



# CHARACTERIZATION OF EPON 862 REINFORCED WITH FUNCTIONALIZED MCNT'S

**Merlin Theodore, Mahesh Hosur, Jonathan Thomas, Shaik Jeelani**  
**Center for Advanced Materials, Tuskegee University, Tuskegee University, Tuskegee, AL 36088**

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## Abstract

*The effects of various functionalized multi-walled carbon nanotubes (MWCNT) on morphological, thermal, and mechanical properties of an epoxy based nanocomposite system were investigated. Chemical functionalization of MWCNT by oxidation (MWCNT-COOH), direct-fluorination (MWCNT-F), and amino-functionalization (MWCNT-NH<sub>2</sub>) were confirmed by Raman spectroscopy. Utilizing in-situ polymerization, a 1 wt % loading of MWCNT was used to prepare the epoxy-based Nanocomposites. Mechanical and thermal properties were tested on the Zwick test system (which utilizes a three point bend test), and Dynamic Mechanical Analysis (DMA). Functionalization not only improved the dispersion of MWCNTs in the polymer matrix but also enhanced the mechanical and thermal properties. Flexural testing performed on the sample using the Zwick showed a 33 – 59% increase in strength and 16 – 55% increase in modulus in these systems, compared to the neat epoxy system. However, only the MWCNT-F nanocomposites showed 10% increase in glass transition temperature ( $T_g$ ). Curing kinetics of these systems with have been studied using Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR). All kinetics parameters (activation energy, rate of reaction, enthalpy change, percent conversion) were determined using thermal kinetics analysis software. The values of the activation energy decreased; and enthalpy change and rate of reaction increased for the MWCNT-COOH and the MWCNT-NH<sub>2</sub>. The MWCNT-F showed a decrease in activation energy and the lowest increase in enthalpy change. All systems somewhat achieved the same degree of conversion.*

## 1 Introduction

Since their discovery in 1991 by S. Iijima [1], researchers have envisioned carbon nanotubes (CNTs) as the prime candidates to dominate the revolution in nanotechnology. CNTs are among the stiffest and strongest fibers known and have remarkable electronic properties. In polymer nanocomposite (PNC) applications, CNT replaces traditional fibers because it requires a lower loading to greatly improve the mechanical properties of the polymer, such as increasing toughness by absorbing energy due to their highly flexible elastic behavior. CNTs are commonly used as fillers in base polymers to fabricate composite materials with superior mechanical, electrical, and thermal properties. Unfortunately, the fabrication of PNC with superior strength as high as the individual CNTs themselves has not been made possible so far. The achievement of such a superior PNC reinforced with CNTs is hindered by the fact that CNTs have a non-reactive surfaces, lack interfacial bonding with matrix, poorly disperse within composite matrices [2] and have very low solubility in most solvents. Overcoming these problems will promote better usage for CNTs in PNC. Chemical functionalization of CNTs is reported by various groups to overcome these challenges promoting increase in overall properties of epoxy nanocomposites system [2-5]. Chemical functionalization alters the CNTs morphology and provides an abundance of reactive sites, thus increasing the possibility of crosslinking with the polymer matrix. Chemical functionalization also promotes separation of agglomerates resulting in a homogeneous dispersion when incorporated into a solvent or polymer matrix, and also improves solubility of the CNTs in an organic solvent. The two main approaches for chemical functionalization are non-covalent (wrapping) and covalent (oxidation sidewall defect) attachment of functional groups onto the walls of CNTs. Non-covalent functionalization creates minimal alteration to

CNTs properties and structure. However, the functional groups attached are held together by weak Van der Waals forces and can be easily separated. Covalent functionalization creates covalent bonds between functional groups and CNTs and may alter the CNTs surface by introducing defects. Compared to non-covalent bonding, covalent attachment of functional groups to the surface of nanotubes has a higher efficiency for load transfer and offers the opportunity for chemical interactions with the epoxy systems. Unfortunately, the introduction of defects by covalent functionalization may cause detrimental effects degrading the overall properties of the CNTs, and also the properties of the PNC reinforced with these CNTs. Several researchers have reported noncovalent and covalent bonding of CNTs and its effects on the CNTs properties or PNC properties when utilized as the reinforcing phase in PNC [6, 7]. Simulation studies by Namilae et al. [8] has shown that the interfacial and mechanical properties of composite increase by increasing the number of functional group attachments through covalent functionalization. Homogenous incorporation of these functionalized MWCNTs into the matrix could improve processability, thereby providing more control over CNTs polymer nanocomposites properties promoting the usage in a wide range of applications. There is a desperate need to develop approaches to achieve the optimum dispersion and processability method, and to provide more control over properties. However, achieving the optimum operating conditions for synthesis, dispersion, and reproducibility of composites are limited by the fact that it is impossible to find one source that provides a variety of functionalized MWCNTs originating from the same batch. Availability of such CNTs is hampered by the fact that certain functionalization may require a unique environment, a particular instrument, and/or very expensive/toxic materials. To date there is very limited or no research being done on head-to-head comparison of epoxy nanocomposites reinforced with functionalized MWCNTs in a particular epoxy matrix.

