

## Research Article

# Three-Phase Carbon Fiber Amine Functionalized Carbon Nanotubes Epoxy Composite: Processing, Characterisation, and Multiscale Modeling

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The present paper discusses the key issues of carbon nanotube (CNT) dispersion and effect of functionalisation on the mechanical properties of multiscale carbon epoxy composites. In this study, CNTs were added in epoxy matrix and further reinforced with carbon fibres. Predetermined amounts of optimally amine functionalised CNTs were dispersed in epoxy matrix, and unidirectional carbon fiber laminates were produced. The effect of the presence of CNTs (1.0 wt%) in the resin was reflected by pronounced increase in Young's modulus, inter-laminar shear strength, and flexural modulus by 51.46%, 39.62%, and 38.04%, respectively. However, 1.5 wt% CNT loading in epoxy resin decreased the overall properties of the three-phase composites. A combination of Halpin-Tsai equations and micromechanics modeling approach was also used to evaluate the mechanical properties of multiscale composites and the differences between the predicted and experimental values are reported. These multiscale composites are likely to be used for potential missile and aerospace structural applications.

## 1. Introduction

The discovery of carbon nanotubes (CNTs) of exceptional mechanical properties combined with low density has led to their novel use as a reinforcing nanofiller in composite materials [1, 2]. The high strength and stiffness of CNTs leads to improved tensile, shear, and flexural properties of multiscale composites [3]. The effectiveness of CNT reinforcement can be proven by the fact that even smaller amounts (<5 wt%) of loading of CNTs result in significant improvements in their mechanical and physical properties. A number of studies have been performed on developing high-performance CNT/polymer composites containing CNTs ranging between 0.1 and 5 wt% [4, 5]. However, the homogeneous and consistent dispersion of CNTs in different polymers is found to be a major difficulty, which often degrades the properties of composites. Another important issue is the poor interfacial adhesion, which is mainly responsible for efficient load

transfer from the CNTs to the matrix [6]. Experimental determination of the interfacial strength of CNT/polymer composites still remains a challenge. Zhang et al. [7] reported that the interfacial shear strength of an epoxy composite reinforced using a CNT/carbon fibre (T300) hybrid is as high as 106.55 MPa, almost 150% higher than that of non-CNT reinforced composites. Limited success has been achieved on the experimental side however; reasonable success has been obtained in theoretical predictions [6]. The interfacial shear stress transfer from the matrix to the reinforcement takes place via the interface, which can be largely improved by chemical functionalisation of the CNT surfaces [8].

Multiscale composites (with CNTs, fibres, and matrix) have drawn significant attention in the field of advanced, high-performance materials. Only a limited number of studies involving three-phase composites have been reported [9–13]. Gojny et al. [9] reported an increase in interlaminar shear strength (ILSS) by 20% due to the amine functionalisation of

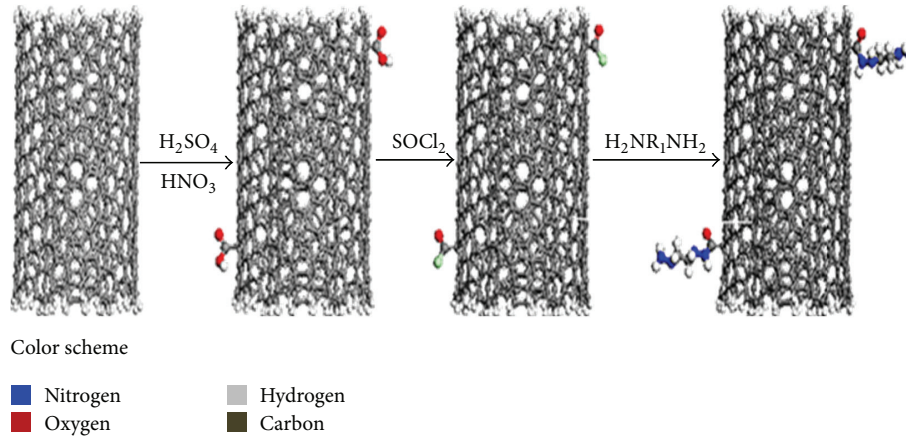


FIGURE 1: Procedure used for functionalisation of MWCNTs.

CNT surfaces. Zhihang et al. [10] reported a 30% increase in ILSS by incorporating CNTs perpendicular to the fibre surface. Thostenson et al. [12] introduced the idea of growing CNTs on the surface of carbon fibres to increase adhesion to the matrix, which was later confirmed experimentally by De Riccardis et al. [13]. Godara et al. [14] conducted tensile testing of unidirectional laminates reinforced with carbon fibre in different directions. They observed a systematic decrease in longitudinal tensile strength by up to 20% in comparison to the laminates produced using pristine CNTs.

An equally exciting, recent, research area is modeling of CNT composites and multiscale (microscale fibres and nanoscale tubes) composites to predict the mechanical properties and behaviour. Currently, for CNT/polymer composites, the Halpin-Tsai equations [15–17] and the Mori-Tanaka method [18–21] are being widely used. Qian et al. [17] considered multiwalled CNTs (MWCNTs)/polystyrene composite films as randomly oriented discontinuous fibre lamina and calculated the tensile modulus of the composite using the Halpin-Tsai equations. Yeh et al. [22] proposed modifying the Halpin-Tsai equations to evaluate the tensile modulus and strength of MWCNT/phenolic composites by adopting orientation and exponential shape factors. Kim et al. [23] obtained the tensile modulus of three-phase woven laminates theoretically as well as experimentally. They found that the theoretical tensile modulus is larger than the measured value by 11.8%; this discrepancy is attributed due to the assumptions made in the theoretical models.

The present research aimed to enhance the understanding of the practical and theoretical aspects related to the processing of three-phase multiscale CNT composites and the influence of the addition of CNTs. The objective of the present work is to obtain a homogeneous dispersion of amine functionalised multiwalled carbon nanotubes (AFMWCNTs) into epoxy, as well as producing a strong interface between them by means of functionalisation of CNTs. Also, several dispersion techniques have been tested in order to get a more homogenous dispersion. This study is also focused on evaluating the effect of CNT functionalisation on mechanical properties of multiscale composites.

TABLE 1: Types of fabricated three-phase composites.

