

## Synthesis and Characterization of Conducting Polymers Multiwalled Carbon Nanotube -Chitosan Composites Coupled with Poly (Ortho-Aminophenol)

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**Abstract:** In this research work, acid functionalized multiwalled carbon nanotubes (MWCNT) were covalently grafted to chitosan by first reacting the oxidized carbon nanotubes with thionyl chloride to form acyl-chlorinated carbon nanotubes which are subsequently dispersed in chitosan and covalently grafted to form composite material, MWCNT–chitosan which was washed several times to remove unreacted materials. Poly (o-amino phenol) is attached with MWCNT which increases electrochemical properties of nanocomposites. This composite has been characterized by FTIR, TGA, SEM and TEM and has been shown to exhibit enhanced thermal stability. XRD spectra showed that the crystalline nature of composite was not affected much by the addition of c-MWCNTs. Fourier transmission infrared spectroscopy (FTIR) analysis provided an evidence for the formation of nanocomposites. The thermal stability of nanocomposites was improved by addition of c-MWCNTs as confirmed by thermo gravimetric analysis (TGA).

**Key words:** Poly (ortho-aminophenol) • Multi-walled carbon nanotube (MWCNT) • Nanocomposites • Oxidative polymerization • Chitosan • SEM • TEM • XRD • TGA • FTIR

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### INTRODUCTION

The discovery of carbon nanotubes has led to huge breakthroughs in the biomedical field. Their chemical and structural properties allow them to be used for a variety of scientific practices on a molecular level. These carbon nanotubes allow research to be conducted on a nanoscale. Researchers are currently conducting studies where they use carbon nanotubes (CNTs) as sensors that can locate harmful toxins that damage DNA, as a drug delivery system and as a tool to destroy cancerous. Carbon nanotubes are one of the most studied nanomaterials in the last fifteen years. Due to their extraordinary physical and chemical properties that this carbon allotrope possesses has emerged as novel nanometric material, promising in most areas of science and engineering. These materials have their own features and properties related to structural arrangement and therefore the carbon nanometric materials find new specific research fields that are raised constantly.

Nowadays, the carbon nanotubes research has been focused on diverse fields, inasmuch as no previous material has displayed the combination of outstanding mechanical, thermal and electronic properties [1].

**Structure of Carbon nanotube:** Carbon nanotubes are allotropes of carbon with cylindrical structure. These are useful for nanotechnology, electronics, optics and other fields of material science and technology. These are members of Fullerene Family. Nanotubes are two types such as single walled carbon nanotube and multiwalled carbon nanotube. Individual nanotubes naturally align themselves into ropes held together by Vander Waals forces. The chemical bonding of nanotubes is composed of sp<sup>2</sup> bonds, similar to Graphite. Because of the promising physical, thermal, mechanical and electric properties, 1,2 carbon nanotubes (CNTs) have attracted extensively scientific interest 3,4 recently [2]. Moreover, applications of multiwalled carbon nanotubes (MWCNTs) in structural materials such as polymer composites are more feasible

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with their mass production, which leads to price reduction. 5,6 Specifically, use of CNTs in polymer/carbon nanotube composites has attracted wide attention. 7,8 In this sense, it has been reported that the matrix properties can be effectively enhanced via the addition of CNTs in different polymer matrices. 9,10 nevertheless, using CNTs as filler in polymer matrix, disadvantageous effects were observed due to aggregation and nonuniform dispersion of CNTs in common solvents. Therefore, two primary conditions are required for application of CNT nanocomposites: the homogeneous dispersion of CNTs in the host matrix and the interfacial interaction [2].

## MATERIALS AND METHODS

**Materials:** Ortho-aminophenol was purchased from Aldrich. Multi-walled CNT (90% purification) used in this study was purchased from Cheap Tubes (USA, 10–20 nm diameter). Other reagents like ammonium persulfate (APS) hydrochloric, sulfuric and nitric acid (Sigma Chemicals) were of analytical grade. The solvents were purified using vacuum rotary evaporator under reduced pressure and their boiling point was checked for their purity. Low molecular weight chitosan, potassium persulfate, 85% lactic acid solution, sulfuric acid, nitric acid and thionylchloride were obtained from Sigma Aldrich. The solvents were purified using vacuum rotary evaporator under reduced pressure and their boiling point was checked for their purity [3].