The objective of this research is to improve fundamental understanding of how surface functionalized MWCNTs affect the curing process, morphology, mechanical, and thermal properties of epoxy based nanocomposites. This research focuses on three different types of functionalization to multi-wall carbon nanotubes (MWCNTs)

incorporated into an epoxy resin (Epon 862). MWCNTs were chemically modified by oxidation, direct-fluorination, and amino-functionalization to attached carboxylic acid (COOH), fluorine atoms, and amine (NH<sub>2</sub>) functional groups to their sidewalls. Characterization and analysis on the effect of the functionalized MWCNTs on mechanical, thermal, morphological properties of the nanocomposites were investigated.

## 2 Experimental Studies

### 2.1 Processing of Functionalized Nanotubes /Epoxy Nanocomposites

In the current research work, functionalization of pristine MWCNTs was performed by oxidation in acid solution (MWCNT-COOH), direct-fluorination (MWCNT-F), and amino-functionalization (MWCNT-NH<sub>2</sub>). A desired amount of Epoxy/Epicure W (100:26.4) was heated and maintained at 60 °C. A 1 wt % loading of the functionalized MWCNTs was placed in acetone (10:2) and sonicated for 30 minutes in an ultrasonic bath. After the sonication process, the solution of MWCNTs and acetone was added to the Epon 862 and mixed using a digital mechanical stirrer at a constant speed of 500 rpm. During the last 15 minutes of mixing the temperature was raised to 70 °C. This was done to ensure complete removal of acetone. The curing agent, which was maintained at the same temperature as the resin, was added and mixing was continued for an additional thirty minutes. The mixture was then degassed under high vacuum at 60 °C. Degassing was performed to remove bubbles that were generated during mixing. The mixture was then poured into desired molds that were preheated at 121 °C for 1 hour. The mixture was then cured in an oven at 121°C for 4 hours after which it was left to cool to ambient temperature.

### 2.2 Characterization

#### 2.2.1 Interfacial interaction

Evidence of Chemical modification by oxidation, direct fluorination, and amino-functionalized on the surface of the pristine MWCNT was confirmed using Raman Spectroscopy. Raman Spectroscopy measurements were performed on a Renishaw in Via Raman Microscope equipped with an ultra low noise Rencam CCD detector and a 785 diode laser.

2.2.2 Mechanical and thermal Characterization

The flexural and thermal properties of the epoxy nanocomposites were tested using Zwick (Roell 2.5) and Dynamic Mechanical Analysis (DMA) Flexural tests under three-point bend configuration were performed according to ASTM D790-02. The machine was run under displacement control mode at a crosshead speed of 2.0 mm/min, and all the tests were performed at room temperature. Storage modulus and glass transition temperature ( $T_g$ ) of the fully cured samples was obtained using a TA Instruments DMA 2980 in the single cantilever mode with an amplitude of 10 $\mu$ m, oscillatory frequency of 1 Hz and heating rate of 3° C/min in air. The test was carried out according to ASTM D4065-01.

2.2.3 Morphological characterization

Microstructures of neat and composite were examined under a Field Emission Scanning Electron Microscope (FE-SEM Hitachi S-900 JEOL JSM 5800). Sputtering was done using Hummer 6.2 system to coat the samples. A 25 kilovolt accelerating voltage was applied to accomplish desired magnification.

2.2.4 Curing Kinetics

A modulated Differential Scanning Calorimeter (TA Instruments Q1000) was used to characterize thermal behavior during the curing process using ASTM E698 method. The samples were heated from 25 - 350°C at different heating rates; 2, 5, 10, 15°C/min<sup>-1</sup>. Fourier Transform Infrared Spectroscopy (FTIR) Measurements were performed using a Nicolet spectrometer equipped with a Specac Golden Gate Attenuated Total Reflectance Accessory (ATR) using 64 scans with a 4 cm-1 resolution step.

3. Results and Discussion

3.1 Characterization of functionalization

Raman spectroscopy is an excellent technique to investigate the low energy elementary excitations in materials as well as to characterize structural, electronic, vibrational and magnetic properties of carbon nanotubes [9]. The main features, shown in fig. 1, of CNTs in the Raman spectrum are the radial mode band (100-400 cm<sup>-1</sup>), D-band (~1350

cm<sup>-1</sup>), G-band (1500-1600 cm<sup>-1</sup>), and G\*-band (~2600 cm<sup>-1</sup>). The D- band represents the measure of degree of disorder if the intensity of the G or D\* band is not affected by disorder or defects[10]. The G-band represents crystalline graphitic structure whereas the D\* represents overtone of disorder in the functionalized MWCNTs. Chemical functionalization of pristine CNTs dramatically increases the intensity of these bands. Oswald et al. [11] reported that in MWCNTs the D-band

