

## Effect of alcoholic treated MWCNT on tensile behavior of epoxy composite

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### Abstract

In this work, the effect of alcoholic treatment of the multi-wall carbon nano-tube (MWCNT) on the mechanical properties of epoxy composites are investigated and compared. Nano-composites were developed by mixing 0.25%, 0.5% and 0.75wt% of MWCNT. Tensile strength, Young's modulus, and Elongation are found to be effectively improved with the addition of alcoholic functionalized MWCNT in epoxy matrix. Increased tensile strength and elastic modulus of epoxy composites loaded with the alcoholic functionalized MWCNT are observed through experimental studies. The results were compared with neat epoxy composite. These findings confirm that the improved dispersion and interfacial interaction in the composites arising from covalent bonds between the MWCNT and the epoxy matrix.

**Keywords:** MWCNT, tensile strength, alcoholic treatment, tensile modulus, epoxy

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### 1. Introduction

Recently, the manufacturing, and application of polymer nano-composites have attracted attention and interest from both academics and industry. This is due to the reason that the addition of nano particles into composites does offer several advantages over general composites, with respect to higher stiffness, higher strength, and excellent chemical resistance, etc. There are several types of nano particles that are quite popular in nano-composites; these include nano-fibers, nano-tubes, metal nano-particles and nano-clay. Each of these fillers does have their own characteristic to improve the properties of composite materials. Mohapatra and Anand (2010) have studied on nano sized magnetite, which exhibits the excellent magnetic properties and used in the applications for biomedical purposes. Many researchers (Bai and Allaoui, 2003; Gojny *et al.*, 2005; Guo *et al.*, 2007; Yang *et al.*, 2007; Liu *et al.*, 2009; Spitalsky *et al.*, 2009) have studied Multi-Wall Carbon Nanotube (MWCNT) because of their inherent desirable mechanical properties and several other potential functional properties. MWCNT-filled polymer composites exhibits higher stiffness, higher strength, and better electrical conductivity even at low concentration of MWCNT's (Bai and Allaoui, 2003; Yang *et al.*, 2007; Gojny *et al.*, 2005; Guo *et al.*, 2007).

Epoxy/MWCNT composites have been extensively investigated due to their industrial and technological applications. The Nano-Composite of such kind is prepared by various means. Guo *et al.* (2007) have prepared these composites using melt mixing or solution mixing methods. A typical procedure for the preparation of composite by melt mixing method is as follows: MWCNTs are directly added to epoxy resin and then sonicated using an ultrasonic machine at an elevated temperature. Curing agent is added into the mixture and the mixture is degassed in a vacuum oven. Finally, mixture is injected into the sample moulds and is cured in an oven. Liu *et al.* (2009) have used solution mixing method and dispersed MWCNTs in alcohol by sonication. Epoxy resin is heated to elevated temperature then dispersed MWCNT are mixed with it. This mixture is mechanically stirred and sonicated in a water bath and hardener is added to it. The author have, reported that in MWCNT-reinforced epoxy composites using polyethylenimine as a dispersant. The covalently modified composites are 10,000 times more resistive than their noncovalent

counterparts. Storage modulus of the composites containing covalently functionalized nanotubes is increased, relative to the noncovalent composites, due to the stronger polymer/nanotube interaction.

Similar results were observed by Spitalsky *et al.* (2009) for H<sub>2</sub>O<sub>2</sub>/NH<sub>4</sub>OH mixture treated MWCNT/epoxy composites. Bai and Allaoui (2003) have reported that the effect of MWCNT length and aggregate size on the mechanical and electrical properties of epoxy/MWCNT composites. The insulator-to-conductor transition was found to occur at 0.5 wt. % of the as prepared MWCNTs. Yang *et al.* (2007) have prepared amide functionalized MWCNT/bisphenol-A epoxy resin/2-ethyl-4-methylimidazole composites. Transmission electron microscopy (TEM) showed that there was an organic thin layer on the MWCNT surface, which contributed to the homogenous dispersion of the MWCNTs in the epoxy matrix and to the improvement of the MWCNT-epoxy interfacial interaction. Thus the impact strength, bending strength, and thermal conductivity of the composites were enhanced. Similar results were observed by Gojny FH *et al.* (2005) for different types of nanofillers-reinforced epoxy nanocomposites. Guo *et al.* (2007) have fabricated epoxy/MWCNT nanocomposites using an ultra-sonication and cast moulding method. The tensile strength improved with the increase of MWCNT addition. In addition, the fracture strain was also distinctly enhanced, implying that MWCNT loading not only elevated the tensile strength of the epoxy matrix, but also increased the fracture toughness.

