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Material and Mechanical Characterization of Multi-Functional Carbon Nanotube Reinforced Hybrid Composite Materials

P.P. A [1] · V. Rajamohan [2] · A.T. Mathew [1]

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Abstract

Fiber reinforced polymer (FRP) composite structures are widely being used in aircraft wings, wind turbine blades, helicopter rotor blades and tail rotors. These structures are often exposed to external dynamic loads which shorten their lifetime. Carbon nanotubes (CNT) reinforced epoxy resin have distinctive characteristic in providing a significant increase in mechanical properties and stiffness of the FRP composite. The present study investigates the micro, macro and structural analysis of composites with and without reinforcement of multi walled carbon nanotubes (MWCNT). The carboxylic acid (COOH) functionalized MWCNT with more than 95% chemical purity having average dimensions of 17 nm outer diameter and 10 μm length were used to characterize their chemical properties and evaluate the mechanical and free and forced vibration response of composites with and without MWCNT reinforcement. Initially, the powder form of the MWCNT was taken for the identification of true density (ρ) using the gas displacement technique. The COOH-MWCNT were then randomly dispersed in low viscosity epoxy resin (LY556) through an organic solvent using the ultrasonic liquid processor. Test samples were fabricated by adding the hardener (HY951) at 10:1 ratio in the sonicated solution to obtain the Young's Modulus (E) of MWCNT using Nano Indentation. Following this, Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Fourier Transform Infrared spectroscopy (FT-IR), Thermo gravimetric analysis (TGA) were also used to quantify the dispersion, distribution, structural integrity, aspect ratio, functional group and purity level of nanotubes. Further, the impact hammer test based on ASTM E1876, tensile test based on ASTM D3039 and free and forced vibration analysis of the hybrid composite beams were carried out to identify the elastic properties, fundamental natural frequencies, damping ratio and transverse deflection of the hybrid structure. It was shown that the addition of 1 wt% of COOH-MWCNT in fiber reinforced composite beam increases the stiffness of the structure and consequently increases the natural frequencies and damping at each resonant response dominant peaks. The strong adhesion of bonding and proper dispersion of CNTs in the wide surface area of composite strengthen the polymer composites substantially than those of the Glass/epoxy composite structures without reinforcement of MWCNT.

Keywords Multi-walled carbon nanotube · Hybrid structures · Nanocomposites · Vibration analysis

Introduction

Fiber based polymer composites are generally being utilized over a wide scope of industrial applications because of their better mechanical properties, lower structural mass, extended life period, and destructive safe properties. However, the usage of these materials is not wide spread because of the limited viscoelastic and damping performance of the fiber reinforced composites. Since 1991, after the discovery of carbon nanotubes (CNT) by Iijima [1], their distinctive physical properties have got a huge consideration from numerous analysts to manufacture the hybrid composite materials with CNT reinforcement to achieve the enhanced mechanical properties of the structure. Godara et al. [2] presented that the mechanical properties of fiber reinforced polymer composites could be enhanced by using the functionalized MWCNT than those of non-functionalized MWCNT. Zhou et al. [3] examined the significant increase in damping ratio of the hybrid composite structures with reinforcing single walled nanotube (SWNT) in the polymer composite. Numerous investigations have also shown that the addition of multi-walled CNTs

✉ V. Rajamohan
vasudevan.r@vit.ac.in

1 School of Mechanical Engineering, Vellore Institute of Technology (VIT), Vellore, Tamil Nadu 632014, India

2 Centre for Innovative Manufacturing and Research (CIMR), VIT, Vellore 632014, India

(MWCNT) in the composite structure improves the mechanical, shear strength, bending, damping, and thermal properties of the polymer based composites [4–6]. Even though SWCNTs and MWCNT are similar in structure, the variation exists in the diameter such that the diameter of MWCNT varies from 17 to 30 nm while it varies from 0.7 to 2.0 nm for SWCNT which results in increase in the number of concentric walls from 6 to 25 or more in MWCNT. Because of their high surface contact area in MWCNT, they provide maximum suspension phenomena in increasing the damping of the MWCNT reinforced composites compared to SWCNTs. Lau et al. [7] identified that the thermal stability, durability and physical properties of the nano composites are enhanced considerably with random distribution of CNTs in polymer composites.

Thostenson et al. [8] reviewed the latest advances made in the research of nanocomposites in terms of reinforcement of nano particle, nano platelet, nano fiber, and CNT in the traditional fiber composites. It was shown that the nanocomposites are found to be effective materials over the other types of fillers due to their better mechanical properties with dispersion, alignment, volume fraction, and weight percentage. Lehman et al. [9] reviewed the effects of dispersion, interfacial adhesion between the CNTs and composites, and the functionalization on the properties of CNT/polymer composites. It was concluded that the insolubility, weak interfacial bond between the CNTs, dispersion and functionalization significantly influence the mechanical properties of nanocomposites. Singh et al. [10] examined the effect of CNT aspect ratio on stiffness of the composite structure and observed that epoxy composites with longer CNT (length > 350 μm) have better mechanical properties than epoxy composite with shorter CNT.

Arash et al. [11] studied the mechanical behavior of CNT/poly methyl methacrylate (PMMA) composite in the interfacial region using molecular dynamics simulation. The result shows that the Young's modulus and yield strength of hybrid composites could be increased by 3% with an increase in the length of polymer chains from 10 to 30 monomer units. It was also shown that the stiffness is increased by 16 times than that of a pure PMMA polymer. Wernik and Meguid [12] presented the physical and mechanical properties of polyvinylpyrrolidone (PVP) adhesive without and with CNT reinforcement. It was found that tensile strength and stiffness of PVP adhesive could be increased by 25% with addition of 3 wt% of CNT. Tarfaoui et al. [13] investigated experimentally the variation in mechanical behavior such as stiffness of textile composites made of carbon and epoxy with CNT reinforcement. It was identified that the mechanical properties of hybrid composites decreases with reinforcement of CNT beyond 2% in epoxy.

Prusty et al. [14] studied the effects of flexural behavior of glass/epoxy/CNT composites under thermal environment using the dynamic mechanical thermal analysis (DMTA). It was observed that a reduction in flexural strength and corresponding modulus was observed in CNT reinforced glass epoxy composites when the temperature is increased from −80 °C to 110 °C. Further, it was noted a decrement in glass transition temperature of epoxy with 0.3 wt% CNT reinforcement. Mahato et al. [15] investigated the tensile strength and modulus of GFRP composites without and with 0.1% to 0.5% wt reinforcement of CNT at different crosshead speeds during tensile test. It was observed that tensile strength increases by 6.11% and 9.28% respectively, with increase in CNT reinforcement from 0.1% to 0.3% wt of polymer composites. However, a sudden reduction in tensile strength was observed at CNT reinforcement in GFRP with 0.5 wt% due to agglomeration and further resulting a slight increase in the glass transition temperature of CNT-GFRP compared to neat GFRP.

Fan et al. [16] showed that the inter-laminar shear strength of glass/epoxy composite could be enhanced by 9.7%, 20.5%, and 33.1%, respectively, by reinforcing epoxy with 0.5%, 1% and 2% wt oxidized multiwalled carbon nanotubes. The CNT proportion and the interfacial agreement between the CNT and the epoxy matrix could influence the stiffness of the hybrid composites. It was observed that the shear strength in inter-laminar part of the woven composites could be increased about 69% with 2% volume fraction (V_f) of CNT reinforcement [17]. Rawat and Singh [18] investigated experimentally the enhancement of inter-laminar shear strength and bending strength of FRP composites with CNT reinforcement using universal testing machine (UTM) and three point bending test. It was identified that interlaminar shear strength and bending strength of FRP composites could be increased by 13.66% and 44.22% respectively, with 0.5% wt of CNT reinforcement.