Code	CNT wt%	Description
CFEC	0	Carbon fibre/epoxy composite
1CNTCFEC	0.25	0.25 wt% CNT three-phase composites
2CNTCFEC	0.5	0.5 wt% CNT three-phase composites
3CNTCFEC	1.0	1.0 wt% CNT three-phase composites
4CNTCFEC	1.5	1.5 wt% CNT three-phase composites

## 2. Experimental

**2.1. Materials.** AFMWCNTs (diameter: 20–30 nm; length: 20–30  $\mu\text{m}$ ; density: 1.8 g/cc; Young's modulus: 400 GPa) were obtained from Chemapol Industries (Mumbai, India). Diethylamine is used for functionalisation in 7.2 : 120 weight ratios of resin. The selection of Diethyl group for amine functionalisation was based on the results of Gojny et al. and Shen et al. [3, 24]. Shen et al. [24] concluded that the Diethyl group of amines is the most effective in enhancing the mechanical properties of CNT epoxy composites. The procedure used for functionalisation of MWCNTs and their chemical structure functionalised has been shown in Figure 1. The Araldite LY 556 epoxy resin obtained from Chemapol Industries (Mumbai, India) has been cured with the aromatic anhydride hardener HY5200. The glass transition temperature of the neat resin was 130–141°C (Chemapol Industries, Mumbai, India) and density was 1.15–1.20 g/cc. Different amounts (0.25, 0.50, 1.0, and 1.50 wt%) of AFMWCNTs were dispersed in epoxy matrix using an advanced ultrasonic probe sonication method. The details of the sonicator used in this study have been presented in the next section. Finally the three-phase multiscale composites were prepared by the hand layup technique for 60% carbon fibre and for different CNT loading, as listed in Table 1. Carbon fibre T700 grade (Toray Co., USA) containing 600 filaments per tow was used in this study. T700 fibre has a high tensile strength (approximately 5000 MPa) with a standard modulus of 230 GPa.

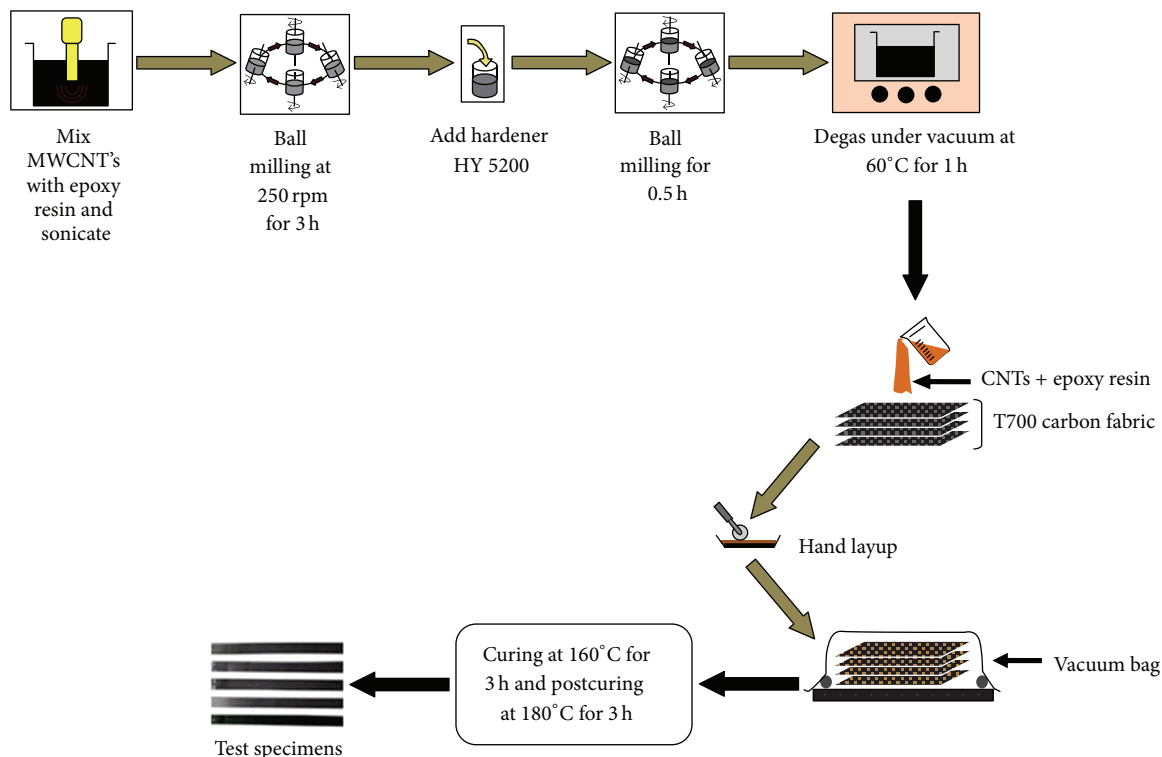


FIGURE 2: Fabrication process of carbon fibre/CNT/epoxy three-phase composites.

**2.2. Fabrication Process.** Precalculated amounts of AFMWCNTs and curing agent were weighed and mixed together with epoxy in a beaker, such that the weight fraction of CNTs was 0.3% with respect to resin and curing agent. Horn Sonicator 3000 ultrasonic probe sonication was employed for 18 min to uniformly disperse the CNTs in the curing agent. Horn Sonicator 3000 has 3.2 mm tip diameter, 100 watts maximum power output, and 22.5 kHz operating frequency. Following this, the epicure AFMWCNT mixture was combined with epoxy and the three component mixture was ball milled at 250 rpm for 3 h for homogeneous dispersion of AFMWCNTs. Next, the hardener HY5200 was mixed and the mixture was further ball milled for 30 min at 250 rpm. The mixture was then degassed in a vacuum oven for 1 h at 60°C and subsequently preheated before spreading uniformly on the carbon fibre, using the hand layup process. Once the carbon fibre had been infiltrated with the LY556/epicure W/MWCNT mixture, it was allowed to cure at 110°C for 2 h and post cure at 180°C for 3 h in a vacuum oven. In this study, the following five carbon fibre reinforced laminates were fabricated: one for neat resin and four with 0.25, 0.50, 1.0, and 1.50 wt% AFMWCNTs dispersed. A schematic illustration of the process used for the fabrication of carbon fibre/CNT/epoxy three-phase composites has been shown in Figure 2. Finally, six samples each were cut in the dimensions set up by the ASTM D 3039 standard for tensile tests and the ASTM D 790 standard for flexural tests.

