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Online Publication Date: 20 Sep 2019

URL: <http://www.jresm.org/archive/resm2019.137ma0702.html>

DOI: <http://dx.doi.org/10.17515/resm2019.137ma0702>

Journal Abbreviation: *Res. Eng. Struct. Mater.*

### To cite this article

Demircan O. Compression after impact properties of glass fiber/epoxy/MWCNT composites. *Res. Eng. Struct. Mater.*, 2020; 6(1): 53-62.

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Research Article

## Compression after impact properties of glass fiber/epoxy/MWCNT composites

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### Article Info

#### Article history:

Received 02 Jul 2019

Revised 13 Sep 2019

Accepted 16 Sep 2019

#### Keywords:

Carbon nanotubes;  
Thermosets  
composites;  
Compression after  
impact;  
Charpy impact  
properties

### Abstract

Glass fiber/epoxy resin/multi-walled carbon nanotubes (MWCNTs) were used to fabricate the nano materials integrated thermoset composite materials in this study. Thermoset composites with and without nano materials were fabricated using resin transfer molding (RTM) methods. The fabricated samples were tested with compression after impact and charpy impact tests. The samples with MWCNTs demonstrated the best improvement of the compression after impact modulus and strength with 31% and 5.6% compared to the samples without carbon nanotubes. The nano materials integrated specimens showed 10.2% improvement of charpy impact strength against specimens without carbon nanotubes in 90° degree direction. Due to the existing of the carbon nanotubes between fiber and polymer matrix was the reason of the improvement of the mechanical properties of carbon nanotubes integrated composites.

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## 1. Introduction

The using of thermoplastics and thermosets polymeric composite materials were considerably developed in recent years. Nano materials can be used as an assistant factor for strengthening of the composites. Carbon nanotubes (CNTs) have superior properties such as, strength and stiffness, with high aspect ratio. Because of unique properties of CNTs (such as Young's modulus of ca. 1 TPa and tensile strength of ca. 200 GPa), CNTs has become an ideal candidate for polymer reinforcement [1].

In the literature, some studies were done about the mechanical properties of CNT modified laminates [2-6]. Flexural properties of glass fiber/epoxy/MWCNT composites were investigated by Demircan et al [2]. In their study, MWCNTs integrated specimens showed the best improvement of the flexural modulus and strength with 19% and 7% compared to the samples without MWCNTs. Bilisik et al. [3] studied short beam shear of nanoprepreg/nanostitched three dimensional carbon/epoxy multiwall carbon nanotubes composites. They found that stitching and MWCNTs addition enhanced the short-beam strength of the composites. Bilisik et al. [4] studied mechanical properties of plain para-aramid/phenolic multiwall carbon nanotubes prepreg/multistitched preform composites. In their study, the fracture toughness (GIC) of the stitching and nanostitched composites showed 42 fold and 41 fold (beam theory), 18 fold and 21 fold (modified beam theory) increased compared to the control. Preparation and mechanical properties of carbon

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DOI: <http://dx.doi.org/10.17515/resm2019.137ma0702>

Res. Eng. Struct. Mat. Vol. 6 Iss. 1 (2020) 53-62

nanotube grafted glass fabric/epoxy multi-scale composites were investigated by Eskizeybek et al [5]. Tensile tests were conducted on fabricated multi-scale composites, indicating the grafting CNTs on glass fabric resulted a decrease (11%) in ultimate tensile strength while toughness of the multi-scale composite laminates were increased up to 57%. Mode I interlaminar fracture toughness of chemically carbon nanotube grafted glass fabric/epoxy multi-scale composite structures were investigated by Eskizeybek et al [6]. Grafting CNTs onto PWGFs improved both initial and steady-state toughness more than double as measured by Mode I interlaminar fracture testing.

In the literature, some articles were found addressing the compression-after-impact (CAI) properties of CNT modified laminates [7-11]. Mannov et al. [7] studied improvement of compressive strength after impact in fibre reinforced polymer composites by matrix modification with thermally reduced graphene oxide. They significantly improved residual compressive properties of the laminates for the modified specimen, with the glass fibre laminates showing the highest improvement of 55% when compared to unmodified specimens. Gorbatikh et al. [8] studied impact and residual after impact properties of carbon fiber/epoxy composites modified with carbon nanotubes. They showed that CNTs network had a positive influence on the properties of the composites. Ye et al. [9] reviewed interlaminar fracture toughness and CAI strength of fibre-reinforced composites with nanoparticles. They reviewed that nanoparticles as additional reinforcing phases in fibre-reinforced polymer (FRP) laminates (especially with brittle thermosetting resins) can enhance interlaminar fracture toughness and CAI strength.

