Flammabilty and Mechanical Performance of MWCNT Incorporated Cyante Ester/Carbon Fiber Composites

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ABSTRACT

The exponential growth in composites and their increased use in military, aerospace, energy, and automotive industry is driven by their high performance and light weight. High performance thermosetting polymers such as cyanate ester have received considerable attention due to its ability of volatile-free curing. It also offers advantages such as excellent radiation shielding, high thermal stability, and hydrophobicity with lots of potential for enhanced mechanical strength. This research article discusses the results of effects of multiwalled carbon nanotubes (MWCNT) at predetermined loading levels of 0.5wt%, 1wt% and 1.5wt% on mechanical, thermal and flammability properties of cyanate ester modified carbon fiber composites. The static mechanical tests indicated 1wt% loading level of MWCNT as optimal loading with an improvement of 19% in tensile strength, 22% in flexure strength, 53% in compressive strength. Thermogravimetric analysis studies revealed that MWCNT has negative effect on thermal stability of cyanate ester resin. The flammability properties assessed based on micro combustion calorimetry studies indicated that the final composites possess excellent flammability properties as indicated by the HRR and HRC.

KEYWORDS: *Cyanate ester resin, Carbon nanotube, Compression molding, Microscopy analysis, Mechanical testing, Thermal analysis, Flammability property.*

1. INTRODUCTION

Cyanate esters are a new class of high-temperature resins traditionally associated with aerospace applications, because of their low dielectric properties and extremely low moisture uptake[1]. The resin also possesses high glass transition temperature (Tg, as high as 350°C), excellent flammability properties, and does not

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release harmful volatile (m-PDA, MDA, etc.) during its curing process[2, 3]. Due to these attractive properties, cyanate ester resin is often regarded as exceptional candidate for high temperature applications, replacing cost-restricted thermoplastic polymers. 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[4]. Polyimide, PMR-15 (polymerization of monomer reactant), developed at NASA, is the most common of these thermosetting formulations because 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. Hence, cyanate ester resins are developed as an alternative to high temperature resins. Cyanate esters (CE) can be formulated for variety of manufacturing methods, such as prepreg, resin transfer molding (RTM), filament 4 winding, tow-preg, syntactic core and adhesive forms[5]. The major research set back on utilizing nanofillers to modify the cyanate ester resin is evaluated by various researchers in the past. However, not much improvement in multifunctional properties of the material system could be derived. Hence, nanomodification of cyanate ester to improve multifunctionality of the resin with a suitable nanofiller is still sought as potential research challenge for its applications.

Earlier research involved utilization of nanoclay[6, 7] as potential nanofiller for modifying the cyanate ester resin. Ganguli et al. reported that nanoclay particles largely influence the cure behavior of the cyanate ester resin as evident from their rheology, DSC and FTIR studies. Although, intercalated morphology proceeding towards exfoliation was observed, due to the catalytic effect of the nanoclay in the resin, the attainment of exfoliated morphology was noted to be difficult due to the rapid curing.[2] In the study by Wooster et al..[8], on the effects of nano clays on rheological and mechanical properties of CE resin, it was observed that the nanofillers have a positive effect on mechanical properties.[8] Silicate nanorods in the form of attapulgite nanorods are used as nano-reinforcement at a concentration of 1wt%, 2wt%, 4wt% and 8wt% in CE resin by Pan et al.. The increase in flexural strength and flexural modulus was observed to be 40% and 42% as compared to neat CE resin, indicating positive effect of attapulgite on mechanical properties. The authors reported rapid gelation of CE resin and a reducing glass transition temperature with increased loading levels[9]. John et al.[10] in their study on effects of nanoclay on mechanical and thermal properties of cyanate ester syntactic foams noted enhancement in toughness, storage modulus. Tensile strength enhancement by 63% and 94%, along with increase in flexural strength improvement by 55% and 97% was observed for a loading level of 2wt% and 4wt% nanoclay. The compression property also has seen an increase by 73% and 150%. However, the improvement in the mechanical properties came at a cost of glass transition temperature. The plasticization of the matrix by addition of nanoclay is attributed for hindrance in the glass transition temperature.[10]

Additionally, POSS[11-15], CNT[16, 17], Nanosilica[18] are also studied as potential nanofillers for nanomodification of cyanate ester resin for enhance multifunctionality of the resultant nanocomposites. Among the few who studied CNT nanoparticles modification of cyanate ester resin, Dominguez et al.[16] studied the influence of MWCNT particles (0.01 – 3wt%) on oligomeric cyanate ester resin. From the studies including DMA to study mechanical behavior and TGA to study thermal stability, it was noted that with addition of MWCNT the storage modulus increases. However, at the loading level of 3wt% MWCNT in CE resin, the storage modulus did not observe any enhancement, where as a 10°C increase in glass transition temperature was observed at 3wt% loading level.[16] In another study by Wang et al.[19], where the mechanical and thermal properties were evaluated on MWCNT modified CE resin, it was observed that 2wt% loading level is optimal for enhanced mechanical and thermal properties. Improvement by 41% in impact strength and 50% in flexural strength by addition of functionalized MWCNT is observed at 2wt% loading level and a significant increase in glass transition temperature was noted[19]. Based on the above studies loading levels upto 2wt% of MWCNTs were selected for this study. Although MWCNT modification of polymers results in excellent multifunctional properties due to their high aspect ratios, they possess undeniably strong attractive forces because of their high surface area causing agglomerations[20].

In this research, three loading rates of MWCNT were selected (0–2wt %) in equal parts, assuming that a loading rate exceeding 2wt% will increase the viscosity of cyanate ester to a point where the processing of resin will be lost. Since, the viscosity of CE resin is directly influenced by the temperautre, preliminary studies were conducted in understanding the maximum dimensions of the test laminates, complete wetting of carbon fabric by hand layup before the temperatures decreased to the point that the processability of CE was lost. 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. One-way analysis of variance (ANOVA) was performed to study the effects of independent variables on the final properties of carbon-reinforced CE nanocomposites.

2. EXPERIMENTAL

Materials and Manufacturing

The resin used in this study was a high-performance thermoset cyanate ester (CE) Primaset® PT-15 obtained from Lonza Corporation. The CE resin features a high glass transition temperature of 350°C and has less than 0.5% volatiles. Graphistrength™ C100 multiwalled carbon nanotubes (MWCNT) were obtained from Arkema. The carbon fabric is supplied by TORAYCA® carbon fibers. Zirconate coupling agent Ken-React ® KZ-TPP is used to cure the composite. The manufacturing process for fabricating a fiber-reinforced nanocomposite was divided into four different stages.

Stage 1: Separation of nanoparticles

MWCNT were milled with ceramic balls in the centrifugal planetary mixer to reduce 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 was achieved.