### 2.3. Sample Characterisation

**2.3.1. FTIR Spectroscopy.** A Fourier transform infrared (FTIR) spectrum was recorded using the SHIMADZU, Kyoto, Japan, IRAffinity-1 spectrometer with the range of 2100  $\text{cm}^{-1}$  peak to peak at the maximum resolution of 0.5  $\text{cm}^{-1}$ . The IRAffinity-1 offers the highest S/N ratio in its class (30,000:1, 1-minute accumulation neighbourhood of 2100  $\text{cm}^{-1}$  peak to peak) and compact dimensions. The interferometer is continuously optimized by a dynamic alignment mechanism and a built-in auto dryer.

**2.3.2. Mechanical Testing.** Carbon fibre/CNT/epoxy composites test specimens were cut in the desired dimensions (Figure 3(a)) out of the laminate panel (Figure 3(b)). The sample dimensions were  $180 \times 10.30 \times 1.44$  mm. Both pure CF-epoxy and three-phase (CNT reinforced) composites were tested according to the ASTM D 3039 standard for tensile properties. A table top model STM series Universal Testing Machine of 50 kN load cell (United Calibration Corporation) was used for tensile testing. The crosshead speed was set at 3.5  $\text{mm}\cdot\text{min}^{-1}$ . Flexural modulus tests were also conducted according to the ASTM D 790 standard on the same machine at a crosshead speed of 10  $\text{mm}\cdot\text{min}^{-1}$  at room temperature, with the sample span of 30 mm. The average values of six test results have been reported here.

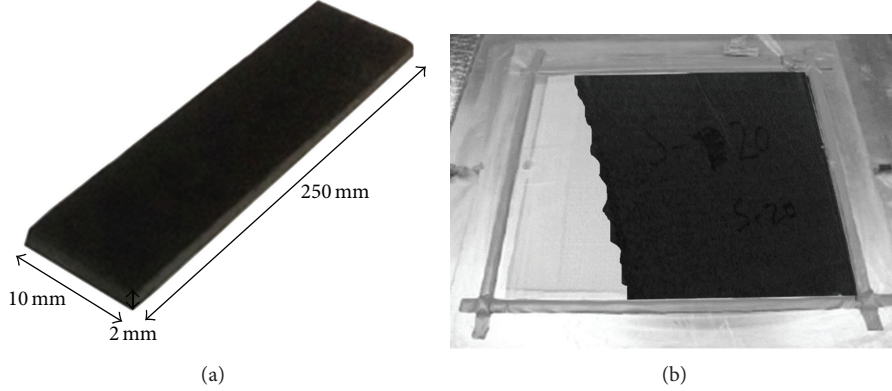


FIGURE 3: (a) Test specimen cut in the desired dimensions from (b) laminate panel sheets.

Morphology of the fractured composite samples surfaces was observed under the JEOL JXA-8100 scanning electron microscope (SEM) in order to investigate the fibre-matrix interface. Further detailed micro- and nanostructural study was carried out using a transmission electron microscope (TEM) (CM 200 from Philips and Tecnai G<sup>2</sup> from FEI) with LaB<sub>6</sub> filament operated at 200 kV. The high resolution imaging was done using the JEOL TEM equipped with a field emission gun operated at 200 kV, capable of providing a point to point resolution. The TEM image for aligned bundles and isolated AFMWCNTs is shown in Figures 4(a) and 4(b), respectively. A fine powder was prepared from the AFMWCNTs sample which was subsequently added to methanol and kept in an ultrasonic bath for 15 min to obtain a uniformly dispersed solution. For carrying out the TEM analysis a small drop from this solution was taken in a capillary tube and poured onto a 300 mesh carbon coated grid of 3 mm diameter and then dried under IR lamp.

**2.4. Micromechanics Modeling.** To predict the mechanical properties of three-phase composites, the Halpin-Tsai equations and theory of micromechanics were applied in hierarchy. First, the Halpin-Tsai equations were applied to calculate the mechanical properties of two-phase CNT/epoxy nanocomposites. The two-phase nanocomposite properties were then applied to compute the mechanical properties of three-phase multiscale composites using the micromechanics rule of mixtures. In the rule of mixtures, the properties of CNT/epoxy composites were used as the properties of the matrix.

**2.4.1. Halpin-Tsai Equations.** One of the primary requirements for obtaining the mechanical properties of three-phase multiscale composites was to compute the material properties of the CNT/epoxy composite. In this study, the results were analyzed with the Halpin-Tsai model for randomly oriented long fibres. This model was developed by Halpin and Kardos [15] to account for the Young's modulus of composites based on polymer matrices filled with particles of high aspect ratio. It produces favourable interactions between the matrix and the filler as well as good filler distribution.

The selected Halpin-Tsai equation, correlating the relative Young's modulus of a composite to the morphological and mechanical properties of its constituents, and the specific geometric characteristics of AFMWCNTs are represented as follows:

$$\begin{aligned}
 E_c = & \frac{3}{8} \left[ 1 + 2 \left\{ \frac{l}{d} \right\} \left\{ \frac{(E_{CNT}/E_{EP}) - (d/4t)}{(E_{CNT}/E_{EP}) + (l/2t)} \right\} \varphi_{CNT} \right] \\
 & \times \left[ 1 - \left\{ \frac{(E_{CNT}/E_{EP}) - (d/4t)}{(E_{CNT}/E_{EP}) - (d/2t)} \right\} \varphi_{CNT} \right] E_{EP} \\
 & + \frac{5}{8} \left[ 1 + 2 \left\{ \frac{(E_{CNT}/E_{EP}) - (d/4t)}{(E_{CNT}/E_{EP}) + (l/2t)} \right\} \varphi_{CNT} \right] \\
 & \times \left[ 1 - \left\{ \frac{(E_{CNT}/E_{EP}) - (d/4t)}{(E_{CNT}/E_{EP}) + (d/2t)} \right\} \varphi_{CNT} \right]^{-1} E_{EP}, \quad (1)
 \end{aligned}$$