In the literature, few articles were found addressing the charpy impact properties of CNT modified laminates [12-13]. Sharma et al. [12] reported impact behavior and fractographic study of carbon nanotubes grafted carbon fiber-reinforced epoxy matrix multi-scale hybrid composites. In this study, CNTs grafted carbon fiber epoxy composites showed 48.7% and 42.2% higher energy absorption compared to reference composites in charpy and izod impact tests. Structural composites hybridized with epoxy compatible polymer/MWCNTs nanofibrous interlayers was studied by Papila et al. [13]. They found that interlayered charpy impact specimens absorbed 20% more energy than the non-interlayered ones.

In the literature, it was found some researchers who they coated the surface of the reinforcements using nano materials. Lagoudas et al. [14] studied effect of carbon nanotubes on the interfacial shear strength of T650 carbon fiber in an epoxy matrix. Their results of the single-fiber fragmentation tests indicated an improvement in interfacial shear strength with the addition of a nanotube coating. Kim et al. [15] studied tensile strength of glass fibers with carbon nanotube-epoxy nanocomposite coating. They found that a more uniform strength distribution and higher strengths of the rovings impregnated with the CNT nanocomposite than those impregnated with the neat epoxy. The effect of adding carbon nanotubes to glass/epoxy composites in the fibre sizing and/or the matrix was reported by Godara et al. [16]. They found that an increasing in resistance of crack initiation fracture toughness by +10% by the presence of CNTs in the sizing, but a lowering in crack propagation toughness of -53%. Interfacial shear strength of a glass fiber/epoxy bonding in composites modified with carbon nanotubes was reported by Gorbatikh et al. [17]. The results of their tests revealed that an increase of interfacial shear strength (IFSS) in specimens.

Wang et al. [18] studied an effective surface modification of carbon fiber (CF) for improving the interfacial adhesion of polypropylene (PP) composites. They significantly enhanced the mechanical performance of PP composites with 0–30 wt. % CFs by CF surface treatment in combination with maleic anhydride grafted PP (MAPP) modification. Demircan et al. [19] investigated the effect of CNTs on the mechanical properties of

LPET/glass fiber thermoplastic composites. They found about 7% and 33% in tensile and flexural modulus and about 3% and 65% in tensile and flexural strength of composites by using carbon nanotubes in the fiber sizing.

In the literature, to the best of the authors' knowledge, it was found no research about the compression after impact and charpy impact properties of the glass fiber/epoxy resin/MWCNTs integrated thermoset composites reinforced with the biaxial warp-knitted fabrics. The purpose of this research was to study the effect of the nano material incorporation on the CAI and charpy impact properties of the thermoset composites. The CAI and charpy impact properties of 0.0 wt% and 0.4 wt% MWCNTs incorporated specimens were investigated. In order to design of the new thermoset composite materials, the results from our research can be used.

## 2. Experimental procedure

### 2.1. Constituents of Thermoset Composites

In order to fabricate nano materials integrated thermoset composites, the non-crimp fabrics (NCF) with glass fibers (Metyx Composites Ltd., Turkey), epoxy resin (DTE 1200, Duratek, Turkey) and hardener (DTS 1155, Duratek, Turkey) were used. The properties of the NCF are shown in Table 1.

Table 1 Properties of non-crimp fabric (NCF) of composites

E glass samples	Biaxial yarn 0° (warp) fibers, tex	Biaxial yarn 90° (weft) fibers, tex	Area weight of 0° warp fibers (g/m <sup>2</sup> )	Area weight of 90° weft fibers (g/m <sup>2</sup> )	Fabric weight (warp, weft and binding fibers) (g/m <sup>2</sup> )
LT1200E 05B 0/90	2400	1200	566	614	1187

The carbon nanotubes were supplied from Ege Nanotek Kimya Sanayi Limited Sirketi, Izmir, TURKEY. The properties of the MWCNTs were demonstrated in Table 2.