Stage 2: Modifying cyanate ester with MWCNT

Thinky planetary centrifugal mixer is used for the dispersion of MWCNTS into CE resin at required loading levels of 0.5wt%, 1wt% and 1.5wt%. The Thinky mixer revolves and rotates at the same time, providing two high speed centrifugal forces, resulting in efficient mixing. Additionally, vacuum is applied to the mixture which will aid in degassing of the mixture. 3mm diameter ceramics balls were used to improve the quality of dispersion of already separated MWCNT into the resin. The grinding media was then separated before further mixing. The resin was heated from 24°C (room temperature) to 120°C, where the viscosity decreased to ~8cP. This temperature was ideal for handling of the resin, as the resin becomes completely liquid eliminating formation of aggregates. At this point, the CE and the Zirconate coupling agent were mixed for 3 minutes at 2000 rpm in the planetary centrifugal mixer. The cycle was repeated 10 times to complete a total mixing time of 30 minutes. For further mixing using stand mixer, the stand mixer was set at the lowest speed for 1 hour and for 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.

Stage 3: Panel fabrication

The mixture was then placed in the oven, where the temperature was increased to 150°C with a heating rate of 3°C/min. The composites are then fabricated using hand layup method with 12 layers of carbon fabric to achieve a thickness of 2mm. After completely wetting the layered laminate, the panel was placed into the compression press (WABASH, G30H-18-CX) using the curing cycle as shown in Figure 1. The load employed during the cure process using compression press is presented in Table 1. Three panels for each formulation (0%, 0.5%, 1%, and 1.5%) were fabricated. Two different curing cycles for CE resin to avoid phase separation was developed by Lao et al.[21]. In our study curing of panels was achieved by using the coupling agent rather than a catalyst, as it would reduce the curing time, making the mixture more stable and does not have a negative impact on glass transition temperature.

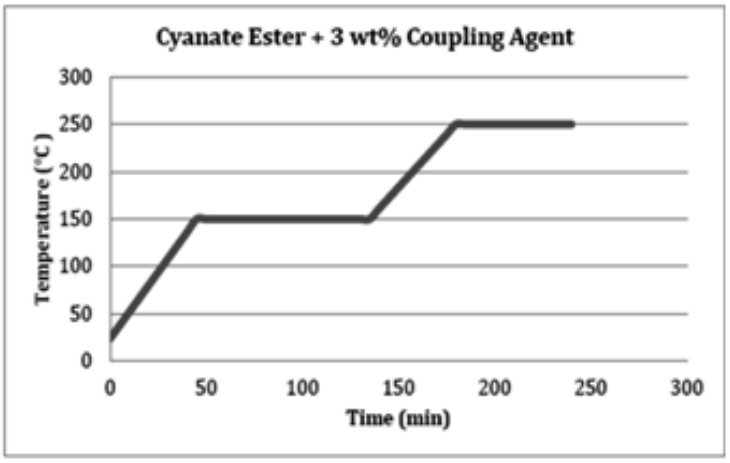


Fig. 1 : Cure cycle for Cyanate Ester using coupling agent

Stage 4: Sample extraction

Samples for tension, short beam shear strength, flexure and compression testing were extracted as per the ASTM standards D3039, D2346, D790 and D6641, respectively. The samples for MCC and TGA according to ASTM standards D7039 and E1131 were extracted. All the samples were extracted using water jet cutting to eliminate edge delaminations which otherwise would hinder the properties.

TABLE 1: Carbon fiber reinforced cyanate ester nanocomposite compression press parameters

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

3. Characterization

3.1 Transmission electron microscopy (TEM)

TEM was employed to study the effect of milling times (15,30 and 45 min) on the entanglement of MWCNT in the CE resin. The nanomodified resin is cured in a gelatin capsule, from which approximately 70nm thin sections were extracted. Upon extraction the sections were transferred onto grids, which were then viewed in JEOL TEM.

3.2 Quality analysis of composites

The quality of composites was determined by evaluating fiber volume fraction, an important parameter which directly affects the load carrying behavior. The fiber volume fraction was calculated using ASTM D2734 density method. Additionally, optical analysis using Nikon MM-880 microscope was performed to observe voids at a macroscopic level.

3.3 Mechanical characterization

The mechanical properties are carried out using MTS 810 hydraulic test system on specimens cut to dimensions at ASTM specified loading rates as provided in Table 2.

3.4 Thermal stability characterization

The thermal stability of the composites was analyzed by Thermogravimetric analysis according to ASTM E1131 on a Shimadzu TGA-50. Two samples in each formulation were analyzed for changes in thermal stability of the composites by heating the sample to 900°C from room temperature at a heating rate of 10°C/min in both air and nitrogen atmosphere. The sample weight ranged from 7 – 10mg.

3.5 Flammability characterization

Microscale combustion calorimetry (MCC) was used to study the flammability characteristics of the formulated

TABLE 2 : Mechanical characterization parameters

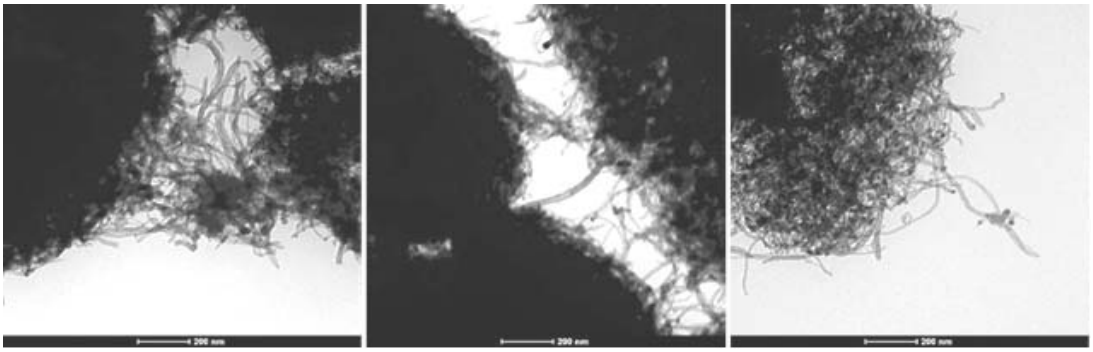
Test	ASTM	Dimensions in mm (L x W x t)	Parameters
Tension	D 3039	254 x 25 x 2	Loading: 2mm/min
Short beam shear strength	D 2344	12 x 4 x 2	Loading: 1mm/min Span: 8mm
Flexure	D 790	64 x 12.7 x 2	Loading: 0.9mm/min Span: 32mm
Compression	D 6641	140 x 12.7 x 2	Loading: 1.3mm/min

composite laminate specimens. The microscale combustion calorimeter MCC-2 from Govmark was developed by Federal Aviation Administration (FCC) to improve research on fire protection safety within aircraft grade materials. The equipment can obtain essential data from very small samples (0.5 to 50mg). Three samples for each formulation were tested according to the standard ASTM D7309.

