

## EFFECT OF ENHANCED CROSSLINK DENSITY ON INTERFACIAL STRENGTH OF E-GLASS/EPOXY COMPOSITES MODIFIED BY AMINO-FUNCTIONALIZED MWCNTS

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### ABSTRACT

Crosslink density is one of the important parameters that govern the physical properties of composite laminates. Enhancement of crosslink density by matrix modification is most effective ways to improve mechanical properties of a composite. In this study, 0.1-0.4 wt. % of amino-functionalized multi-walled carbon nanotubes (MWCNTs) was incorporated to modify an epoxy resin system combining sonication and calendaring dispersion techniques. E-glass/ epoxy nanocomposites were then fabricated at elevated pressure and temperature with the modified resin by compression hot press. Flexural and Interlaminar shear properties of E-glass/epoxy nanocomposites from three point flexure test and Short beam shear test showed an increasing trend in properties up to 0.3 wt. % MWCNTs loading. Micrographs of MWCNTs incorporated epoxy and e-glass/epoxy samples revealed uniform dispersion in epoxy, good interfacial bonding between CNTs and epoxy as well as between glass fiber and epoxy at 0.3 wt. % loading. An improved dispersion and hence an improved crosslink interaction between MWCNTs and epoxy lead to the enhanced mechanical properties of the composite.

**Keywords:** Crosslink Density, Multi-Walled Carbon Nanotubes, Sonication.

### 1. INTRODUCTION

Due to its low cost, high strength, high chemical resistance and excellent insulating properties, glass fiber has become a good choice as reinforcement for fiber reinforced composites (FRC) in many structural applications like automotive, sporting goods, marine and infra-structure sectors etc. Epoxy resin has been excellent candidate as matrix in glass fiber reinforced polymer (GFRP) composites for its good stiffness, strength, excellent chemical resistance, dimensional stability and excellent adhesion with fillers, fibers and other substrates. Basically in FRC, fiber plays a major role in the tensile load carrying capacity of a composite structure while compressive, inter-laminar shear, in-plane shear properties depend on the selection of matrix polymer. Recently, for the modification of the properties of epoxy polymer, a number of researches have been successfully used inorganic nanoparticles as reinforcing materials [1-3]. Among them carbon nanotubes (CNTs) have emerged as potential candidates for modification of polymeric materials because of their excellent mechanical, thermal and electrical properties. Most significant feature of CNTs is their high surface area which provides desirable interfaces for stress transfer and a large potential for obtaining functional properties into composite material. On the contrary, this feature induces undesirable strong attractive forces between CNTs which leads to excessive agglomeration behavior. Many researchers have investigated effective

methods to disperse CNTs uniformly in the epoxy polymer matrix [4-5]. Some researchers found that chemical functionalization on the CNT surface enhances interfacial interaction between CNTs and matrix and hence the dispersion of CNTs into the matrix [6-7]. Still, the ability to control the dispersion of CNTs in polymer matrix remains a technical challenge in producing high performance CNTs reinforced nanocomposites.

Interlaminar shear strength (ILSS) of fiber reinforced composites is a limiting design characteristic. Enhancement of ILSS in FRC has been a major concern in this field for the successful application in various sectors subjected to transverse load. In the last two decades, very few numbers of studies have been conducted regarding improvement in ILSS properties of GFRP composites incorporated with MWCNTs. Fan et al. [1] introduced a novel injection and double vacuum assisted resin transfer molding (IDVARTM) method. They found that adding 2 wt. % MWCNTs into glass fiber reinforced epoxy composites increased the ILSS by 33%. Gojny et al. used high shear mixing process for dispersion and produced GFRP by RTM process [2]. They gained 19% improvement in ILSS by adding 0.3 wt. % amino-functionalized double-walled carbon nanotubes (DWCNTs) into fiber reinforced epoxy composites. Wichmann et al. [8] also got 16% enhancement of ILSS at 0.3 wt. % loading of MWCNTs.

In the present work, MWCNTs reinforced e-glass/epoxy nanocomposites were processed by

combining sonication and calendaring dispersion techniques, utilizing functionalized MWCNTs, combining fabrication processes and curing the composites at higher temperature. Thermo-mechanical tests were performed to investigate the effect of crosslink density on interlaminar properties of e-glass/epoxy composites. Effect of combined sonication and calendaring techniques on MWCNTs dispersion in epoxy suspension were investigated using transmission electron microscope (TEM). In addition, failure morphology was investigated using scanning electron microscope (SEM).

