Solvent free, efficient, industrially viable, fast dispersion process based amine modified MWCNT reinforced epoxy composites of superior mechanical properties

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ABSTRACT

Dispersion of multiwalled carbon nanotubes (MWCNTs) into epoxy resin is a challenging task for the process to be viable on industrial scale. Herein, amine functionalized MWCNTs (Am-MWCNTs) were reinforced into epoxy resin using industrially viable, fast, efficient, solvent free, high speed homogenizer dispersion technique. Am-MWCNTs ranging from 0.1 to 0.75% by w/w were loaded in epoxy and the effects of loading of Am-MWCNTs on mechanical properties of epoxy composites are investigated. The flexural strength of Am-MWCNTs based epoxy composites reached up to 163 MPa for 0.5 wt% MWCNTs loaded sample compared to 95 MPa for pure cured epoxy sample; an overall improvement of 72% in the flexural strength. In addition to this, the flexural modulus value reached to 3795 MPa for 0.75 wt% Am-MWCNTs loaded sample from 2250 MPa for pure epoxy sample, an improvement of 69%. The enhancement in the mechanical properties was correlated with the dynamic scanning calorimeter results, TEM and SEM images of fractured surface. The substantial improvement in the mechanical properties of the epoxy resin at such low CNT loading can open a venue for the preparation of structurally strong structures for aerospace, defence, automobile and sports industries. Copyright © 2015 VBRI Press.

Keywords: Multiwalled carbon nanotubes; functionalization; mechanical properties; dispersion; high speed homogenizer.

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Introduction

Epoxy resin is one of the most important and widely used thermosetting polymer matrix used for the development of advanced composites displaying a number of promising characteristics. Because of very unique mechanical properties, chemical resistance, low cost, ease of processing and good adhesion to many substrates [1, 2], it can be used in number of applications from electronics to aerospace [3].

Due to its exceptional mechanical properties, carbon nanotubes (CNTs) have attracted a lot of attention towards its use as reinforcement with the epoxy resin for enhancing the mechanical properties. Unfortunately, as-synthesized CNTs are insoluble in all the solvents; therefore, their interaction/bonding/adhesion with polymer is very poor. As a result, the mechanical properties of CNTs based polymer composites have not been fully exploited. The chemical functionalization is the easiest way to modify the surface of CNTs with functional groups which are compatible with the polymer matrix. Basically epoxy system is the combination of prepolymer (generally in the form of di-glycidyl ether of bisphenol A) and cross linking agent/hardener (preferably in the form of amine). Therefore, the modification of CNTs surface using amine has been found to be very important for enhancing the mechanical properties due to the formation of covalent linkage between CNT and epoxy.

In addition to functionalization, dispersion process is also very important for viability of commercialization and enhancement in the mechanical properties simultaneously. A number of processing techniques for making nanotube-reinforced composites have been developed and summarized in a review article [4]. For processing nanotube composites using thermoset matrix materials, such as epoxies or vinyl esters, most approaches involve several processing techniques including high speed mixing [5, 6], high-energy sonication and solution-evaporation processing [7-9], surfactant-assisted processing through formation of a colloidal intermediate, or functionalization of nanotubes with the polymer matrix [10, 11].

Most of these approaches are limited in scalability and are not amendable to high volume or high rate production. To evaluate key engineering properties such as strength, toughness and electrical/thermal conductivity, it is crucial to fabricate many macroscopic nanocomposite test specimens. Various dispersion techniques used in literature includes sonication (ultrasonication, pulsed sonication), stirring, kneading, shear mixing, ball milling, calendaring, and micro compounding.

A common technique used to disperse CNT's is the sonication. A pulsed ultrasound exfoliates agglomerates and disperses CNTs in the matrix effectively. However, this method is limited by the reduction of the vibrational energy with increasing distance from the sonic tip and thus only a small quantity can be exfoliated at a time. In one study by Lau et al. [12], different solvents were used to disperse CNTs. Only acetone-dispersed nanocomposites displayed improvement in flexural strength over pure epoxy resin. Flexural strength increased from 74.3 MPa (neat epoxy) to 75.6MPa (with 0.5 wt% SWCNTs) with acetone as a solvent. In another study by Breton et al. [13], Young's modulus increased by 16% for 6wt% MWCNTs loaded composites. In the study by Yu et al. [14], time dependent sonication experiments revealed that the dispersion of

MWCNTs is related to UV absorbance of the solution. The surfactant molecules adsorbed on the surface of the MWCNTs prevents reaggregation of MWCNTs and thus the stability of MWCNTs dispersion can be maintained for several months. Gojny et al. [9] investigated the CNT/epoxy-nanocomposites using TEM and provided evidence for improved interfacial interaction between the functionalized nanotubes and the matrix. Yang et al. [15] used sonication cum stirring technique to disperse CNTs in epoxy resin and observed that impact strength reached to 15.24 kJ/m^2 for composites with as such CNTs from 11.32kJ/m^2 for pure epoxy (an increase of 35%). Impact strength of triethlyene tetra amine (TETA) modified CNTs (0.6 wt %) was 20.83 kJ/m^2 (84% improvement) and bending strength reached to 95.85 MPa for 0.6wt% as such-MWCNT loaded sample from 85.67MPa for neat epoxy (an increase of 12%). Bending modulus increased to 2.41 GPa from 2.21 GPa (a rise of 9%) for TETA modified CNTs (0.6 wt %). Herna´ndez-Pe´rez et al. [16] used sonication cum magnetic stirring for the dispersion of CNTs into epoxy resin. In their studies, the tensile strength improved from 47.3 MPa to 47.9 MPa but elastic modulus decreased from 1.97 GPa to 1.77 GPa. Kathi et al. [17] also used sonication cum stirring technique for dispersion and they found an improvement in flexural strength from 61 MPa to 83 MPa and flexural modulus from 2100 MPa to 2550 MPa. Yang et al. [15] also used sonication cum magnetic stirring technique for the dispersion and they found an improvement in the bending strength from 85 MPa to 111 MPa and bending modulus from 2.2 GPa to 2.7GPa. Peng et al. [18] also used ultrasonication for the dispersion and the flexural strength improved from 107 MPa to 125 MPa with incorporation of 0.25 wt% silane MWCNTs. Guo et al. [19] used high power ultrasonication for the dispersion and the tensile strength of composites improved from 43 MPa to 70 MPa with incorporation of 8 wt% carboxylic-MWCNTs. Shen et al. [20] used magnetic stirring followed by sonication for the dispersion of CNTs into epoxy resin and flexural strength improved from 58.5 MPa to 128.94 MPa with 1 wt% 4, 4-diaminodiphenylmethane treated MWCNTs. Shen et al. [21] also used magnetic stirring followed by sonication for the dispersion of CNTs and the flexural strength improved from 71.6 MPa to 144.3 MPa (for 1 wt% amino functionalized MWCNTs) and the flexural modulus from 2.85 GPa to 3.39 GPa (for 0.25 wt% amino functionalized MWCNTs).