4. RESULTS AND DISCUSSIONS

4.1 Transmission Electron Microscopy (TEM)

Figure 2 displays TEM images for various milling times (15 min, 30 min, and 45 min) of 1.5wt% MWCNT loading level in CE resin. 45 minutes of milling time of MWCNT exhibited better reduction in entanglement as compared to other milling times. The MWCNT aggregates are visible in the TEM images, indicating that better dispersion techniques are needed for homogenous dispersion. Higher shear forces as offered by three roll mill and high shear mixer or higher energies as offered by horn type ultrasonication may be alternative dispersion processes as they can debundle and reduce the size of aggregates promoting uniform dispersion. MWCNTs that were milled for 45 minutes were pursued to manufacture the panels for mechanical, flammability, and thermal testing, to see their effect on the final composite.



a b c

Figure 2: TEM images of 1.5wt% MWCNT in CE resin for (a) 15 min, (b) 30 min and (c) 45 min of milling time

4.2 Quality analysis of composites

The most widely used method to compute the fiber volume fraction of composites material, because its simplicity is the density method. All the fabricated panels showed no variation during the manufacturing process. The average overall fiber volume fraction was found to be 0.49 ± 0.02. Optical characterization results as indicated in figure 3, showed voids which were a resultant of entrapped air in the final composite. The manufacturing procedure employed in this study due to its open mold nature results in higher volumes of void content. The agglomerates of MWCNTS due to insufficient dispersion might have resulted in the formation of voids. However, from this study there is no evidence to discuss the effects of nanomodification of resin on the void formation. The presence of voids can lead to delamination, high variation on the results and a detrimental effect on the mechanical properties.

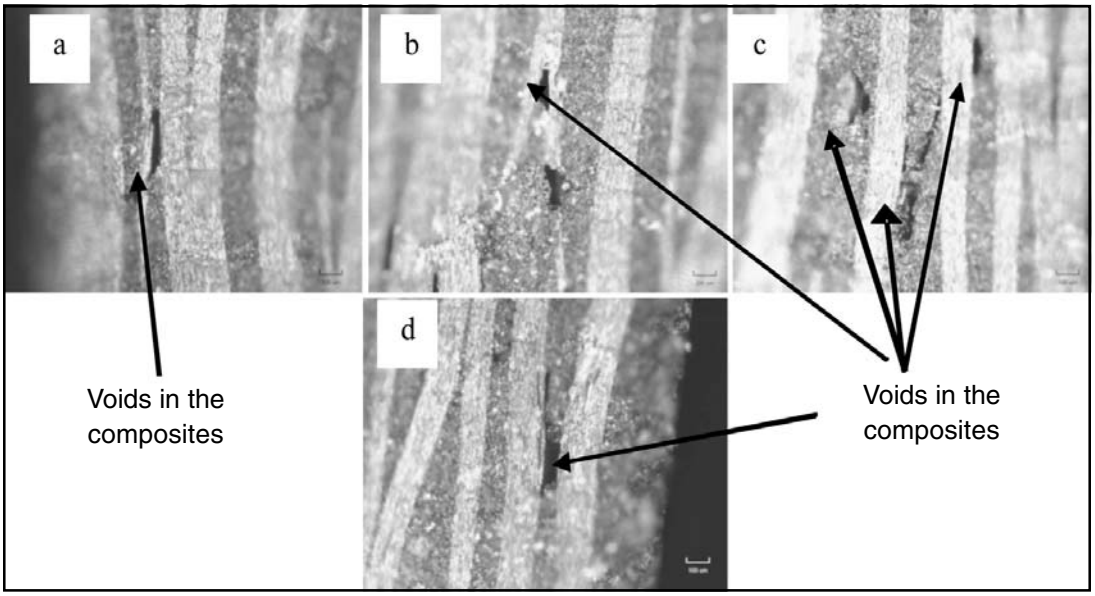


Fig. 3: Microscopic images showing voids in (a) Control (b) CE + 0.5 wt% (c) CE + 1.0wt% and (d) CE + 1.5wt% of MWCNT incorporated carbon fiber composites at a magnification of 100X.

4.3 Mechanical Characterization

4.3.1 Tensile property

Results of tension tests performed in accordance with ASTM D3039 with a loading rate of 2mm/min on five samples in each category are represented in consecutive figures below. The samples were tabbed prior to testing to ensure that the failure takes place in the gauge region instead of the grips to gain better understanding on damage. Figure 4 represents the stress-strain plot variation in the samples under tensile loading. It was observed that nano modification of CE resin with MWCNT had an overall positive effect on the tensile properties.

The effects of MWCNT in CE resin is more readily visible in terms of the ultimate tensile strength (UTS) values as shown in figure 5a. However, these improvements in the values is not exploratory because of the agglomerations as observed due to inefficient dispersion. Nanofillers in the polymer tend to act as crack propogation inhibitors or crack defelctors and efficiently distributes the loading on the composite before failing. The more homogenous distribution of nanofillers contribute to torturous path which delays the cracks from reaching the interface of fiber-matrix. The maximum improvement in UTS is recorded for the 1wt% loading level modified CE composites where in the composite sample survived an average strength value of 1238 MPa as opposed to 1041 MPa of control sample. As the loading level increased to 1.5 wt% the property has seen a decline close to control samples. Carbonaceous nanomaterials due to their highly reactive surface groups tend to pull the adjacent particles. As the percentage of

MWCNT increase in the CE resin, the agglomerates increase in size, promoting stress concentration which causes premature failure before reaching their full potential. Figure 5a illustrâtes the variation in ultimate tensile strength values with the changing loading level of MWCNT. Figure 5b shows tensile modulus values of the four formulations. The tensile modulus is calculated in the elastic region as indicated in the stress-strain plot. In this study, it was observed that 1wt% and 1.5wt% MWCNT modification resulted in inferior property as compared to control samples. An 8% enhancement of tensile modulus property is observed for 0.5wt% loading level MWCNT in CE resin.

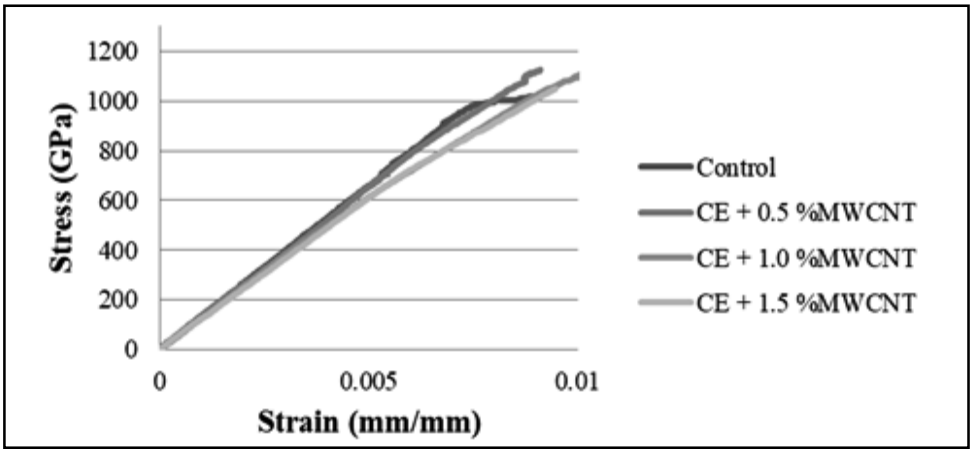


Fig. 4 : Tensile stress-strain plot of carbon fiber reinforced CE nanocomposites

4.3.2 Flexure property

The trend observed in the flexure properties are presented graphically in figure 6. As observed in figure 6, flexure properties increased appreciably with the incorporation of MWCNT, which decreases as the loading level increase to 1.5wt%. However, just as observed for tensile properties, the flexural properties peaked at an MWCNT loading level of 1wt%, indicating that the specified loading level could prove viable in enhancing mechanical properties.