**Oxidation of MWCNTs:** Typically, MWCNTs were reacted with Nitric Acid and distilled water (3:1) was refluxed for 24 hours at 70°C. After cooling to room temperature they were vacuum filtered through 0.2µm Millipore polycarbonate membrane. Then washed with deionized water until a natural pH of the filtrate was reached.

Then MWCNT-COOH was formed and it was treated with thionyl chloride (-SOCl<sub>2</sub>) for 24h at 60-75°C. This results corroborated the successful carboxylation of MWCNTs. Subsequently, upon reacting with thionyl chloride (-SOCl<sub>2</sub>), the -COOH was transformed into acyl chloride functional groups and the distinctive stretching vibration of -COCl should have been observed [4].

**Synthesis of MWCNT-Chitosan Derivative:** The MWCNT-COCl (400 mg) was reacted with chitosan (2 g) in 100 ml 2% acetic acid at 75°C for 24 hours while stirring. After the reaction was stopped, the product was washed three times with 2% acetic acid to remove unreacted chitosan [5].

## MECHANISM

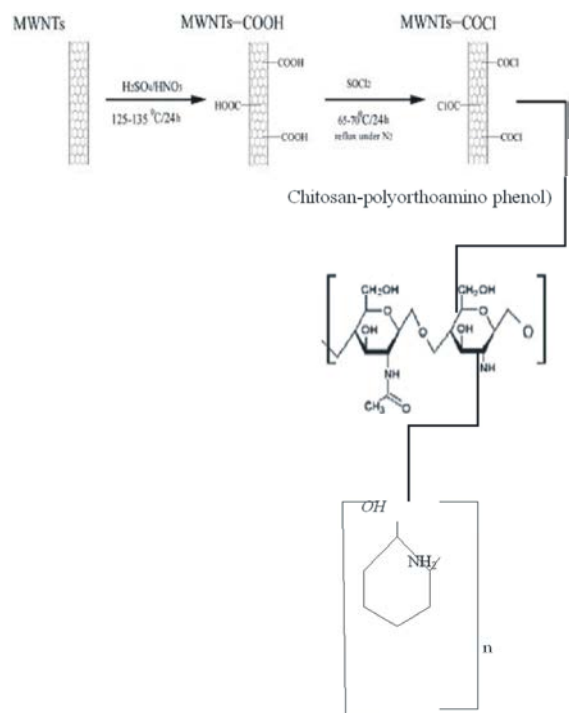


Fig. 1: Structure of Functionalization of Ortho- Amino Phenol/C-MWCNT

**Preparation of Orthoamino Phenol/C-MWCNTs Nanocomposites:** 5 wt% c-MWCNTs (based on the weight of Ortho aminophenol) was dispersed in the solution of 0.015 mol ortho- aminophenol in 100 ml of 0.1 M HCl by ultra sonication for 10–15 min. Then, the solution of 0.015 mol APS in 50 ml of 0.1 M HCl was added drop by drop into the previous solution which was stirred constantly in an ice bath in a period of 30 min to initiate the polymerization. The reaction was kept for 24 h. Acetone was then poured into the reaction mixture to stop polymerization and to precipitate the Ortho aminophenol /c- MWCNTs nanocomposite. The purification and drying procedures were the same as those for the synthesis of the bare polymer [6].

## RESULTS AND DISCUSSION

### Characterization

**FTIR Analysis:** Figure 2 shows the FTIR spectra of MWNTs and MWNTs-COOH. All the peaks, characteristic of MWNTs, at 1600–1450 cm<sup>-1</sup> (aromatic ring), 1352 cm<sup>-1</sup> (-C-O), 3393 cm<sup>-1</sup> (-OH) and 1642 cm<sup>-1</sup> (-C=C-), appear in both spectra. Closer inspection revealed two unique peaks in the spectrum of MWNTs-COOH, one appearing around 1721 cm<sup>-1</sup>,