Gojny et al. [22] introduced a calendaring approach to disperse amine-functionalized nanotubes. This approach represents a significant advancement toward development of solvent-free, scalable manufacturing technique. This technique is readily scalable from laboratory to manufacturing setting and can achieve high throughput (for cost-effectiveness). They used mini calander for high shear mixing. In their study, three different types of CNTs SWCNT, DWCNT and MWCNTs. The surface of the CNTs was also modified. The highest improvement in strength (+10%) from 63.80 to 67.66 MPa, stiffness (+15%) from 2599 MPa to 2790 MPa and fracture toughness (+43%) from 0.65 to 0.85 MPa m$^{1/2}$ were attained with 0.5 wt% amino-functionalized DWCNTs content. In another study, Gojny et al. [23] used calendaring approach and the Young's modulus improved

from 3.29 GPa (neat resin) to 3.5 GPa (0.1 wt% of DWCNT-NH$_2$), tensile strength was approximately same (62 MPa for neat as well as CNTs reinforced) and fracture toughness K$_{IC}$ =0.65 MPa m$^{1/2}$ (neat) and 0.76 MPa m$^{1/2}$ (with 0.1 wt % DWCNT).

In another study, Nadler et al. [24] used three roll mill and flexural strength increased from 104 MPa to 134.6MPa (with 1.5 wt % modified CNTs) and flexural modulus from 2.57GPa to 3.4GPa.

In the study by Zheng [25], impact strength increased from 8.5 kJ/m^2 for pure epoxy to 15.5 kJ/m^2 for 0.6 wt% MWCNT-NH$_2$ loaded sample (a rise of about 80%). The bending modulus of the composite increased from 1550 to 2450 MPa (a rise of 58%) and the bending strength of composite raised from 33 MPa to the maximal value of 45MPa (a rise of 36%). Recently, some other studies have also been carried out to investigate the mechanical properties of CNT reinforced epoxy composites [26-29].

All these studies reveal that deagglomeration and dispersion of CNTs in epoxy matrix has been recognized as one of the major challenges in utilizing CNTs in commercial applications. The method used to de-agglomerate CNTs or to proper disperse them into epoxy matrix should be efficient, economical, and scalable.

Therefore, in this study, amine functionalized MWCNTs (Am-MWCNTs) were reinforced in epoxy resin using industrially viable, solvent free, fast and high speed homogenizer dispersion technique with loading ranging from 0.1 to 0.75% by w/w. The effect of loading of Am-MWCNTs in the epoxy resin on the mechanical properties has been investigated and the results correlated with the SEM of the fractured surface, HRTEM and DSC studies. The reaction mechanism is also proposed for the interaction between Am-MWCNT and epoxy resin.

Experimental

Materials

Di-glycidyl ether of bisphenol A (DGEBA) type epoxy resin (LY-556, Huntsman Co. Inc.) was used as the matrix material. Aradur (HY5200, Huntsman Co. Inc.) was used as a curing agent. MWCNTs were synthesized using toluene as a carbon source and ferrocene as catalyst precursor in a chemical vapour deposition (CVD) set-up developed in the laboratory [30, 31]. The MWCNTs produced were of ~26 nm [32] average diameter. These were 90 % pure with 10 wt% of Fe catalyst. These shall be designated as o-MWCNTs. Nitric acid, ethanol, thionyl chloride, tetrahydrofuran and benzene were purchased from Merck India, Qualigens one chemicals, Mumbai, India and RANKEM, New Delhi, India, respectively.

Chemical modification of MWCNTs

Surface modification of MWCNTs was carried out using nitric acid treatment (oxidation) followed by amine treatment (amidation) through thionyl chloride route (chlorination). Typical reflux set up is used for the oxidation of MWCNTs with nitric acid [33-36]. The oxidation of MWCNTs was performed by refluxing 1 g of as-produced MWCNTs with 200 ml concentrated nitric acid (60% (v/v)). The mixture was refluxed for 24 h at 70°C

and cooled down to room temperature. After refluxing, the MWCNTs were filtered and washed with distilled water in order to remove the acid completely while noting down the pH of the water. Final washing was carried out using acetone in order to make sure that no water molecules are trapped inside the tube bundles. The thoroughly washed tubes were then placed inside an oven for overnight at a temperature of 110 °C. These acid modified MWCNTs shall be designated as COOH-MWCNTs. A 100 mL-flask was charged with 1 g of COOH-MWCNTs dispersed in 30 mL of anhydrous benzene (C$_6$H$_6$). Then, 30 mL of thionyl chloride (SOCl$_2$) was added to it and was refluxed for 10 h. After the reaction, the reaction mixture was filtered and the solid residue was washed several times with anhydrous tetrahydrofuran (THF) and dried overnight at 50 °C. These chlorinated MWCNTs were designated as COCl-MWCNTs. 0.5 g of COCl-MWCNTs was suspended in THF and refluxed in the presence of excess Aradur 5200 (aromatic diamine which was also used as curing agent with the epoxy resin) for about 90 h to produce amine modified MWCNTs. After functionalization, MWCNTs were washed with ethanol (in order to dissolve excess amine) and deionized water followed by drying under vacuum prior to use. This amine modified MWCNTs shall be designated as Am-MWCNTs.
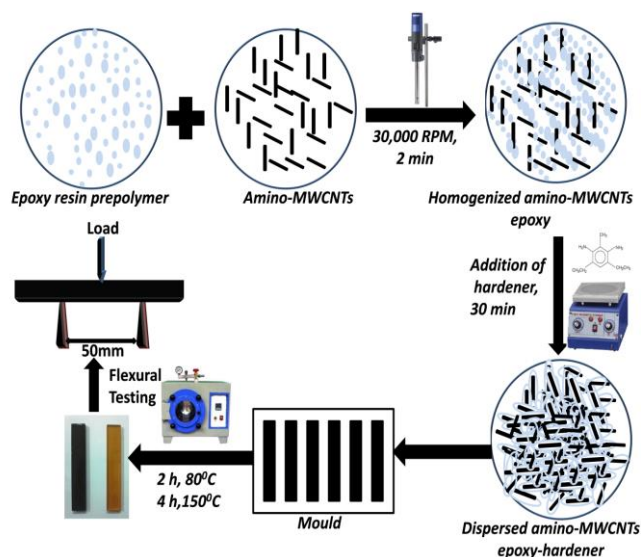

Fig 1. Schematic representation of the fabrication of Am-MWCNT epoxy composites.