Farrash et al. [19] investigated the free vibration responses of beam made of neat epoxy, glass/epoxy, Carbon/epoxy, without and with reinforcement of 0.25% wt CNT in the composite structures. It was shown that the fundamental natural frequencies of CNT/glass/epoxy composite could be increased by 9.4% with 12.3% decrease in damping ratio over the glass/epoxy. Further, it was shown that 13.9% reduction in the fundamental frequencies of CNT/carbon/epoxy with 31.5% improvement in damping ratio over the carbon/epoxy. Coleman et al. [20] identified that the durability, structural strength, damping and mechanical properties of the composite fibers could be improved greatly by the CNT reinforcement. Jakkamputi and Rajamohan [21] investigated the dynamic responses of the GFRP composites without and with 0.5% wt CNT reinforced in the composite beam under clamped free (CF) and clamped clamped (CC) end conditions at room and elevated temperatures. It was shown that the fundamental natural frequency of CNT-GFRP composite could be increased by 17.43% and 18.46% than those of with the GFRP composite under CF and CC conditions at room temperature. In addition, the fundamental frequency of CNT-GFRP decreases by

3.47% and 11.90%, whereas, the damping factor at the first mode increases by 22.64% and 35.41% under CF and CC conditions, respectively, at an elevated thermal environment from 30 to 60 °C. Khan et al. [22] observed experimentally a significant increase in the characteristics of damping of carbon fabric reinforced composites with reinforcement of 0.5% and 1% MWCNT in the structure. Even though various researchers have focused on characterization and reinforcement of CNTs in polymer composites, the materials and mechanical characterization of CNTs reinforced hybrid composites in terms of micro and macro level within elastic limit of structures have not yet been explored in detail.

In the present study, the material, mechanical and free vibration characterizations of multi-walled carbon nano tube (MWCNT) reinforced fiber reinforced polymer composite material are investigated. The micromechanical analysis of hybrid composite material has been carried out using the Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and thermo gravimetric analysis (TGA) to quantify the dispersion, structural integrity, aspect ratio, functional group and purity level of nanotubes. In addition, true density and Young's modulus of MWCNT are identified using the gas displacement technique (AccuPyc II 1340) and nano indentation technique (Agilent G200), respectively. Followed by this, the impact hammer test (ASTM E1876), tensile test (ASTM D3039) and free and forced vibration analysis were carried out to identify the elastic properties, fundamental natural frequencies, damping ratio and the transverse deflection of the hybrid composites. The structural analysis was performed on the test specimens made up of glass fiber reinforced polymer composites without and with 1% wt reinforcement of MWCNT. The strong bonding and proper dispersion between the CNTs and epoxy in the wide surface area of composites strengthen the polymer composites significantly than those of the glass/epoxy composite structures without CNT reinforcement. The results reveal that the addition of 1 wt% of COOH-MWCNT in fiber reinforced composite beam increases not only the stiffness but also the damping of the structure at each resonant response dominant peaks.

Materials and Methods

The carboxylic acid (COOH) functionalized multi walled carbon nanotubes (MWCNT) supplied by United Nanotech Innovations Private Limited® with more than 95% chemical purity having average dimensions of 17 nm outer diameter and 10 μm length were used for the present study to perform the micro, macro and structural analysis of composites with and without reinforcement of multi walled carbon nanotube (MWCNT). The carboxylic acid (COOH) functionalized MWCNT were randomly dispersed in low viscosity epoxy resin through an organic solvent (SRL extra pure acetone) using the ultrasonic liquid processor. The micromechanical analysis of hybrid composite material was carried out using the SEM, TEM, FT-IR and TGA to quantify the dispersion, structural integrity, aspect ratio, functional group and purity level of nanotubes. In addition, the macro mechanical analysis was carried out using the gas displacement technique (AccuPyc II 1340) and nano indentation technique to identify the true density (ρ) and Young's modulus (E) of MWCNT, respectively.

The test specimens of glass fiber reinforced polymer composites were made without and with reinforcement of MWCNT using hand layup method. Initially, 1% wt MWCNT was added into the solvent and stirred thoroughly using the mechanical shear mixture for half an hour. Then the mixture was sonicated using the ultrasonic liquid processor having 12.5 mm diameter of titanium probe with pulsed on-off cycles with period of 5 s for 1 h at room temperature to separate the entangled MWCNT. The measured quantity of epoxy resin (LY556) was added into the mixture of MWCNT/acetone and the mixture was sonicated again using the ultrasonic liquid processor for 2 h to achieve the dispersion. Then, the mixture of acetone/epoxy/CNT was kept in hot air oven at 75 °C operated for 48 h to evaporate the solvent (acetone). Further, the homogenous dispersion of CNTs in epoxy resin was enhanced by using shear mixture for 30 min. The hardener (HY951) was then added into the homogenously sheared epoxy/MWCNT mixture with 1:10 ratio. Finally, the glass fiber reinforced polymer composite test specimens were fabricated without and with MWCNT reinforcement using hand-layup method, by adding 1:10 ratio of hardener into the epoxy/MWCNT mixture, prepared earlier and reinforced with E-glass unidirectional fabrics (220 GSM). Further, the specimens were cured in oven at 75 °C operated for 1 h and then post cured at room temperature for 24 h.

Once the composite samples were fabricated, the impact hammer test based on ASTM E1876, tensile test based on ASTM D3039 and structural responses of hybrid composite using modal analysis experimental test setup accompanied with the DEWESOFT version 7.1.1 software were carried out for the CNT reinforced hybrid composite beams made up of E-glass unidirectional fibers.

Material Characterization

Material Characterization Using Scanning Electron Microscopy (SEM)

SEM is the most commonly used reliable microscope to characterize the morphologies and dimensions that uses a high vitality electron beam centered to get an interminable number of scattered electron signals from the surface of strong samples and yields a three-dimensional (3D) picture of nanoparticles. Most of the SEM equipments are suitable to resolve structures higher than 5 nm in diameter and the greatest sophisticated SEM can accomplish point resolutions less than 1 nm using field emission microscopes having monochromators.

In this study, the SEM analysis was carried out using the carboxylic acid functionalized moisture less CNT nanotube particles which are intertwined with each other and may develop irregular shapes of aggregates. At this stage, the MWCNT couldn't blend homogeneously in the epoxy resin matrix due to the presence of entangled structure of the nanoparticles. Figure 1a demonstrates the accumulation of nanotubes entrapped with each other before sonication. To overcome this lump amalgamation of CNTs, the most proficient ultrasonicator liquid processor was employed to disintegrate the required amount of nanoparticles precisely without affecting the aspect ratio of the nanotubes. The test was carried out with the magnification range from 3.00 KX to 24 KX and the scaling range from 1 μm to 10 μm by using the ZEISS (EVEO18 Research). Figure 1 demonstrates the SEM image of the functionalized MWCNT before sonication, and after sonication process. The isolated nanotubes from the ultra-sonication process were again taken for the investigation using SEM. The test was conducted by engaging the gold coated sonicated CNT samples with 15.00KX magnification and fixing the scaling at 2 μm.