4.3.3 Compression property

Typical compressive stress-strain plots were plotted in figure 7. It was observed that 1wt% and 1.5wt% MWCNT modification of CE resin resulted in enhanced deformation resistance of resultant composites under compressive load. Among the compared composite specimens, 1wt% modification resulted in higher deformation resistance and higher compression load sustaining behavior. Since, the MWCNT nanofillers are not treated prior to dispersion, the increase in the property is mainly related to better adhesion of MWCNT with the chains of CE resin promoting efficient load transfer. The ultimate compressive load values of MWCNT modified CE resin composite specimens is significantly higher as compared to control composites indicating positive reinforcing effects of MWCNT.

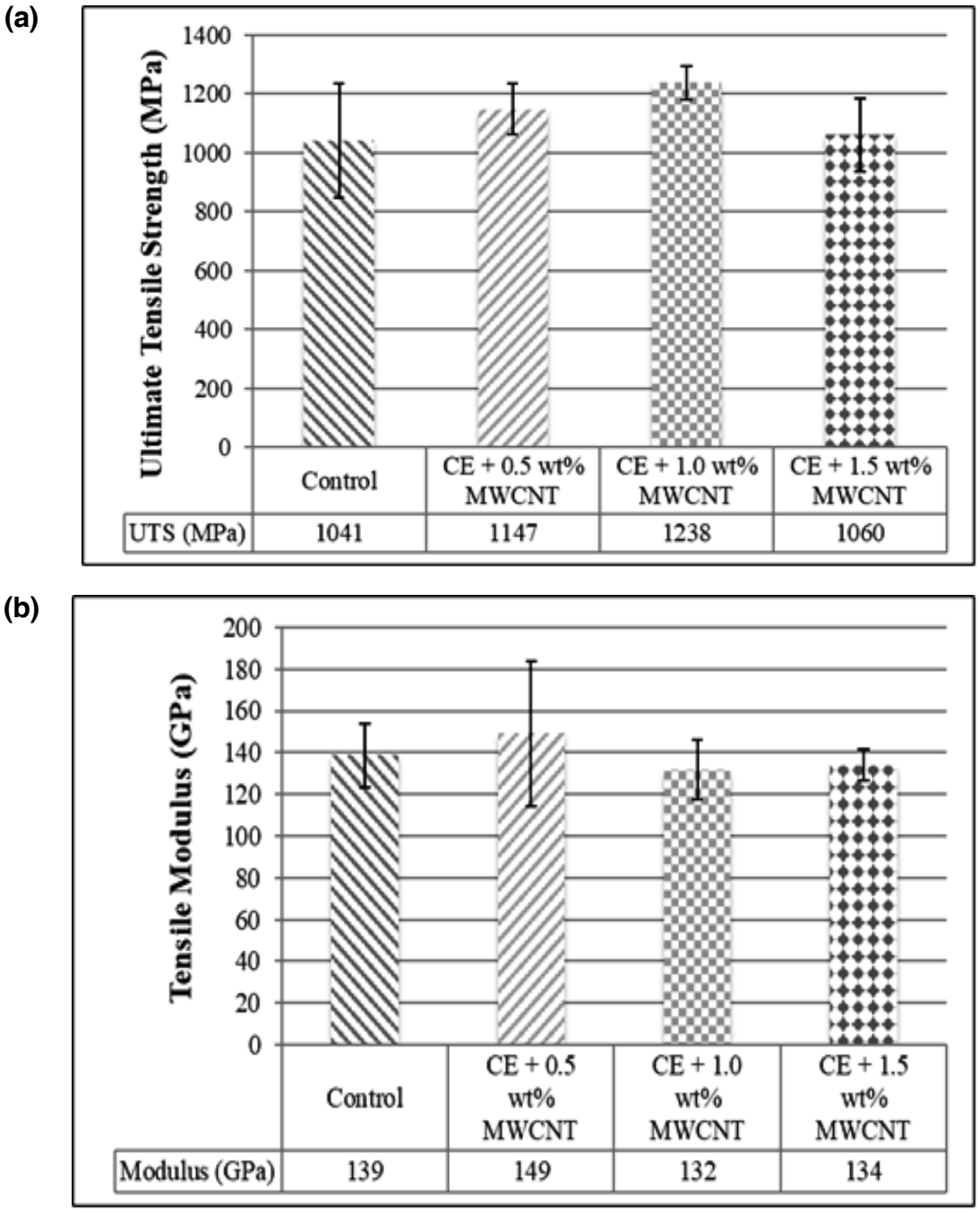


Figure 5 : Carbon fiber reinforced CE nanocomposites (a) Ultimate Tensile Strength, (b) Tensile Modulus

