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# Synthesis and Characterization of Multi-walled Carbon Nanotubes from Pine Oil and their Impact on Carbon Fiber-Reinforced Epoxy Hybrid Nanocomposite

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## ABSTRACT

This work is aimed at the synthesis and characterization of MWNT from the used natural precursor of pine oil and catalytic supported materials by the Spray Pyrolysis method. This study includes the impact of MWNT on carbon fiber-reinforced epoxy hybrid nanocomposite. MWNT were prepared over Fe, Co & Mo as catalytic support on silica with pine oil at three various temperatures. Characterization studies such as SEM, HR-TEM and RAMAN were taken for prepared MWNT using pine oil at three different temperatures 550 °C, 650 °C and 750 °C. The study has clearly shown that MWNT has good morphology and well-graphitization at 650 °C, with better yield. The mechanical properties such as tensile strength and modulus, flexural strength and modulus of MWNT-filled and unfilled carbon fiber reinforced epoxy hybrid nanocomposites were also investigated. Thermal properties were studied by using Thermogravimetric Analysis (TGA) for various wt. % of MWNT. Water absorption and chemical resistance tests were conducted for MWNT composite material to know the capability of resistance in water absorption and chemicals. The findings of this study encourage the use of MWNT and its composite materials in several areas with higher efficiency.

**Keywords:** Multi-walled Carbon Nanotube; MWNTs/Carbon composite material; Pine oil.

## 1. INTRODUCTION

The newly-discovered Carbon nanotubes (CNTs) are one of the most important components of nanotechnology. The CNTs are highly graphitic in structure with the orientation of the basal carbon planes parallel to the tube axis, whereas CNFs are the structures with the other orientations of the graphitic lamella that will leave a smaller or no central channel (Vander Wal *et al.* 2001). CNTs are prepared by three common methods, *viz.* Arc discharge, Laser ablation and Chemical vapor deposition (CVD). Kroto *et al.* (1985) made an important contribution to carbon nanotube research by discovering a wide family of all carbon compounds known as fullerenes. Iijima *et al.* (1991) discovered the carbon nanotube (CNT) while searching for novel carbon structures; CNTs are formed on graphite cathode surfaces during the electric-arc discharge process, which is frequently used to produce fullerene powder. Filamentous carbons without or with an insignificant central channel are denoted as 'CNF's, regardless of their graphitic structure reported by several authors (Pérez-Cabero *et al.* 2004; Pan *et al.* 2004).

Recently carbon nanotube and graphene have been used as effective electrodes in supercapacitors due to their specific surface area excellent electrical and mechanical properties (Chen *et al.* 2013). Thermal expansion of Carbon nanotubes is beneficial for carbon-carbon composites. Interesting to note that in multi-walled carbon nanotubes, only the outer shell participates in electrical conduction (Frank *et al.* 1998) and electrons can move between adjacent shells only by tunneling. Difficulty occurs to prove the covalent attachment of molecular species to fully $sp^2$-bonded carbon atoms on the nanotube sidewalls. Therefore, nanotubes can be considered as usually chemically inert (Lordi *et al.* 2000; Thillaikkarasi *et al.* 2020). It is expected that low-defect CNTs will have very low coefficients of thermal expansion (Pop *et al.* 2006). Compared with other properties such as mechanical, electrical and electrochemical properties of the carbon nanotubes are have several practical uses and are well established.

The present analysis reveals the synthesis of one-dimensional carbon nanomaterials from pine oil fractions. This is followed by multi-walled filled carbon fiber reinforced epoxy hybrid nanocomposites are prepared by hand laying process on the laboratory scale. The mechanical properties in terms of tensile strength and tensile modulus, flexural strength and flexural modulus, thermal characteristic studies (using TGA), as well as water absorption behavior and chemical resistance properties, were investigated and reported as per American Society for Testing Materials (ASTM) standards. Morphological structure of as-grown Multi-walled carbon nanotubes (MWNTs) were characterized by SEM, HR-TEM and RAMAN.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of MWNTs

The Fe-Co-Mo catalysts (0.5 g) were put in the quartz boat and inserted into the middle of a quartz tube, placed in the electrical heating furnace. To remove air and produce a nitrogen environment, the reaction furnace was run through with the carrier gas nitrogen (200 mL min-1). The temperature was increased from room temperature to 550 °C – 750 °C, the ideal temperature for MWNT growth. The carbon precursor pine oil was then sprayed into the quartz tube at a rate of 20 mL per hour using a spray nozzle. The deposition took 45 minutes at the chosen temperature. The nitrogen flow was maintained until the furnace achieved a normal operating temperature. Then the product was weighed and kept in an airtight container for analysis purposes.

