

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

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**Abstract:** The carbon nanotube is currently the focus of intense research. This system also provides us with an opportunity to apply to many of the techniques of band structure calculation. The current interest in carbon nanotubes is a direct consequence of the synthesis of buckminsterfullerene, C<sub>60</sub>, in 1985 and its derivatives thereafter. The discovery that carbon could form stable, ordered structures other than graphite and diamond stimulated many researchers in the world to search for other allotropes of carbon. This further led to another key finding in 1990 that C<sub>60</sub> could be produced in a simple arc-evaporation apparatus readily available in most laboratories. Functionalization or modification of cnts has become a major activity Within the interdisciplinary fields of nanoscience, nanotechnology, bioengineering and bionanotechnology, As it promises to be the best approach for improving the solubility and compatibility of cnts. functionalization of mwcnts can be achieved by many functional groups followed by acid treatment. In the present research program 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 were subsequently dispersed in chitosan and covalently grafted to form composite material, MWCNT-chitosan which was washed several times to remove un-reacted materials. Poly para toluidine attached to chitosan attached MWCNT which increases electrochemical and other properties of nanocomposites. The FTIR SEM, TEM and XRD methods were adopted to characterize these composites.

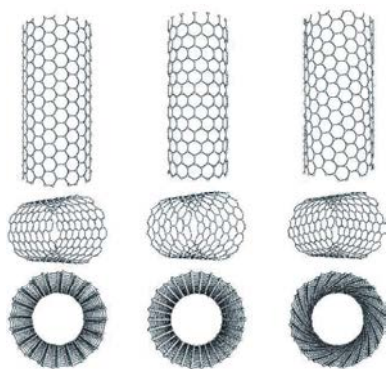
**Key words:** Poly (paratoludene) • Multi-walled carbon nanotube (MWCNT) • Nanocomposites • Oxidative polymerization • Chitosan • SEM • TEM • XRD • TGA • FTIR

### INTRODUCTION

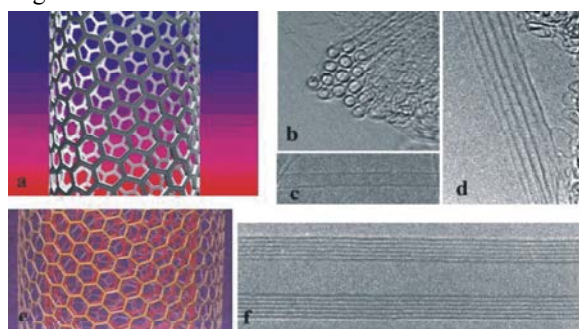
Multiwalled carbon nanotubes (MWCNTs) consist of two or more concentric layers of carbon nanotubes with a hollow core typically 2-30 nm in diameter. For example, double-walled carbon nanotubes have two concentric layers. MWCNTs may be stiffer than SWCNTs and may potentially be of greater health and safety risk due to the possibility of piercing the body's pleural tissue. Multi walled carbon nanotubes (MWCNTs) consist of two or more concentric layers of carbon nanotubes with a hollow core typically 2-30 nm in diameter. For example, double-walled carbon nanotubes have two concentric layers. MWCNTs may be stiffer than SWCNTs and may potentially be of greater health and

safety risk due to the possibility of piercing the body's pleural tissue. Carbon nanotubes (CNTs) are cylindrical carbon molecules with novel properties outstanding mechanical, electrical, thermal and chemical properties: 100 times stronger than steel, best field emission emitters, can maintain current density of more than  $10^{-9}$  A/cm<sup>2</sup>, thermal conductivity comparable to that of diamond) which make them potentially useful in a wide variety of applications (e.g. optics, an electronics, composite materials, conductive polymers, sensors, etc.). CNTs are of two types, namely, single-walled carbon nanotubes (SWCNTs) and multiwalled nanotubes (MWCNTs) nanotechnologies. [qc. ca/projets/nanotubes](http://www.qc.ca/projets/nanotubes)). SWCNT were discovered in 1993 and most of these have a diameter close to 1 nm, with a tube length that may be

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Single walled carbonnanotube Discovered in 1993!



Application of Carbon Nanotubes

Fig. 1: Figure (a-f) shows single wall edcarbonn anotube (SWCNT) and figure (e-f) shows multi wall edcarbon nanotubes (MWCNT).

manythousands of times larger and up to orders of centimeters by Weisman and Subramoney in this issue.) by Jaldappagari Seetharamappa, Shiva raj Yellappa and Francis D'Souza The structure of a SWCNT can be conceptualized by wrapping a one-atom-thick layer of graphite (or graphene) into a seamless cylinder. The way the graphene sheet wraps can be represented by a pair of indices  $(n, m)$  called the chiral vector [1].

## MATERIALS AND METHODS

**Experimental Details:** Paratoludene 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 [2].

## Mechanism

**Oxidation of Mwcnts:** Typically, MWCNTs were reacted with  $\text{H}_2\text{SO}_4:\text{HNO}_3$  (3:1), then tip sonicated for 30 minutes using an ultrasonic processor with amplitude at 30% and 7s pulse to yield carboxylic acid functionalized MWCNTs (MWCNT-COOH) [3].