It can be seen from Fig. 1b the snared nanoparticles of the CNTs are isolated independently with irregular conveyance and distributed randomly into the organic solvent. The clusters of CNT particles have been disintegrated into individual parts for enlightening the efficacy of the nanocomposites with random distribution of CNTs in epoxy. After ensuring the disintegration of CNTs, the organic solvent (acetone) is allowed to evaporate using the hot air oven at 75 °C operated for 48 h. Followed by this process, sonicated CNTs were mixed homogeneously with the epoxy resin. Then the test specimens were fabricated with and without addition of CNTs to observe the distribution of CNTs reinforced in the epoxy resin (Fig. 2a, b). Moreover, the strong bonding due to the Vander Waals force exist between the nanotubes and epoxy LY556 material can be witnessed in these images.

Material Characterization Using Transmission Electron Microscopy (TEM)

TEM is an advanced steadfast electronic equipment used to identify the structural integrity and aspect ratio with high resolution compared to the specification of SEM. It utilizes a great vitality electrons centered strong light waves to obtain the transmitted electrons specifically pointed on the test samples and passes the signs all through the whole surface of the test specimen and furnishes a 2D picture with clear details of the data taken from the cross sectional perspective of nanotube. The TEM has the greatest magnification about 50 million and has the resolution of 0.5 Å.

The TEM analysis was carried out to quantify the length, diameter, alignment, orientation, nanotube purity, chemical composition and the sectional view of transparent structural information of nano particles per unit area by using FE1-TECHNAI G2–20 TWIN. The procured MWCNT test sample was analysed with 200KX magnification and the focused scaling was about 10 nm. The images of MWCNT from TEM analysis shows the clear picture of the multi layered wall (Fig. 3). These multi layered carbon nanotubes could enhance the stiffness and damping performance of the nanocomposites due to the presence of more surface contact area in tube form. Figure 3 demonstrates the nanotube images of MWCNT before and after sonication process.

After sonication, the clustered form of CNT particles has been separated into individual parts without affecting the structural integrity which helps to enhance the bonding of polymer chains between the epoxy and nanotubes with the influence of the Vander Waals force. Figure 3a shows the outer diameter,

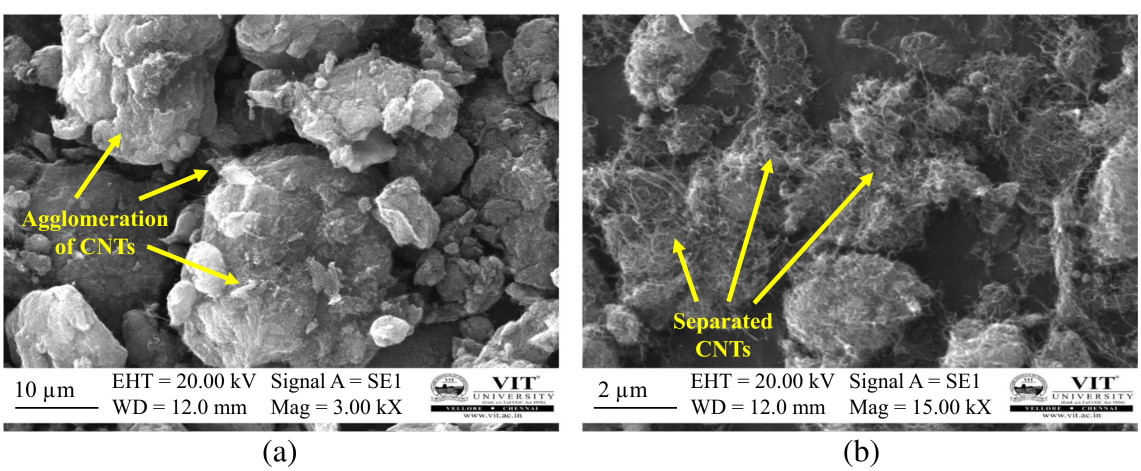

Fig. 1 SEM images of MWCNT (**a**) before sonication (**b**) after sonication

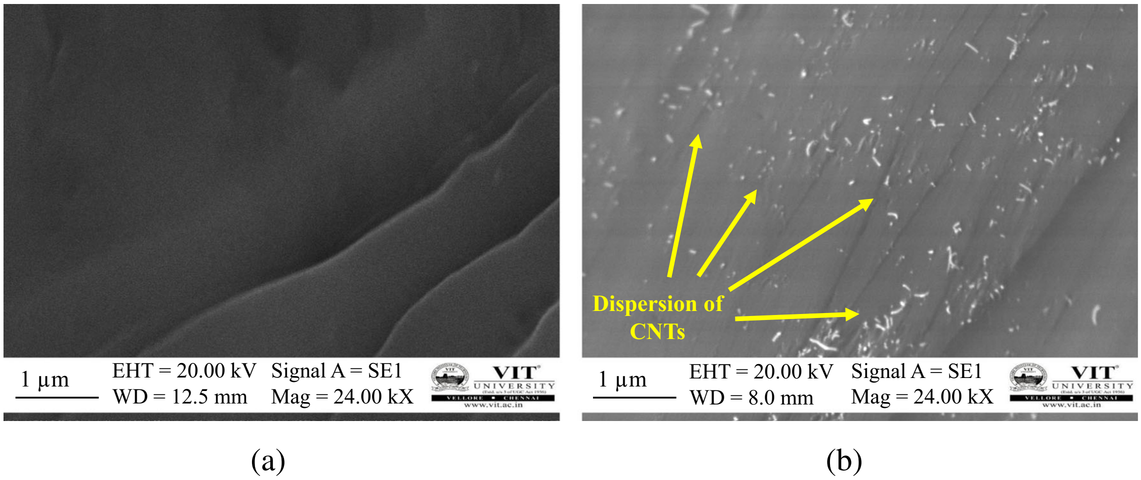

Fig. 2 SEM images of surface of test specimens (**a**) epoxy without CNT (**b**) CNTs dispersion in epoxy resin

inner diameter, individual wall thickness and number of walls of nanotubes before and after the sonication process and were observed as an average unit of 16.96 nm, 7.94 nm, 0.353 nm, and 17 walls on both sides of MWCNT without changing the structural integrity, aspect ratio and multi layers walls. In addition, the chemical purity has been observed as 95.82% of carbon (C). The remaining impurities such as copper (Cu) 3.23%, Oxide (O) 0.40%, Iron (Fe) 0.36%, Calcium (Ca) 0.12%, Sulphur (S) 0.05%, and Chloride (Cl) 0.02% were also identified in the sonicated functionalized CNT.

Material Characterizations Using Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is the advanced equipment with better efficiency in transmitting the infrared signal to the solid, gas and powder materials. The functionalization of CNTs will not only alter their wettability in various surfactants but also the toxicity [11]. It is quite reliable to collect the details of sensitive sample from the extensive variety of signal of the spectrum and provides the clear output about the functional group of the test samples.

