structures that can be developed into new products for use in engineering, science, and medicine [48]. Nanoparticles have existed for many years. In fact, nanoparticles are produced as the result of many chemical and physical processes of the human body and the nature. For example, natural nanoparticles can be found in volcanic ash, ocean spray, fine sand and dust, and viruses [49]. People have been dealing with nanoparticles created as byproduct of human activities such as a running fuel engines and large-scale mining [49]. However, these nanoparticles have different shapes and compositions, and their exposure to the human body and the environment are controlled and regularized by organizations such as the National Institute of Occupational Safety and Health (NIOSH) [48]. The problem emerged when scientific advancements improved the capability to synthesize specific particulates in a size range from 1 to 100 nm. These engineered

nanoparticles have been specifically designed and deliberately synthesized by human beings to have precisely controlled sizes, shapes, and compositions. The manipulation of particles at this scale has the potential to affect the quantum mechanics effects of materials, which has opened whole new branches of research areas. Nanoparticles are so useful in technology because of its high surface area to mass ratio, large quantum effects, deformability, durability, tendency to aggregate, optical sensitivity, hydrophobicity, high reactivity, rapid dissolution (for soluble particles), electrical conductivity, and great tensile strength [50]. Interestingly, several studies have shown that the toxicity of particles increases for the exact same reasons [48, 51-54]. Inhaled nanoparticles have the ability to translocate in the body as much as 80 % of the deposited mass and are capable of traveling freely in the blood throughout the body and reach the organs like liver, lungs, and brain [55]. Figure 37 shows a summary of the diseases associated to nanoparticle exposure [56].

### DISEASES ASSOCIATED TO NANOPARTICLE EXPOSURE

C. Bicaia, I. Pacheco, & K. Robbie, Nanomaterials and nanoparticles: Sources and toxicity, Biointerphases 2 (2007) MR17-MR71

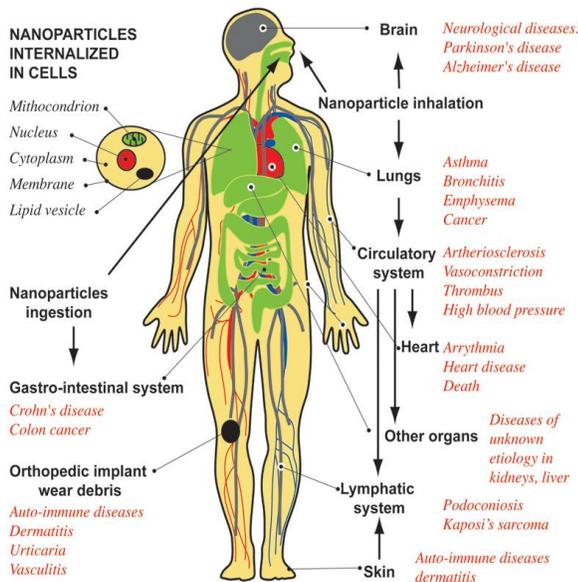


Figure 37. Diseases associated to nanoparticle exposure

In the last decade human exposure to nanoparticles has become inevitable since nanotechnology made myriad inroads into mainstream society through products such as coatings on cell phones, antimicrobial socks, static-free pants, self-cleaning toilets, food packaging, solar paint, lighter and stronger baseball bats, lighter and damage-tolerant wind turbine blades, and fuel cells. Engineered nanoparticles have changed the abundance, chemical composition, and physical characteristics of very small particles in potential workplaces and environmental exposures. However, while the number of nanoparticle types and applications continues to increase, studies to characterize their effects after exposure and to address their potential toxicity are few in comparison [48]. Thanks to the accelerated rate of improvement of this technology a significant increase of the market value of nanotechnology products was estimated from \$254 billion in 2009 to \$2.5 trillion in 2015 [57]. The benefits that nanotechnology could bring with it are promising, but it is essential to control and regularize the way in which these nanoparticles should be handled. Current regulations permit the commercial production and use of most nanoparticles without additional safety testing, using standards developed for larger breathable particulates of the same chemical composition [48, 58]. Ongoing nanoparticles exposures in students and workers increase the urgency of the studies. The toxicology of most particles generated during industrial processes has been studied for a long time [59], but the size of these particles has changed therefore the toxicology must be studied again. New regulations that considered sizes, shapes and not only chemical composition are needed for engineered nanoparticles.