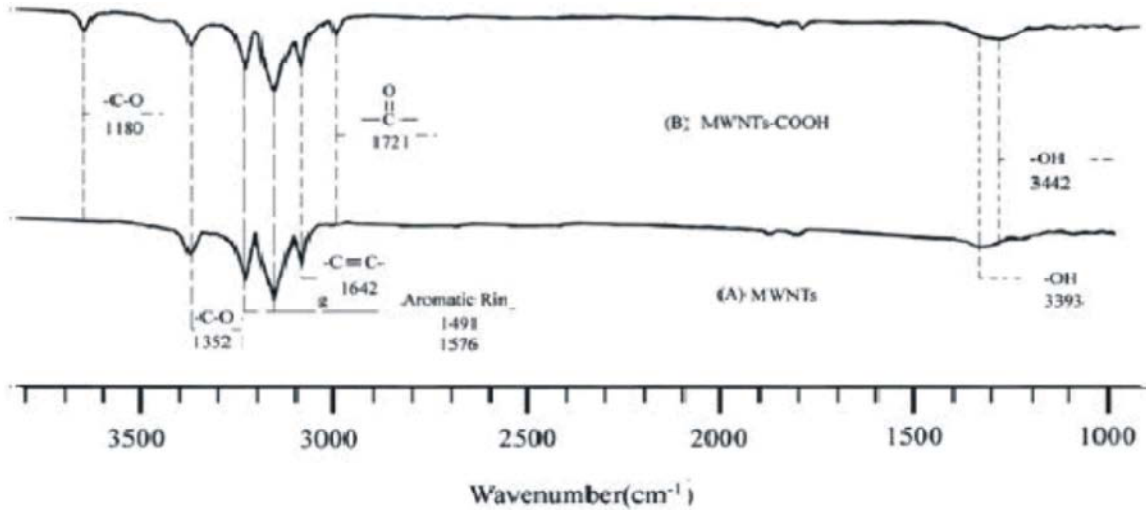


Fig. 2: FTIR spectrum of (A) MWCNT & (B) MWCNT-COOH

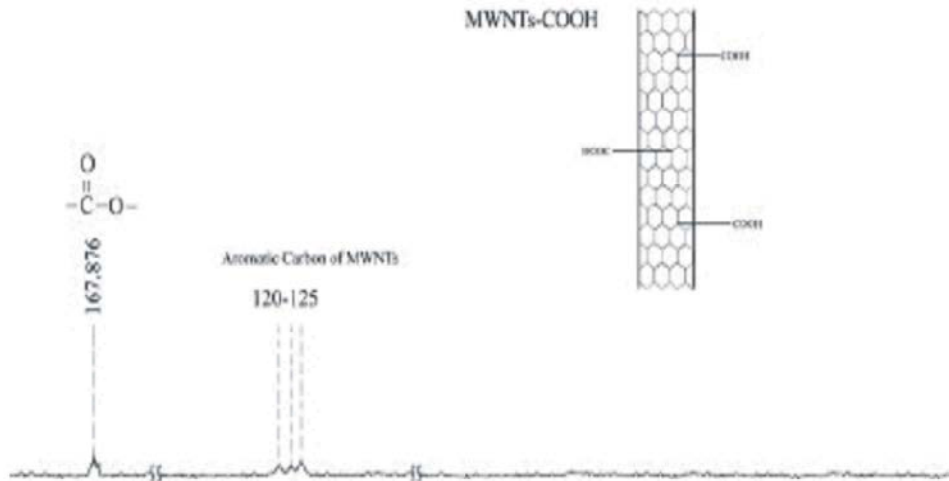


Fig. 3: NMR of MWCNT-COOH

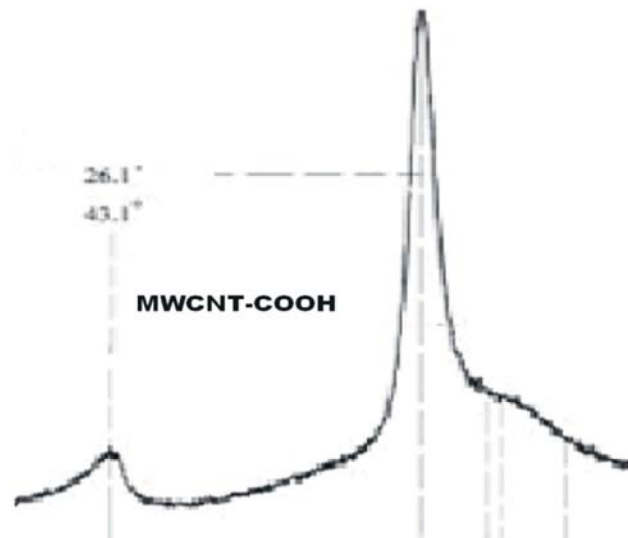


Fig. 4: X-RAY Diffraction of MWCNT -COOH

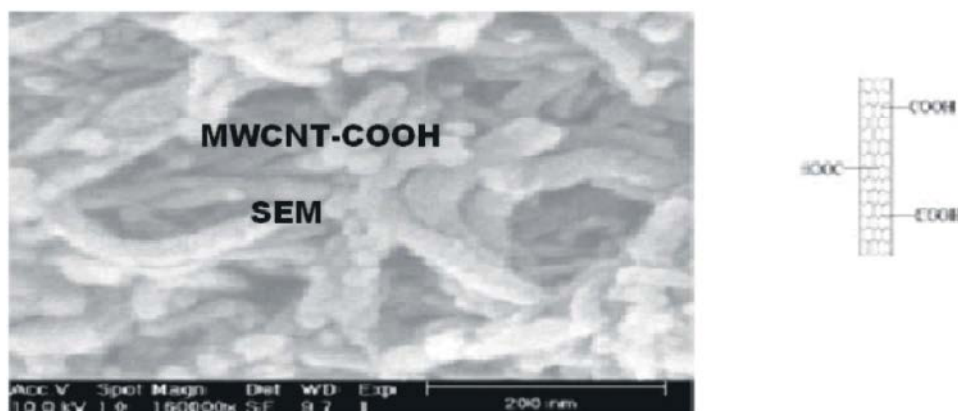


Fig. 5: Sem Micrograph of MWCNT-COOH

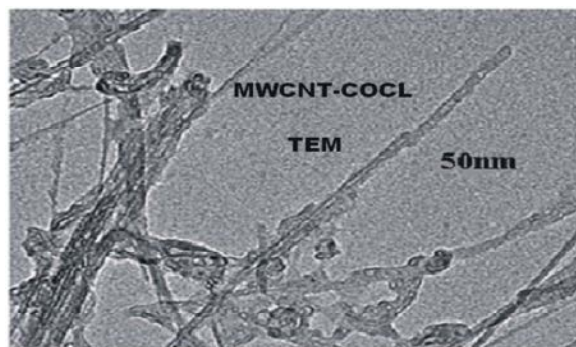


Fig. 6: Tem of MWCNT-COCL

arising from the stretching vibration of the  $C=O$  group, 12,33 and one at  $1180\text{ cm}^{-1}$ , arising from the stretching vibration of the  $C=O$  group, both therefore due to the existence of  $-COOH$  caused by chemical oxidation when treated with acid. To better understand the carboxylic acid-functionalized MWNTs, the expanded FTIR spectra between  $3300$  and  $3500\text{ cm}^{-1}$  was inspected [7].

In Figure 3 MWCNTs-COOH, this peak is seen shifted to  $167.876\text{ ppm}$  because of the removal of Ni and, measured at the same signal-to-noise ratio, is also more intense. The increased intensity thus confirmed the additional carboxylation of MWCNTs via chemical served as direct evidence for the functionalization of MWCNT [8].

In this Fig 4 shows X-ray diffraction was used to examine the crystalline structures of pure MWCNT-COOH, because there is a peak at about at  $2\theta = 26.18$  and  $43.18$  in the spectrum of MWCNTs-COOH was observed [9].

The entangled clusters seen in the SEM photo of MWCNTs-COOH are the result of insufficient dispersion and poor interfacial adhesion between filler and matrix [10].

In this Figure shows that TEM indicated that the coatings were clearly visible on the surface of MWCNT-COOH and that the functionalized MWCNTs had attached to the  $-COCL$  group(MWCNT-COCL). Energy Dispersive Spectroscopy (EDS) scans showed the presence of atoms present in each sample and indicated the presence of impurities [11].