The FT-IR analysis was carried out to find the functional group of the Carboxylic acid (COOH) functionalized MWCNT by using IR AFFINITY SHIMADZU®. Initially, the least quantity (i.e., 1 mg) of CNT particles were taken for the analysis by passing the strong infrared signal on the test samples which were reflected by the COOH existed in the nanotubes. The amount of infrared active modes is purely independent on diameter of the nanotubes and highly a sensitive function for detecting the position of the peaks. Figure 4 shows the functional group for functionalized MWCNT. In this, the X-pivot represents the wave numbers (1/cm) and the Y- pivot signifies the transmittance signal in percentage (%T). The result from the FT-IR graphical data represents the existence of functional group of COOH through the two dominant peaks with respect to the wave numbers for C=O (1737.86) and O-H (1213.23) in the range between 2000 and 1000 cm^{-1} for MWCNT. Similar observations were made by Kouklin [23], Misra [24] and Osswald [25]. At this stage, the MWCNT could blend uniformly in the epoxy material due to the presence of functional group of COOH which influences the polymer chain building units between the epoxy and CNT.

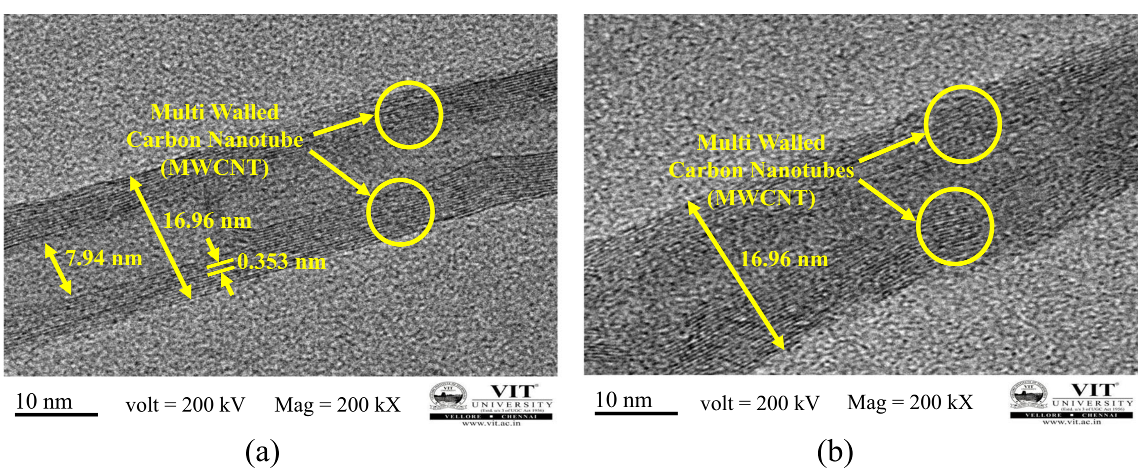

Fig. 3 TEM images of aspect ratio of (**a**) CNT before sonication (**b**) CNT after sonication

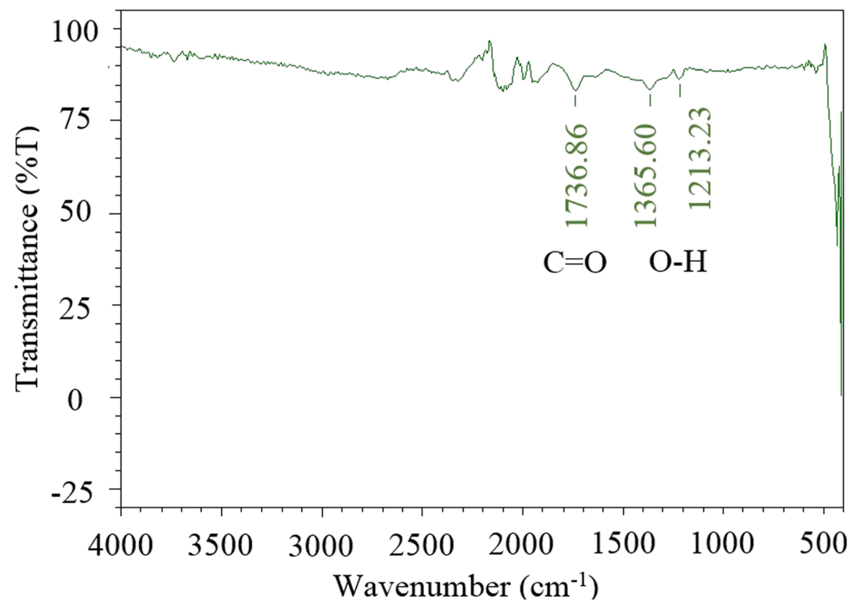

Fig. 4 Graphical representation of COOH group functionalized MWCNT

Material Characterizations Using Thermogravimetric Analysis

The TGA (SDT Q600 V20.9 Build 20) Universal V4.5A TA instrument has been employed to acquire the purity and thermal stability of the test samples of epoxy without and with CNT reinforcement. Initiation temperature, oxidation temperature (i.e., thermal stability) and residual mass (remains after heating) were measured using TGA. Initially, the analysis was carried out by taking the few milligrams of epoxy without CNT and epoxy with CNT samples at elevated thermal environment from 20 to 600 °C and 25 to 800 °C. Figure 5 shows the comparison between the epoxy and epoxy/MWCNT. Purity of carbon content has been observed as 95% from the remaining residual mass of COOH functionalized nanoparticles after heating. Moreover, the existence of 90.30% weight of residual mass of epoxy/CNT inside the hot chamber could be observed even after the temperature exceeds above 800 °C compared to the epoxy sample without CNT reinforcement. This is due to the fact that the functionalized CNTs and their reinforcement with epoxy are more effective due to the alignment of polymer chains and the presence of functional group "COOH" at the surface of CNTs.

Further, the functionalization of CNTs effectively block the polymer chain movements thermally due to the interaction between epoxy/CNT and yield the coefficient of thermal expansion (CTE) as very minimal, and even zero CTE at few occasions. This may provide a high thermal stability and yield a significant change in thermal stability of CNT reinforced epoxy [2]. Thereby the residual mass of the epoxy with CNT sample remains 90.30% and 6.50% for epoxy sample without CNT.