Table 2 Properties of MWCNTs

Parameter	Value
Outer diameter (nm)	10-20
Interior diameter (nm)	5-10
Length (µm)	10-30
Surface area (m <sup>2</sup> /g)	>200
Color	black
Electrical conductivity (S/cm)	>100
Density (tap) (g/cm <sup>3</sup> )	0.28
Density (true) (g/cm <sup>3</sup> )	2.1

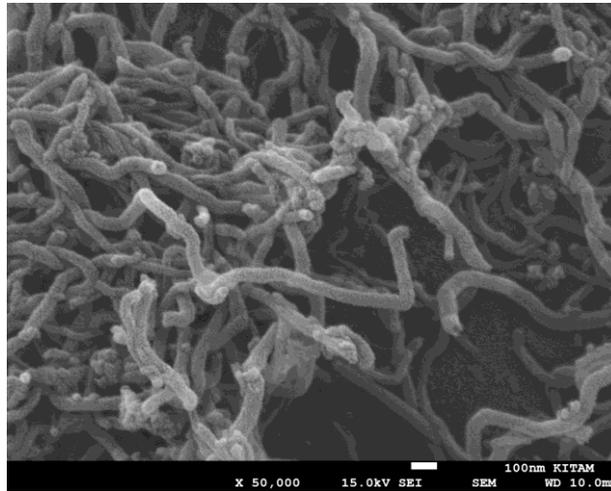


Fig. 1 SEM images of MWCNTs

## 2.2. Fabrication Method of Thermoset Composites

In order to fabricate the thermoset composites with nano materials, the resin transfer method (RTM) was chosen to manufacture four layers biaxial warp-knitted (BWK) reinforced composites plates as shown in Figure 2.

At first ethanol and MWCNTs solutions were prepared to coat each faces of the NCFs. MWCNTs were dispersed in ethanol using a magnetic stirrer device. After that the solution of MWCNTs and ethanol were stayed in an ultrasonic bath. Later, each faces of the NCFs were coated using of the solution of MWCNTs and ethanol. After coating of the NCF with the MWCNTs solution, the specimens were left for two days in the room temperature to evaporate of the ethanol. Then, MWCNTs coated four layers fabrics were laid in mold cavity in a symmetrical stacking sequence  $[(90_{wa}/0_{we}/90_{wa}/0_{we})_s]$  of the RTM system (Figure 3).



Fig. 2 The RTM apparatus

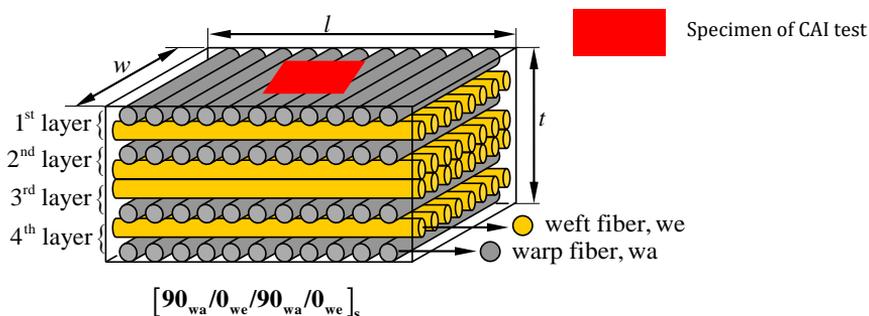


Fig. 3 Schematic drawing of the thermoset composites. Here, l: length, w: width and t: thickness of the fabricated composite plate

Table 3 Fiber volume fraction and thickness of fabricated composites

Composites	Weft Vf (%)	Warp Vf (%)	Binding Vf (%)	Total (warp, weft and binding) Vf (%)	Thickness (mm)
0.0 wt % MWCNT	17.4	16.1	0.66	34.2	5.4
0.4 wt % MWCNT	16.8	18.2	0.28	35.3	5.0

### 2.3. Characterization of Thermoset Composites

Zwick Roell Z250 KN Universal test equipment was used for both low velocity drop weight impact and CAI tests. The weight and diameter of the impactor was 6490 g and 12.9-mm. After completing the low energy impacts tests with 43 J, the damaged samples were used for the CAI tests. Impactor was able to damage the surface of the composite plate at 43 J. Therefore, 43 J impact energy level was chosen. The CAI tests were conducted on specimens with constant displacement of 0.5 mm/min. A 250 kN unit cell was used in the CAI tests. The CAI tests were performed on specimens using EN 6038 test standard. Three specimens were tested in the CAI tests. In the CAI tests, the specimens were placed in an anti-buckling jig where both loaded edges were fully clamped. In order to prevent global buckling the sides were simply supported in the CAI tests. The sample dimensions were: 150 mm in length, 100 mm in width and 5.0-5.4 mm in thickness in the compression after impact tests.