It is necessary to study the morphology of the MWCNTs and polymer blends, since the mechanical properties depend on it. In general, good dispersion of MWCNTs in the matrix and strong interfacial adhesion between the two phases are required to obtain a composite material with satisfactory mechanical properties. Scanning electron microscopy was used to study the tensile fracture surfaces of composite samples of MWCNT-COOH (5 wt %) blends, in which the major component forms the matrix and the minor component (MWCNTs) the dispersed phase [12].

This Fig. 7 shows that TEM was used to give an indication of the attachment of chitosan and eventually chitosan to the functionalized MWCNT. TEM indicated that coatings were clearly visible on the surface of CNTs and that the functionalized MWCNTs had attached to the chitosan surface [13].

SEM was performed to assess the morphology of the MWCNTs and chitosan derivatives. While the SEM for chitosan resembles previous results, it also indicated the attachment of chitosan to the functionalized MWCNT as indicated by the thin strings in scans [14].

In this figure FTIR peaks for pure show the broad peaks at  $3450\text{ cm}^{-1}$  due to the stretching vibration  $-OH$  superimposed on  $-NH$  stretching band and broaden due to inter hydrogen bonds of polysaccharides. The  $1656\text{ cm}^{-1}$  attributed to the presence of acetyl unit with  $-CO$  stretching;  $1579\text{ cm}^{-1}$  attributed to  $N-H$  bending, the  $1376\text{ cm}^{-1}$  attributed to  $-CH_3$  symmetrical