Gong *et al.*(2000) have investigated the effect of a non-ionic surfactant on the thermo-mechanical properties of epoxy/CNT composites. With the surfactant (C12EO8) as the processing aid, the addition of only 1 wt. % CNTs in the composite increases the glass transition temperature (T<sub>g</sub>). Miyagawa and Drzal (2004) have reported on the thermo-physical properties and impact strength of diglycidyl ether of bisphenol F epoxy nanocomposites reinforced with fluorinated Single Wall Carbon Nanotubes (FSWCNTs). The T<sub>g</sub> decreased approximately 30°C with the addition of 0.2 wt. % FSWCNTs. Kim and Park (2010) have studied the effect of ammonized MWCNTs (NH-MWCNTs) on the mechanical interfacial properties of epoxy nanocomposites. The mechanical interfacial properties of the nanocomposites were remarkably improved with increase of the NH-MWCNT content. Similar results were observed by Jung *et al.* (2010) for amine epoxy adducts/thin MWCNT composite particles. Lee *et al.*(2009) have investigated the surface treatment effect of reinforcement filler on the dynamic mechanical properties of epoxy/MWCNT composites. The storage modulus of the epoxy/MWCNT composite was enhanced about 1.27 times through oxy fluorination of MWCNTs at 25<sup>0</sup>C. As per the best knowledge of authors, earlier researchers have studied the effect of other organic solvents on MWCNTs. However, the effect of alcohol treated MWCNT’s on the characteristics of composite are limited. In the present work an effort is made to study the effect of alcohol treated and un-treated MWCNT on the tensile properties of epoxy composites are investigated and results were comparedfor optimization.

## 2. Materials and methods

### 2.1 Materials

The present investigation has been carried out with MWCNT loaded in epoxy resin (LAPOX L-12) under room temperature with a curing hardener (K-6). All these polymer products were supplied by Atul India Pvt. Limited, Polymer Division, Gujarat, India. Senthil Saravanan *et.al.* (2010) have proposed a simplified arc discharge method for synthesis of MWCNTs. MWCNT used inthis work was research grade supplied by Sigma Aldrich, USA with a purity of 95%. The properties of Epoxy and MWCNT are tabulated in Table (1) and (2).

**Table 1: Physical Appearance and Properties of Epoxy**

<b>Lapox L12</b>	<b>Unit</b>	<b>Limiting Value</b>
Appearance	-	Clear yellowish Viscous liquid
Viscosity at 25 °C	cPs	7000 to 15000
Gel time at 160 °C	Sec.	60 to 120(Resin Mix.)
Epoxy content	Eq/Kg	5.0 to 5.6
Epoxy Elevating Temp.(P.E.T)	°C	185 to 210

**Table 2: Physical and Mechanical properties of MWCNT**

<b>Specifications</b>	<b>Dimensions</b>
Diameter	10–30 (nm)
Length	1–2 (mm)
Purity	0.95 (%)
Surface area	350 (m <sup>2</sup> /g)
Bulk density	0.05–0.17 (g/cm <sup>3</sup> )
Density	1.8 (g/cm <sup>3</sup> )
Tensile strength	3500 (N/mm <sup>2</sup> )
Length of fiber	5 (mm)
Fiber thickness	0.3(mm)

**2.2 Preparation of epoxy/MWCNT composites**

Nano-composites were developed by mixing 0.25%, 0.5% and 0.75wt% of MWCNT. Study has been made to find the effect of treated and un-treated ethanol on MWCNT. Henceforth, in the following section Type-I is used for un-treated ethanol of MWCNT and Type-II is used for with alcoholic treatment of MWCNT. The detailed procedure of the preparation of Type-I and Type-II composites are as follows:

**Type-I**

1. According to the dimension of mould the volume of the mould has been calculated, which is equal to the volume of composite ( $v_c$ )
2. Use theoretical equation  $V_m + V_f = 1$ , then obtain  $V_m$ , where  $V_m$  = volume fraction of matrix and  $V_f$  = volume fraction of fiber/filler, which is in our case =0%, 0.25%, 0.50% and 0.75 wt%. We have,  $V_m = \frac{V_m}{v_c}$ ; Obtain,  $v_m$  which is volume of matrix and get required mass of the matrix.
3. Calculated amount of Epoxy is heated to a temperature of 60°C, such that semisolid form of epoxy is converted into the liquid form, at the same time put magnetic bid into liquid epoxy and stir it for 5 to 10 minutes until all bubbles present in epoxy will disappear.
4. After reaching the temperature of Epoxy to 60°C, mix the required quantity of MWCNT and stir it using magnetic stirring thoroughly for five minutes; Keep the beaker into ultra sound sonication bath for 30 minutes to ensure homogeneity.
5. Add the hardener (10% of  $v_m$ )to mixer of Epoxy/MWCNT, and stir the mixture for three minutes and pour into the mould. Keep the mould at controlled temperature for about 24 hours.
6. Composites are manufactured using hand layup method of moulding. Specimens are machined as per ASTM D638 Standard dimensions using constant speed electric cutter.

The detailed calculations involved in the preparation of the samples are shown in Table. 3. The sample preparation procedure along with the equipment is shown in Fig.1. The size of the mould,  $V_c = 170 \times 180 \times 4 = 122,400 \text{ mm}^3$ .

**Table. 3** Calculated values of different Weight of MWCNT

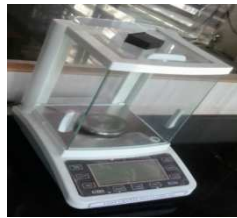
Weight Percentages of MWCNT	$V_f$	$V_m$	$V_c$	Weight of Epoxy	Weight of MWCNT
Plane Epoxy	0	1	$1.224 \times 10^{-5} \text{ m}^3$	145 gm	0
0.25% MWCNT	0.25%	99.75%	$1.224 \times 10^{-5} \text{ m}^3$	145gm	0.3625 gm
0.5% MWCNT	0.50%	99.50%	$1.224 \times 10^{-5} \text{ m}^3$	145gm	0.7250 gm
0.75% MWCNT	0.75%	99.25%	$1.224 \times 10^{-5} \text{ m}^3$	145gm	1.0875 gm



Aluminum foiled mould



Heater used for the Experimentation



Chemical Balance



Ultrasound Sonication Bath



Composite slab

**Fig. 1.** Mould and Equipment used for fabrication of Nano-Composites

**Type-II**

The steps involved in fabrication of Type II specimen are same as Type-I preparation except in-place of plain MWCNT, a 10ml of ethanol is added into weighed MWCNT in glass spatula and subjected to sonication for 20 minutes and heat the sonicated mixture until ethanol is completely evaporated. But care should be taken that temperature should not exceed 75°C. Finally, add alcoholic treated MWCNT into epoxy mixture and further follow the same steps of Type-I.

**2.3 Tensile test**

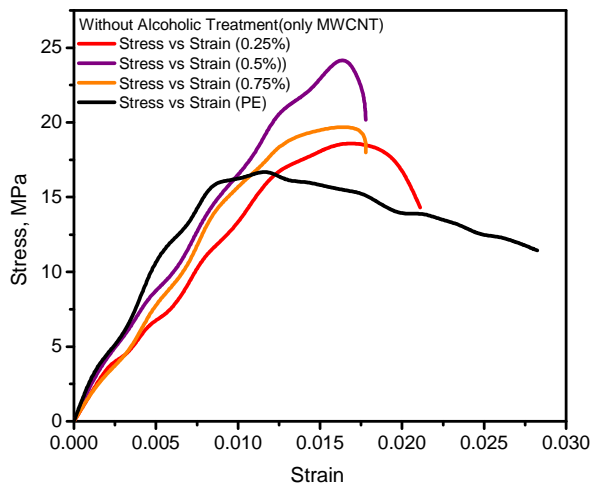
Tensile test is performed on Type-I and Type-II specimens to determine the elastic properties of the composite. The most commonly used specimen geometries are the dog-bone specimen and straight-sided specimen with end tabs. The tension test is performed by taking five samples as per ASTM D 638 with monotonic uniaxial tension at a strain rate of 2 mm/min under room temperature. The plot of stress versus strain, the values of yield stress, ultimate stress and percentage elongation were recorded.