Fabrication of composites

MWCNTs were dispersed in epoxy resin (LY-556, Huntsman) using high speed homogenizer (MICCRA D-9, from ART Prozess & Labortechnik GmbH &Co. KG) at ~30000 RPM for 2 min. Hardener (HY 5200, Aradur) in a ratio of 100:23 by wt. (epoxy: hardener) was added to MWCNTs dispersed epoxy and magnetically stirred for 30 min. The mixture was placed in a mould of size 70X12.7 X 3.2 mm^3. Then, the mixture was cast into mould and placed in vacuum oven for curing (80°C for 2 h   followed by 150°C for 4 h). The composite samples with varying Am-MWCNTs loadings i.e. 0.1, 0.2, 0.3, 0.5, 0.75 were prepared and designated as Am-MWCNTs-0.1, Am-MWCNTs-0.2, Am-MWCNTs-0.3, Am-MWCNTs-0.5,

Am-MWCNTs-0.75. A neat epoxy (0% MWCNTs) sample was also prepared under similar conditions and designated as cured epoxy. A schematic for the fabrication of the composites is shown in **Fig. 1**.

The surface morphology of as produced MWCNT, Am-MWCNTs and fracture surface of Am-MWCNT-epoxy composite samples were analysed using scanning electron microscopy (SEM, Zeiss EVO MA-10). HRTEM studies of as o-MWCNTs and Am-MWCNTs were carried out using Tecnai G20-stwin, 300 kV instrument. For the TEM study of CNTs, these were dispersed in ethanol and put over the carbon-coated copper grids. In order to prepare the samples for TEM studies of the polymer composite, the thin composite piece was ground to make it thinner (~200 nm). A circular slice of 2.3 mm is cut using an ultrasonic cutter. The slice is polished and dimple ground to make it electron transparent (~50 nm at centre) and then TEM studies were carried out by keeping them between two copper grids.

Characterization

Raman studies of the o-MWCNTs, COOH-MWCNTs and Am-MWCNTs were carried out using a Renishaw inVia Reflex Raman spectrometer, UK, with an excitation laser source of 514 nm wavelength. The Raman spectra were recorded from 1000 cm^{-1} to 2000 cm^{-1} with 5 mW laser power and 10 s of exposure time. FTIR of as-produced MWCNTs, COOH-MWCNTs and Am-MWCNTs were carried out to find out the functional groups introduced during functionalization i.e. acid functionalization and amine functionalization. The samples were ground and dried to eliminate the absorbed moisture. The dried samples were mixed with KBr and the mixture was pressed into pellets. The FTIR spectra were recorded on Nicolet 5700 in transmission mode in the wave number range 500-4000 cm^{-1} by averaging over 50 scans. TGA/SDTA 851e thermal analysis (Mettler Toledo) system was also used to study the effect of functionalization on the MWCNTs which provided the information regarding amounts of functional groups retained on the surface of MWCNTs. A heating rate of 10°C/min was used to study the thermal behaviour of as-produced MWCNTs, COOH-MWCNTs and Am-MWCNTs in air. The flexural strength and modulus of pure epoxy and MWCNT-epoxy composites were measured on an Instron machine model 4411. The specimen of size 70 X 12.7 X 3.2 mm^3 was bended with the support span of 50 mm at a cross head speed of 0.5 mm/min. Differential scanning calorimeter (DSC1/700, Mettler Toledo) was used to measure the change in heat of reaction with the addition of Am- MWCNTs in the epoxy resin. 10 mg of sample (e.g. pure epoxy resin with hardener and CNTs dispersed epoxy with hardener) was heated from room temperature to 300°C at a heating rate of 10°C/min under N_2 atmosphere. Heat of reaction was determined by calculating the area under the curve using the inbuilt software in DSC. X-ray photoelectron spectroscopy (XPS) was carried out on ESCA-3000 model (V.G. Scientific, U.K.) operated at a pressure of 6 X 10^{-8} Pa with non monochromatized Al Kα X-ray source (1486.6 eV photon). The XPS survey spectra were obtained with 50-eV pass energy and a 0.5-eV step size. Core level spectra were obtained at 20-eV pass energy with a 0.05-eV step size. All binding energy values were charge corrected to C 1s =285 eV as an internal standard.

Results and discussion

Characteristics of o-MWCNTs and Am-MWCNTs

Structural Properties of o-MWCNTs, COOH-MWCNTs and Am-MWCNTs: Fourier transforms infrared spectroscopy (FTIR), Raman spectroscopy and energy dispersive X-ray (EDX) analysis were used to investigate the structure and chemical composition of the o-MWCNTs and Am-MWCNTs samples. **Fig. 2** (**a**, **b** and **c**) show the FTIR spectra of o-MWCNTs, COOH-MWCNTs and Am-MWCNTs, respectively.