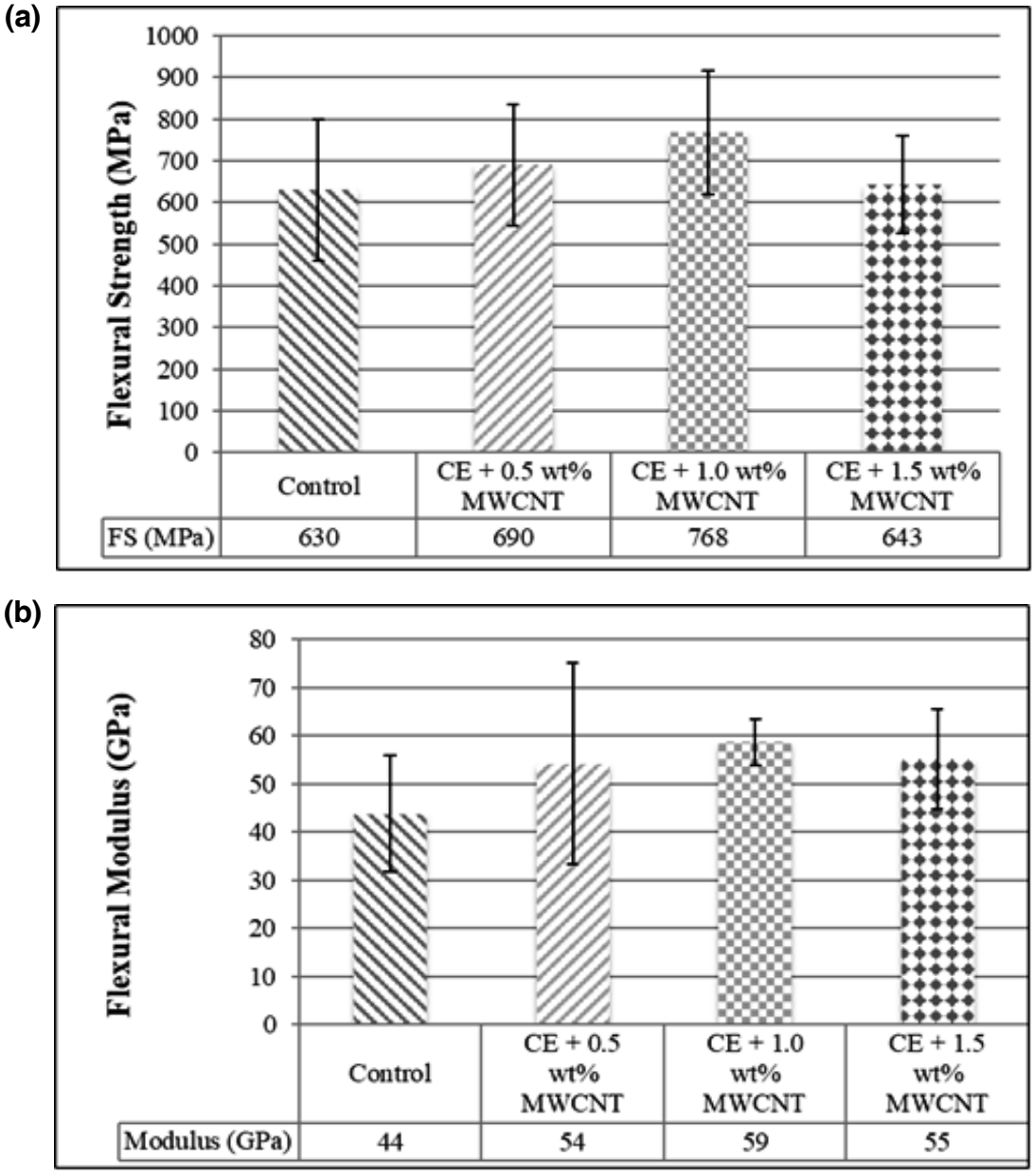


Fig. 6 : Carbon fiber reinforced CE nanocomposites (a) Flexure Strength, (b) Flexure Modulus

The comparative compression strength and compression modulus values of the MWCNT modified composites are shown in figure 8a and figure 8b. The 1wt% MWCNT loaded carbon fiber reinforced cyanate ester resin nanocomposites outperformed all the other

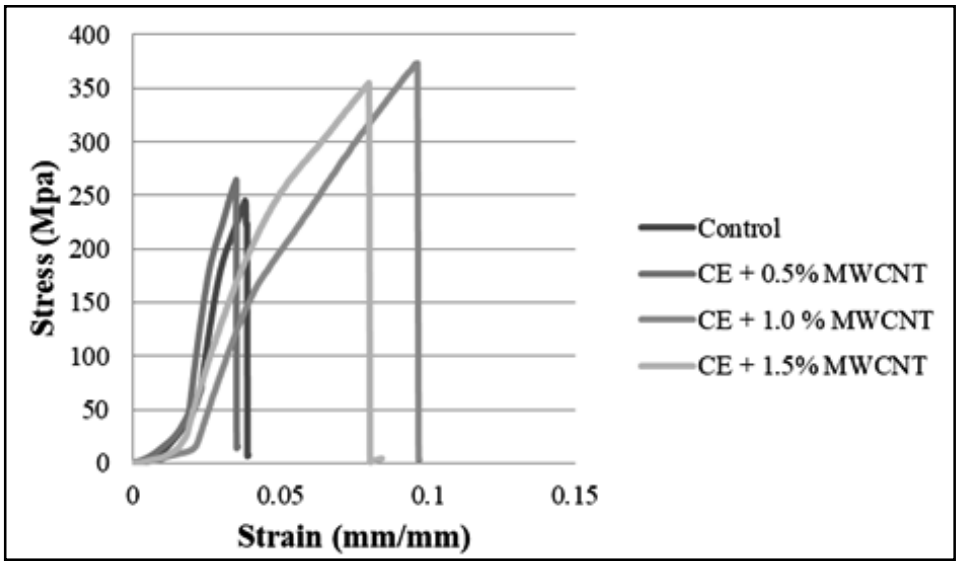


Fig. 7 : Compressive stress-strain plot of carbon fiber reinforced CE nanocomposites

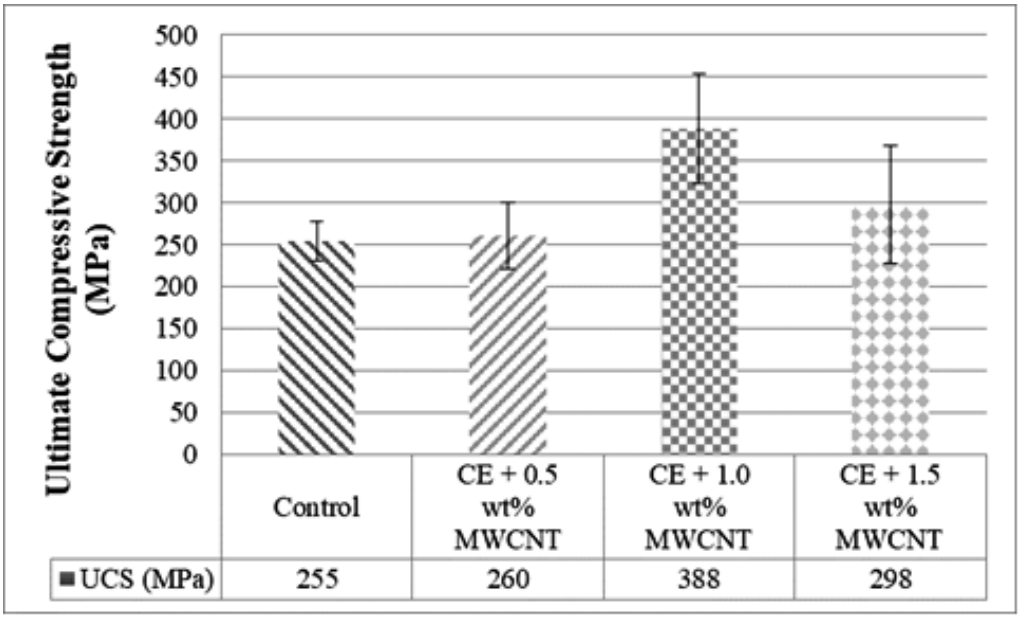
material systems with an enhancement in compression strength by 52.1% and compression modulus by 60.3%.

4.3.4 Short beam shear property

The short beam shear strength property of the laminated composite materials gives the interlaminar shear stress between individual layers of the laminate. Composite laminates due to their layered structure typically encounter delamination failure reducing the efficiency in stress transfer between the layers. The consequence would be reduced strengths and premature failure of the composite laminates under loading. The test employs a typical three-point flexure test setup and is a qualitative measure of interlaminar shear strength for quality control evaluation.

Figure 9a, gives the typical stress-strain plot of the short beam shear strength. In a short beam shear test damage evaluation, the failure modes might involve local crushing at the point of loading or flexural failure, making it too difficult to assess the damage initiation. Thus, a stress-strain plot and peak load data are most viable approach to evaluate the interlaminar shear strength of the composite. As observed from the figure 9a, there is large variation in stress-strain plot which would not be sufficient to evaluate the resistance to interlaminar shear. From figure 9b, it can be observed that there is significant reduction in the 1wt% and 1.5wt% MWCNT modified composites indicating that the presence of aggregates might not have been efficient in crack deflection. As opposed to other mechanical properties, 0.5wt% MWCNT modified composites showed good short beam shear strength. The presence of less amounts of nanofillers promoted good bonding of the nanofiller + CE resin + carbon fibers, thus positively contributing to enhanced stress values.