### 2.2 Preparation of MWNT-filled Carbon Fiber-Reinforced Epoxy Hybrid Nanocomposite

Hybrid nanocomposite materials were prepared by mechanical stirring and ultra-sonication process by maintaining a constant time. In order to understand the effect of MWNT addition under the constant dispersion processing time (Mechanical stirring for 45 minutes and Ultra-sonication for 45 minutes) is followed. Pre-calculated amounts of MWNT and epoxy Diglycidal ether of bisphenol-A (DGEBA) resin were mixed together. Priorly, the epoxy resin was pre-heated to lower the viscosity and to facilitate better wetting of the particles. As-grown MWNT mixture and resin matrix were mixed using a mechanical stirrer for 45 minutes for initial mixing and under a high-intensity ultra-sonicator for 45 minutes. To reduce the chances of voids, the MWNT-dispersed resin is kept under vacuum for 60 minutes. Once bubbles were trapped, the required amount of Triethylenetetramine (TETA) hardener was added and manually mixed for 10 minutes.

### 2.3 Preparation of Composite Laminates

Composite laminates were prepared by Hand layup technique. The stacking procedure consists of placing a resin system (epoxy + hardener + MWNT) impregnated fabrics one above the other by hand layup process (8 plies). To ensure the uniform thickness of the sample, a spacer of size 3 mm was used. Along with the release agent, the mold plates were sprayed. The whole assembly was reserved in a hydraulic press and a temperature of 100 $^{o}$C was applied for 2 hours and the whole setup was cooled gradually to room temperature and permitted to cure for a day in order to diminish the residual thermal strains. The MWNT contents were varied from 0.0 % to 0.4 wt. % based on the weight of the matrix and the influence of MWNT weight fraction on act of composite was estimated.

### 2.4 Characterization

The morphological structure of as-grown Multi-walled carbon nanotube was characterized by SEM, HR-TEM and RAMAN analyses. Thermal properties of MWNT unfilled and MWNT-filled carbon fiber-reinforced epoxy hybrid nanocomposites were ascertained by using Thermogravimetric Analysis (TGA). Water absorption and Chemical resistance tests were conducted using ASTM D570 and ASTM 543-95 standards, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1 Optimization of Temperature for Maximum Yield of MWNTs and its Characterization

The effect of temperature on the yield of MWNTs from natural precursor of Pine oil at a feed rate of 20 mL per hour over Fe-Co-Mo catalysts supported on Silica is studied. In this present study, the low yield of carbon deposit was produced at 550 °C. Noticeably high yield of carbon deposit was observed for the reaction temperature at 650 °C and a further increase in temperature to 750 °C resulted in a decrease in the yield. The well-grown MWNTs with diameter in the range of 20-40 nm was reported using SEM (Fig. 1). Fig. 2 shows the well-crystalline graphitic layers of MWNTs grown at 650 °C and were reported using HR-TEM. The inner and outer diameters of MWNTs synthesized were in the range of 10-12 nm and 16-22 nm, respectively.