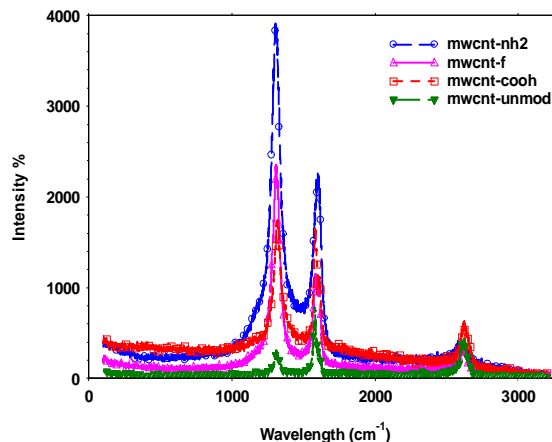


Fig. 1 Raman Spectroscopy of functionalized MWCNTs

originate from defects in the tube walls. The ratio of G-band/D-band or D\*-band/G-band, listed in Table 2, is used to characterize the order/disorder in the graphite structure. The G –band is less affected by defects from functionalization as compared to the D-band. An increase in  $I_D/I_G$  or decrease in  $I_{D^*}/I_G$  indicates higher defect concentration or a higher degree of disorder as well [10]. Also, the lower the  $I_D/I_G$  ratio, the higher will be the concentration of amorphous, which is evident in table 1. In the current study, the radial breathing mode (RBM) in the Raman Spectra was not evident. The radial mode band is a direct measurement of the core nanotube diameter [12, 13]. Since MWCNTs used in the current study contained a minimum average of about 20 layers in height the Raman spectra of these CNTs would correspond to a radial mode band with very low frequency and weak intensity.

Table 1. Disorder/order ratio of MWCNTs

MWCNT	$I_D/I_G$	$I_{D^*}/I_G$
MWCNT-UNMOD	0.39	0.60
MWCNT-COOH	1.06	0.37
MWCNT-F	2.00	0.33
MWCNT-NH <sub>2</sub>	1.78	0.21

### 3.2 Curing Kinetics by DSC and FTIR

Knowledge of the degree conversion of the thermosetting reaction is critical to the development of complete understanding of the curing process recommended by the manufacturing. The study of cure reaction after the introduction of carbon nanotubes into a polymer is very important for accessing their reinforcement role [14]. The curing kinetics of the uncured epoxy nanocomposites were studied at different scanning rates (2, 5, 10, 15°C/min<sup>-1</sup>) from 25 – 350°C using thermal stability kinetics on the DSC. The heat evolved during the curing process was measured and used to calculate kinetic results such as activation energies, rate constants, enthalpy, and % conversion using the equations:

$$d\alpha/dt = Ze^{E_a/RT}(1-\alpha) \quad (1)$$

$$\Delta H_{reaction}^0 = \Sigma\Delta H_f^0(P) - \Sigma\Delta H_f^0(R) \quad (2)$$

where  $da/dt$  = reaction rate (s<sup>-1</sup>);  $\alpha$  = fractional conversion;  $Z$  = pre-exponential factor (s<sup>-1</sup>);  $E_a$  = activation energy (J/mol),  $R$  is the universal gas constant;  $T$  is the temperature (in kelvin); and  $\Delta H_r$  = standard enthalpy change of reaction;  $\Delta H_f^0(P)$  = enthalpy of products;  $\Delta H_f^0(R)$ . enthalpy of reactants. The evolution of the percent material converted,  $\alpha$ , versus time at 121°C is shown in fig. 2. All systems were not 100% fully cured due to the crosslinking initiation in the thermoset, around 1-3%, reported in table 2, remained uncured.. The functionalized MWCNTs have disturbed the curing behavior by catalyzing the reaction creating a decrease in the activation energy and an increase in standard enthalpy change. The rate of reaction is highest for the MWCNT-COOH and MWCNT-NH<sub>2</sub> simply because the reaction rate increased with higher concentration of reactive sites for the MWCNT-COOH composites; and the crosslinking concentration is highest for the MWCNT-NH<sub>2</sub>. The MWCNT-NH<sub>2</sub> acts as an initiator for the curing process, resulting from the excess amounts of amine groups. A study on differentiating the stoichiometry ratio and its effects on interfacial interaction is currently being investigated. concentration of MWCNTs in the systems is highest for MWCNT-COOH because oxidation decreases the length of the MWCNTs by more than half its original length doubling the concentration of MWCNT-COOH with open end caps creating a higher concentration of reactive sites catalyzing the

reaction rate. Too much of an increase in reaction rate is not suitable for proper wetting of CNTs by the polymer, but that was not the

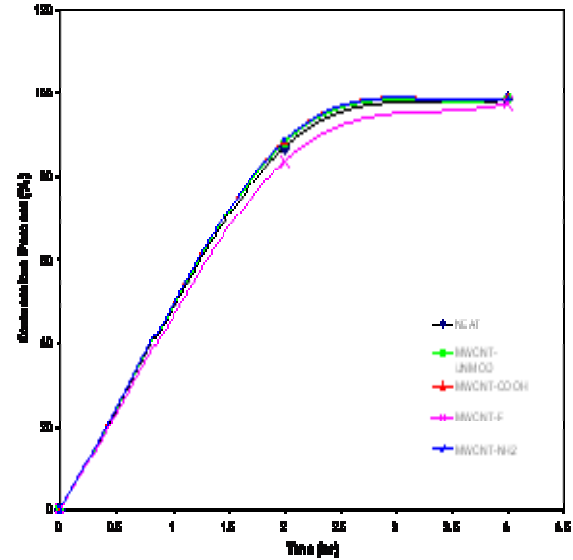


Fig. 2 Conversion % of nanocomposites

case as seen in the fracture surface of this system discussed in section 3.4. Higher increases in rate of reaction will subsequently lead to the highest heat of reaction seen in table 2. The activation energy, heat of reaction, and rate of reaction was lowest for the MWCNT-F, merely because the MWCNT-F reacts initially with the curing agent as seen in the reaction schematic in fig. 3c. Schematic of the MWCNT-COOH, MWCNT-NH<sub>2</sub> systems are shown in fig. 3a and 3c.