(a)



(b)

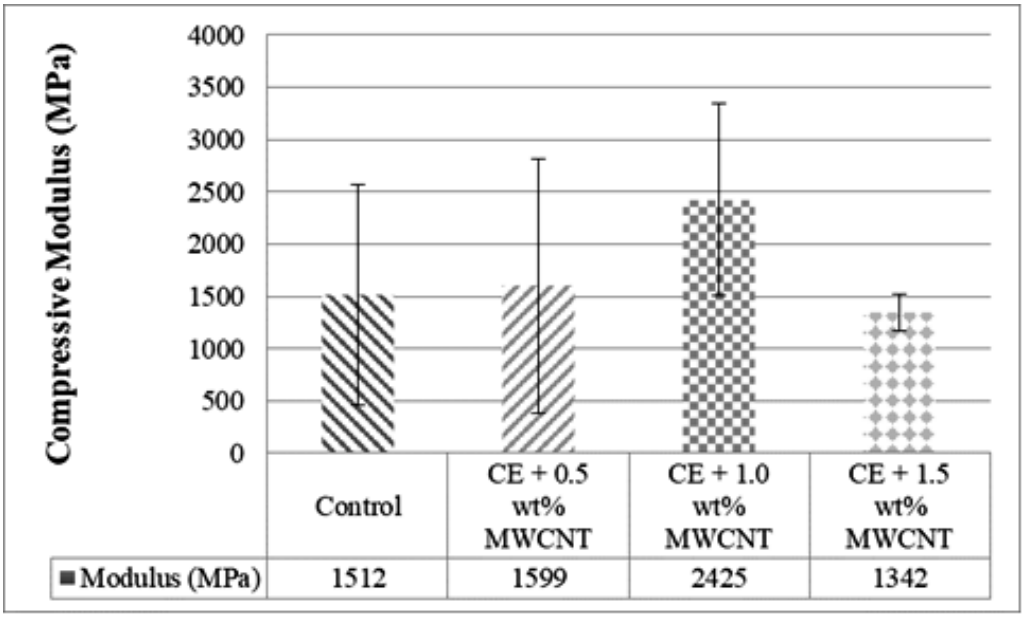
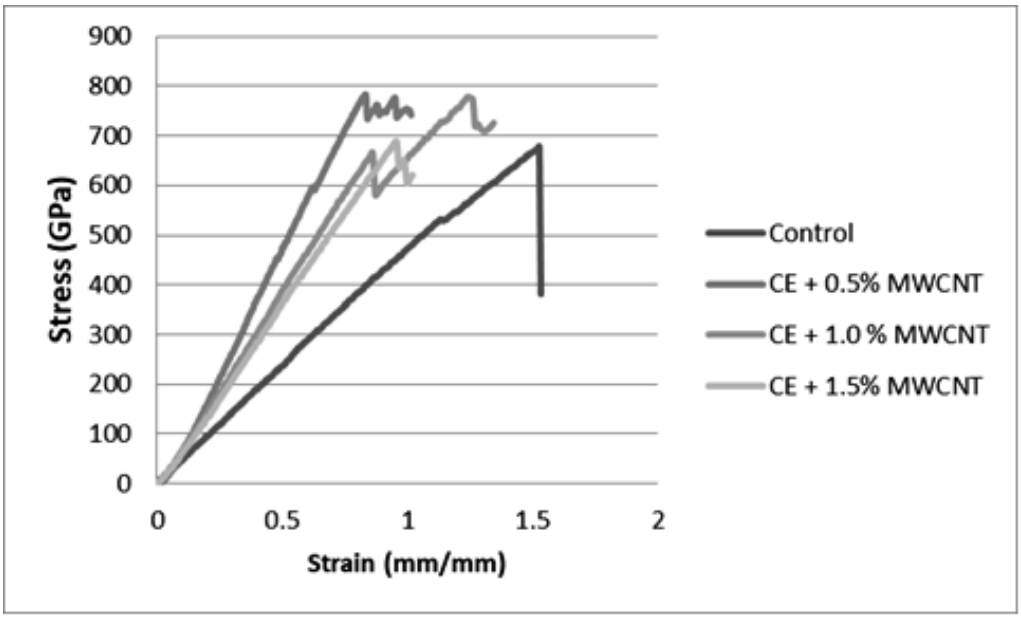


Fig. 8 : Carbon fiber reinforced CE nanocomposites (a) Compressive Strength, (b) Compressive Modulus

(a)



(b)

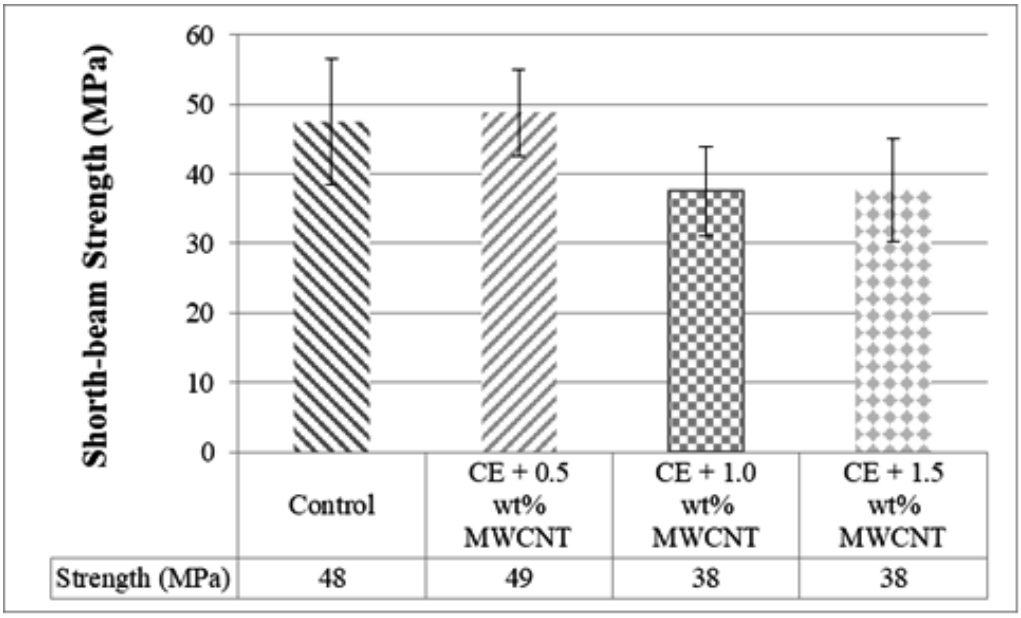


Fig. 9 : Carbon fiber reinforced CE nanocomposites (a) Short Beam Shear stress-strain plot, (b) Short Beam Shear Strength

4.4 Flammability characterization

4.4.1 Microscale combustion calorimetry (MCC)

Flammability of polymers and composites are mainly evaluated through ignitability, flame spread and heat release. When aiming for high temperature applications, polymeric composites typically need to meet certain large scale flammability performance requirements. Microscale combustion calorimetry employed for the flammability characterization in this study typically need a sample size of 2-10mg and can give us variety of information such as heat release rate, peak pyrolysis temperature, heat of combustion, ignition and combustion temperature.