## 2. EXPERIMENTAL

### 2.1 Materials

SC-15 epoxy resin system, amino functionalized MWCNTs and woven e-glass plain weave fiber fabric were used to fabricate composite laminates. The matrix SC-15 resin, a two part cyclo-aliphatic amine type epoxy resin (Part A: diglycidylether of bisphenol A, aliphatic diglycidyl and Part B: hardener) was manufactured and supplied by Applied Poleramics Inc. As reinforcement in composites, commercially available e-glass woven fabric with a density of  $2.58 \text{ g/cm}^3$  and a single fiber diameter of  $14\text{-}16 \text{ }\mu\text{m}$  was supplied by Fibre Glast Development Corporation. Amino functionalized MWCNTs were purchased from Nanocyl, Belgium, having average diameter of  $10 \text{ nm}$ , length of  $1 \text{ micron}$  and carbon purity  $>95\%$ .

### 2.2. Manufacturing Process

#### 2.2.1 Resin Preparation

A novel technique to disperse MWCNTs effectively into the resin through a combination of calendaring process and sonication process was employed. At first, MWCNT-NH<sub>2</sub> was mixed with epoxy resin Part A as per calculated weight ratio. The mixture was then sonicated at room temperature for 1 hour at 35% amplitude and 40 second on/ 20 second off cycle pulse mode. Sonication process induces elevated pressure and temperature in the system, so the mixture was cooled down by keeping the container in a refrigerator cooler maintained at  $5^\circ \text{ C}$ . To further improve the dispersion, the sonicated mixture was then passed through three rollers as shown in Fig. 1. In this three roll process, roller 1 and 3 rotate in the same direction whereas the roller 2 placed in between rotates in the opposite direction thereby generate high shearing in the mixture. A varying gap setting between the rolls and multiple passes of  $20 \text{ }\mu\text{m}$  (1<sup>st</sup> pass),  $10 \text{ }\mu\text{m}$  (2<sup>nd</sup> pass) and  $5 \text{ }\mu\text{m}$  (3<sup>rd</sup> pass) was used to generate high shear force in the mixture to further de-agglomerate and improve the dispersion of CNTs in resin. Roller speed of  $150 \text{ rpm}$  was maintained constant in all the three passes. The hardener Part B was added as per stoichiometric ratio (Part A: Part B= $10:3$ ) to the modified mixture after completion of sonication and calendaring process and mixed with a high speed mechanical stirrer for 10 minutes at approximately  $800 \text{ rpm}$ . The mixture was then placed in desiccators for 20 minutes to remove the volatile materials and entrapped air bubbles that were generated due to intense mechanical mixing.

#### 2.2.3 Fabrication of Laminates

E-glass/epoxy nanocomposite laminates were fabricated by using a combination of hand lay-up technique and a hot press process to ensure uniform resin distribution into the fabrics and good compaction. The fabrics were cut into square of  $250 \text{ mm} \times 250 \text{ mm}$ . The layers were properly stacked into 7 plies of woven fabrics so as to achieve approximately  $3.25 \text{ mm}$  thickness upon curing. The orientation of fiber within the fabric was kept constant all the time during lay-up process. Consolidation of the laminates was achieved by applying  $133 \text{ kN}$  force in a hot press machine. The composite laminates were first cured at  $60^\circ \text{ C}$  for a period of 2 hours according to the manufacturer's instructions. After completion of curing, the laminates was taken out from the press and thermally post cured at  $100^\circ \text{ C}$  for 4 hours in a mechanical convection oven. The final thickness of the panel was found to be  $3.25 \text{ mm}$ . The whole process is shown in figure 1.