The extent of cure was also determined by FTIR. The FTIR method involves the decrease in the absorbance of the epoxy group, which has a characteristic absorbance peak around 920 cm<sup>-1</sup>. The decrease of this peak as a function of cure time (4 hrs) for the neat and the functionalized MWCNTs systems were determined. A ratio of the peak to that of the internal reference band is taken. This ratio is then used in the following equation to calculate the degree of conversion,  $\alpha$ , reported in table 3.

$$\alpha = A_{t=4}/A_{t=0} \quad (3)$$

where  $A_{t=4}$  and  $A_{t=0}$  are the area under the epoxy band at the end of curing time and  $t = 0$ . The FTIR

results are in good agreement (table 3) with DSC kinetics results for percent conversion.

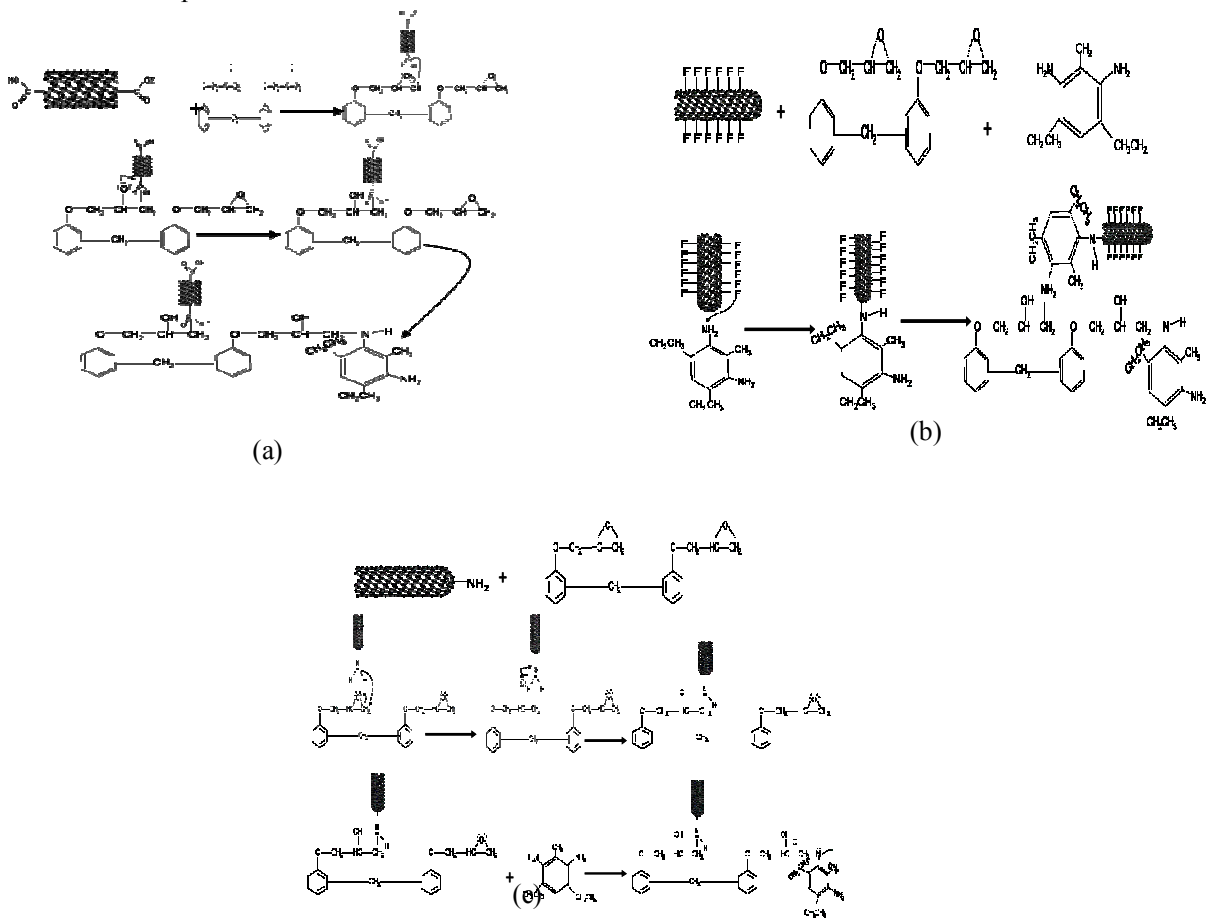


Fig. 3 Chemical reactions (a) mwcnt-cooh/epoxy resin (b)mwcnt-f/epoxy resin (c) mwcnt-nh<sub>2</sub>/epoxy resin

Table 2. DSC curing kinetics results

Material	Activation Energy (Kj/mole)	Enthalpy (J/g)	Reaction Rate (1/min)	Conversion % @ 121 for 4hrs
Neat	57.7± 2.3	263.8 ± 15.3	0.0168	98
MWCNT-UNMOD	55 ± 0.6	258.3 ± 16.5	0.0174	99
MWCNT-COOH	55.2 ± 1.8	304 ± 4.8	0.0182	99
MWCNT-F	54.5 ± 3.8	267.5 ± 0.5	0.0147	97
MWCNT-NH <sub>2</sub>	56.2 ± 3.1	286.5 ± 9.8	0.0181	99

Table 3. DSC and FTIR degree of conversion (%)