Some organizations with processes that involve the production and/or use of engineered nanoparticles have shown the interest for learning about the hazards of

exposing their workers to these kinds of materials [60, 61]. However, the lack of national or international regulations to deal with nanoparticles have forced them to be creative to generate new ideas that enable the measurement the level of exposure and the analysis of the effects of nanoparticles in the human body. Seeing the necessity to organize, control, and replicate these efforts, the NIOSH established a nanotechnology field research team whose primary goal was to visit facilities and evaluate the potential for release of nanomaterials and worker exposure. All the measurement techniques and instruments to assess potential inhalation exposures in facilities that handle or produce engineered nanomaterials are compiled in the nanoparticle emission assessment technique (NEAT) [61]. One of the reports of progress from NIOSH showed the plan to fill the gaps for safe handling of nanotechnology in the workplace [62].

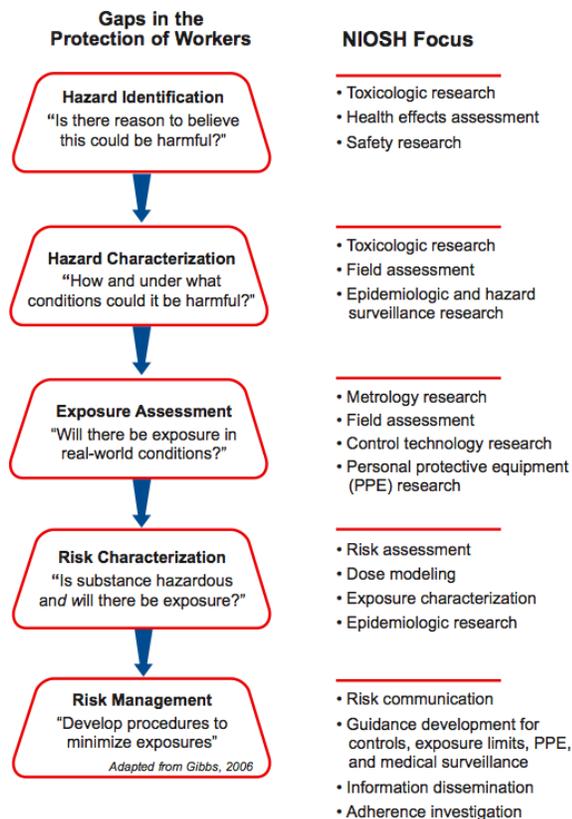


Figure 38. Plan to fill the gaps for safe handling of nanotechnology in the workplace

The Advanced Composites Lab at Texas State University, worried about the exposure of their students and researches to nanoparticles, echoed this information and established internal rules to handle nanoparticles with safety. A nanoparticle containment room (negative-pressure clean room) to be used in manufacturing or scientific research that deals with nanoparticles was built. The room also serves as permanent storage of nanomaterials and contaminated equipment. This room maintains negative pressure and it has a dedicated exhaust. The filters used are ULPA (ultra-low penetration air) filters rated 99.999 percent efficient with particles of 120 nm in diameter. Researchers who would like to use this room must wear gloves, safety glasses, lab coats, and half-mask respirator for which is necessary to pass a pulmonary function test and undergo respirator training. Therefore, only people instructed by the personal are allowed to enter this room.

In addition, Texas State University and the University of Texas at Tyler have received a NSF-NUE (Nanotechnology Undergraduate Education) grant, to develop introductory and advanced curricula that address “nanotechnology safety issues” including social, ethical, environmental, health, and safety. The main objective of this effort is to create awareness in the next generation of engineers and prepare them to deal social, ethical, and environmental issues related to nanotechnology, particularly health and safety issues [63].

As a technology under development, there is still a long way to go to balance the researches between the applications of nanotechnology and the effects and risks of the exposure to nanotechnology, but important initiatives have started to show significant progress in this area.

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