Fig. 7: Sem of MWCNT-COCL

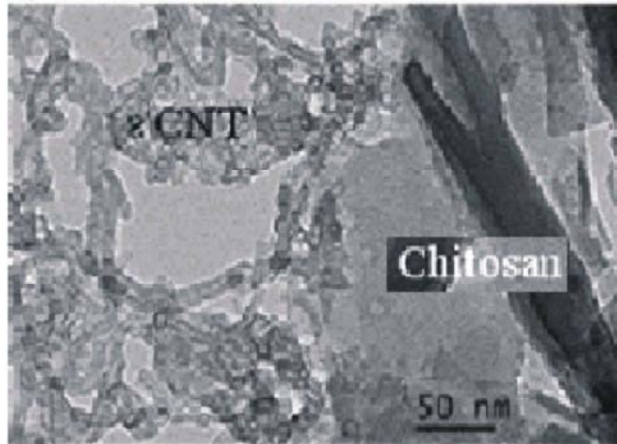


Fig. 8: Tem of MWCNT-CHITOSAN

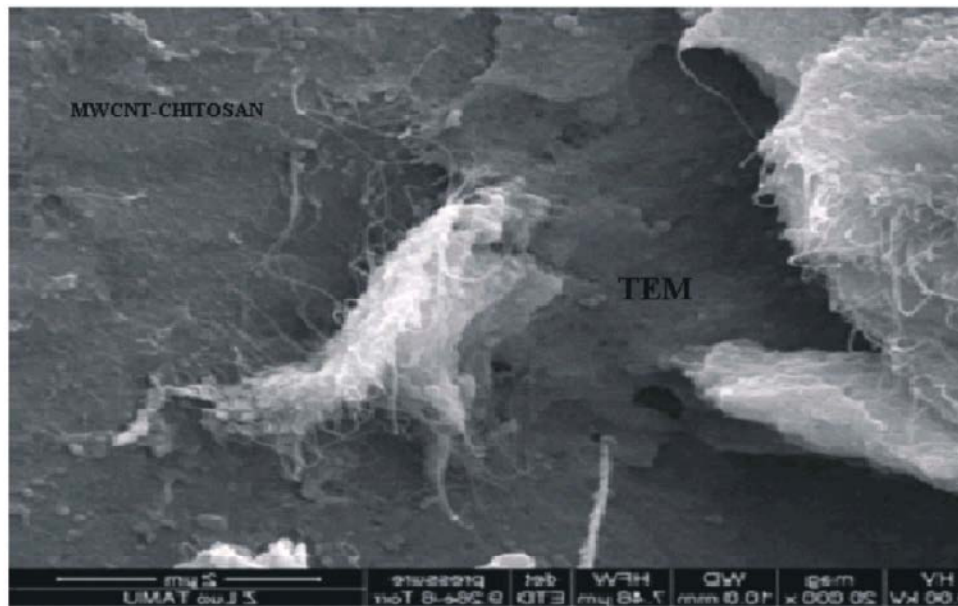


Fig. 9: Sem of MWCNT-CHITOSAN

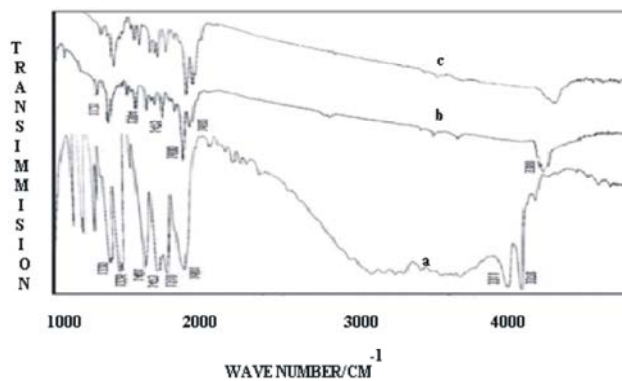


Fig. 11: Ftir Spectrum of Ortho-Aminophenol\C-MWCNT

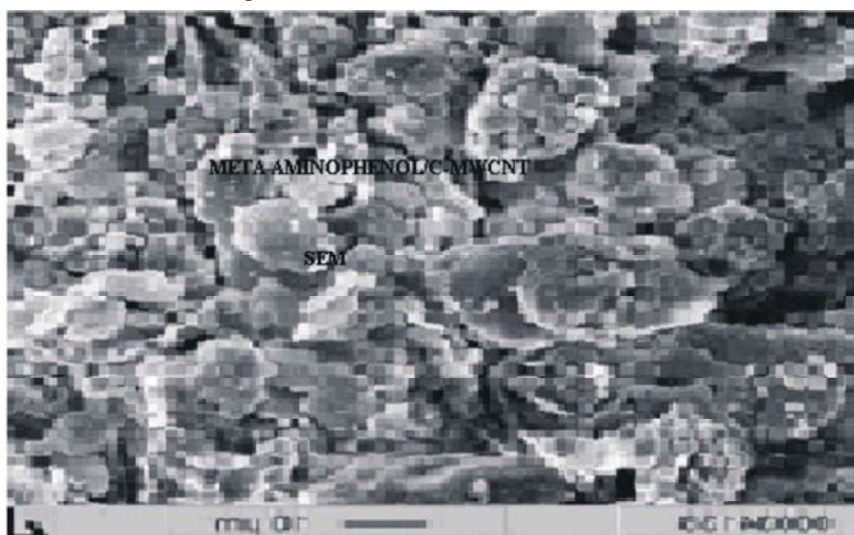


Fig. 12: Sem of Ortho Aminophenol\C-MWCNT

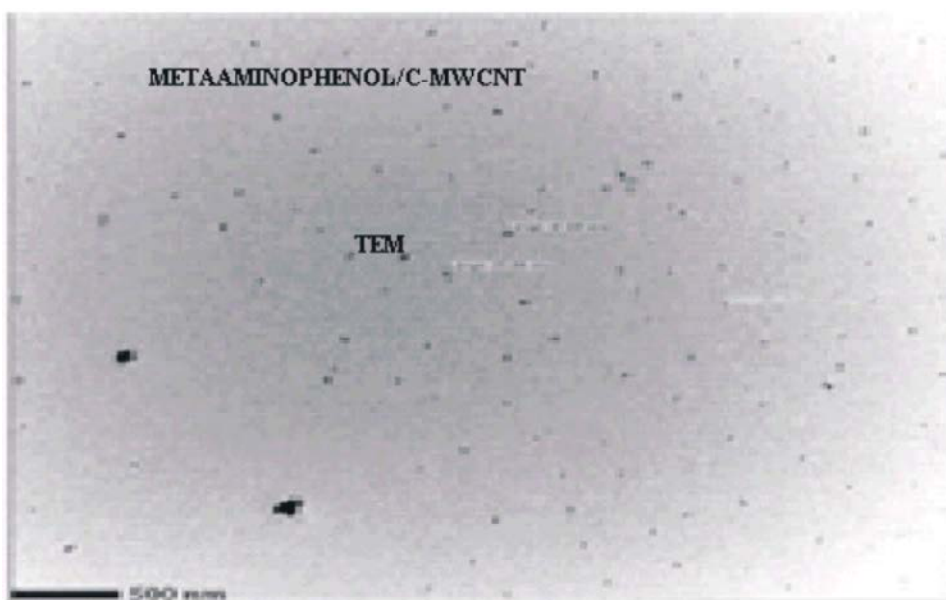


Fig. 13: TEM Image of orthoaminophenol/ C-MWCNTs

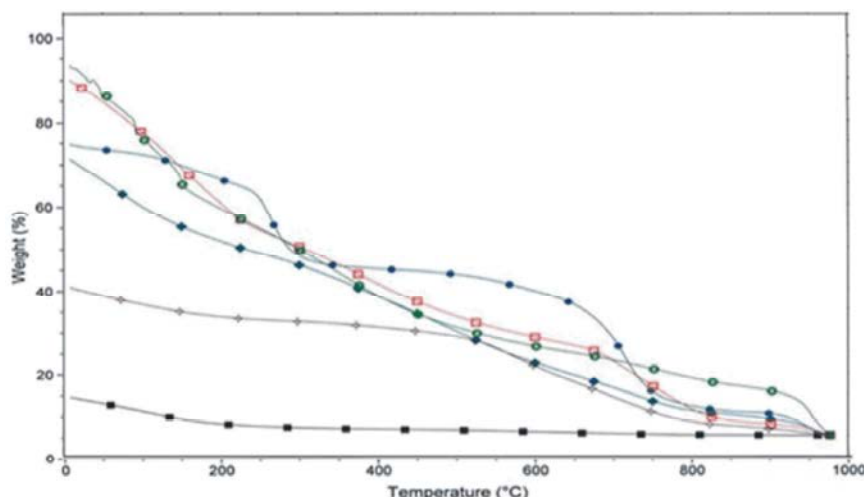


Fig. 14: TGA Analysis of MWCNT, MWCNT-COOH, MWCNT-COCL, MWCNT-CHITOSAN, ORTHO AMINOPHENOL/C-MWCNT

angular deformation;  $1153\text{ cm}^{-1}$  attributed to  $\beta$  (1,4) glycosidic bonds; and  $1091\text{ cm}^{-1}$  attributed to C–O–C stretching vibration [16].

**SEM Analysis:** The morphology of the synthesized poly (ortho-aminophenol) nano compound was measured by SEM and is shown in Fig. 12. From the figure it was evident that the morphology of the resultant nano compound is flakes in shape. This confirms that the synthesized meta amino phenol/ MWCNTs falls under the category of nano compound [17].

In this Figure 13 the TEM image of orthoaminophenol/ c-MWCNTs shows that the size of the synthesized metaaminophenol nano compound measured by

Transmission electron microscopy is given in Fig. 13. The result clearly indicates that the size of the nano compound is found to be 25-42nm at 12K with the magnification of 20,000x. This confirms that the synthesized ortho-aminophenol/MWCNTs falls under the category of nano compound [18].