Charpy impact tests were performed in accordance with the ISO 179 testing standards with an impact hammer of 5 J energy capacity. In the charpy impact tests, three specimens were tested in the 90° directions for each type of the composite panels. The sample dimensions were: 90 mm in length, 15 mm in width and 5.0-5.4 mm in thickness in the charpy impact tests.

### 3. Results and Discussion

The surface morphologies of glass fibers after grafting CNTs are investigated via SEM as shown in Figure 4. The glass fiber surface was fairly grafted by CNTs but non-grafted regions were also observed (Figure 4a). According to this observation, the carbon nanotube grafting process forms of CNT inlets on the glass fiber surfaces. The high magnification SEM image of the individual CNT grafted glass fiber is shown in Figure 4b. The grafted CNTs on the fiber surface exhibit randomly oriented with non-uniform dispersion and fairly agglomerated areas were also observed.

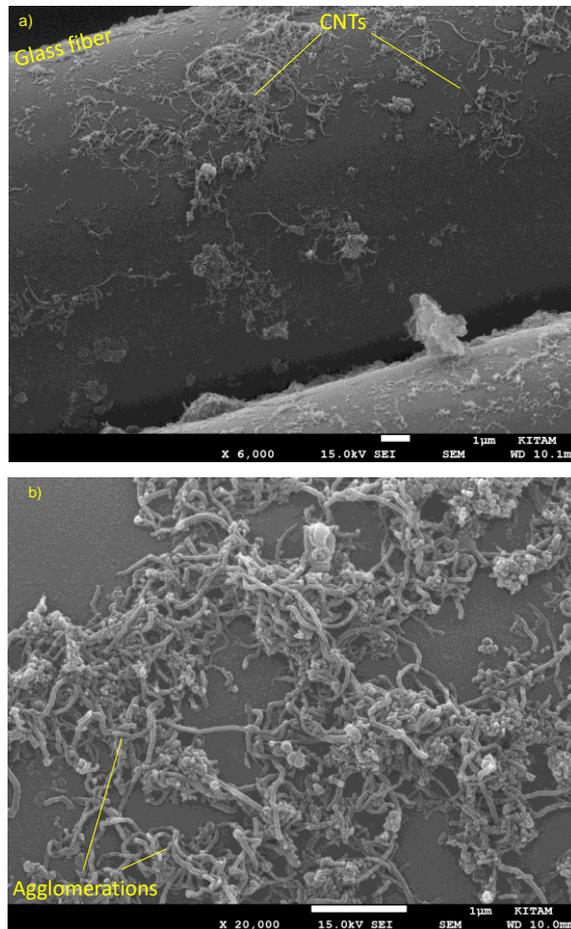


Fig. 4 SEM images of surface morphologies of glass fibers after grafting CNTs

Figure 5, 6 a and b represent the results of the CAI stress-strain curves and modulus and strength of the specimens of the thermoset composites with 0 wt% and 0.4 wt% MWCNTs. The CAI modulus and strength of the specimens with 0 wt% and 0.4 wt% MWCNTs were 0.55 GPa and 177.6 MPa and 0.80 GPa and 188.3 MPa. The CAI modulus and strength of the specimens with 0.4 wt% MWCNTs were 31% and 5.6% higher compared to the 0.0 wt% MWCNTs.

The RTM fabrication process of the composite laminates includes the post-curing step at 80 °C and this step could induce the formation of chemical bonds between functional groups on the MWCNTs and the glass fiber surfaces. The possible reason for the obtaining the improved CAI properties for the specimens incorporated with the MWCNTs was the synergy between fiber and matrix, which was created by the MWCNTs in the composite material. Since the CNTs having superior mechanical properties with large surface area, they improve mechanical properties of composites.

Comparing these results with others found in the literature, 0% and 7% in improvements in CAI strength for laminates with 5 wt% and 10 wt% of cup-stacked CNTs was reported by Yokozeki et al. [10]. 12–15% increase in CAI strength for nano-enhanced laminates containing 0.5 wt% MWCNTs was reported by Kostopoulos et al. [11]. 55% increase in CAI strength for nano-enhanced laminates containing 0.5 wt% MWCNTs was reported by Mannov et al. [7]. The good agreement between our results and literature supported our mechanical tests.