FTIR spectrum of o-MWCNTs showed a peak at 1630 cm^{-1} corresponding to the stretching mode of the C=C double bond which forms the framework of the carbon nanotube sidewall [37]. It does not show any other significant peak. Although, there are chances of functional groups or defective sites being created during synthesis of MWCNTs at low temperature CVD technique at atmospheric pressure. But the concentration of these functional groups is very less which could not be observed in the FTIR.
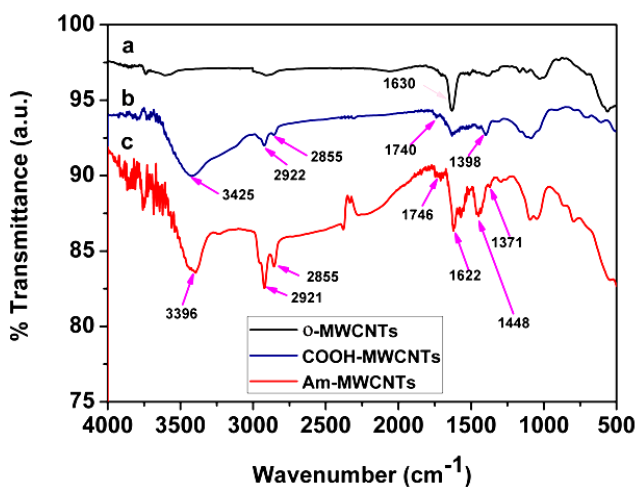

Fig 2. FTIR spectra of (a) o-MWCNTs, (b) COOH-MWCNTs and (c) Am-MWCNTs.

In case of COOH-MWCNTs (**Fig. 2 b**), the broad peak at 3425 cm^{-1} is due to O—H stretching vibration of hydroxyl groups and the peak at 1740 cm^{-1} correspond to the carboxylic (C=O) group attached to MWCNTs. These two peaks are indication of acid functionalization. The peaks at 2922 cm^{-1} and 2855 cm^{-1} were assigned to C−H stretching vibration of methylene produced at the defect sites of acid-oxidized MWCNT surface. The FTIR spectrum of Am-MWCNTs (**Fig. 2c**) confirmed the formation of amide groups on the MWCNTs surface. The peaks at 1263 cm^{-1} and 1448 cm^{-1} were ascribed to C–N stretching of amide groups, while the peak at 3396 cm^{-1} can be assigned to the N–H stretching vibrations. The peaks at 1622 and 1371 cm^{-1} correspond to the N-H bending and C-N stretching of amine, respectively [1].

For further verification of the attachment of functional groups, EDX analysis was carried out and the results are shown in **Fig. 3** (**a**, **b** and **c**) for o-MWCNTs, COOH-MWCNTs and Am-MWCNTs, respectively. The elemental compositions in wt% and at% are given in inset of each **Fig 3**.
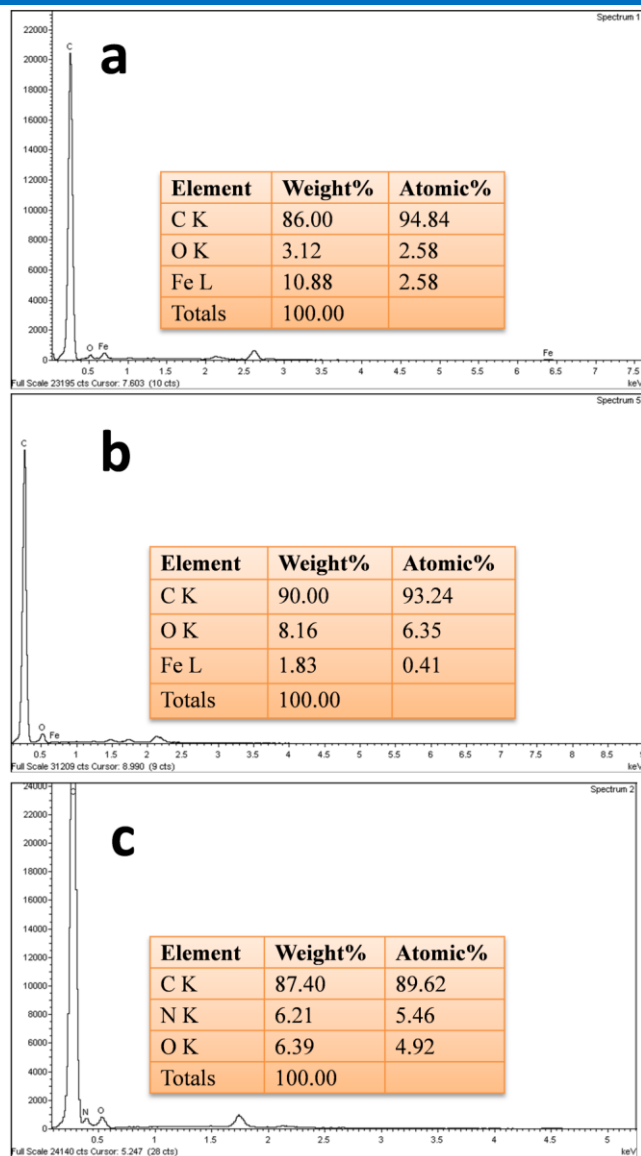
Fig 3. EDX spectra of (a) as-produced MWCNTs, (b) COOH-MWCNT and (c) Am- MWCNTs. In the inset, the compositional analysis is given.

The EDX of as-produced CNTs showed ~3.1 wt% oxygen. It may be due to the presence of defect sites on the surface of as-produced CNTs, as the synthesis was carried out at lower temperature and under atmospheric pressure. Further, the EDX of COOH-MWCNTs (**Fig. 3b**) showed the presence of ~8.2 wt% oxygen which confirmed the substantial attachment of carboxylic groups. The EDX of Am-MWCNTs showed the presence of 6.2 wt % nitrogen, which further confirms the attachment of substantial amounts of amino groups on the surface of MWCNTs.

In order to study the thermal behaviour of MWCNTs, TGA studies have been carried out and the results are presented in **Fig 4**. **Fig. 4** shows the thermal degradation behaviour of o-MWCNTs, COOH-MWCNTs and Am-MWCNTs in air. Thermo-oxidative behaviour of o-MWCNTs shows only one step decomposition and weight loss starts at 475^oC; whereas the weight loss in functionalized CNTs occurs at lower temperature ~200^oC. The weight loss in functionalized CNTs shows two and three step decomposition for COOH-MWCNTs and Am-MWCNTs, respectively. TGA study of Am-MWCNTs