**3. Results and Discussions**

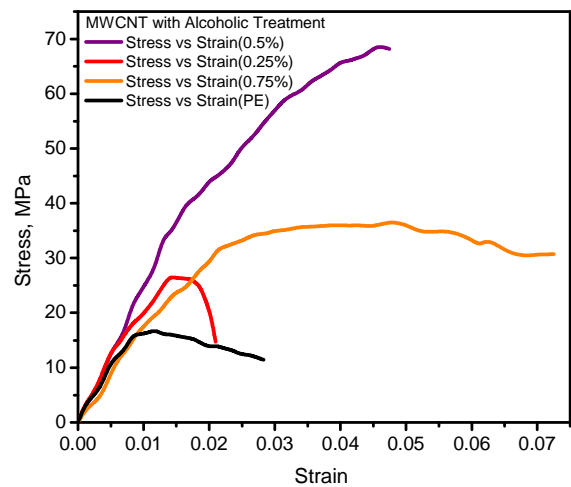
Experiments have been carried out to characterize the candidate for Type-I and Type-II Composite material. The analysis of the results and the influence of alcoholic treatment on the properties of MWCNT epoxy composite are summarized under the following Section.

**3.1 Tensile behavior**

Tensile test were conducted in accordance with ASTM D 638 for five specimens in each compositions of prepared composite. The dimensions of the test specimens were 165 mm in length, 13 mm in width and 3.5 mm in thickness respectively. A total of 35 specimens were tested at a cross-head speed of 2 mm / min under room temperature. The Fig. 2 and 3 shows stress versus strain plots for Type-I and Type-II oftreated and un-treated MWCNT epoxy composite samples.



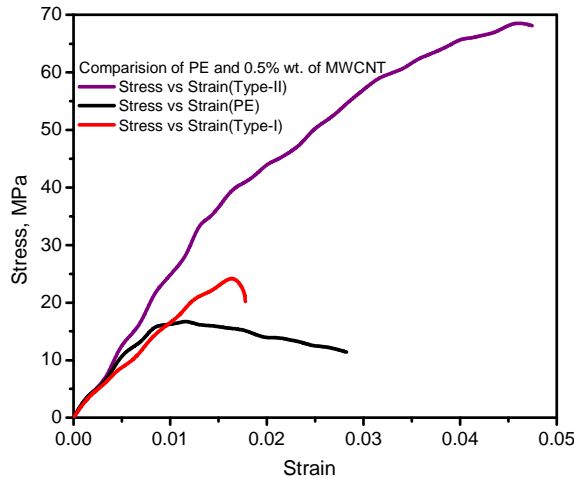
**Fig. 2:**Stress strain behavior of Epoxy/MWCNT without ethanol treatment



**Fig. 3:**Stress strain behavior of Epoxy/MWCNT with Ethanol treatment

Tensile behaviour in terms of stress versus strain for ethanol treated and un-treated MWCNT with varying weight percent are shown in Fig. (2) and (3). At low value of stress the elongation is high in Plane Epoxy(PE) samples shown in Fig.2 as compared to 0.25%,0.5% and 0.75wt % un treated MWCNT epoxy composites (Type-I). There will be similar value of Young’s modulus with higher value of stress in case of 0.5wt% and 0.75wt % loaded MWCNT un-treated epoxy composite samples has been observed. This behaviour indicates the samples loaded with MWCNT withstand higher loads as compared to plane epoxy composite samples. Among type-I, the specimens loaded with 0.5wt % MWCNT gives better tensile strength and stiffness.The low stress with low elongation has been observed in Fig.3 for plane epoxy and 0.25wt% loaded with treated MWCNT composite samples.The samples loaded with 0.5wt% treated MWCNT have higher value of tensile strength and stiffness as compared to 0.75wt% treated MWCNT composite samples has been observed but these strength and stiffness enhancement still higher than the plane epoxy and 0.25wt% loaded with treated MWCNT composites. In type II specimens also the tensile strength and stiffness has been observed better in case of 0.5wt% of MWCNT.