where  $E_c$  = Young's modulus of nanocomposite,  $E_{EP}$  = Young's modulus of neat epoxy,  $E_{CNT}$  = Young's modulus of AFMWCNTs,  $l/d$  = aspect ratio of dispersed AFMWCNTs,  $d$  = diameter of AFMWCNTs,  $l$  = length of AFMWCNTs,  $t$  = thickness of graphite layer (3.4 Å), and  $\varphi_{CNT}$  = volume fraction of AFMWCNTs given by the following equation:

$$\varphi_{CNT} = \frac{1}{[(\rho_{CNT}/\rho_{EP}) \times (M_{EP}/M_{CNT})] + 1}, \quad (2)$$

where  $\rho_{CNT}$  is density of CNT,  $\rho_{EP}$  is density of epoxy,  $M_{EP}$  is mass volume fraction of epoxy, and  $M_{CNT}$  is mass fraction of CNTs, calculated to be 0.143% based on the CNT and epoxy densities of 2.1 and 1.2 g/cc, respectively [25, 26]. The estimated diameter, length and modulus of AFMWCNTs are 20 nm, 30 μm and 400 GPa, respectively. Calculated tensile modulus equal to 3.10 GPa of neat epoxy and (1) yields the CNT/epoxy composite tensile modulus of 3.46 GPa at 0.25 wt% CNT loading, which translates to a 11.61% increase over the neat epoxy modulus. In the calculations, the CNT composites were regarded as isotropic as the AFMWCNTs which were assumed to be uniformly distributed and randomly oriented throughout the matrix. As the amount of CNTs was small, the Poisson's ratio of the CNT

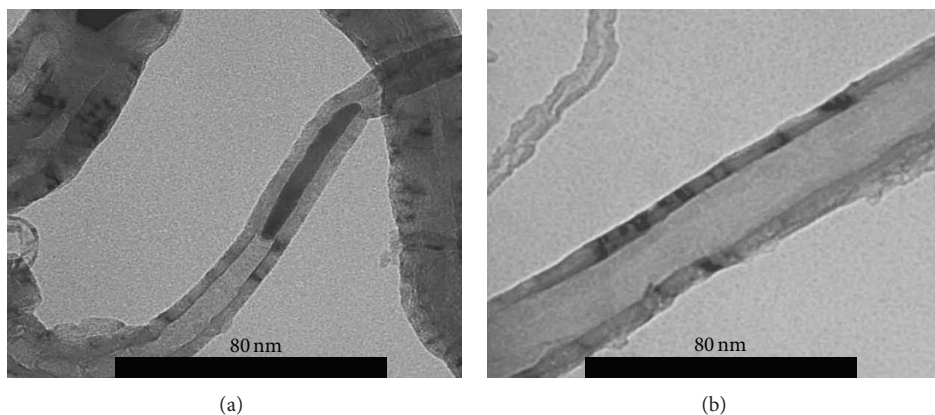


FIGURE 4: TEM image of AFMWCNTs showing (a) aligned bundles and (b) isolated MWCNT.

composite was assumed to be the same as that of epoxy, that is, 0.35 [27]. Considering isotropy, the shear modulus can be calculated using the following equation:

$$G_C = \frac{E_C}{2(1 + \nu)}, \quad (3)$$

where  $G_C$  is shear modulus and  $\nu$  is Poisson's ratio of CNT/epoxy composites. Table 2 shows the results of elastic properties of CNT/epoxy composites for varying percentage of CNTs. At 0.25 wt% CNT loading the shear modulus increased by 11.30%. Table 3 shows the elastic properties of ICFCFEC and CNTCFEC multiscale three-phase composites. For multiscale composites, the mechanical properties of CNT composites were used as matrix properties. The composite was considered to be unidirectional fibre reinforced and the mechanical properties were calculated by CADEC, a micromechanics software by Barbero [27]. The composites have been theoretically tested for longitudinal Young's modulus up to 5 wt% of CNT reinforcement; this is because of the continuously increasing trend of modulus. The mechanical reinforcement of different wt% CNTs in epoxy matrix shows an improvement of 25.83% in longitudinal tensile modulus, while moderate improvement has been observed in transverse tensile modulus and in-plane shear modulus. This can be attributed to CNT reinforcement in the longitudinal direction that is fiber dominated.

### 3. Experimental Results and Discussion

First, the functionalisation of AFMWCNTs was verified using FTIR spectroscopy, and in the second phase, five specimens of each type of composites have been tested and analyzed. For multiscale composites tensile, flexural and shear tests were performed and the results are discussed in this section.

**3.1. Effect of Functionalisation.** FTIR spectroscopy has shown limited ability to probe the structure of AFMWCNTs owing to their poor infrared transmittance. Because of their black character, the AFMWCNTs exhibit a strong absorbance and often are unable to be distinguished from the background noise, making it necessary to use a very weak concentration

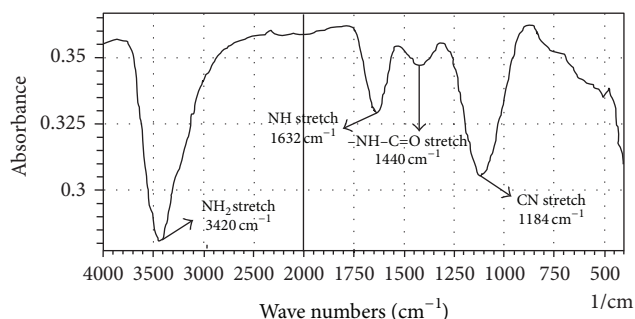


FIGURE 5: FTIR spectrum of AFMWCNTs.

of the nanotubes in potassium bromide (KBr) powder. As shown in Figure 5, the peak at  $3420 \text{ cm}^{-1}$  corresponds to the  $\text{NH}_2$  stretch and peaks at  $1632$  and  $1184 \text{ cm}^{-1}$  correspond to the NH in-plane and C-N bond stretching, respectively, in AFMWCNTs. The  $3420 \text{ cm}^{-1}$  peak produced by the flexible fluctuation of primary amine ensures the presence of amine group in MWCNTs.