shows three steps decomposition i.e. due to of decomposition of CNTs, attached amino groups and residual oxygenated groups that have not reacted with amine. The weight loss in Am-MWCNTs is comparatively higher than COOH-MWCNTs in the low temperature region. It is due to the attachment of bulky amine groups on the surface of MWCNTs. This thermo-oxidative study further confirms the presence of substantial amount of functional group on the surface of MWCNTs.
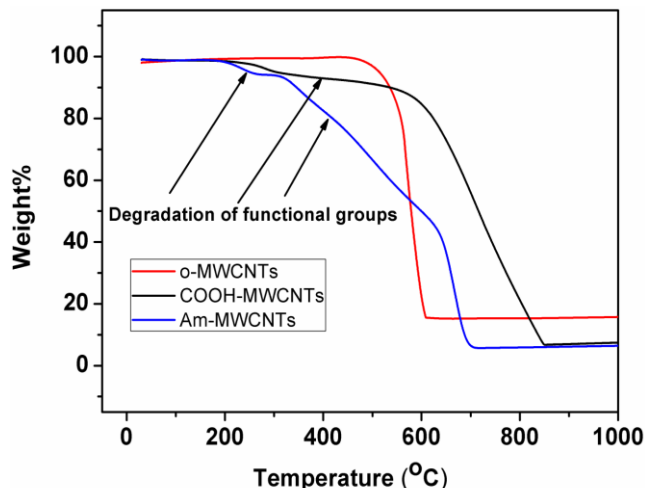
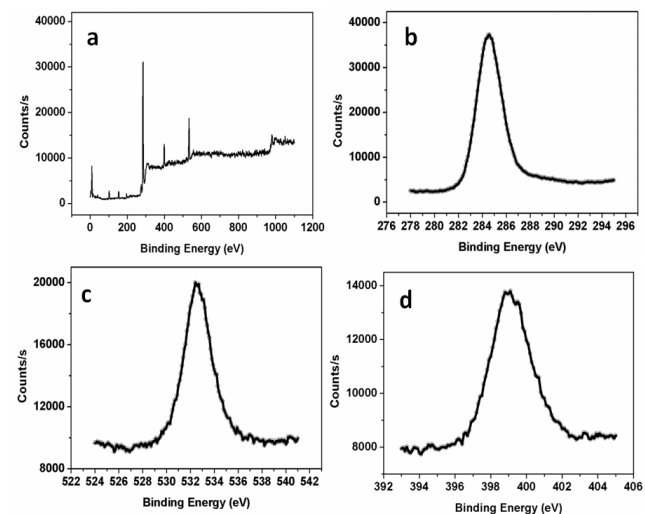**Fig 4.** TGA plot of (a) o-MWCNTs, (b) COOH-MWCNTs and (c) Am-MWCNTs.

Fig 5. XPS spectra of Am-MWCNTs (a) complete (b) C1 bonding energy region (c) O1 bonding energy region and (d) N1 bonding energy region.

High-resolution XPS spectra for amine functionalized MWCNTs are shown in **Fig. 5**. Samples were degassed within the XPS chamber prior to analysis of the sample. The general survey spectrum was taken to locate the element present. The C 1s, N 1s and O 1s core level spectra for amino-functionalized MWCNTs samples are shown in **Fig. 5a**, **b** and **c**, respectively. The C 1s, O 1s, N 1s peaks were studied between 278-295 eV, 524-541 eV and 393-405 eV, respectively. The presence of N in the XPS data and presence of amino group in the FTIR data clearly indicate that amino-group is attached on the surface of MWCNTs.

Surface morphology and micro structural characterization of o-MWCNTs and Am-MWCNTs

Fig. 6 (**a–f**) shows the SEM micrographs of o-MWCNTs and Am-MWCNTs. As can be seen in **Fig. 6a**, the o-MWCNTs are in the form of long bundles. These bundles broke down into separate tubes due to extensive refluxing during acid treatment followed by amine functionalization (**Fig. 6** (**b**, **d** and **f**)). Treatment of MWCNTs with strong acids followed by amine treatment usually shortens the length of the MWCNTs. In the present study, we have also observed such shortening of the tube length. A closer look at the micrographs reveals that the amino functionalized MWCNTs are relatively shorter compared to o-MWCNTs (**Fig. 6** (**a**, **c**)).
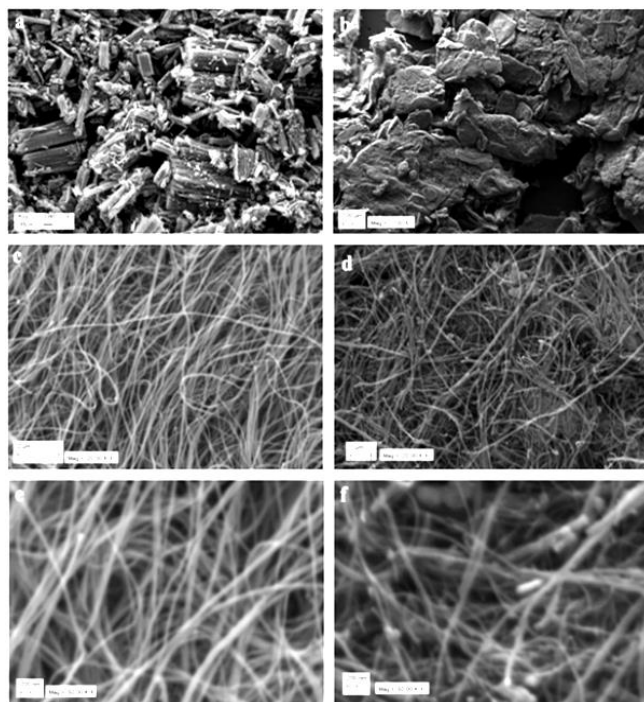
Fig 6. SEM images of (a) o- MWCNTs at 100X, (b) Am-MWCNTs at 100X, (c) o-MWCNTs at 20000X, (d) Am-MWCNTs at 20000X, (e) o-MWCNTs at 50000X and (f) Am-MWCNTs at 50000X magnification.
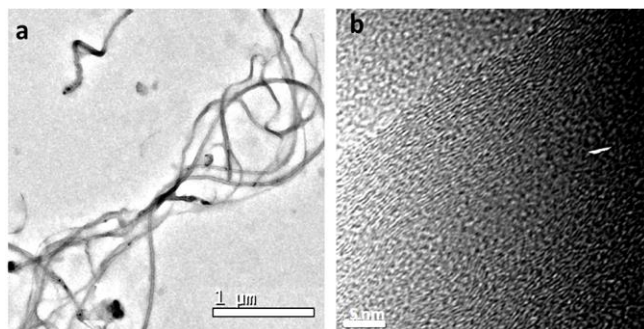
Fig 7. TEM images of o-MWCNTs at different magnification.