Since better results have been observed for the addition of 0.5wt %MWCNT in epoxy, hence comparison has been made to understand this enhancement with plane epoxy and ethanol treated and un-treated composites samples are shown in Fig 4. It has been evidenced that there will be increase in the value of yield strength by 65% for un-treated ethanol epoxy composite samples. The reason behind this increase in the value of yield strength has been explained in below paragraph. The Young’s modulus, Yield strength, Ultimate strength and percentage elongation for without ethanol treated MWCNT for various composition specimens tested are tabulated in Table 4.



**Fig. 4:** Stress strain behavior of Epoxy 0.5% wt MWCNT for Type-I and Type-II along with Plane Epoxy

**Table 4:** Elastic properties of specimens without ethanol treated MWCNT

Composition	Young's Modulus (MPa)	Yield Strength (MPa)	%Elongation
Pure Epoxy	1892	16.30	15.00
Epoxy/0.25% MWCNT	1300	15.87	18.98
Epoxy/0.50% MWCNT	1597	22.54	13.55
Epoxy/0.75% MWCNT	1574	15.75	07.89

The Young's Modulus, Yield strength, Ultimate strength and % Elongation for without ethanol treated MWCNT for various compositions based on mean values of specimens tested were tabulated in Table 5.

**Table 5:** Elastic properties of specimens with ethanol treated MWCNT

Composition	Young's Modulus (MPa)	Yield Strength (MPa)	Elongation (%)
Pure Epoxy	1892	16.30	15.00
Epoxy/0.25% MWCNT	1872	26.60	07.69
Epoxy/0.50% MWCNT	1941	58.67	07.89
Epoxy/0.75% MWCNT	1433	36.00	07.69

The probable reason may be due to change in the morphology and microstructure of multi-walled carbon nano-tubes (MWCNTs) when treated with ethanol. According to Guojun Yuet.al 2006, the etching by OH radicals and deposition of C radicals on the carbon nano-tubes were considered to be responsible for the modification of the MWCNT structures and the formation of new carbon nanostructures. After ethanol treatment the nano-tube surface become rough and a large number of nano-lumps are formed on the surface. The SEM images of MWCNTs, before treatment and after treatment were shown in the work of Guojun Yuet.al 2006. Three chemical equations were proposed to demonstrate the decomposition of ethanol and etching reaction of MWCNTs by OH radicals, which are in agreement with the discussion in Maruyama et al. (2002).





The CO gas can further react with OH radicals to produce CO<sub>2</sub> gas ( Zen *et al.*, 1999; Brennkmeijer *et al.*, 1999)



This etching of ethanol may be going to enhance the cross linking reaction of Epoxy and Hardener, hence the homogeneity of MWCNT dispersion is increasing which is going to enhance the tensile property of Epoxy/MWCNT composite.

#### 4. Conclusions

Adding Carbon Nano materials in polymer composites has attracted attention and interest from both academics and industry. This is due to the reason that addition of Nano materials into composites does offer higher stiffness, higher strength, excellent chemical resistance etc. over conventional polymer composites. In this study the Nano composites samples were successfully processed and developed using hand layup method of manufacturing. Samples loaded with MWCNT withstand higher loads as compared to plane epoxy composite samples. The samples loaded with 0.5wt% treated MWCNT have higher value of tensile strength and stiffness as compared to 0.25%wt and 0.75wt% treated MWCNT composite samples. Yield strength and Young's modulus were increased by 17.7% to 65% for 0.5wt% treated MWCNT compared to untreated composite samples. Since most of the Nano composites materials can find their use in aerospace, surgical and automotive engineering. Due to the high diversity, properties, and advantages of Nano particles in polymer composite-based applications have been envisioned to be practical application in near future. These Nano materials in composites coupled with affordable cost will soon be seen in the global market.

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