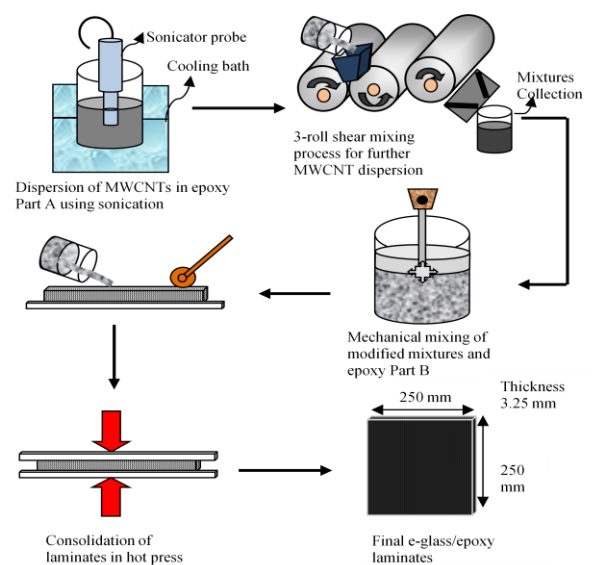


Fig 1. Schematic of E-glass/epoxy nanocomposite fabrication.

### 2.3. Thermo-Mechanical Characterization

Thermo-mechanical behavior of nanophased epoxy composites was investigated by dynamic mechanical thermal analysis (DMTA) according to ASTM D4065-01 [9]. Storage modulus in glassy state as well as in rubbery state and glass transition temperature was determined from this test.

From the theory of rubber elasticity, crosslink density of a polymer based composites can be calculated from the storage modulus in rubbery regions or at a temperature well above glass transition temperature which can be determined from this test. In this test, the width of the samples was  $12 \text{ mm}$  and span length to thickness ratio was 10. The test was conducted in dual cantilever beam mode with a frequency of  $1 \text{ Hz}$  and amplitude of  $15 \text{ }\mu\text{m}$  in DMA 2980 machine. The temperature was ramped from  $30$  to  $180^\circ \text{ C}$  at a rate of  $5^\circ \text{ C/min}$ . Minimum of five specimen samples of each type were tested.

### 2.4. ILSS Characterization

Interlaminar shear strength (ILSS) of the

E-glass/epoxy nanocomposites was measured by carrying out short beam shear test method according to ASTM D-2344-00 [10]. The test was performed using a MTS Hydraulic machine. The specimen was loaded in three points bending which was placed by two cylindrical supports and a cylindrical head was moved to apply a force at the centre until the first failure was observed. The load at failure was then used to calculate interlaminar shear strength. The apparent shear strength was measured as follows using classical beam theory:

$$SH = 3P_b/4bd \quad (1)$$

Where,  $P_b$  is the breaking load,  $b$  is the width of specimen,  $d$  is the thickness of specimen. According to ASTM D2344-00, the ratio of span length to thickness is chosen as 6:1 and width to thickness is 2:1. The span length of samples between two supports was 19.5 mm and width was 6.5 mm with a thickness of 3.25 mm. Samples were loaded in displacement control mode with crosshead speed of 1.2 mm/min. Load-deflection data and graph for each sample was collected and from this data, Inter-laminar shear strength was calculated. Minimum of five samples of each type were tested and the average value of them was determined.

## 2.5. Electron and Optical Microscopy

Inter-laminar fracture pattern was investigated by optical microscopy. Dispersion state of MWCNTs in epoxy resin was investigated by transmission electron microscopy (TEM) using a Zeiss EM10 Transmission Electron Microscope operated at 60kV. The analysis of neat and nano epoxy composites was carried out using a JEOL JSM-6400 scanning electron microscope (SEM) at 5 kV accelerating voltage. Specimen surfaces were coated with a thin gold film to increase their conductance for SEM observation.

## 3. RESULTS AND DISCUSSION

### 3.1. Storage Modulus

Storage modulus as a function of temperature obtained from DMTA test for the neat epoxy resin and its nano-composites is shown in fig. 2. From the graph, an enhancement in the storage modulus in glassy regions as well as in the rubbery region with the addition of the nanotubes is clearly observed. This increase of the storage modulus was seen up to 0.3 wt. % loading. The behavior can be attributed to the better dispersion and an improved interaction between the CNTs and epoxy due to the formation of covalent bonds between them. Increased interfacial interaction reduces the molecular motion of the epoxy matrix chain around the nanotubes by increasing crosslink density. When the nanotubes loading was 0.4 wt. %, a decrease was observed in storage modulus. Increase of viscosity and inability to completely de-agglomerate causes a reduction in formation of crosslink or exposing the reaction sites on CNTs to epoxy molecules to interact. As a result, the molecular motion and movement of chain becomes easier and a drop in storage modulus is observed. It is also possible that clustered CNTs slide relative to each other resulting in reduced stiffness and hence storage

modulus.