The surface of Am-MWCNTs is also roughened compared to o-MWCNTs which are due to the attachment of functional groups. The surface roughness and shortening of the MWCNTs during amine functionalization were further confirmed by HRTEM studies (**Fig. 7a-b** for o-MWCNTs and **Fig. 8 a-f** for Am-MWCNTs). HRTEM images of the Am-MWCNTs suggest that the surface roughness of Am-MWCNT (**Fig. 8 d-f**) is much higher than the o-MWCNT (**Fig. 7b**). The surface roughness can therefore be attributed to the presence of functional groups. The length of Am-MWCNTs (**Fig 8a**) is also shorter compared to o-MWCNTs (**Fig 7a**). Therefore, shortening of the length and pronounced surface roughness of CNTs is due to the attachment of functional groups.
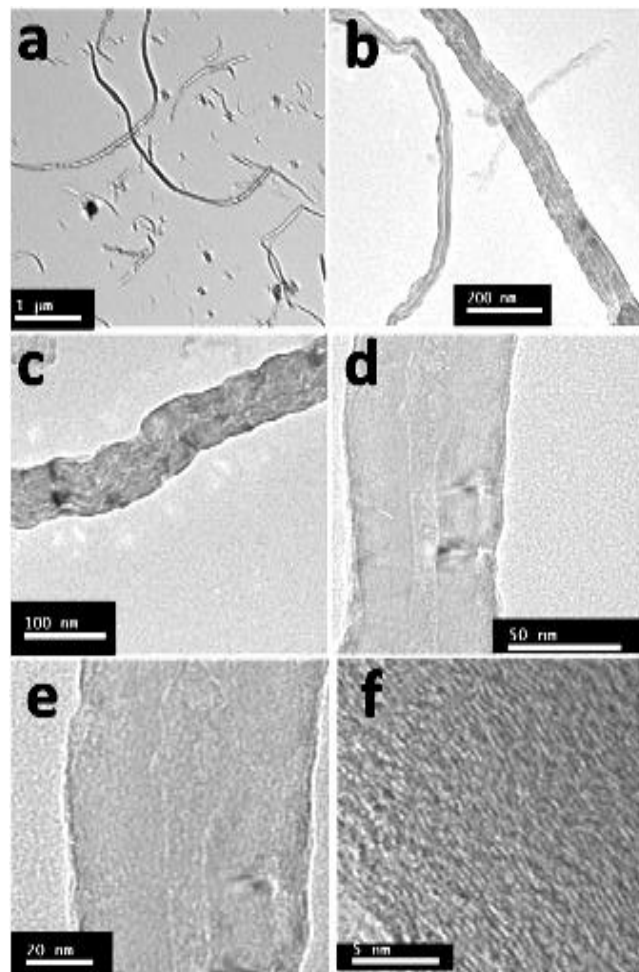

Fig 8. TEM images of Am-MWCNTs at different magnification.

Curing behaviour of epoxy resin in the presence of o-MWCNTs / Am-MWCNTs

The curing behaviour of epoxy resin in absence/presence of o–MWCNTs or Am-MWCNTs were investigated by recording the DSC traces. The procedure of a dynamic mode involves ramping ~10 mg of uncured sample from room temperature to 350°C with a heating rate of 10°C/min. **Fig. 9** shows the DSC trace of pure epoxy (0% MWCNTs), 0.3% Am-MWCNTs, 0.5% Am-MWCNTs and 0.75% Am-MWCNTs based epoxy. In all these samples the ratio of epoxy resin to hardener was kept constant i.e. 100:23. In all the samples a curing exothermic was observed. The curing exothermic was analysed by noting the following parameters- T_{onset} : temperature at which curing starts; T_p: exothermic temperature; T_{end} : Temperature at which curing is complete
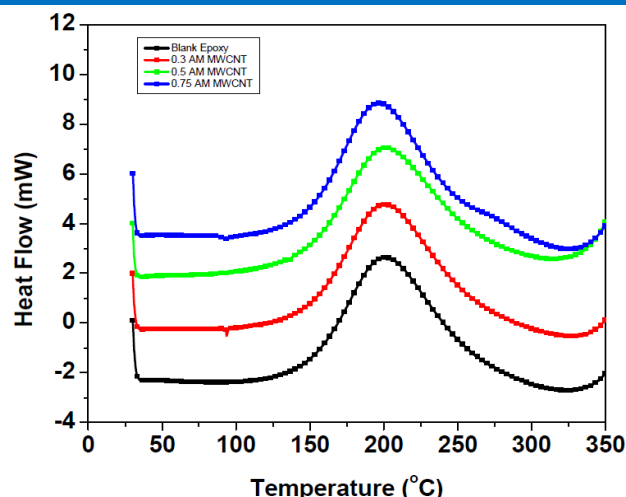ΔH: heat of curing.

Fig 9. DSC traces of epoxy resin: hardener [100:23 by wt.] in the absence/presence of varying amounts of Am-MWCNTs in N_2 atmosphere [heating rate 10°C/min].

The results of DSC traces are given in **Table 1**. The heat of reaction for pure epoxy system is 202 J/g which increased to 283 J/g in the presence of 0.3 wt. % o-MWCNTs. The higher value of ΔH could be due to interaction of MWCNTs with epoxy; reaction of epoxy with oxygenated functional groups present on as produced MWCNTs. This interaction is responsible for the improvement in the flexural strength from 95 MPa for pure epoxy to 125 MPa for 0.3 wt. % o-MWCNTs loaded epoxy [25]. Further, for amine functionalized samples, the heat of reaction increased to 313 J/g for 0.3 wt. % Am-MWCNTs. The higher value of ΔH for Am-MWCNTs based epoxy composites is due to the formation of covalent bond between amine groups attached to the CNTs and epoxy resin. Upon further increasing the Am-MWCNTs loadings to 0.5 wt. %, the ΔH value increases slightly to 317 J/g but decreased substantially to 222 J/g for higher Am-MWCNTs loadings (0.75 wt.%). This is due to the formation of agglomerates at higher loadings which does not provide sufficient sites for the interaction between the amine groups of CNTs and epoxy resin. Thus, most of the amino groups must be remaining unused due to the formation of agglomerates.