Samples	FTIR Degree of conversion (%)	DSC Degree of Conversion (%)
Neat	98	98
MWCNT- -UNMOD	97	99
MWCNT-COOH	95	99
MWCNT-F	98	97
MWCNT-NH <sub>2</sub>	98	99

### 3.3 Mechanical and thermal characterization

Mechanical and thermal properties were tested on the Zwick test system (which utilizes a three point bend test), and DMA. Functionalization not only improved the dispersion of MWCNTs in the polymer matrix but also enhanced the flexural properties as shown in fig. 4, results of which are listed in table 4. Interaction between the MWCNTs and the polymer matrix improved and is evident in the flexural properties and dispersion. The dispersion of the MWCNTs in epoxy resin influences its strengthening effect [5]. However, flexural testing performed on the sample using the Zwick showed a 33 – 59% increase in strength and 16 – 55% increase in modulus in these systems. Brittle failure was observed in all systems, figure 4, a good indication of an increase in crosslinking, better dispersion, and improved interfacial interaction between the MWCNTs and the matrix. PNC becoming more brittle with the incorporation of CNTs is a common problem seen in most research. MWCNT-NH<sub>2</sub> composites exhibited the highest increase in strength, due to the fact that the MWCNT-NH<sub>2</sub> creates a covalent bond with the polymer matrix, thus becoming an integral part of its structure forming a very strong hybrid material that increased the elongation of the composite by 8%. Subsequently, the amount of energy needed to break the sample also increased. MWCNT-NH<sub>2</sub> improves the dispersability by increasing the surface polarity inducing the incorporation of MWCNTs into the matrix resulting in a larger improvement in the ultimate strength [15]. The MWCNT-F composites showed the best dispersion, however the mechanical properties was the lowest

for this system, but still higher than the neat. This observed behavior may be due to degradation of the sample during curing. The premature degradation is presumably catalyzed by hydrofluoric acid, HF, which evolves from the MWCNT-F during the curing process. Shofner [7] and Valentini [16] also found that residual fluorine functional groups start to detached as HF up to temperatures as high as 185° C. HF etches the polymer matrix damaging its structure causing a loss in strength. When flouronanotubes are incorporated into the polymer matrix at high temperatures during processing defluorination might occur. Vigorous mixing at high speed causes fluorine atoms to detach from the surface of the nanotube. These free fluorine atoms attract and bond with hydrogen atoms on the polymer matrix chain. This new bond formed is strong enough to pull and separate itself from the polymer chain resulting in the formation of hydrofluoric gas (HF). The separation sites on the polymer chain and MWCNTs surface opens the opportunity for more reactive sites and other covalent bonding to occur. Flouronanotubes also offer the opportunity for insitu chemical interaction with the amine curing agents [6] in the presence of a catalyst at high temperature [16], and the possibility of intermolecular elimination of HF in the reaction. The degradation mechanism is still under investigation. Another explanation for this low increase would be due to the fact that the rate of reaction and enthalpy change for this system has the lowest values(refer to curing kinetic) indicating that there may possibly be no chemical interaction between the resin and the MWCNT-F.

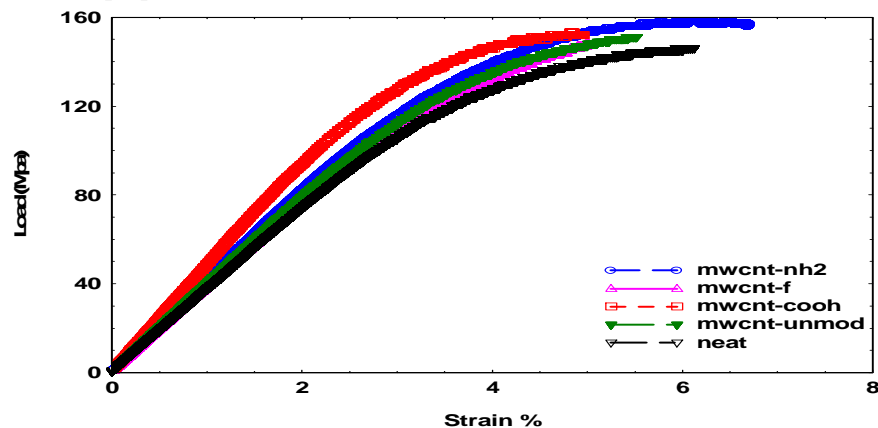


Fig. 4 3-point bend flex test results

Table 4. Mechanical properties of epoxy nanocomposites

Material	Max. Strength, (MPa)	% increase	Modulus, (GPa)	% increase
Epon 862 neat	102.4 ± 5.6	-	3.1 ± 0.3	-
Nanocomposite/ MWCNT -UNMOD	152.1 ± 20.2	49%	4.1 ± 0.2	32%
Nanocomposite/ MWCNT -COOH	151.1 ± 14.9	48%	4.8 ± 0.6	55%
Nanocomposite/ MWCNT -F	136.1 ± 12.2	33%	3.6 ± 0.0	16%
Nanocomposite/MWCNT-NH <sub>2</sub>	162.8 ± 4.60	59%	4.2 ± 0.1	35%