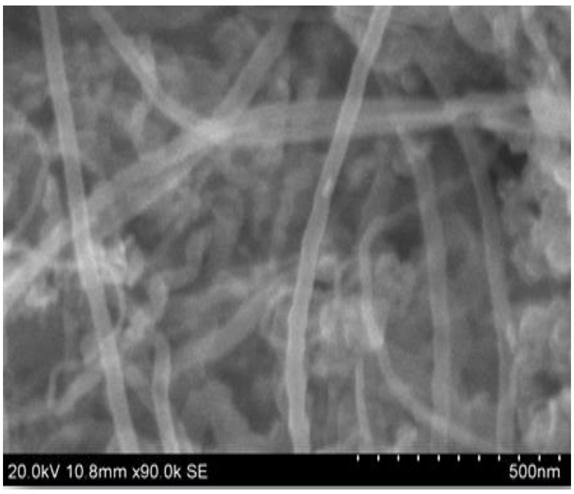


**Fig. 1: SEM image of MWNTs grown at 650°C**

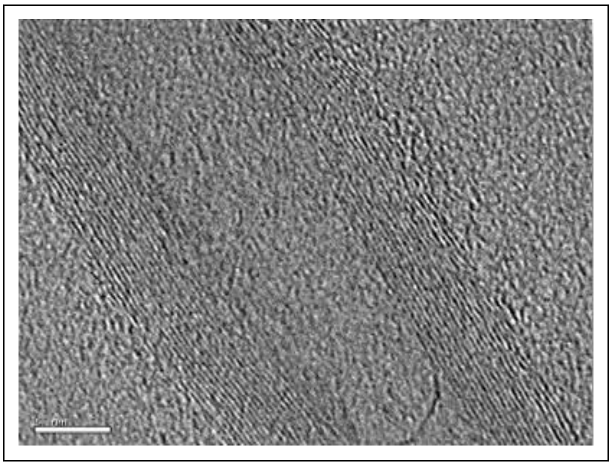

**Fig. 2: HR-TEM image of MWNTs grown at 650°C**

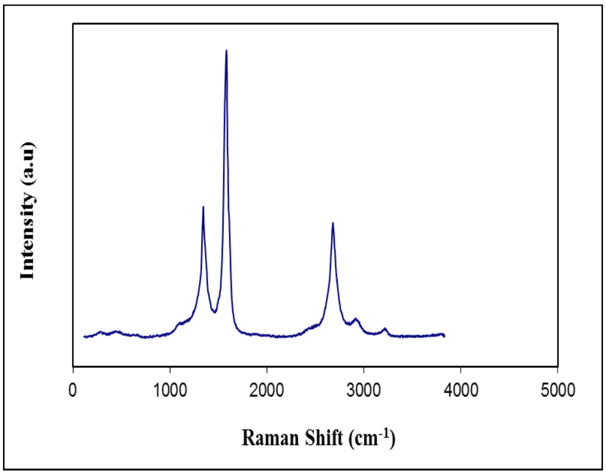


**Fig. 3: Raman Spectra of MWNTs grown at 650 °C**

Fig. 3 shown the Raman spectrum of as-grown MWNTs synthesized using pine oil at 650 °C. The D and G peaks were observed at 1346 $cm^{-1}$ and 1592 $cm^{-1}$, respectively, for the CNTs prepared at 650 °C. The $I_G/I_D$ ratio calculated from the peak area is 1.9; the high value indicating the well-graphitization of the MWNT synthesized. Among the chosen experimental temperatures, the highest $I_G/I_D$ ratio was observed for 650 °C, indicating the formation of highest quality CNTs at 650 °C.

## 3.2 Mechanical Properties of MWNT-filled Carbon Fiber-Reinforced Epoxy Hybrid Nanocomposite

The effects of MWNT loading on mechanical characteristics such as tensile strength, tensile modulus, flexural strength and flexural modulus of unfilled and MWNT-filled carbon fiber-reinforced epoxy hybrid nanocomposites were studied in this section of the research.

## 3.3 Effect of MWNT Loading on Tensile Properties

Unfilled carbon fiber-reinforced composite tensile strength & modulus values were 153.8 MPa and 5.82 GPa, respectively, as shown in Fig. 4 and 5. It is proved that the properties are increasing up to 0.2 wt. % of MWNT prepared from pine oil and reached the highest values of 346 MPa and 9.5 GPa, respectively; then the tensile properties decrease for further increase in MWNTs up to 0.4 wt. %.