The flammability properties of the resultant carbon fiber reinforced MWCNT cyanate ester nanocomposites were evaluated using microscale combustion calorimetry (MCC) on three samples of each formulation according to ASTM D7309 standard. The samples were pyrolyzed in nitrogen atmosphere from 75°C to 900°C and the resulting gaseous particles were combusted in air at 950°C. The heat release rates (HRR) for the formulations are presented in figure 10. Additional information of peak heat release rate (PHRR) and total heat release for the formulations is presented in Table 3. The samples modified with 0.5wt% and 1wt% MWCNT observed higher HRR than the control specimens. Increase in loading level of MWCNT upto 1.5wt% showed a drastical decrease in HRR. However, the peak temperature at which the heat release rate peaks remained the same. As observed from the HRR plot in figure 10, there is an initial delay in the heat release rate indicating the materials temperature is below pyrolysis temperature of the matrix. The initial delay period of MWCNT modified composites is less as expected indicating the effectivness of MWCNT in delaying the time to reach pyrolysis temperatures. Once after reaching the peak HRR, there is a sharp decline in the curve which might be due to the formation of char layer effectively decreasing decomposition rate of subsequent layers. The progressive decline in the reaction rate is also effected by the resin content in the composites and in our study, it was observed that MWCNT modification has subsequently reduced decomposition of resin, making the resin available to further reduce combustion rate.

4.5 Thermal characterization

4.5.1 Thermogravimetric analysis

In order to assess the thermal decomposition behavior of the formulated composite materials, thermogravimetric analysis was performed in inert nitrogen and air atmosphere. The degradation of a polymer in a fiber reinforced polymer composites is a combination of thermal and chemical degradation mechanisms.[22] In an actual environment in this case air, the test generally give an understanding of the oxidative degradation and thermal resistance in case of char layer formed during combustion. Inert atmosphere thermal analysis is carried out inorder to eliminate the unwanted oxidative reactions which could hinder better understanding of polymer degradation. Figure 11a and 11b, shows the behavior of the samples tested in air and nitrogen atmosphere respectively. Table 4 displays the resulting 10% mass loss temperatures extracted from the plot of samples tested in air and nitrogen

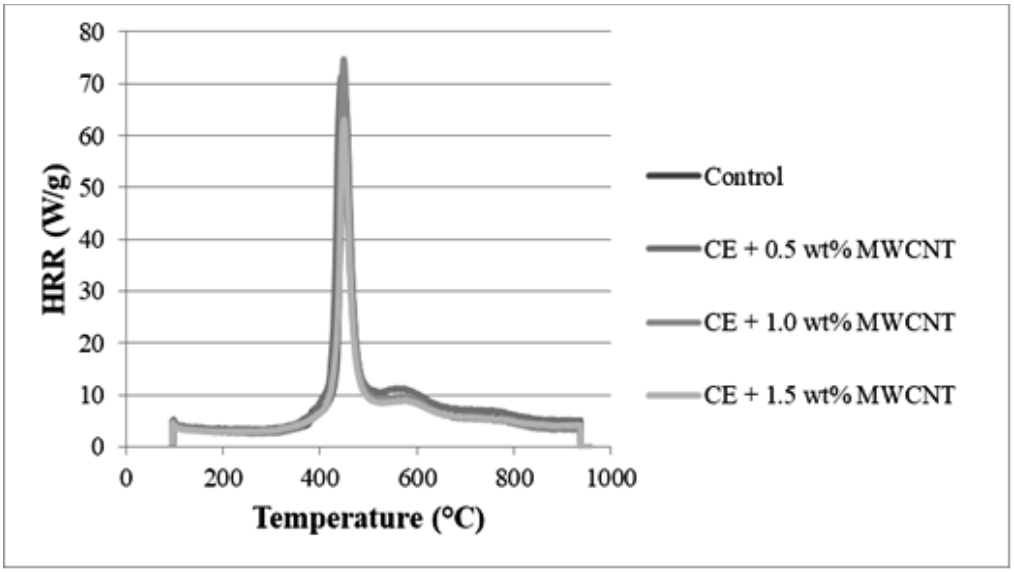


Figure 10 : Carbon fiber reinforced CE nanocomposites Heat Release Rates (HRR)

TABLE 3: Parameters from MCC testing on carbon fiber reinforced cyanate ester nano composites.

Formulation	HR capacity	Peak HRR	Total HR (L x W x T)	Temperature
	J/g-K	W/g	kJ/g	C
Control	43.67	63.8	2.27	450.17
0.5wt% MWCNT-CE/CF	47.00	69.36	2.43	446.67
1wt% MWCNT-CE/CF	49.33	72.73	2.53	447.43
1.5wt% MWCNT-CE/CF	40.67	59.56	2.17	448.33

atmosphere respectively. The first stage of decomposition in a TGA plot while assessing the thermal stability properties on a composite material, can be attributed to the degradation of matrix and the second stage to the combined decomposition of matrix and fiber.[23] In this study, 10wt% mass loss is considered for analysis to assess the effects of MWCNT in the cyanate ester resin on the thermal stability of the resultant composites.

As observed in figure 11a, where the TGA analysis is conducted in air atmosphere, there are two decomposition steps, the first one occuring at ~ 380°C – 450°C and the second at ~ 500°C – 925°C. The first step is typically associated with the weight loss due to decomposition of residual volatiles. The second step is typical due to the oxidation reaction happening and the decomposition is a result of the burning of composites in the presence of oxygen in air, which is a result of homolytic cleavage of backbone of the polymer. As observed from $T_{10\%}$ for the formulation in air, MWCNT have a negative effect on the thermal