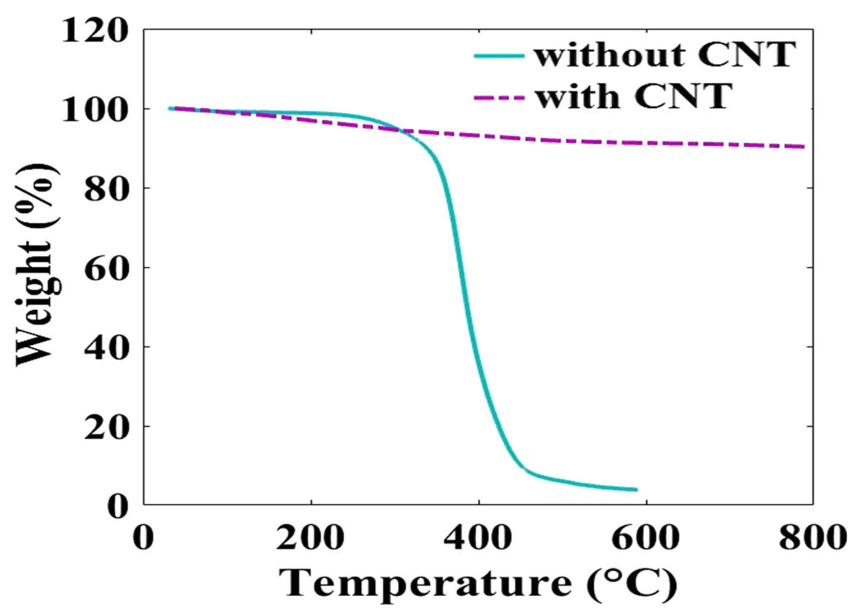

Fig. 5 TGA analysis of epoxy without and with CNT

Identification of True Density of MWCNT

In general, density is well-defined as the quantity of matter accumulated in a three-dimensional volume of an object whose atoms are closely packed together. It plays a significant role among the mechanical properties of the materials being used for the engineering applications which can be measured precisely based on the principle of gas displacement technique to identify the various type of densities, such as: True density, Skeletal (Apparent) density, Envelope density, Bulk density and Tapped density. The most commonly used density among all is the absolute or true density which provides very accurate result for powder samples, by suspending the volume of inter and intra-particular voids exist in between the open and closed porous region of the material. Conversely, rest of the density types were considered for the nano/micro solid particles without neglecting the voids or pores which is not suitable for the sample material in the form of nanotubes. Therefore, the preliminary study was carried out to identify the true density of the MWCNT using the advanced reliable equipment AccuPyc II 1340″, from micromeritics®. Figure 6 shows the step by step procedure carried out for the preparation of test sample to find the true density of COOH group functionalized MWCNT. Initially, the sample MWCNT of mass (m_s) 0.7399 g were kept for the heat treatment at 75 °C for 30 min under closed condition. Then, the unwanted moisture content was removed through the sealable enclosed desiccator (used as a preserver for moisture sensitive items) kept in the vacuum assisted thermal oven. Following this, the sample was taken out and placed in the filling chamber provided to facilitate the expansion process based on the principle of gas displacement technique using the AccuPyc II 1340. The Helium inert gas was passed to pressurize the sample chamber and the expansion chamber was set about 19.5 psi which was then released from the Pycnometry system. Initially, this cyclic process was continued for 10 times through the purges to clean the samples by just blowing the gas over them.

Afterwards, the analysis was carried out for 7 times and maintained to fill the pressure equally at the equilibrium rate of 0.005 psig/min. The pressures at the sample filled and expansion chambers (P_1 and P_2) were recorded. Then, the true density (ρ) of CNTs is calculated such that:

$$\rho = \frac{m_s}{V_s}$$
$$V_s = V_c - \left(\frac{V_{\exp}}{\left(\frac{P_1}{P_2}\right) - 1} \right) \quad (1)$$

where, m_s is mass of the sample, V_s is the volume of sample, V_c is the cell volume, V_{exp} is the expansion volume, P_1 is pressure in sample filled chamber and P_2 is the pressure in expansion chamber. The true density of CNTs was identified as 2514 kg/m^3.

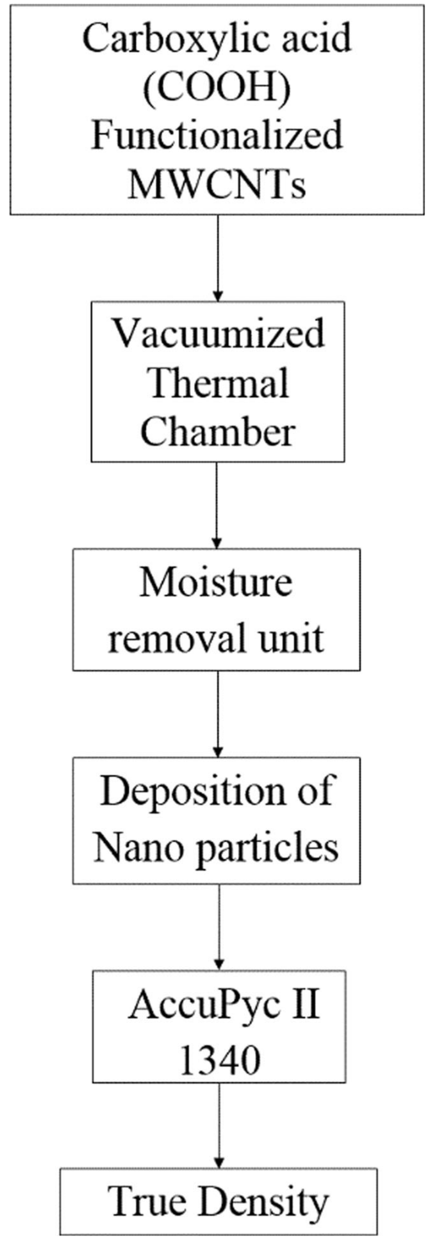

Fig. 6 Representation of the process used to find the true density of MWCNT

Evaluation of Young's Modulus of MWCNT

The nano indentation techniques are widely being used to quantify the Young's modulus, hardness, fracture toughness, friction co-efficient, crack propagation etc., without any loss in the structural integrity of the materials with high accuracy. Young's modulus of the MWCNT was identified using the nano-indentation equipment Agilent G200 integrated with Berkovich indenter having pyramid geometry made of diamond. Figure 7 shows the step by step procedure carried out for the preparation of the test sample to find the Young's modulus of MWCNT.

Firstly, 1% wt CNT reinforced composite was fabricated by adding the moisture less functionalized MWCNT into the