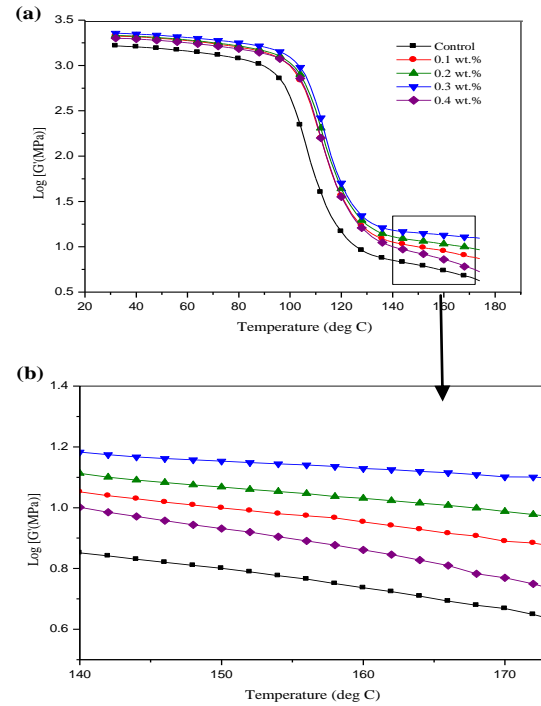


Fig 2.(a) Storage modulus with respect to the temperature and (b) storage modulus at 140-175 °C.

### 3.2. Crosslink Density

Here the value of crosslink density,  $\lambda$  of epoxy networks was determined from elastic modulus above the glass transition temperatures using rubber elasticity theory. As it is postulated that covalent interfacial interaction increases crosslink density, value of crosslink density can be calculated by using following relationship according to the theory of rubber elasticity:

$$\lambda = \frac{G}{RT} \quad (2)$$

Where  $\lambda$  is the cross-link density expressed in moles of elastically effective network chains per cubic centimeter of sample,  $G$  is the storage modulus in the rubbery region at a temperature well above glass transition temperature,  $R$  is the universal gas constant and  $T$  is the absolute temperature at which experimental modulus is selected [11]. The above relationship shows that the cross-link density increases with an increase of storage modulus in the rubbery region/space.

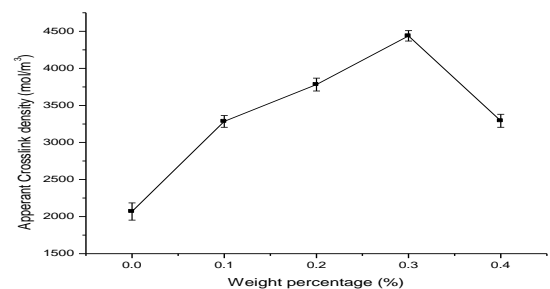


Fig 3. Crosslink density for control and epoxy nanocomposites.

Figure 3 shows apparent cross-link density calculated

using the formula at different weight percentages of nanotubes loading. Crosslink density increased up to a loading of 0.3 wt% CNTs and then decreased. As shown in Fig. 4, addition of nanotubes to the epoxy results in a shift of the glass transition temperature. The glass transition temperature was shifted from 99 deg C for control samples to 107 deg C for 0.3 wt% loading CNTs. This gain in thermo-stability can again be interpreted as a reduction of the mobility of the epoxy matrix around the nanotubes by the formation of interlocking structure type crosslink sites. The change in the glass temperature with increasing cross-linking has a linear relationship. Fig. 5 shows plot of the glass transition temperatures of the networks as a function of crosslink density.

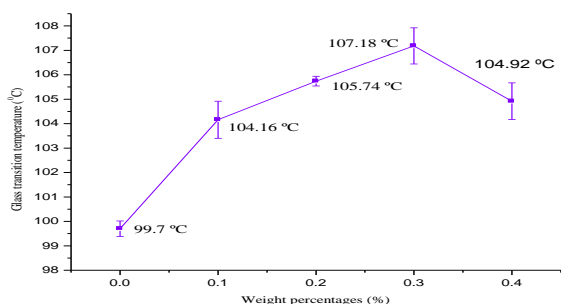


Fig 4. Glass transition temperature as a function of weight percentages of MWCNTs.