**Synthesis of MWCNT-COCl:** The MWCNT was treated with thionyl chloride ( $-\text{SOCl}_2$ ) for 24h at 60-75°C. This results corroborated the successful carboxylation of MWCNTs. Subsequently, upon reacting with thionylchloride ( $-\text{SOCl}_2$ ), the  $-\text{COOH}$  was transformed into acylchloride functional groups and the distinctive stretching vibration of  $-\text{COCl}$  should have been observed.

**Synthesis of CNT-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 [4].

**Preparation of Paratoludene/C-mwcnts Nanocomposites:** 5 wt% *c*-MWCNTs (based on the weight of paratoludene) was dispersed in the solution of 0.015 mol paratoludene in 100 ml of 0.1 M HCl by ultrasonication 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 paratoludene/*c*-MWCNTs nanocomposite. The purification and drying procedures were the same as those for the synthesis of the bare polymer [5].

## Characterization

**FTIR Analysis:** Figure 3 shows the FTIR spectra of MWNTs and MWNTs-COOH. All the peaks, characteristic of MWNTs, at 1600-1450  $\text{cm}^{-1}$  (aromatic ring), 1352  $\text{cm}^{-1}$  ( $-\text{C}-\text{O}$ ), 3393  $\text{cm}^{-1}$  ( $-\text{OH}$ ) and 1642  $\text{cm}^{-1}$  ( $-\text{C}=\text{C}-$ ), appear in both spectra. Closer inspection revealed two unique peaks in the spectrum of MWNTs-COOH, one appearing around 1721  $\text{cm}^{-1}$ , arising from the stretching vibration of the  $\text{C}=\text{O}$  group, 1233 and one at

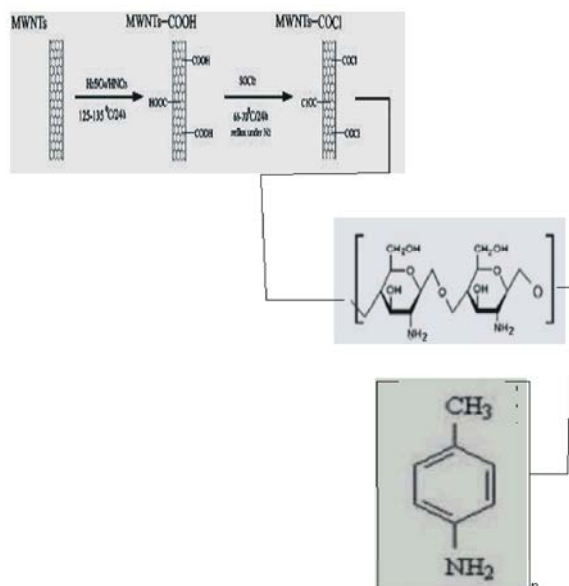


Fig. 2: Structure of functionalization of poly (paratoludene)-c-mwcnt

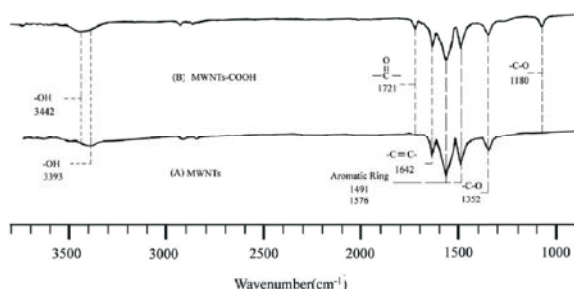


Fig. 3: FTIR spectrum of (A) MWCNT & (B) MWCNT-COOH

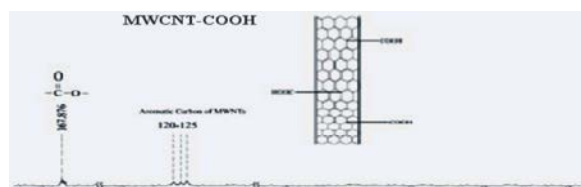


Fig. 4: Nmr of Mwcnt-cooh Fig-5-x-ray Diffraction of MWCNT -COOH

1180  $\text{cm}^{-1}$ , arising from the stretching vibration of the  $\text{C}/\text{O}$  group, both therefore due to the existence of  $\text{--COOH}$  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 [6].

In Figure 4 shows that (MWCNTs-COOH), this peak is seen shifted to 167.876 ppm because of the removal of Ni and, measured at the same signal-to-noise ratio, is also

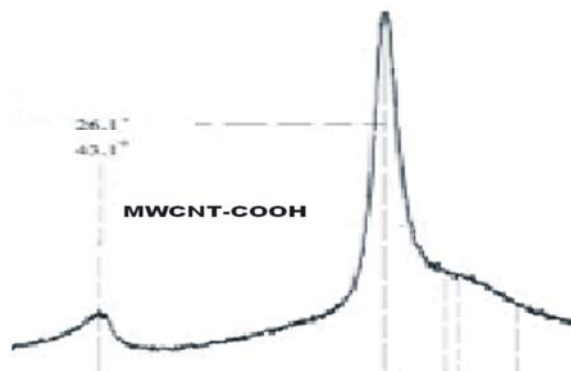


Fig. 5: X-Ray Diffraction of Mwcnt -CooH



Fig. 6: Sem Micrograph of Mwcnt-cooh

more intense. The increased intensity thus confirmed the additional carboxylation of MWCNTs via chemical served as direct evidence for the functionalization of MWCNT [7].