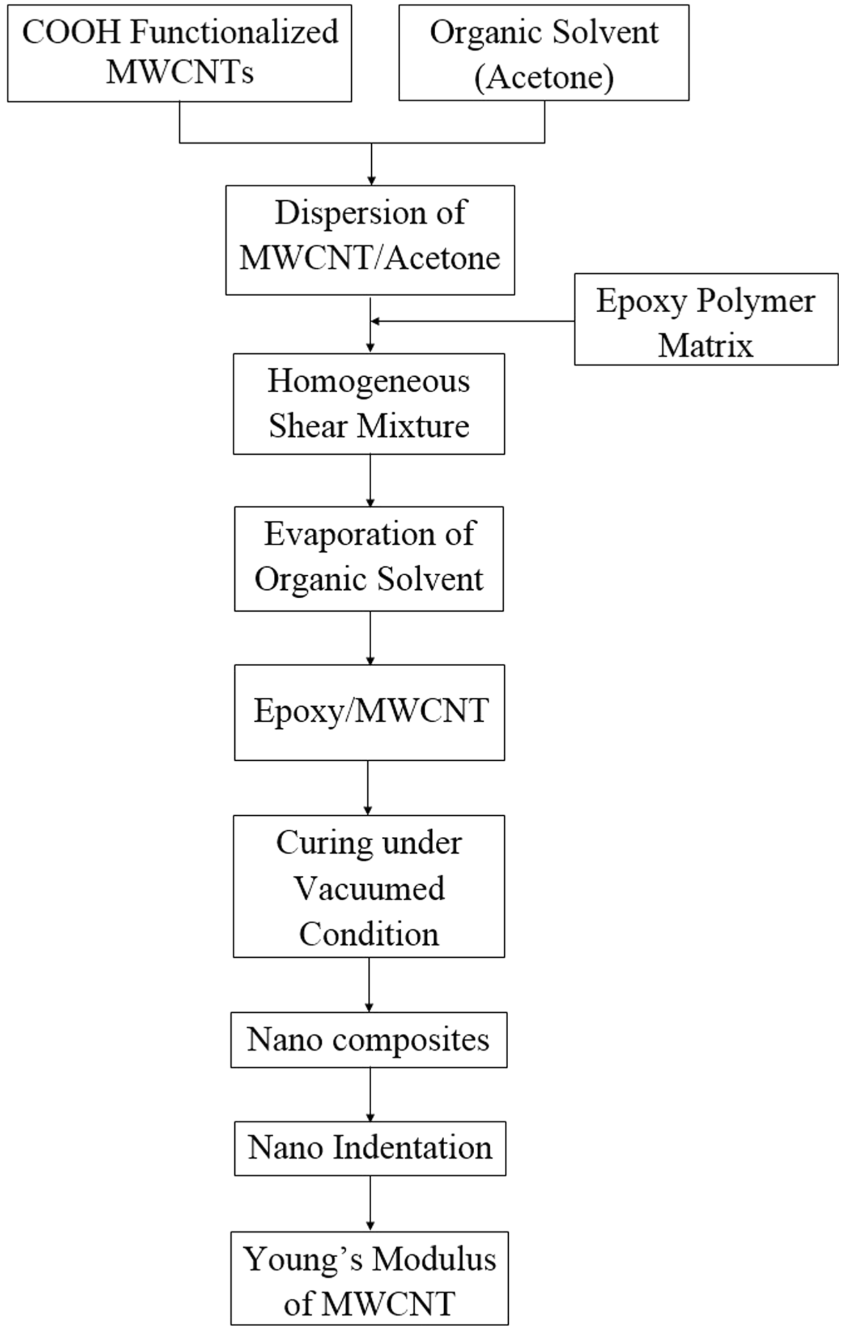

Fig. 7 Representation of the process to evaluate the Young's Modulus of MWCNT

organic solvent (SRL extra pure acetone) to disintegrate the agglomeration using the ultrasonic liquid processor with pulsed on-off time cycles with a period of 5 s for 30 min at room temperature. Once the MWCNT were disintegrated, they were dispersed homogeneously into the epoxy resin LY556 using shear mixture with pulsed on-off cycles with a period of 5 s for 30 min at room temperature.

Afterwards, the mixture was kept in the homogenous shear mixture at 1500 rpm to remove the existence of the organic solvent. Finally, hardener HY951 was added in the epoxy/MWCNT with 1:10 ratio which was then poured into the mold to fabricate the test sample of standard dimension 20 mm × 20 mm × 5 mm to carry out the nano indentation test. The test was carried out for 10 times on the 5 mm thickness of solid sample samples of with and without MWCNT having

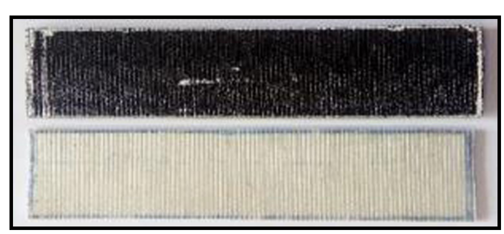

Fig. 8 Photograph of the test specimens

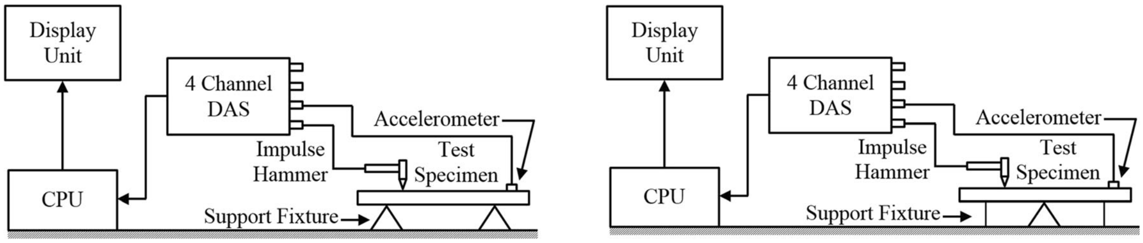

Fig. 9 Block diagram of the experimental setup used to measure the elastic properties

0.05 nm/s of allowable drift rate with 45 Hz of frequency, 2 nm of harmonic displacement, and 0.05 s-1 strain rate, targets up to 2000 nm of depth limit and followed by the penetrated indenter unloading about 90% of the 5 mm thickness of solid sample. The reciprocating motion of the Berkovich indenter was carried out with a vertical loading/penetration angle of 65.03° at a strain rate of 0.05 s-1 using Agilent G200 and the results were noted. It was identified that the Young's modulus of the epoxy with and without MWCNT reinforcement are 4.5 GPa and 4.1 GPa, respectively.

Mechanical Characterization of Hybrid Composites

In this section, the mechanical characterization and structural responses of hybrid composites without and with CNT reinforcement in the epoxy and glass/epoxy/CNT composites are presented. The elastic properties of the CNT reinforced hybrid composites were identified based on the American Society for Testing and Materials (ASTM). Further, the structural analysis of the hybrid composite beam has been carried out to identify the fundamental natural frequency, damping ratio and transverse response of the hybrid composites with and without CNT reinforcement.

Evaluation of Elastic Properties

The impact hammer vibration analysis was carried out based on ASTM E1876 [26] to identify the elastic modulus such as Young's moduli and Shear modulus of Glass/epoxy and CNT/Glass/epoxy composite materials. Figure 8 shows the test specimens of 150 mm × 50 mm × 5 mm size with $[0°]_{20}$ and $[90°]_{20}$ ply orientations with and without CNT reinforcement fabricated as followed by the same procedure presented in sample preparation section.

The analysis was performed by using the special type of out of plane and torsion fixture experimental setups as shown in Fig. 9a, b. Impulse hammer-5800SL (Roving hammer) was used as the exciter to energize the test specimen kept for analysis. A uniaxial accelerometer was mounted on the top surface of the specimen to measure the responses due to the excitation applied. These acceleration signals were received and converted into frequency response function by adapting four channel digital data acquisition system (Model: ATA-DAQ042451).

The natural frequencies of Glass/epoxy and CNT/Glass/epoxy under flexure and torsion were subsequently observed from the peaks provided in the frequency response function by using the DEWESOFT (version 7.1.1) software. Young's modulus, shear modulus of composites with and without CNTs were calculated by substituting the frequency in the equations (2–3) such that:

Dynamic Young's modulus

$$E = 0.9465 \times \left(\frac{M f_f^2}{b}\right) \times \left(\frac{L^3}{t^3}\right) \times T_1 \tag{2}$$

$$T_1 = \left[1.000 + 6.585\left(\frac{t}{L}\right)^2\right] \tag{3}$$

where, m is mass of the bar, f_f is the fundamental resonant frequency of bar in flexure b is width of the bar, mm, L is length of the bar, mm, t is thickness of the bar, mm; T_1 is

Table 1 Evaluation of elastic properties of Glass/epoxy and Glass/epoxy/CNT using ASTM E1876

Composite Materials	Frequency used to measure Young's modulus along the fiber direction (Hz)	Frequency used to measure Young's modulus along the transverse direction of fiber (Hz)	Frequency used to measure shear modulus (Hz)	Flexural Young's modulus along the fiber direction, E_1 (GPa)	Flexural Young's modulus along the transverse direction of fiber, E_2 (GPa)	Shear modulus, G_{12} (GPa)
Glass/epoxy without CNT	932.600	442.770	933.011	26.035	5.869	3.292
Glass/epoxy with CNT	1062.000	562.100	943.010	33.732	9.446	4.239