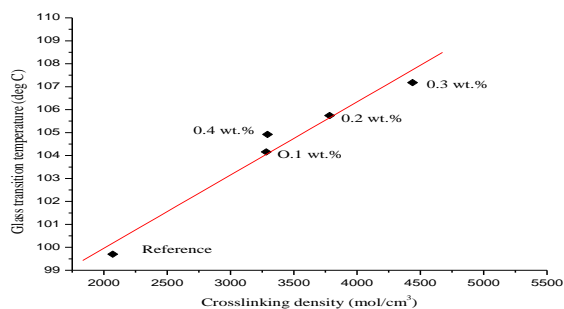


Fig 5. Relationship between crosslink density and glass transition temperature.

### 3.3 Inter-Laminar Shear Strength (ILSS)

ILSS depends on the matrix properties such as matrix strength, matrix volume fraction and fiber-matrix interfacial shear strength rather than fiber properties. It can be improved by increasing matrix strength, matrix volume fraction and fiber-matrix adhesion. It also depends on the size of specimens as well as fabrication process. In this study, ILSS for glass fiber reinforced epoxy matrix composite samples was obtained using span length to thickness ratio of 6:1 according to short beam shear test. Matrix volume fraction was 30-32% obtained by matrix digestion test method according to ASTM D 3171-99(2004). In this research, prime focus was to improve the ILSS by increasing matrix strength and fiber-matrix interfacial strength through the infusion of amino-functionalized MWCNTs in matrix. Load versus deflection plots of inter-laminar shear testing for various weight percentages of nanocomposites are presented in Fig. 6. In all cases the relation was seen to be

nonlinear. After reaching the peak load, there is a sudden drop in load in some samples where there was shear failure (fig 6a) and a gradual reduction in load due to continuous matrix failure (fig 6b). These failure modes were identified in optical microscopy studies and are discussed later.

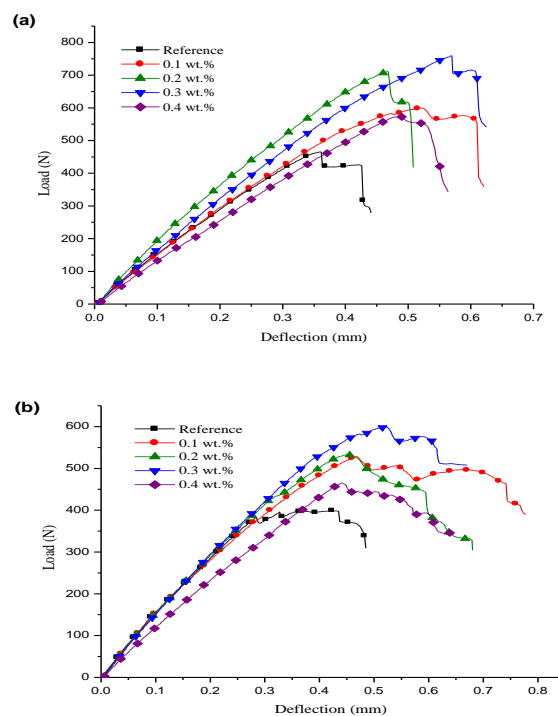


Fig 6. Load vs. deflection plots of short beam shear test.

ILSS of the composites is improved up to 0.3 wt. % of CNT loading as shown in fig. 7. Then the strength decreased at 0.4 wt. % loading of nanotubes. The strength of 0.3 wt. % loading is best with a 49% strength enhancement in comparison of reference samples. Considering the low concentration of nanotube loading, this improvement in ILSS is noteworthy.

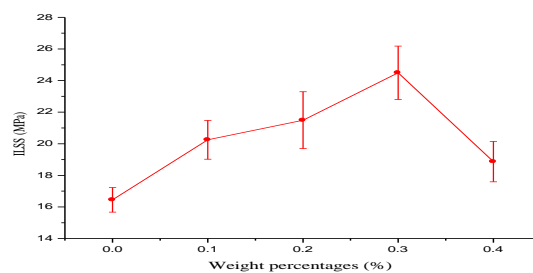


Fig 7. Effects of MWCNT-NH<sub>2</sub> on interlaminar shear strength of e-glass/epoxy nanocomposites.