DMA was used to measure the ability of a material to return or store energy (storage modulus), lose energy (loss modulus), and the ratio of these effects (Tan Delta), identifies transition regions in plastics, such as the glass transition temperature (operating range of the composite, T<sub>g</sub>), and may be used for quality control or product development. Moreover, the testing allows one to detect molecular motions and to develop property-structure or morphology relationships. Unlike the quasi-static testing where in the modulus is measured in the initial linear region of a stress strain curve, DMA calculates modulus from a material response to the sine wave sweeping across a temperature or frequency range [17]. The addition of functionalized MWCNTs has a tremendous effect on the storage modulus, reported in table 5 and illustrated in fig. 5. The

MWCNT-COOH, MWCNT-F, MWCNT-NH<sub>2</sub> epoxy nanocomposite showed a 39%, 37%, and a 46% increase in storage modulus, respectively as compared to the neat. Despite having the lowest mechanical properties, the epoxy-nanocomposites prepared with the MWCNT-F showed the highest increase of 10% in the glass transition temperature (T<sub>g</sub>) as shown in figure 5b with a shift from 128°C to 141 °C. This increase in T<sub>g</sub>, indicates that both the MWCNT-NH<sub>2</sub> inhibits the mobility of the polymer chain causing an increase in T<sub>g</sub>. This effect will basically appear around and above the T<sub>g</sub> due to the limited potential movement of the polymeric matrix [3]. There was a 2 to 5% decrease in the MWCNT-NH<sub>2</sub> and MWCNT-COOH composites system. Strangely, these two systems have the highest reaction rates and enthalpy change.

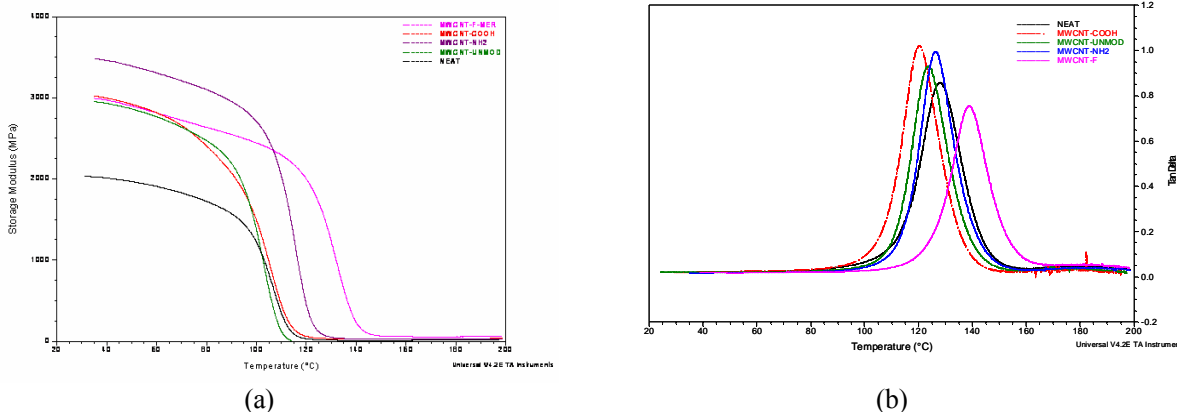


Fig. 5 DMA (a) storage modulus (b) glass transition temperature

Table 5. DMA mechanical and thermal properties

Material	Storage Modulus (MPa)	% increase	Glass transition temp. (T <sub>g</sub> ), °C	% difference
Epon 862 neat	2268 ± 15	-	128.0 ± 4.6	-
Nanocomposite/ MWCNT -UNMOD	2827 ± 532	25%	121 ± 10	-5%
Nanocomposite/ MWCNT -COOH	3144 ± 120	39%	121 ± 6	-5%
Nanocomposite/ MWCNT -F	3112 ± 230	37%	141 ± 1	10%
Nanocomposite/MWCNT-NH <sub>2</sub>	3300 ± 188	46%	125 ± 1	-2%

### 3.4 Morphology of Fracture Surface

SEM was employed to determine the morphology and dispersion of the functionalized MWCNTS in the matrix. The fracture surface of the samples from the three point bend test was investigated. Figures 6-9 illustrate the scanning electron micrographs of the samples observed under the microscope after the flexure tests. Most common failure observed in polymer nanocomposites reinforced with short fiber as well as continuous fibers are fiber fracture, fiber pullout, debonding/crack bridging, or matrix cracking [18]. From Fig 6a, it is obvious that the neat composite has a clean and smooth surface. Incorporation of pristine MWCNT into the matrix increases the roughness. These nanocomposites contain agglomeration of MWCNTS that seem to be sitting on top of the matrix as opposed to being embedded into the matrix (Fig. 6b). These results are signs of poor dispersion resulting from poor interfacial interaction and adhesion to the matrix.

surface of composite shows that it is resisting or delaying the fracture process by forming vivid ridges which dissipate energy during their formation promoting a higher resistance to material separation. It is believed that randomly oriented MWCNT is responsible for such resistance. The increased number of features on the surface (vivid ridges) gives rise to a larger area for fracture energy absorption, simultaneously, increasing the stress intensity factor. In the MWCNT-COOH composites a continuous and uniform river pattern was formed at the fracture surface and the MWCNT-COOH were very well dispersed (Fig. 7). Kime et al. [19] also reported that this effect is caused by the increased interfacial bonding between the MWCNTs and matrix resin when the impurities are removed from the CNTs and the functional groups are formed by acid treatment. In the MWCNT-F composites, matrix cracking is observed creating debonding in some areas (Fig. 8). As mentioned earlier, the matrix cracking could be the consequences resulting from the damages created