**3.2. Tensile Test.** Figure 6 shows the fractured specimen after tensile testing. Five test specimens were tested for each composite type as listed in Table 1. Figure 7(a) shows the typical stress-strain plots for different compositions while Figures 7(b) and 7(c) show the mean values (along with standard deviation error bars) of tensile modulus and tensile strength, respectively, of different multiphase composites. In general, the longitudinal tensile modulus and tensile strength of unidirectional multiphase composites exhibit a fibre dominated behaviour. This is clearly observed for longitudinal tensile modulus plotted in Figure 7(b). Figure 7(c) demonstrates that the tensile strength of the three-phase composite increases from 1.25 GPa (CFEC) to 1.90 GPa (3CNTCFEC), that is, 51.46%, but for 4CNTCFEC it decreases. This may be attributed to the formation of the covalent bond between AFMWCNTs and epoxy matrix, leading to more effective stress transfer.

TABLE 2: Tensile properties of neat epoxy and CNT/epoxy composites.

% CNT in CNT/epoxy composite	Tensile modulus $E$ (GPa)	Poisson's ratio $\nu$	Shear modulus $G$ (GPa)
0.0% CNT (neat epoxy)	3.10	0.35	1.15
0.25%	3.46	0.35	1.28
0.50%	3.83	0.35	1.42
1.00%	4.26	0.35	1.58
1.50%	4.41	0.35	1.63

TABLE 3: Elastic properties of carbon fibre/epoxy and carbon fibre/CNT/epoxy multiscale composites.

Composite description	Longitudinal tensile modulus $E_{11}$ (GPa)	Transverse tensile modulus $E_{22}$ (GPa)	In-plane Poisson's ratio $\nu_{12}$	In-plane shear modulus $G_{12}$ (GPa)
CFEC	98.92	7.59	0.284	2.75
1CNTCFEC	124.48	8.46	0.284	3.07
2CNTCFEC	128.94	9.34	0.284	3.39
3CNTCFEC	138.35	10.36	0.284	3.77
4CNTCFEC	142.58	10.72	0.284	3.89

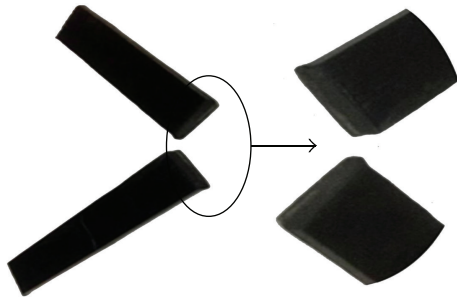


FIGURE 6: Fractured specimen of multiscale composites.

Young's modulus has been increased by 40.4% for 1CNTCFEC when compared with CFEC, as shown in Figure 7(c). This is because of the fact that the longitudinal tensile modulus and tensile strength for unidirectional composite laminates in general show fibre dominated behaviour. The AFMWCNTs prove to be even more effective due to the alignment of the polymer chains along the CNTs in the axial direction. This may be due to the presence of  $-\text{NH}_2$  functional groups at the surface of CNTs. This results in reduction in the average free polymer chain length and improvement cross-linking of the polymer chains with CNTs, leading to an obvious increase in the tensile strength and longitudinal tensile modulus. However, a decrease was observed for the 4CNTCFEC (reinforcement above 1.0 wt%); this may be due to the enhancement in stress which has been built up around the fibres.

In case of CFEC, the theoretical tensile modulus was found to be larger than the experimental value by approximately 16%, as shown in Figure 8. This may be attributed to the assumptions implicated in the Halpin-Tsai equations, namely, perfect fibre-matrix bonding, good dispersion, and high  $l/d$  ratio. The carbon fibre/CNT/epoxy interface was investigated by observing the morphology of the fractured

surface using SEM. The specimen investigated by SEM was initially coated with gold before examination under the microscope. The SEM images shown in Figures 9(a) and 9(b) illustrate weak bonding at the fibre-matrix interface.

**3.3. Shear Test.** Figure 10 shows the specimen after testing in shear. For the shear test, five test specimens were tested for each composite type. The experimental results in Figure 11 are the mean values of the five test specimens with standard deviation bars. The test results show a systematic increase in ILSS up to 3CNTCFEC and further decrease of 38.76% on addition of more CNTs. This was increased by 27% for 3CNTCFEC as compared to CFEC. The increase in ILSS by addition of AFMWCNTs is due to surface modification, which results in a strong interfacial interaction. Similar results were also reported by Gojny et al. [9] and Zhihang et al. [10]; however, they used a different matrix (name it here). Godara et al. [14] reported an ILSS value of 68 MPa for modified MWCNTs which was 13.33% higher than the unmodified MWCNTs.

The other possible reasons are less damaged CNT surface, maintained aspect ratio, and the optimized level (up to 10%) of  $-\text{NH}_2$  functional groups added during the CNT functionalisation process. Additional factors like step time and temperature can also influence the grafting of a number of functionalised groups at the CNT surface. Park et al. [25] reported such an influence on the CNT/epoxy composite in terms of decreased matrix toughness, with an increase in temperature. They also elaborated the importance of the optimisation of CNT surface functionalisation, as it strongly influences the polarity and level of interaction of CNT surface with the matrix. In addition, Ci and Bai [26] explained the minimum influence of CNT reinforcement on the properties of composite if the matrix is extremely tough. Therefore, it is difficult to observe any effect on the strength of the epoxy matrix for any CNT type. They also revealed that soft and