Table 1. Results of DSC traces for epoxy: hardener (100:23 by wt.) in absence/presence of o-MWCNTs/Am-MWCNTs.

Sample designation	Wt. % of filler	T_{onset} °C	T_p °C	T_{end} °C	ΔH (J/g)
Neat epoxy	0	135	201	292	202
o-MWCNTs-0.3	0.30	112	201	315	283
Am-MWCNTs-0.3	0.30	106	201	322	313
Am-MWCNTs-0.5	0.50	98	202	320	317
Am-MWCNTs-0.75	0.75	122	200	292	222

The onset temperature of curing (T_{onset}) and the exothermic temperature (T_p) are given in **Table 1**. The exothermic temperature is almost constant at 201 °C for all

the composites but the onset temperature decreased by 37 °C (a significant change) for Am-MWCNTs based epoxy composites as compared to neat epoxy. It is clear that all kinds of CNTs facilitated the curing initially by lowering the onset temperature of curing. The Am-MWCNTs demonstrated the most noticeable effect on T_{onset} (lowering it by 37 °C for 0.5 wt. % compared to neat epoxy). The as-produced MWCNTs based epoxy exhibited a modest effect on T_{onset} (lowering it by 23 °C). Similar effect has been observed in a SWNTs-filled bisphenol A-type epoxy resin and carbon fibre/carbon nanofibre/carbon black-filled bisphenol F-type epoxy resins [38]. Although, the CNTs induced curing to start at lower temperatures, there was no obvious effect on the exothermic peak temperature. These results clearly indicate that incorporation of MWCNTs facilitated the curing of epoxy resin.

Mechanical Properties of Am-MWCNTs reinforced epoxy composites

Fig. 10 a and **b** show the variation in flexural strength and flexural modulus of composites, respectively for different Am-MWCNTs loadings. **Fig. 10 a** shows that with increasing loading of Am-MWCNTs, flexural strength of composites increases gradually and reaches a maximum value of 163 MPa for Am-MWCNTs-0.5 composites compared to 95 MPa for cured epoxy. This shows an overall improvement of 72%. The flexural modulus of composites also improved from 2250 for pure cured epoxy to 3795 MPa, an overall improvement of 69% (**Fig 10b**).
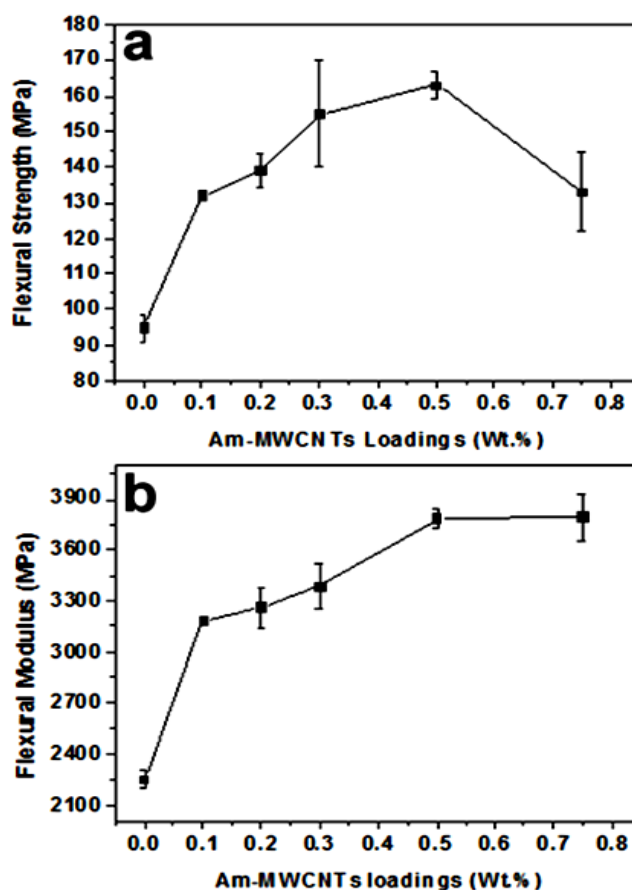

Fig 10. Variation of **(a)** flexural strength and **(b)** flexural modulus with Am-MWCNTs loadings in epoxy resin.

Such high improvement is due to proper bonding of Am-MWCNTs with the epoxy resin. It is clear from the above DSC data that there is a substantial enhancement in the ΔH value with the addition of Am-MWCNTs compared to non-functionalized CNTs and pure epoxy which is responsible for the improvement in the flexural strength. The strong interaction between Am-MWCNTs and matrix therefore results in further increase in flexural strength of composites i.e. upto 155 MPa for Am-MWCNTs-0.3; an improvement of ~24% in the flexural strength compared to non-functionalized MWCNTs based composites [25].

In addition to this, the flexural strength increased with further loadings of MWCNTs but the improvement was not significant. The behaviour was different than non-functionalized MWCNTs based composites in which the strength start declining beyond 0.3 wt. % loading [1, 25].

This could be due to the formation of CNTs agglomerates beyond 0.3 wt. % loading. However, in the case of Am-MWCNTs, due to better dispersion and proper interaction between epoxy and Am-MWCNTs, the flexural strength improved beyond 0.3 wt. % loading. The flexural strength increased to 163 MPa for Am-MWCNTs-0.5 from 155 MPa for Am-MWCNTs-0.3. Similarly, increase in the heat of reaction was also lesser i.e. 313 J/g for Am-MWCNTs-0.3 and 317 J/g for Am-MWCNTs-0.5. Beyond 0.5 wt. % loading the flexural strength of composites dropped to 133 MPa for Am-MWCNTs-7.5. It may be due to the formation of agglomerates at higher loadings. The heat of reaction also decreased from 317 J/g to 222 J/g. The formation of CNTs agglomerates inhibits exposure of interfacial surface for the bonding between epoxy and attached amino groups at the surface of MWCNTs. This increase in the heat of reaction increases the crosslink density of the matrix which is also responsible for the enhancement in the mechanical properties of composites [39].