As shown in figure, the standard deviation is considerably high. In case of inter-laminar shear failure, it was found that failure occurs through a combination of fiber rupture, micro buckling and inter-laminar shear cracking [12] though it was supposed to fail only by inter-laminar shear cracking. So all sample do not fail by only transverse shear failure mode in short beam shear test. Some of them fail by pure fiber-matrix interfacial de-bonding, some due to matrix micro cracking and some of them by a combination of both which was

evident clearly in optical micrograph as shown in Fig. 8. Fig.8 (a) shows pure inter-laminar shear failure in the samples where Fig. 8(b) and Fig 8(c) shows matrix cracking and combination of fiber rupture, matrix micro cracking and ILSS failure in the samples respectively.

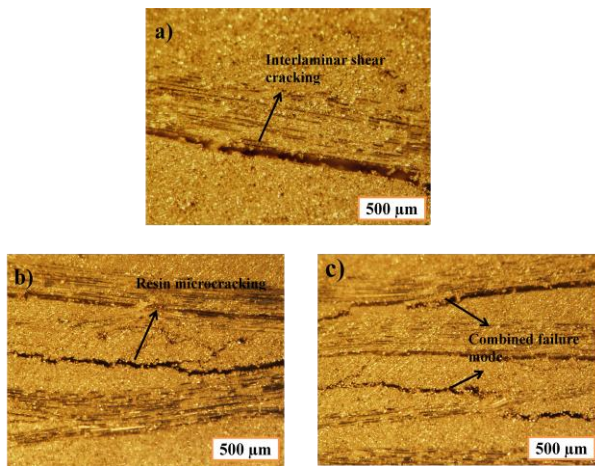


Fig 8. Optical micrograph of (a) interlaminar shear failure, (b) resin microcracking and (c) combination of both failure modes in short beam shear test.

As the sample has to withstand a bending force, the surface under the central loading zone is subjected to compression and the composite may undergo localized buckling which results micro-cracking of resin in the samples. For these two types of failure, we obtained two types of clearly distinct graphs in our load vs. deflection curve plot. figure 6(a) shows a gradual rise and then sudden fall which reflects ILSS failure with a better strength. On the contrary figure 6(b) shows a gradual rise with a gradual fall which reflects matrix micro-cracking with less strength than ILSS failure.

One of the obvious factors that contribute to the improvements in ILSS properties is the increased load transfer capability between the epoxy matrix and nanotubes. It has been reported that effective stress transfer between epoxy matrix and amino-functionalized MWCNTs contributed in enhancing of mechanical properties of fiber-reinforced composites [13]. An improved dispersion of CNTs in matrix facilitates to enhance interfacial reactions and forms covalent bond between them that induces different cross-linking region in the epoxy matrix. This cross-linking results inter-locking structure which restricts mobility of polymer matrix chain. So the noticeable increase in ILSS up to 0.3 wt. % loading can be ascribed to better dispersion of CNTs. We observed a decrease in 0.4 wt% loading composite samples due to excessive agglomeration.

### 3.4 Dispersion State of MWCNTs in Epoxy

Figure 9(a) and 9(b) show the TEM micrographs which have revealed the dispersion state of amino-MWCNTs at 0.3 wt. % and 0.4 wt. % loading in SC-15 epoxy polymer. At 0.3 wt. % loading, MWCNT exhibit a uniform and homogenous dispersion within the epoxy matrix without considerable agglomerates. As

shown in Fig 9 (b), the achieved dispersion for 0.4 wt. % of MWCNTs in the epoxy matrix contains considerable small bundles or agglomerates and few larger agglomerates.

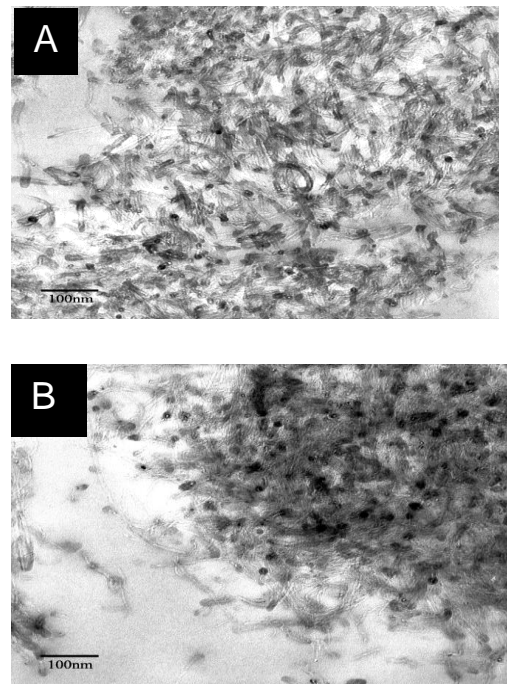


Fig 9. TEM micrograph showing the dispersion state of (a) 0.3 and (b) 0.4 wt.% loading of amino-functionalized multi-walled carbon nanotubes into SC-15 epoxy resin.