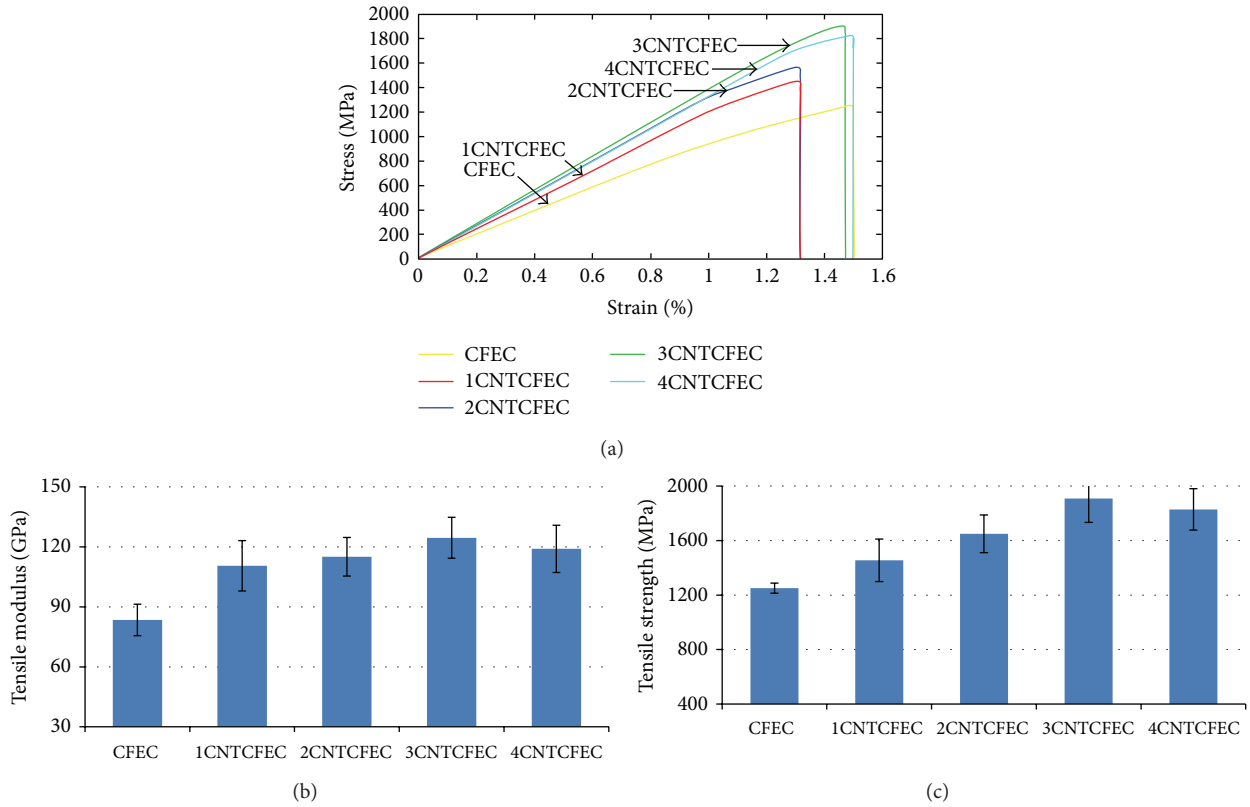


FIGURE 7: (a) Stress-strain plots, (b) tensile modulus, and (c) tensile strength of different multiphase composites.

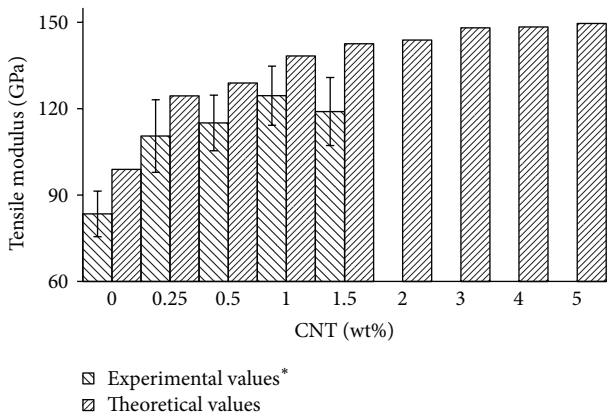


FIGURE 8: Comparison of theoretical and experimental longitudinal tensile modulus. \*Experimental values were determined only up to 1.5 wt% of CNT reinforcement.

ductile matrices allow better interface adjoining, whereas the interfacial interaction is poor due to complete cross-linking of polymer molecules surrounding the CNTs in the stiff matrix. The matrix used to fabricate laminates in the present study has a modulus of about 3.10 GPa, which is well above the limit mentioned by Ci and Bai [26].

The significant decrease of ILSS for 4CNTCFEC is attributed to a combination of higher matrix rigidity and higher interfacial interaction. Such a behaviour suggests

an optimisation of the inert sites of the CNT surface for the optimal level of interaction with matrix. The surface modification using amine functionalisation shows positive effects in comparison with the CFEC composite system. As expected, the increased physical affinity between the AFMWCNTs and epoxy resin system worked positively in this case.

**3.4. Flexural Test.** Figure 12 shows the improvement in flexural strength of multiscale composite with increased content of CNTs. When compared with CFEC, the 2CNTCFEC and 3CNTCFEC composites showed a 24.69% and 38.04% increase in flexural strength, respectively. This enhancement was due to the reinforcing effect of the CNTs, as flexural properties are matrix dominated rather than being fibre dominated. The reduced flexural strength of 4CNTCFEC, when compared to 3CNTCFEC, can be inferred from the fact that there exists a more dominant factor than the degree of CNT dispersion that governs the matrix dominated mechanical properties. Another comparing factor may be the degree of cure of the epoxy resin at the time of infusion. Incomplete fibre wetting due to high viscosity of the mixture tends to weaken the crosslinking between polymer molecules to conform to the fibre preform and infiltrate the interfilament spaces. In addition to this, heat buildup during prolonged sonication and ball milling may contribute to premature curing, and this possibility warrants further investigation [23]. However, a maximum enhancement in flexural modulus