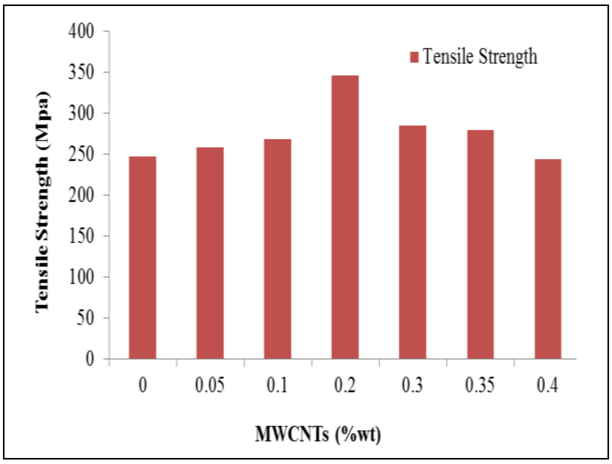


**Fig. 4: Tensile strengths for different wt. % of MWNT derived from pine oil for MWNTs nanocomposites**

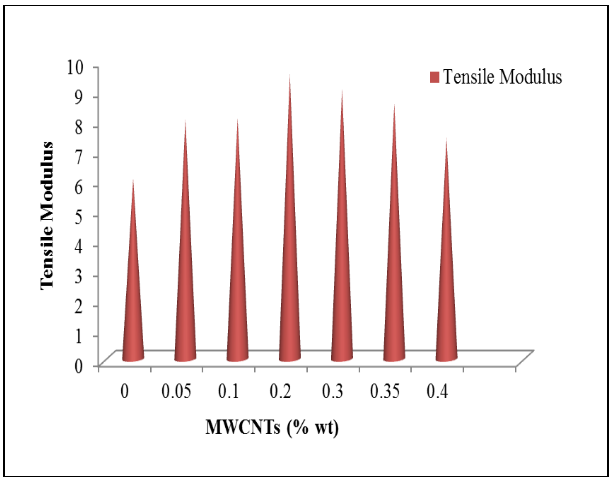


**Fig. 5: Tensile modulus for different wt. % of MWNTs derived from pine oil for MWNTs nanocomposites**

## 3.4 Effect of MWNTs Loading on Flexural Properties

For unfilled and filled carbon-reinforced epoxy composite, flexural strength and modulus values were observed as 340.5 MPa and 25.74 GPa, as evident from Fig. 6 & 7.

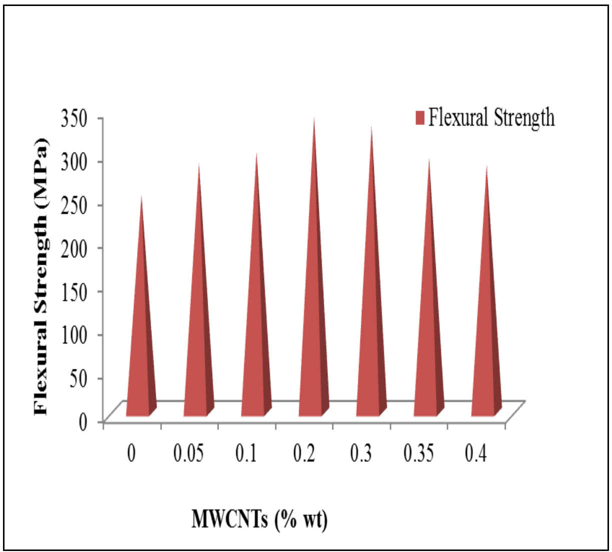


**Fig. 6: Flexural strengths for different wt. % of MWNTs derived from pine oil for MWNTs nanocomposite**

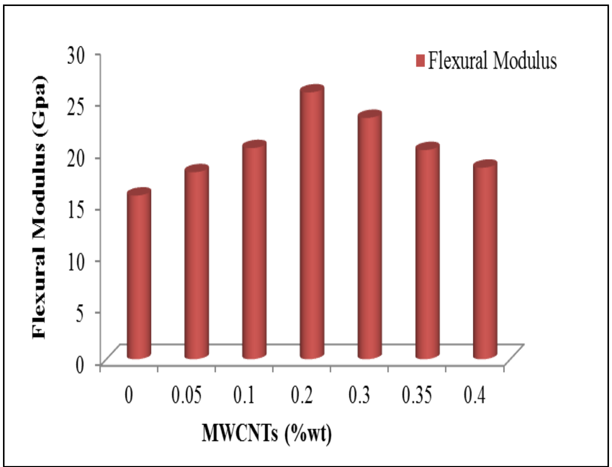


**Fig. 7: Flexural modulus for different wt. % of MWNTs derived from pine oil for MWNTs nanocomposites**

It can be seen that the flexural strength and flexural modulus of MWNT-filled carbon fiber-reinforced epoxy hybrid nanocomposites were higher than that of unfilled EP/CF composites irrespective of the weight fractions of MWNTs. Flexural modulus increased up to 0.2 wt. % MWNTs; then it gradually dropped as MWNTs increased further to 0.4 wt. %. Optimal values were obtained at 0.2 wt. % of MWNTs. It was concluded that the enhancement in the flexural properties might be due to the improved interfacial properties responsible for the transfer of stresses and elastic deformation in the presence of nanofiller.

## 3.5 Thermal Properties of Unfilled and MWNT-filled Carbon Fiber-reinforced Hybrid Nanocomposite

This investigative method utilizes a sensitive balance to determine the weight loss of a sample through a range of temperatures. During the TGA analysis, time was short and the sample weight required was small. The sample weight loss was measured as a utility of temperature during the investigation.