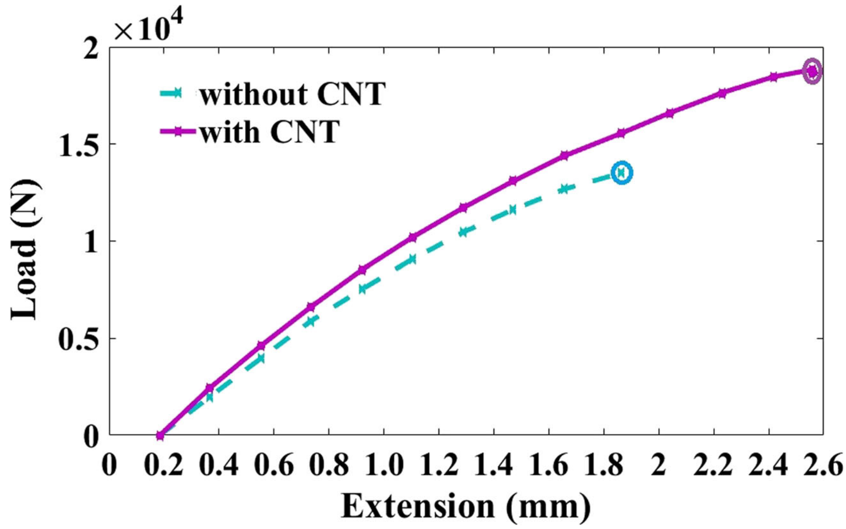

Fig. 10 Variation of extension with tensile loading of the composite samples without CNT and with CNT reinforcement

correction factor for fundamental flexural mode to account for finite thickness of bar.

The Dynamic shear modulus:

$$G = \left(\frac{4Lmf_t^2}{bt}\right) \times R \tag{4}$$

$$R = \left[\frac{1+\left(\frac{b}{t}\right)^2}{4-(2.521)\times\left(\frac{t}{b}\left(1-\frac{1.991}{e^{\pi\frac{b}{t}}+1}\right)\right)}\right] \tag{5}$$

$$\times\left[1+\frac{0.00851\,n^2b^2}{L^2}\right]-0.060\left(\frac{nb}{L}\right)^{\frac{3}{2}}\times\left(\frac{b}{t}-1\right)^2$$

where, f_t = fundamental torsional resonant frequency of bar, Hz; n = the order of the resonance, here $n = 1$. Table 1 presents the elastic properties of Glass/epoxy and CNT/Glass/epoxy derived from impact hammer test.

It was observed that Young's modulus along the fiber and matrix directions and shear modulus of CNT reinforced composite specimen increase by 22.82%, 37.87%, and 22.34% respectively, as compared with Glass/epoxy composite beam without CNT reinforcement.

This is due to the strong adhesion and proper dispersion of CNTs in the wide surface area of composite which strengthens the polymer composites substantially over the Glass/epoxy composite materials without reinforcement of CNT.

Evaluation of In-Plane Tensile Properties of Hybrid Composites

The tensile test was carried out based on ASTM D3039 [27] to identify the in-plane tensile properties of Glass/epoxy and Glass/epoxy/CNT composites having length (L) 250 mm, width (W) 15 mm, and thickness (T) 2 mm with 0° and 90° ply orientations to evaluate E_1 and E_2 of unidirectional glass fabric without and with MWCNT reinforcement. The tensile test was carried out with loading along longitudinal direction of fibers at the extension rate of 1 mm/min operated under the room temperature by using the Universal INSTRON 8801 hydraulic testing machine. Figure 10 shows the results obtained in terms of loading with variation of extension along the axial direction of the composites without and with reinforcement of MWCNT. It can be seen that the failure load of the composite structure with CNT reinforcement is higher than compared to that of structure without CNT reinforcement.

Table 2 Tensile properties of Glass/epoxy and CNT/Glass/epoxy

Tensile properties	Glass/epoxy Without CNT	Glass/epoxy With CNT	Percentage Improvement (%)
Young's modulus, E_1 (GPa)	27.621	32.220	14.27
Young's modulus, E_2 (GPa)	7.454	10.957	31.97
Ultimate Tensile Stress (GPa)	0.209	0.300	30.33
Tensile strain at Maximum Load (%)	1.077	1.472	26.83
Load at Break (kN)	13.470	18.490	27.15
Tensile stress at Break (MPa)	207.190	295.830	29.96
Tensile strain at Break (%)	1.082	1.484	27.09

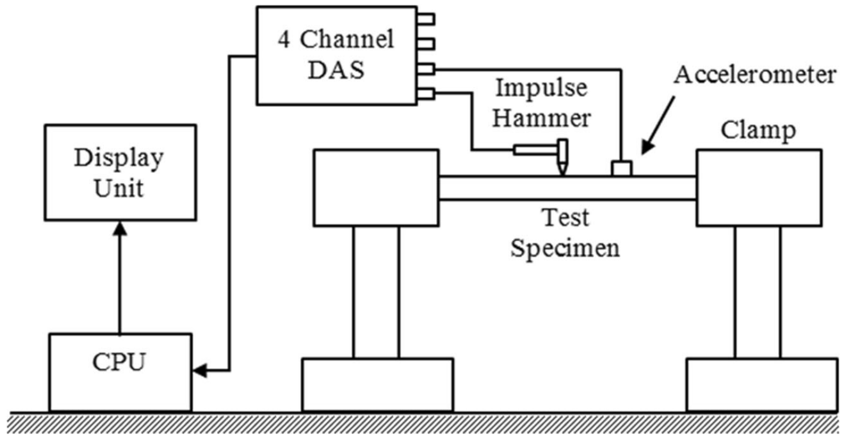

Fig. 11 Block diagram of the experimental setup used to perform the free vibration analysis

At particular load the extension of the CNT reinforced composite structure is much less than that of without CNT reinforcement. Table 2 shows the elastic tensile properties of Glass/epoxy and Glass/epoxy CNT derived from Fig. 10.

It can also be observed that Young's modulus, ultimate tensile stress (UTS), tensile strain at maximum load (%), load at break (kN), tensile stress at break (MPa), and tensile strain at break of hybrid composite increases by 14.27%, 31.97%, 30.33%, 26.83%, 27.15%, 29.96%, and 27.09%, respectively, compared to those of composite structures without reinforcement of CNT. This is once again related to the strong adhesion, proper dispersion and increment of stiffness of composite material with addition of CNTs in the wide surface area of composite which consequently strengthens the polymer composites substantially over the Glass/epoxy composite materials without reinforcement of CNT.

Structural Analysis of Hybrid Composites

Free Vibration Responses

The dynamic characterization of hybrid composite beam was carried out to identify the efficacy of CNTs in the glass fiber reinforced polymer composites in enhancing the natural frequency and damping factor of the composite structure. The composite beam having dimensions of length (*L*) 350 mm, width (*W*) 30 mm, and thickness (*T*) 3.5 mm were fabricated with ply orientation of $[0°/90°]_{3S}$ with glass fiber 0.513 wt%. Figure 11 shows the block diagram of experimental setup used to perform the dynamic analysis on laminated composite beam structures.

The structural responses in terms of damping and natural frequencies were identified using the roving hammer-5800SL as an exciter to energize the test specimen. A uni-axial accelerometer was mounted on the beam top surface to get the responses due to the applied excitation.