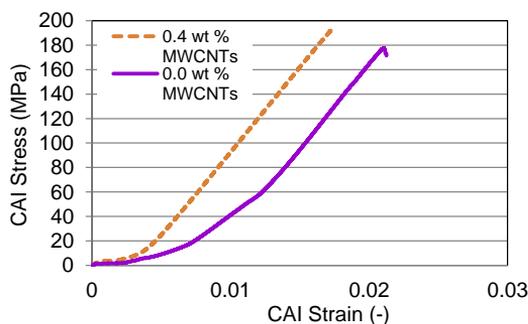


Fig. 5 Results of CAI stress-strain properties of thermoset composites

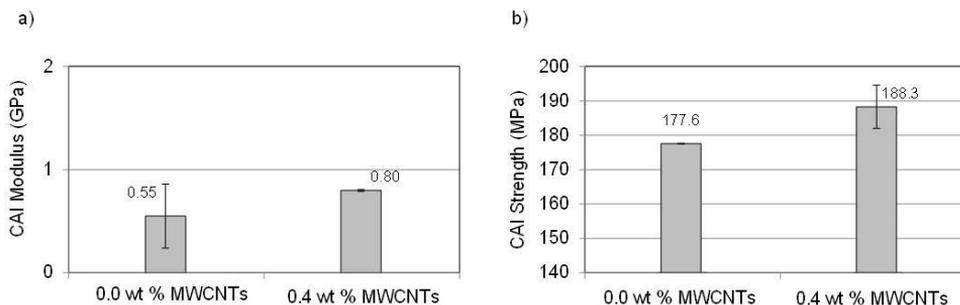


Fig. 6 Results of CAI modulus and strength properties of thermoset composites

Figure 7 shows the results of the charpy impact properties of the specimens of the thermoset composites with 0 wt% and 0.4 wt% MWCNTs in the 90° direction. The charpy impact strength of the specimens with 0 wt% and 0.4 wt% MWCNTs were 162.9 kJ/m<sup>2</sup> and 181.4 kJ/m<sup>2</sup> in 90° direction. The CNT integrated specimens showed 10.2% improvement of the charpy impact strength against specimens without CNTs in the 90° degree direction. As mentioned earlier, the possible reason for the improvement in the

Charpy impact strength might be the synergy between the fiber and matrix, which was created by the MWCNTs in the composites.

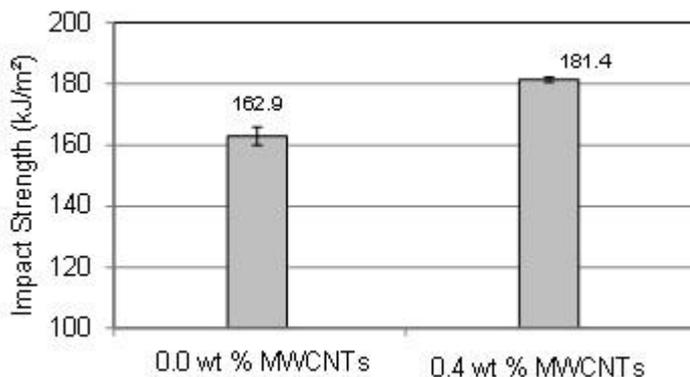


Fig. 7 Results of Charpy impact properties of thermoset composites

The influence of addition of CNTs on the energy absorption properties of composites has been studied by various researchers. 48.7% higher energy absorption in Charpy tests from the fabricated composites with MWCNTs was reported by Sharma et al. [12]. 20% increase in the Charpy impact energy absorbance in the presence of 0.2 wt % MWCNTs interlayers was reported by Papila et al. [13].

#### 4. Conclusions

The addition of the carbon nanotubes on the surface of the reinforcements enhanced the CAI modulus and strength and impact strength of the thermoset composites.

From the results of this study, the following conclusions can be drawn:

- The best improvement of the CAI modulus and strength with 31% and 5.6% were obtained from the specimens with 0.4 wt% MWCNTs due to the superior properties of carbon nanotubes.
- The highest results of Charpy impact strength were achieved with 0.4 wt% MWCNTs.
- There was a good agreement of results of the CAI and impact tests of nano materials integrated composites from literature and from us.

In future study, we will try to investigate the interlaminar shear strength properties of the nano materials integrated composite materials with the NCFs reinforcements.

#### Acknowledgment

The author thanks to the Research Fund of Ondokuz Mayıs University (Project Numbers: (PYO.MUH.1904.16.004 and PYO.MUH.1904.16.005) for funding of this study.

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