Weight loss details of nanocomposites at 400 °C, 600 °C and 750 °C were mentioned in Table 1. It clearly reveals that the weight loss at each temperature significantly lowers with an increase in weight % of MWNTs content in the hybrid nanocomposite. This again demonstrated that the relative thermal stability of the blends depends on the weight % of MWNTs. This reveals that the char residue of unfilled and MWNT-filled carbon fiber-reinforced epoxy hybrid nanocomposites significantly increased in comparison to the unfilled carbon fiber-reinforced epoxy hybrid nanocomposites. Increasing the char residue enhances the thermal stability, as the formation of char hinders the diffusions of the low volatile decomposition products.

**Table 1. Weight Losses of MWNT-filled Carbon Fiber Reinforced Epoxy Hybrid Nanocomposites at various Temperatures**

| Name of the Sample | Loss of Weight (%) | | | Residue Weight % |
|---|---|---|---|---|
| | 400°C | 600°C | 750°C | |
| A | 61.35 | 85.37 | 93.94 | 7 |
| B | 60.05 | 84.80 | 92.12 | 6.3 |
| C | 56.46 | 77.60 | 85.45 | 15.30 |
| D | 52.00 | 70.20 | 78.18 | 20.82 |
| E | 41.78 | 51.80 | 64.22 | 38.00 |
| F | 36.78 | 49.80 | 54.10 | 42.90 |
| G | 26.22 | 35.30 | 43.17 | 56.10 |

The results have shown that 0.4 wt. % of MWNT-filled carbon fiber reinforced epoxy hybrid nanocomposites (Sample G) have given the lowest weight loss (i.e., highest char) at all the specified temperatures indicating better resistance towards thermal aging.

**Table 2. Chemical resistance properties of unfilled and MWNT-filled carbon fiber-reinforced epoxy hybrid nanocomposites with different weight proportions of MWNTs**

| Chemicals Name | EP/CF/MWNTs nanocomposites as a function of MWNTs | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 wt. % | 1 wt. % | 2 wt. % | 4 wt. % | 6 wt. % | 8 wt. % | 10 wt.% |
| 1N HCl | +1.46 | +0.61 | +0.55 | +0.52 | +0.68 | +0.45 | +0.71 |
| 10N $CH_3COOH$ | +2.21 | +1.10 | +2.72 | +1.18 | +2.07 | +2.45 | +2.62 |
| 1N $HNO_3$ | +1.52 | +0.96 | +0.98 | +0.84 | +2.10 | +2.58 | +3.05 |
| NaOH g/L | +0.85 | +1.17 | +0.89 | +0.26 | +0.75 | +0.91 | +0.43 |
| $Na_2CO_3$ g/L | +0.18 | -0.61 | -0.58 | +0.27 | +0.48 | +0.63 | +0.75 |

### 3.6 Chemical Resistance Behavior of Unfilled and MWNT-filled Carbon Fiber-Reinforced Epoxy Hybrid Nanocomposites

Table 2 demonstrates the weight gain (+) and weight loss (-) of experimental results of the unfilled carbon fiber reinforced epoxy nanocomposites and MWNT-filled carbon fiber reinforced epoxy hybrid nanocomposites as functions of MWNTs' weight fraction when the samples were immersed in acids, alkalis and solvents. The results clearly reveal that the weight expansion was observed for all the chemical reagents used. This change in weight indicates that the nanocomposites are swollen by the chemical reagents rather than getting dissolved. This chemical resistance behavior study clearly demonstrated that nanocomposites could be used for handling chemicals in various engineering fields.

## 4. CONCLUSION

The utilization of the Fe, Co and Mo as catalytic supports on Silica for the synthesis of well-graphitized multi-walled carbon nanotubes with high yield at low-temperature conditions using the spray pyrolysis method is reported successfully. The influence of reaction temperature on the yield and morphological studies of MWNTs synthesized from chosen precursors have revealed that 650 °C was the most favorable temperature for the formation of well-graphitized MWNTs with better yield.

The addition of multi-walled CNTs derived from pine oil epoxy carbon fiber-composite laminates enhanced all the mechanical properties when compared with unfilled laminates. The thermal characteristics of unfilled and MWNT-filled carbon fiber-reinforced epoxy hybrid nanocomposite were studied using TGA and found that the addition of MWNT remarkably increased the thermal stability.

The chemical resistance study clearly indicates that nanocomposites can be applied for handling chemicals in several engineering fields.

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## CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.



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