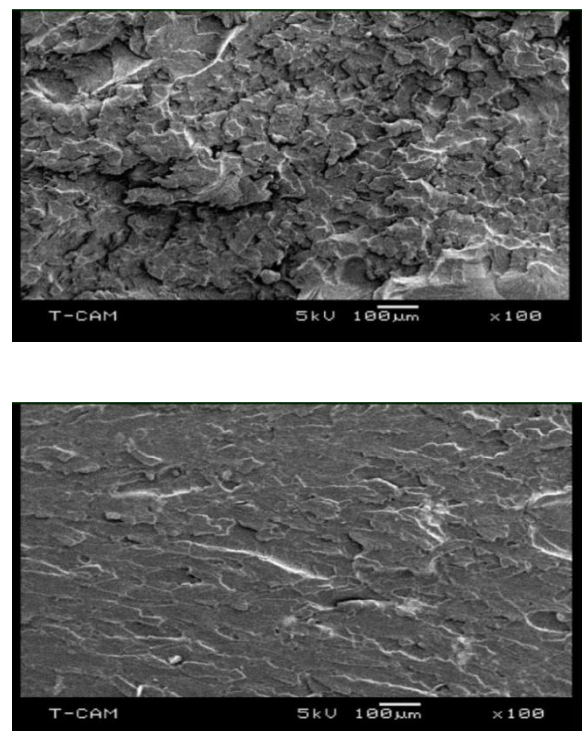


Fig 10. Micrograph of (a) 0.3 wt. % MWCNTs reinforced epoxy and (b) control composite fractured sample.

### 3.5 Morphology Analysis

It mentioned earlier that a bonding between the CNTs and the polymer matrix i.e. crosslink is essential to obtain the highest possible enhancement in properties. A uniform dispersion of CNTs in matrix provides more cross-linking sites for polymer-matrix interaction as well as presence of amino- functional groups on the outer ring of MWNTs forms a strong covalent bond with the epoxy resin. Zhou et al. reported that the crack propagation changes direction as it crosses CNTs during failure process due to bridge effect which prevents crack opening [14]. CNTs may provide bridging in the pores of matrices and improves the interfacial strength between glass fabrics and matrix. Due to this, crack initiation and propagation may become difficult within the matrix and at glass/matrix inter-phase than that without reinforced CNTs. We observed control and nanophased epoxy samples after fracture. More rugged fracture surface is observed in nanophased fracture samples as shown in Fig. 10 (a) which reveals distorted path of crack tip and hence makes more difficult in crack propagation. In contrast, a smoother fracture surface in the matrix and poor interfacial bonding was observed in control composites in comparison to MWCNTs reinforced epoxy nanocomposites as shown in Fig 10(b).

### 4. CONCLUSION

Based on the experimental results, the following conclusions were reached:

(1) MWCNTs incorporation at quite low concentration in glass fiber reinforced epoxy composites increased ILSS property of the composites. In this study 0.3 wt. % CNT loading into the composites is the optimum loading below or above which the properties of the samples were lower. ILSS test results shows 49% improvement in strength at 0.3 wt. % loading of CNTs in glass fiber reinforced nanocomposites systems with respect to reference sample.

(2) The improvement up to optimum loading explores a good interfacial interaction and effective load transfer between CNTs and epoxy system due to better dispersion. At 0.3 wt. % loading, apparent crosslink density is found to be highest which is due to increased number of crosslink sites. Morphological studies have revealed that amino-functionalized MWCNTS promote good adhesion between glass fiber and epoxy matrix by modifying the matrix adhesive properties.

(3) Overall this work proved that amino-functionalized MWCNTs can be easily used to modify fiber-reinforced composite materials.

### 5. ACKNOWLEDGEMENTS

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