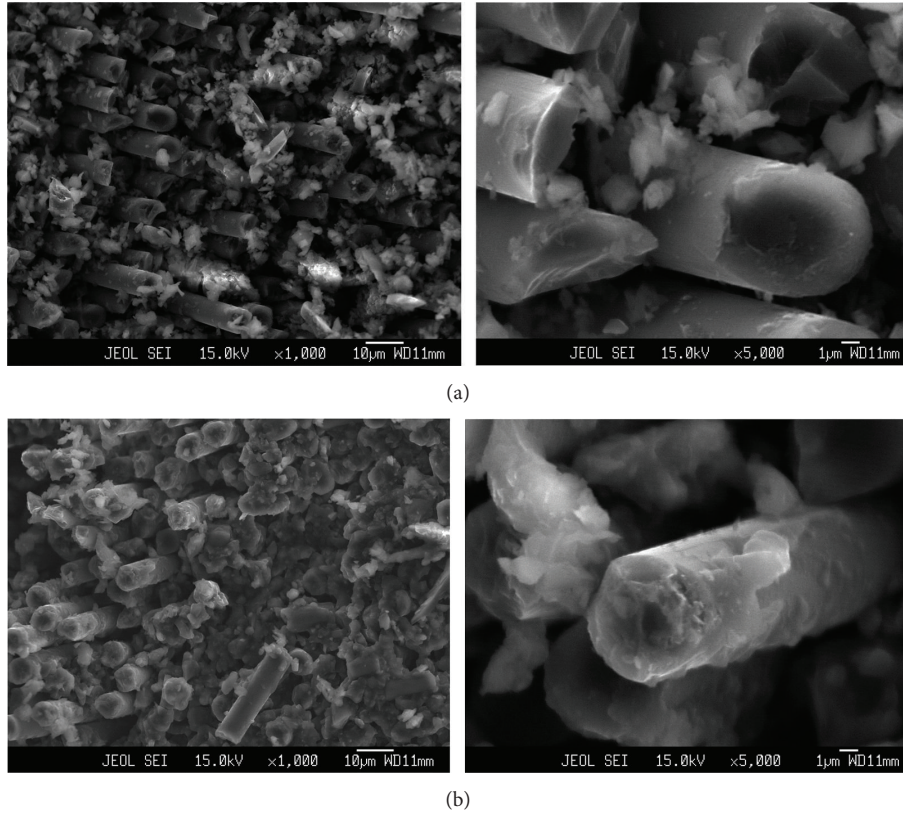


FIGURE 9: SEM images of carbon fibre epoxy interface showing debonding and void in (a) 2CNTCFEC and (b) 3CNTCFEC sample.



FIGURE 10: Shear tested specimen of multiscale composite.

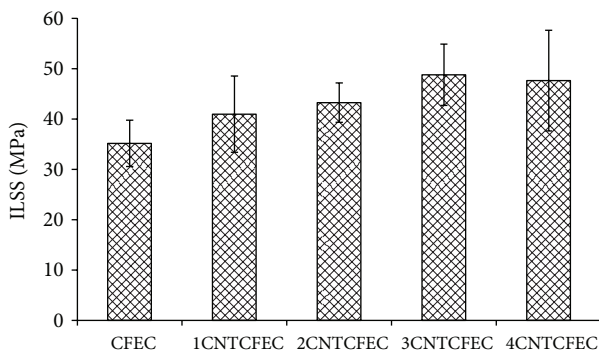


FIGURE 11: ILSS variation with CNT concentration (wt%).

by 35% and a 5% improvement in flexural strength have been shown by [28] for small addition of CNTs (0.025, 0.05, and 0.1 wt%) in epoxy resin.

For optimising the advantage of reinforcing effect of CNTs, it is crucial to achieve a strong interface between the CNTs and the matrix. In particular, it is important to reinforce the interface between the carbon fibre and the matrix using CNTs so that the load can be transferred from the fibre to the matrix, and at the same time, the gap between the highly mismatched properties of the matrix and the fibre can be bridged [9]. Optimized functionalisation of the CNT surfaces may be the most effective solution for successful load transfer between the CNTs and matrix, results of which increase the mechanical properties of multiscale composites considerably.

#### 4. Conclusion

Carbon fibre/CNT/epoxy multiscale composites were fabricated and characterised in this research. A detailed analysis of the experimental results obtained has been presented in this paper. Good dispersion and perfect bonding were the two major issues for significant improvement of the mechanical properties of carbon fibre/CNT/epoxy three-phase composites. AFMWCNTs were uniformly distributed in the carbon fibre-epoxy matrix using ultrasonic treatment assisted or combined with high speed mechanical steering or stirring. The dispersion technique used for AFMWCNTs led to a significant improvement in the mechanical properties of the three-phase multiscale composites. Dispersion of only 1.0% AFMWCNTs in the matrix improved the Young's modulus and tensile strength of carbon fiber/epoxy composites by

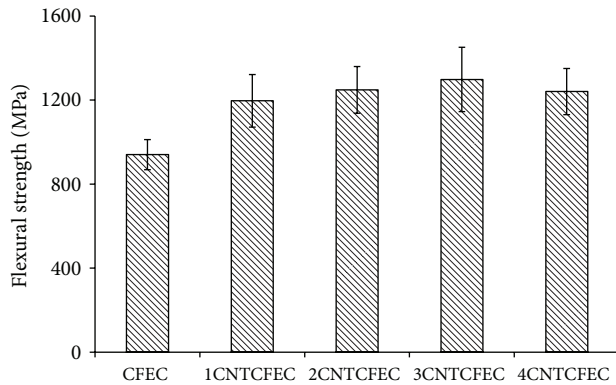


FIGURE 12: Flexural strength variation with CNT concentration (wt%).

49% and 52%, respectively. Similarly, the ILSS and flexural strength improved by 37% and 38%, respectively. Improved mechanical properties of multiscale composites are attributed to the formation of strong interface between the carbon fibres and the epoxy matrix in the presence of AFMWCNTs.

Three-phase composite modeling was performed in parallel to predict the tensile properties. The Halpin-Tsai equations and conventional micromechanics rule of mixtures were combined to calculate Young's modulus of three-phase composites. Theoretical Young's modulus of carbon fiber/epoxy composites was higher by 16% than the experimental Young's modulus. This may be attributed to the assumptions implicated in the Halpin-Tsai equations, namely, perfect fibre-matrix bonding, good dispersion, and high  $l/d$  ratio.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

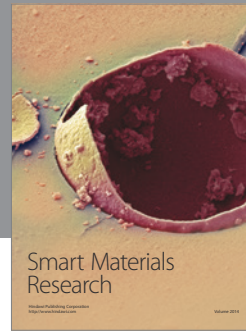
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## References