For further confirmation of the substantial improvement in the mechanical properties of CNT-epoxy composites, HRTEM studies of these composites were carried out and results are shown in **Fig. 11a** and **b**. **Fig. 11a** clearly reveals the coating of the epoxy on the CNTs which is due to the proper interaction of Am-MWCNT and epoxy resin which forms the covalent bond as shown in reaction mechanism (**Fig. 12**).
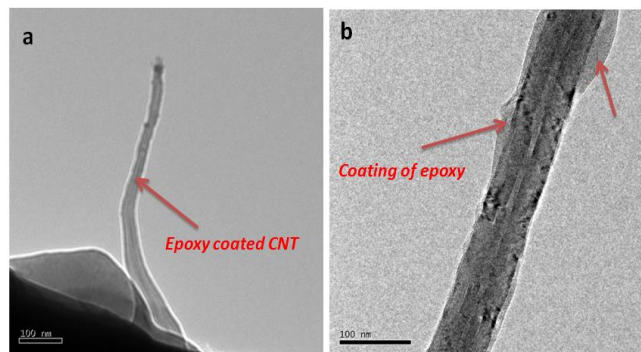

Fig 11. (**a** and **b**) TEM micrograph of 0.3 wt% Am-MWCNT-epoxy composites. Sample from the bulk was made by gridning, dimpling and polishing the sample.

The bonding between the CNTs and epoxy is shown in the proposed reaction mechanism. The opening of the

oxirane ring and bonding of the Am-MWCNT with epoxy matrix is also shown. The formation of covalent bond between Am-MWCNTs and epoxy resin is responsible for the significant enhancement in the mechanical properties. This can also be inferred from the SEM images of the fractured surfaces of composite samples (**Fig 13**). SEM images of fractured surfaces of composites clearly shows that MWCNTs are embedded in the polymer matrix. Coating of epoxy resin over the MWCNTs can also be seen.

It is to be noted that Garg et al [1] reported bending strength value of 14o MPa for addition of 0.3 wt% amino functionalized CNTs into the epoxy.
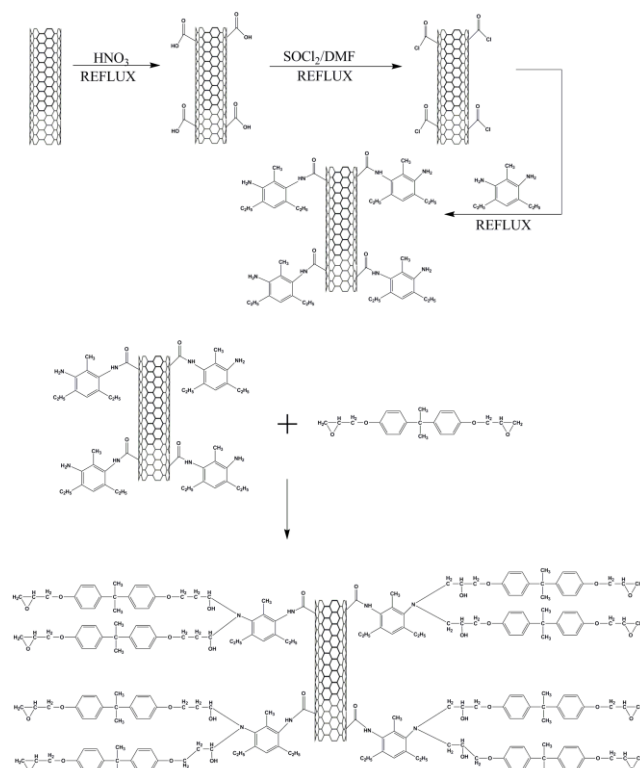

Fig 12. Reaction mechanism responsible for the formation of covalent bond between Am-MWCNT and epoxy resin.
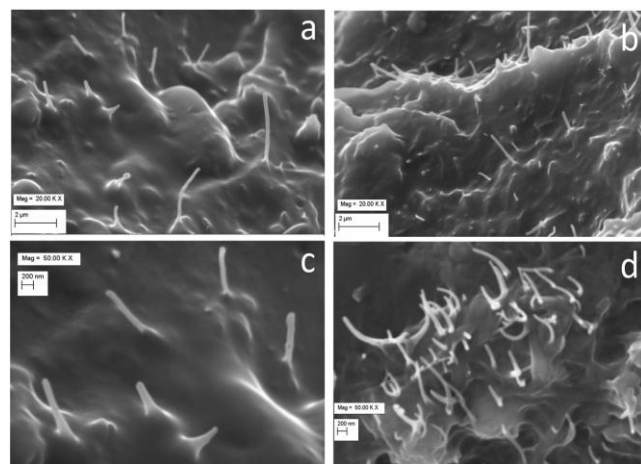

Fig 13. SEM images of fractured surface of (**a**) 0.3 wt% Am-MWCNT-epoxy composites at 20,000 magnifications, (**b**) 0.5 wt% Am-MWCNT-epoxy composites at 20,000 magnification, (**c**) 0.3 wt% Am-MWCNT-epoxy composites at 50,000 magnification and (**d**) 0.5 wt% Am-MWCNT-epoxy composites at 50,000 magnifications.

In another condition **[1]**, they observed flexural strength value of 140 MPa. Apart from these two studies, the flexural strength values of CNT epoxy composites were reported in the range of 64-135 MPa. The value reported by Garg et al. **[1]** was significant but the dispersion technique used by Garg et al. **[1]** was ultrasonication of CNTs in acetone followed by magnetic stirring for 24 h. Thus, there was a scope to look for an efficient approach which can be industrially viable for large scale fabrication of CNT epoxy composites. In this study, the amino modified CNT-epoxy composites were fabricated using a fast of dispersion process using high speed homogenizer and it showed a high value of flexural strength in the range of 163 MPa. The modified epoxy with improved strength can be used for the fabrication of carbon fibre based epoxy hybrid composites for structural applications **[40-43]**.

Conclusion

High speed homogenization was found to be a successful industrial viable technique for the fabrication of CNT-epoxy composites on a large scale. Am- MWCNTs and reinforced epoxy composites were fabricated using this technique and a flexural strength value of 163 MPa with the addition of merely 0.5 wt. % Am-MWCNTs were achieved. The SEM studies of fractured surface of these Am-MWCNT-epoxy composites clearly revealed a strong interaction between CNTs and epoxy matrix which was also confirmed by the heat of reaction values obtained by dynamic scanning calorimetric studies on various CNT-epoxy samples. These CNT epoxy composites having high value of flexural strength can be used for the development of super strong carbon fibre based epoxy hybrid composites for structural applications.

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