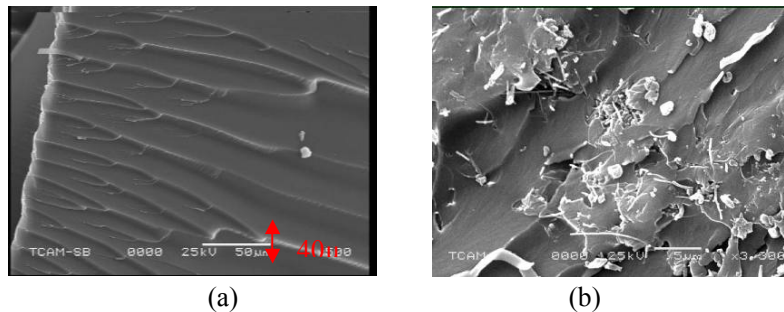


Fig. 6 Fracture surfaces of the flexure samples: a) neat composite, b) mwcnt-unmod composite

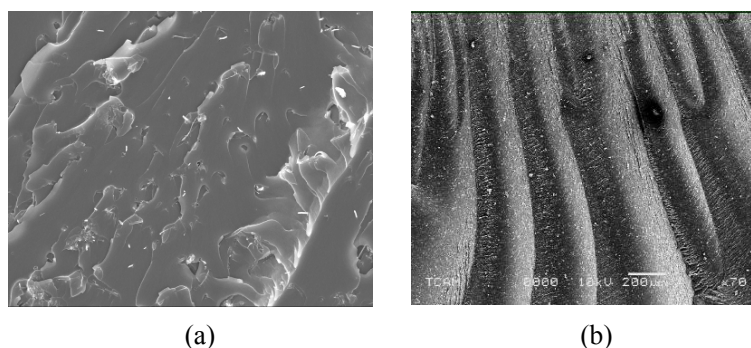
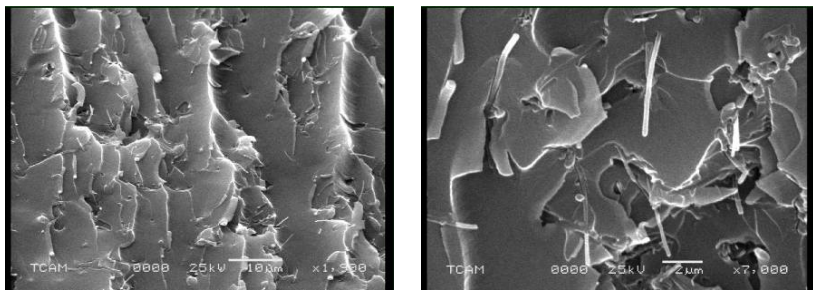


Fig. 7 Fracture surface of the mwcnt-cooh composites flexure sample at different magnifications

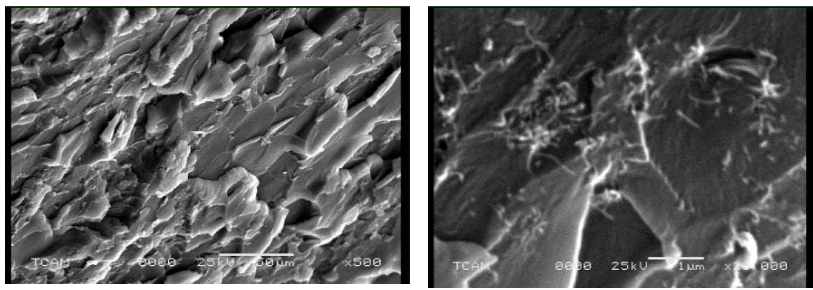
Incorporating functionalized MWCNTs increased the roughness to an even higher degree making the composites more resistant to deformation. It also improves dispersion within the matrix. The fracture

by the HF. The MWCNT-NH<sub>2</sub> contains the most rigid fracture surface with some agglomeration-rich areas and fiber fracture (Fig. 9). The concentration was still less than that of the MWCNT-UNMOD.





(a) (b)  
 Fig. 8 Fracture surface of the mwcnt-f composites flexure sample at different magnifications



(a) (b)  
 Fig. 9 Fracture surface of the mwcnt-nh<sub>2</sub> composites flexure sample at different magnifications

Even though dispersion was not the best in MWCNT-NH<sub>2</sub>, breaking of the MWCNTs indicate that interfacial interaction between the MWCNT-NH<sub>2</sub> and polymer matrix is the strongest. Increase in roughness, improvement in dispersion, and fiber fracture are all indications of enhancement in interfacial interaction.

#### 4. Conclusions

In this study, MWCNTs were functionalized through oxidation, fluorination and amine modification. The modified as well as unmodified MWCNTs were then dispersed in EPON 862 polymer at 1% loading by weight. Performance of the nanocomposites samples was compared with that of neat epoxy. The effect of functionalization was characterized through, Raman Spectroscopy. Curing kinetics were studied utilizing DSC (thermal stability kinetics) and FTIR to determine curing kinetics parameters such as activation energy, enthalpy change, rate of reaction, and percent conversion. 3-point flexure and dynamic mechanical analysis were carried out on the sample to determine the mechanical and Thermomechanical behavior of the samples.