- [1] J. Njuguna, K. Pielichowski, and J. R. Alcock, "Epoxy-based fibre reinforced nanocomposites," *Advanced Engineering Materials*, vol. 9, no. 10, pp. 835–847, 2007.
- [2] J. Njuguna, K. Pielichowski, and J. R. Alcock, "Polymer nanocomposites for aerospace applications: characterization," *Advanced Engineering Materials*, vol. 6, no. 4, pp. 204–210, 2004.
- [3] F. H. Gojny and K. Schulte, "Functionalisation effect on the thermo-mechanical behaviour of multi-wall carbon nanotube/epoxy-composites," *Composites Science and Technology*, vol. 64, no. 15, pp. 2303–2308, 2004.
- [4] K. Lau and S. Shi, "Failure mechanisms of carbon nanotube/epoxy composites pretreated in different temperature environments," *Carbon*, vol. 40, no. 15, pp. 2965–2973, 2002.
- [5] R. G. de Villoria, A. Miravete, J. Cuartero, A. Chiminelli, and N. Tolosana, "Mechanical properties of SWNT/epoxy composites using two different curing cycles," *Composites B*, vol. 37, no. 4–5, pp. 273–280, 2006.
- [6] M. Abdalla, D. Dean, D. Adibempe, E. Nyairo, P. Robinson, and G. Thompson, "The effect of interfacial chemistry on molecular mobility and morphology of multiwalled carbon nanotubes epoxy nanocomposite," *Polymer*, vol. 48, no. 19, pp. 5662–5670, 2007.
- [7] F. Zhang, R. Wang, X. He, C. Wang, and L. Ren, "Interfacial shearing strength and reinforcing mechanisms of an epoxy composite reinforced using a carbon nanotube/carbon fiber hybrid," *Journal of Materials Science*, vol. 44, no. 13, pp. 3574–3577, 2009.
- [8] A. Eitan, K. Jiang, D. Dukes, R. Andrews, and L. S. Schadler, "Surface modification of multiwalled carbon nanotubes: toward the tailoring of the interface in polymer composites," *Chemistry of Materials*, vol. 15, no. 16, pp. 3198–3201, 2003.
- [9] F. H. Gojny, M. H. G. Wichmann, B. Fiedler, W. Bauhofer, and K. Schulte, "Influence of nano-modification on the mechanical and electrical properties of conventional fibre-reinforced composites," *Composites A*, vol. 36, no. 11, pp. 1525–1535, 2005.
- [10] F. Zhihang, H. S. Michael, and S. Advani, "Interlaminar shear strength of glass fiber reinforced epoxy composites enhanced with multi-walled carbon nanotubes," *Composites A*, vol. 39, no. 3, pp. 540–554, 2008.
- [11] T. Yokozeki, Y. Iwahori, and S. Ishiwata, "Matrix cracking behaviors in carbon fiber/epoxy laminates filled with cup-stacked carbon nanotubes (CSCNTs)," *Composites A*, vol. 38, no. 3, pp. 917–924, 2007.
- [12] E. T. Thostenson, W. Z. Li, D. Z. Wang, Z. F. Ren, and T. W. Chou, "Carbon nanotube/carbon fiber hybrid multiscale composites," *Journal of Applied Physics*, vol. 91, no. 9, pp. 6034–6041, 2002.
- [13] M. F. De Riccardis, D. Carbone, T. D. Makris, R. Giorgi, N. Lisi, and E. Salernitano, "Anchorage of carbon nanotubes grown on carbon fibres," *Carbon*, vol. 44, no. 4, pp. 671–674, 2006.
- [14] A. Godara, L. Mezzo, F. Luizi et al., "Influence of carbon nanotube reinforcement on the processing and the mechanical behaviour of carbon fiber/epoxy composites," *Carbon*, vol. 47, no. 12, pp. 2914–2923, 2009.
- [15] J. C. Halpin and J. L. Kardos, "The Halpin-Tsai equations: a review," *Polymer Engineering and Science*, vol. 16, no. 5, pp. 344–352, 1976.
- [16] S. Peeterbroeck, L. Breugelmans, M. Alexandre et al., "The influence of the matrix polarity on the morphology and properties of ethylene vinyl acetate copolymers-carbon nanotube nanocomposites," *Composites Science and Technology*, vol. 67, no. 7–8, pp. 1659–1665, 2007.
- [17] D. Qian, E. C. Dickey, R. Andrews, and T. Rantell, "Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites," *Applied Physics Letters*, vol. 76, no. 20, pp. 2868–2870, 2000.

- [18] X. Li, H. Gao, W. A. Scrivens et al., "Reinforcing mechanisms of single-walled carbon nanotube-reinforced polymer composites," *Journal of Nanoscience and Nanotechnology*, vol. 7, no. 7, pp. 2309–2317, 2007.
- [19] G. D. Seidel and D. C. Lagoudas, "Micromechanical analysis of the effective elastic properties of carbon nanotube reinforced composites," *Mechanics of Materials*, vol. 38, no. 8–10, pp. 884–907, 2006.
- [20] B. Jiang, C. Liu, C. Zhang, B. Wang, and Z. Wang, "The effect of non-symmetric distribution of fiber orientation and aspect ratio on elastic properties of composites," *Composites B*, vol. 38, no. 1, pp. 24–34, 2007.
- [21] T. Mori and K. Tanaka, "Average stress in matrix and average elastic energy of materials with misfitting inclusions," *Acta Metallurgica*, vol. 21, no. 5, pp. 571–574, 1973.
- [22] M. Yeh, N. Tai, and J. Liu, "Mechanical behavior of phenolic-based composites reinforced with multi-walled carbon nanotubes," *Carbon*, vol. 44, no. 1, pp. 1–9, 2006.
- [23] M. Kim, Y. Park, O. I. Okoli, and C. Zhang, "Processing, characterization, and modeling of carbon nanotube-reinforced multiscale composites," *Composites Science and Technology*, vol. 69, no. 3–4, pp. 335–342, 2009.
- [24] J. Shen, W. Huang, L. Wu, Y. Hu, and M. Ye, "Study on amino-functionalized multiwalled carbon nanotubes," *Materials Science and Engineering A*, vol. 464, no. 1–2, pp. 151–156, 2007.
- [25] S. Park, H. Jeong, and C. Nah, "A study of oxyfluorination of multi-walled carbon nanotubes on mechanical interfacial properties of epoxy matrix nanocomposites," *Materials Science and Engineering A*, vol. 385, no. 1–2, pp. 13–19, 2004.
- [26] L. Ci and J. Bai, "The reinforcement role of carbon nanotubes in epoxy composites with different matrix stiffness," *Composites Science and Technology*, vol. 66, no. 3–4, pp. 599–603, 2006.
- [27] E. Barbero, *Introduction to Composite Materials Design*, vol. 17, pp. 29–35, Taylor & Francis, 1999.
- [28] T. Peijs, F. Inam, D. W. Y. Wong, and M. Kuwata, "Multiscale hybrid micro-nanocomposites based on carbon nanotubes and carbon fibers," *Journal of Nanomaterials*, vol. 2010, Article ID 453420, 12 pages, 2010.



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