In this Figure 14 Thermogravimetric analysis showed a total weight loss of about 50% at 800°C. It is most likely that acid oxidation using concentrated HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixtures also led to cutting of carbon nanotubes and creation of more defect sites, it is therefore not too surprising that the total weight loss of 50% at 800°C is observed [19]. The thermal analysis of pure chitosan shows two distinct weight losses, below 450°C, a 20% weight loss observed can be attributed to amine side or N-acetyl side groups' presence in chitosan. This degradation appears to be delayed in MWCNT–COOH

and MWCNT-CHITOSAN in An indication that the presence of carbon nanotubes in the chitosan enhanced the thermal stability in chitosan. The second weight loss occurred between 600 and 800°C and may be attributed to oxidative removal of the glycosidic linkage [20].

## CONCLUSION

Carbon nanotubes (CNTs) have been analyzed and chemically modified aiming to diversify their properties and be incorporated into an engineering polymer matrix successfully. The oxidation approaches in these materials have been an important technique to attach or link diverse chemical moieties. FTIR, SEM, TEM, X-ray diffraction and TGA analysis confirm the bonding of the carbon nanotubes and the chitosan. Future work will focus on the bioactivity studies both in simulated body fluid to establish apatite forming ability especially if envision for application in bone tissue engineering.

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