The vibration signals from transducer (accelerometer) were received by four channel digital data acquisition system (DAS), Model: ATA-DAQ042451 and converted into digital form of frequency response function which were processed in Fast Fourier transform (FFT) to obtain the natural frequencies. The natural frequencies of the Glass/epoxy and CNT/Glass/epoxy beam with clamped - clamped (CC) and Clamped - Free (CF) end conditions were consequently observed from the dominant peaks provided in the frequency response function by using the DEWESOFT (version 7.1.1) software. The damping factor was calculated by adapting the half power

Table 3 Natural frequencies and damping ratio of Glass/epoxy and CNT/Glass/epoxy composite beam structures under CC and CF boundary conditions

Mode Number	Clamped – Clamped (CC)				Clamped – Free (CF)			
	Glass/epoxy Without CNT		Glass/epoxy With CNT		Glass/epoxy Without CNT		Glass/epoxy With CNT	
	Natural Frequency (Hz)	Damping ratio (ζ)	Natural Frequency (Hz)	Damping ratio (ζ)	Natural Frequency (Hz)	Damping ratio (ζ)	Natural Frequency (Hz)	Damping ratio (ζ)
1	83.60	0.025	97.37	0.033	17.19	0.027	21.88	0.056
2	197.13	0.011	235.17	0.028	84.60	0.014	109.38	0.036
3	309.38	0.015	356.25	0.017	221.88	0.021	257.87	0.029
4	448.06	0.019	481.25	0.025	387.12	0.023	414.06	0.033
5	639.17	0.028	692.19	0.034	598.44	0.037	640.94	0.048

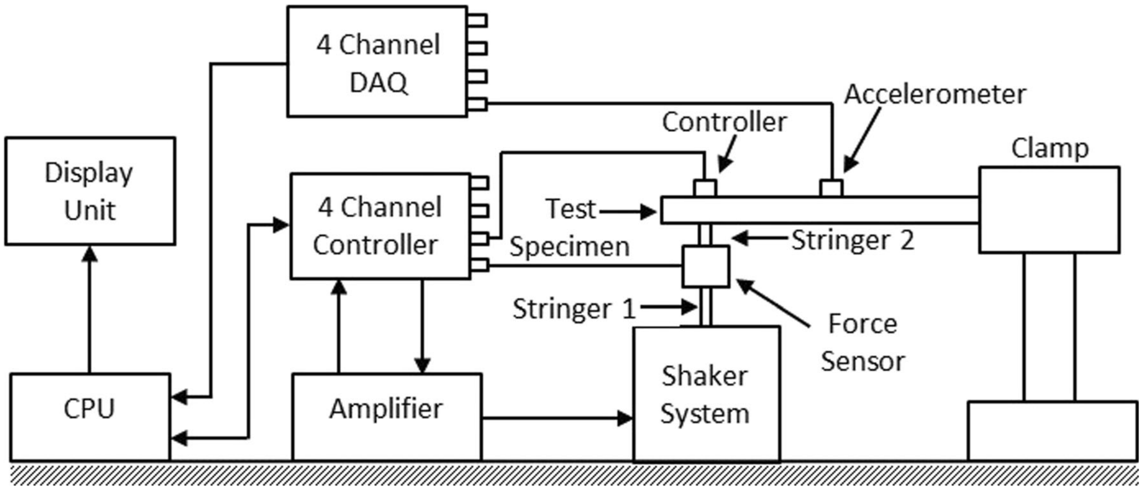

Fig. 12 Block diagram of the experimental setup used to evaluate the transverse vibration response

bandwidth method and the results are presented in Table 3. It was observed that fundamental natural frequency and damping factor of CNT reinforced composite beam at 1st mode increases by 14.14% and 24.24% under CC end conditions and 21.44% and 51.79% under CF end conditions respectively, as compared to those of with Glass/epoxy composite beam without CNT under CC boundary condition.

It can also be observed that the natural frequency and damping factor of the composite beam with CNT reinforcement are higher than that of without CNT reinforcement under all modes considered. This is due to the strong adhesion bonding and maximum surface contact of CNTs in composite which strengthens the polymer composites which substantially improves the bending stiffness and damping ratio over the composite beam without reinforcement of CNT. Furthermore, it was clearly shown that the natural frequencies and damping of Glass/epoxy composite beam could be increased significantly with reinforcement of CNTs without any significant change in mass of the composite beam.

Forced Vibration Responses

The forced vibration responses of the composite beam reinforced with and without CNT are investigated under CF boundary condition. The beam was subjected to a sinusoidal excitation of magnitude below 1 N using the Dongling ESS-005 electrodynamic shaker attached at a distance of 270 mm from the fixed end of the beam as shown in Fig. 12.

A uni-axial accelerometer was mounted on the mid node point of the beam top surface to get the responses due to the applied excitation. The vibration signals from transducer (accelerometer) were received by four channel digital data acquisition system (DAQ), Model: ATA-DAQ042451 and converted into digital form of frequency response function which were processed in Fast Fourier transform (FFT) to obtain the transverse vibration response of the beam. The transverse displacement evaluated corresponding to resonance conditions at each natural frequency are presented in Table 4.

It was observed that the transverse vibration amplitude at all the peaks of the CNT reinforced composite beam is less than compared to those of amplitudes of the beam without CNT reinforcement. This is due to the fact that the stiffness of the composite beam increases with CNT reinforcement which consequently decreases the amplitude of the vibration. Hence, it can be concluded that CNT reinforcement in the composite beam not only increases the stiffness of the structures but also increase the damping factor without any significant change in mass of the existing structures.

Table 4 Transverse vibration response of Glass/epoxy and Glass/epoxy/CNT composite beam under CF boundary condition

Mode Number	Glass/epoxy composite beam without CNT reinforcement		Glass/epoxy composite beam with CNT reinforcement	
	Natural Frequency (Hz)	Displacement (mm)	Natural Frequency (Hz)	Displacement (mm)
1	17.19	0.2522	21.88	0.1396
2	84.60	0.1650	109.38	0.0079
3	221.88	0.0032	257.87	0.0023
4	387.12	0.0019	414.06	0.0010
5	598.44	0.0009	640.94	0.0003

Conclusions

In this study, the micro, macro and structural analysis of composites with and without reinforcement of CNTs are investigated. The specimens were fabricated with proper distribution of CNTs in the composite with 1% wt. The material characterization of CNT was carried out to ensure the purity, quality and dispersion in polymer based composites under various aspects. The Carboxylic acids functionalized CNTs before and after sonication, and its distribution, length and diameters were identified. Further, the number of windings of roll in a multi walled carbon nanotube and the cross section view were predicted by using the TEM analysis. The functional group of CNTs functionalized with Carboxylic acid (COOH) was found by using the FT-IR analysis. The purity of the functionalized CNT was obtained by using the TGA analysis. Then, the mechanical characterization of Glass/epoxy and CNT/Glass/epoxy was carried out based on ASTM E1876. It was observed that the elastic properties of CNT reinforced composites are significantly higher than those of composites without CNT reinforcement. Further, the transverse vibration amplitude at all the peaks of the CNT reinforced composite beam decreases compared to those of amplitudes of the composite beam without CNT reinforcement. It was also seen that the natural frequencies at all the modes considered shift to higher level with CNT reinforcement in the composite structures. Hence, it can be concluded that CNT reinforcement in the composite beam not only increases the stiffness of the structures but also increase the damping factor without any significant change in mass of the existing structures.

The present study could be expanded by developing a mathematical model to investigate the dynamic responses of the hybrid composite structures such as beams, plates and shells which will provide the guidelines for the designer. Further, the study could focus on identifying the percentage increase in mechanical properties reinforcement of CNTs at elevated temperatures.

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Compliance of Ethical Standards

Disclosure of Potential Conflicts of Interest The authors declare that they do not have any conflict of interest.

Research Involving Human Participants and/or Animals The authors declare that the research does not involve any human participants and or animals which are harmful to them.

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