Finally, the flexure samples were observed under scanning electron microscope to understand the failure modes. Following conclusions were made: Chemical functionalization, in most cases, is a useful method to improve dispersion, mechanical, and thermal properties. Raman spectroscopy is a very efficient and a useful tool for confirmation of disorder or degree of functionalization on the MWCNT surface. Curing kinetics studies show evidence of how these functionalized MWCNT affect the curing process by lowering activation, and increasing change in enthalpy. SEM investigation of the fracture surface showed evidence of improvement in the dispersion of MWCNTs in the matrix and the chemical interaction between them. Improvement in interfacial interaction and dispersion also manifested itself by improving the mechanical and thermal properties of the composites. The improvements in the mechanical properties of the polymer matrix by addition of functionalized MWCNTs are the results of two major factors, dispersion and surface modification.

## References

- Iijima, S., *Helical microtubules of graphitic carbon*. Nature, 1991. **354** (6348): p. 56.
- Yaping, Z., Aibo, Z., Jiaoxia, Z., Rongchang, N. *Functionalized effect on carbon nanotube/epoxy nano-composites*. Materials Science and Engineering A, 2006. **435-436**: p. 145-149.
- Gojny, F.H. and K. Schulte, *Functionalisation effect on the thermo-mechanical behaviour of multi-wall carbon nanotube/epoxy-composites*. Composites Science and Technology, 2004. **64**(15 SPEC ISS): p. 2303-2308.
- Chen, G.-X., Kim, H.-S., Park, B., Yoon, J.-S. *Multi-walled carbon nanotubes reinforced nylon 6 composites*. Polymer, 2006. **47**(13): p. 4760-4767.
- Zhu, J., Peng, H., Rodriguez-Macias, F., Margrave, J., Khabashesku, V., Imam, A., Lozano, K., Barrera, E. *Reinforcing epoxy polymer composites through covalent integration of functionalized nanotubes*. Advanced Functional Materials, 2004. **14**(7): p. 643-648.
- Khabashesku, V.N., J.L. Margrave, and E.V. Barrera, *Functionalized carbon nanotubes and nanodiamonds for engineering and biomedical application*. Diamond and Related Materials, 2005. **14**(3-7): p. 859-866
- Shofner, M.L., V.N. Khabashesku, and E.V. Barrera, *Processing and mechanical properties of fluorinated single-wall carbon nanotube-polyethylene composites*. Chemistry of Materials, 2006. **18**(4): p. 906-913.
- Namilae, S. and N. Chandra, *Multiscale model to study the effect of interfaces in carbon nanotube-based composites*. Journal of Engineering Materials and Technology, Transactions of the ASME, 2005. **127**(2): p. 222-232.
- Eklund, P.C., J.M. Holden, and R.A. Jishi, *Vibrational modes of carbon nanotubes; spectroscopy and theory*. Carbon, 1995. **33**(7): p. 959-972.
- Liang, E.J., Ding, P., Zhang, H.R., Guo, X.Y., Du, Z.L. *Synthesis and correlation study on the morphology and Raman spectra of nanotubes by thermal decomposition of ferrocene/ethylenediamine*. Diamond and Related Materials, 2004. **13**(1): p. 69-73.
- Osswald, S., Flahaut, E., Ye, H., Gogotsi, Y. *Elimination of D-band in Raman spectra of double-wall carbon nanotubes by oxidation*. Chemical Physics Letters, 2005. **402**(4-6): p. 422-427.
- Jorio, A., Saito, Hafner, J., Lieber, C., Hunter, M., Dresselhaus, G., Dresselhaus G.M., *Structural (n, m) determination of isolated single-wall carbon nanotubes by resonant Raman scattering*. Physical Review Letters, 2001. **86**(6): p. 1118-1121.
- Jiang, C., Zhao, J., Therese, H., Friedrich, M., Mews, A. *Raman imaging and spectroscopy of heterogeneous individual carbon nanotubes*. Journal of Physical Chemistry B, 2003. **107**(34): p. 8742-8745.
- Kun, T Yang, S., Grunlun, J., Kin, Y-S., Dang, B., Deng, Y., Thomas, R., Wilson, B., Wei, X. *Effects of carbon nanotube fillers on the curing processes of epoxy resin-based composites*. Applies Polymer Science, 2006. **102**: p 5248-5254
- Gojny, F.H., Wichmann, M., Fiedler, B., Schulte, K. *Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites - A comparative study*. Composites Science and Technology, 2005. **65**(15-16 SPEC ISS): p. 2300-2313.
- Valentini, L., Puglia, D., Armentano, I., Kenny, J. *Sidewall functionalization of single-walled carbon nanotubes through CF plasma treatment and subsequent reaction with aliphatic amines*. Chemical Physics Letters, 2005. **403**(4-6): p. 385-389.
- Menard, K.P., *Dynamic Mechanical Analysis: A Practical Introduction*. 1st ed. 1999, Boca Raton, London, New York, Washington DC: CRC. 224.
- Thostenson, E.T., C. Li, and T.-W. Chou, *Nanocomposites in context*. Composites Science and Technology, 2005. **65**(3-4): p. 491-516.
- Kim, J.A., Seong, D., Kang, T., Youn, J. *Effects of surface modification on rheological and mechanical properties of CNT/epoxy composites*. Carbon, 2006. **44**(10): p. 1898-1905.

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