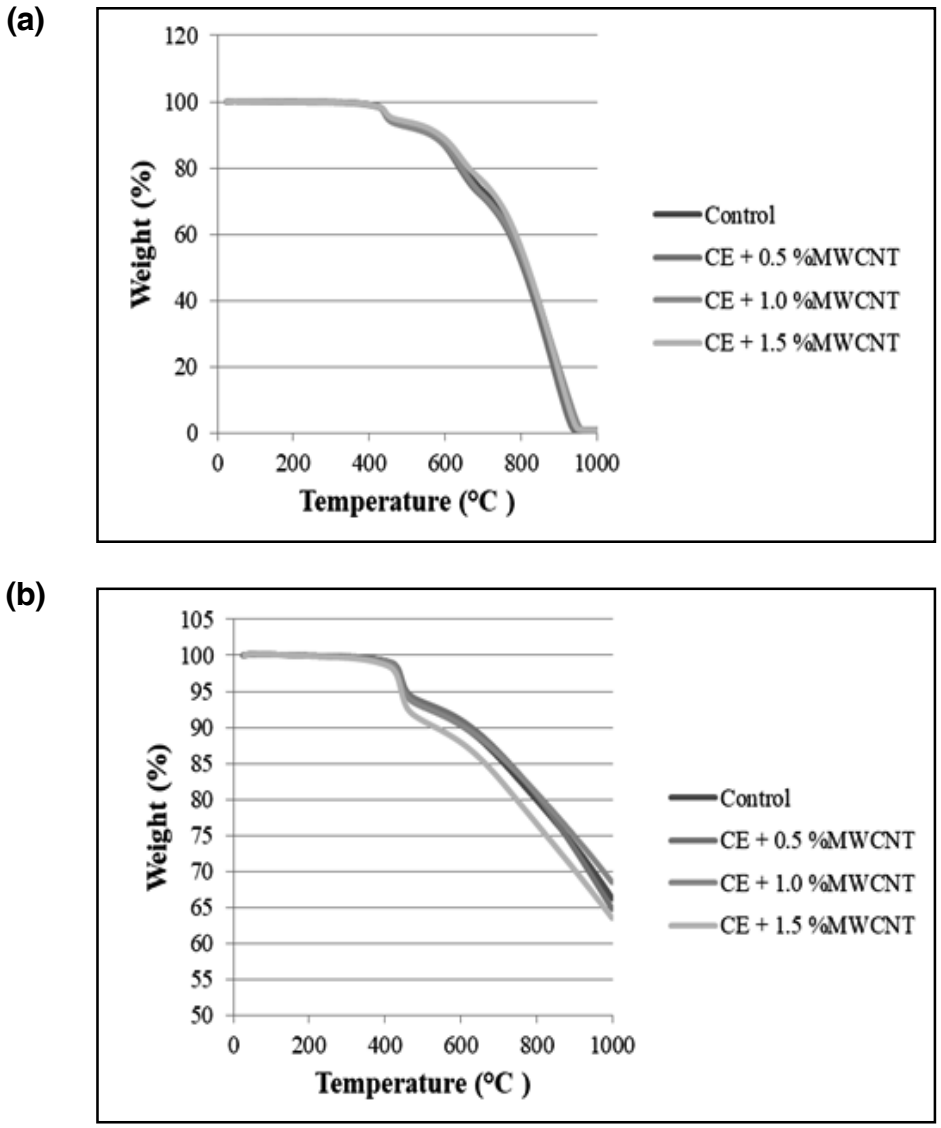


Fig. 11 : Carbon fiber reinforced CE nanocomposites (a) TGA plot in air atmosphere, (b) TGA plot in Nitrogen atmosphere

stability. However, at 1.5wt% MWCNT loading, the decomposition temperature at 10% mass loss was increased by 15°C. The presence of more amount of MWCNT, restricts the movement of the chains of the polymer thus by allowing more heat to be absorbed before the degradation occurs.

Contrast to the results in air atmosphere, TGA analysis of composites conducted in nitrogen atmosphere showed a single step

TABLE 4 : Carbon fiber reinforced CE nanocomposites : properties extracted from TGA plots

Formulation	10% mass loss in air		10% mass loss in nitrogen	
	$T_{10\%}$ (°C)	Δ (%)	$T_{10\%}$ (°C)	Δ (%)
Control	571.03	-	609.98	-
0.5wt% MWCNT-CE/CF	564.64	-1.12	629.10	3.13
1wt% MWCNT-CE/CF	563.35	-1.35	610.31	0.05
1.5wt% MWCNT-CE/CF	586.55	2.72	534.43	-12.39

decomposition as shown in figure 11b. In the absence of oxygen, the chemical decomposition is a result of the pyrolysis. The major decomposition step as indicated at ~ 400°C – 500°C is a result of the decomposition of residual volatiles and the decomposition after that is observed to be continuous. The composite thermal decomposition did not stabilize even at 1000°C, indicating increase in greater char yields. This behavior is typical to carbon fiber degradation in nitrogen atmosphere where in a protective layer of char is formed which retards further decomposition. When compared for 10wt% mass loss of MWCNT modified composites to the control composites, 0.5wt% MWCNT-CE/CF the thermal stability temperature increased by 20°C approximately, indicating positive effects of MWCNT. At further loading levels, there was no improvement in the thermal stability. At 1.5wt% loading level, a sharp decrease was observed, which might be due to dispersion defects.

4.6 Analysis of variance (ANOVA)

The primary goal of this research is to evaluate the effectiveness of the MWCNT at three different loading levels on the flammability properties of the cyanate ester carbon fiber composites without comprimising mechanical properties. In order to evaluate the siginificance of the result, on-way ANOVA was performed with a 95% confidence level. The difference between the mean values are statistically significant if p-value is below 0.05. The one-way ANOVA parameters calculated and collected for mechanical properties and flammability properties are represented in Table 5 and Table 6 respectively. The ' F' value in the Table represents the ratio of two mean squares and in general the value should be closer to 1.0 most of the time. A larger F value mean that there is lot of variance in the test data. The p values are calculated from the F ratio.

As observed from Table 5, analysis of variance shows that the mechanical properties of the composites at varying loading levels of MWCNTs are statistically insignificant. When considering nanofillers in the resin system it is obvious that many parameters including the dispersion, processability, change in physical properties and chemical properties play a crucial role in determining consistency. As observed from various results of tests in this study, including agglomerates formed during dispersion process might have resulted in not significant values. The flammability properties evaluated and ANOVA results tabulated in Table 6 showed that these results are statistically significant. However, the probability to obtain a significant difference by modifying CE with

TABLE 5 : One-way ANOVA of mechanical properties of CE-CF nanocomposites

	F	F_{crit}	p-value	Recommendation
Tensile Strength	2.59972	3.15991	0.08393	Reject
Tensile Modulus	0.73075	3.15991	0.54701	Reject
Flexural Strength	0.96572	3.19678	0.43163	Reject
Flexural Modulus	1.25870	3.19678	0.31995	Reject
Compressive Strength	7.48475	3.34389	0.00315	Accept
Compressive Modulus	0.22695	3.34389	0.87607	Reject
Short Beam Strength	3.09929	3.41053	0.06396	Reject

TABLE 6 : One-way ANOVA of flammability properties of CE-CF nanocomposites

	F	F_{crit}	p-value	Recommendation
Heat Release Rate	9.29538	4.06618	0.00551	Accept
Heat Release Capacity	3.98077	3.86255	0.04652	Accept

various loads of MWCNT is low. IN consequence, it can be considered that there is no enough evidence to affirm an effect of MWCNTs in the composite.

5. CONCLUSION

Carbon fiber reinforced cyanate ester nanocomposites modified with 0.5wt%, 1.0wt% and 1.5wt% MWCNTs, were characterized for their mechanical and flammability properties in this research. A fiber volume fraction of 49±0.02 was found for all panels, which reveals good precision within the manufacturing process. Tension, flexure, compression, and short-beam tests were performed to evaluate the behavior of carbon fiber reinforced cyanate ester nanocomposites under mechanical loading. The thermal stability was evaluated by running TGA in an atmosphere of air, and nitrogen. The flammability of the carbon fiber-reinforced cyanate ester composite was evaluated with MCC analysis.

- Overall, an improvement of the mechanical properties was observed for the nanomodified formulations when compared with the control samples. 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 as évident from experimental data.
- 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.
- 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.
- The compressive strength improved by 3, 53, and 17% for weight loading rates of 0.5, 1.0 and 1.5%, respectively.

- Short Beam Shear Strength property 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. 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.
- The results for TGA in air showed a variation of ± 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 ±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 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.

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