**X-Ray Diffraction:** Fig 5 shows X-ray diffraction was used to examine the crystalline structures of pure MWCNT-COOH, because there is a peak at about at  $2\theta \approx 26.18$  and  $43.18$  in the spectrum of MWCNTs-COOH was observed [8].

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 [11].

**Transmission Electron Microscope (Tem) Studies of MWCNT-COCL:** In this Figure 7 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  $\text{--COCL}$  group (MWCNT-COCL). Energy Dispersive Spectroscopy (EDS) scans showed the presence of atoms present in each sample and indicated the presence of impurities [9].

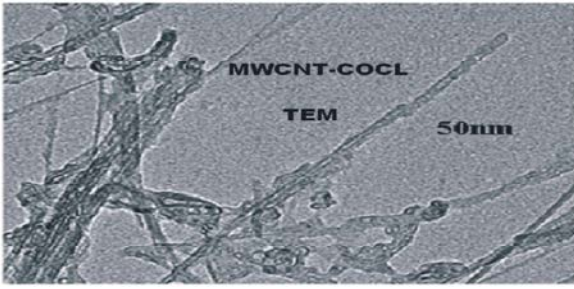


Fig. 7: TEM of MWCNT-COCL

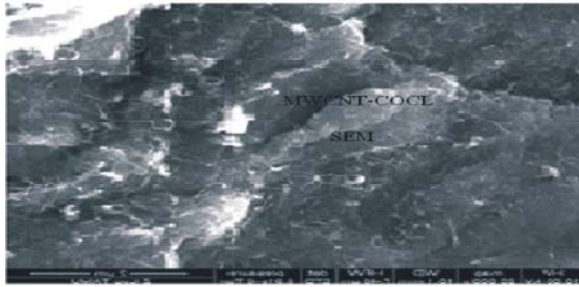


Fig. 8: SEM of mwcnt-cocl

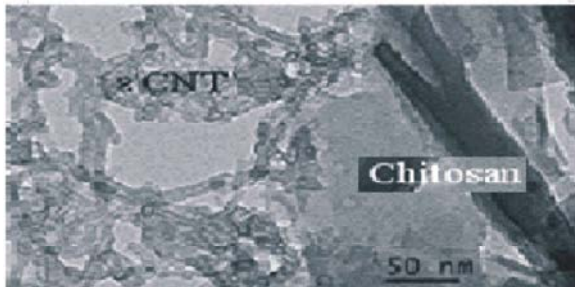


Fig 9: Tem of Mwcnt-chitosan

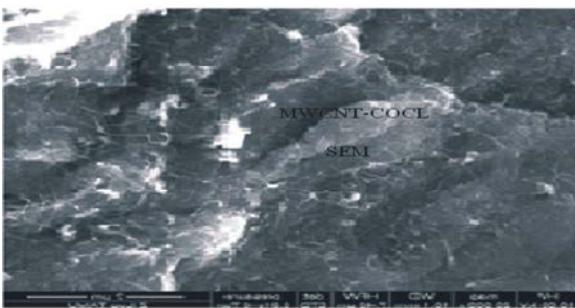


Fig. 10: SEM of mwcnt-chitosan

**SEM Studies of MWCNT-COCL:** It is necessary to study the morphology of the MWNTs and polymer blends, since the mechanical properties depend on it. In general, good dispersion of MWNTs 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

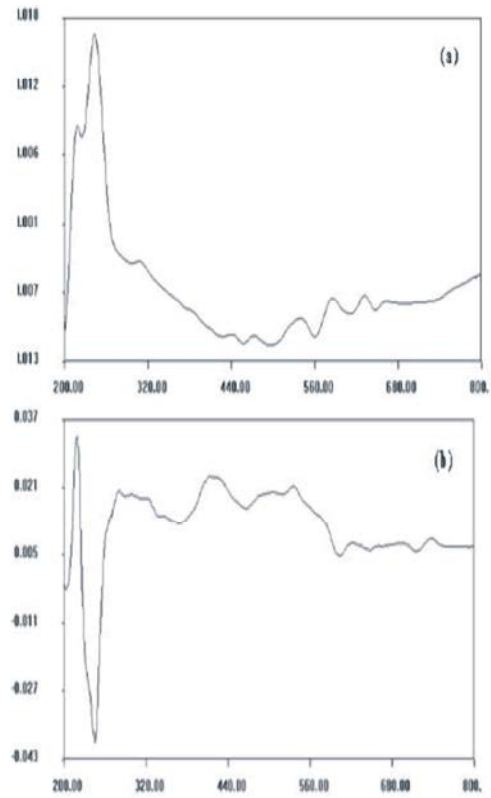


Fig. 11: UV-Vis absorption spectrum of paratolueneMWCNTs

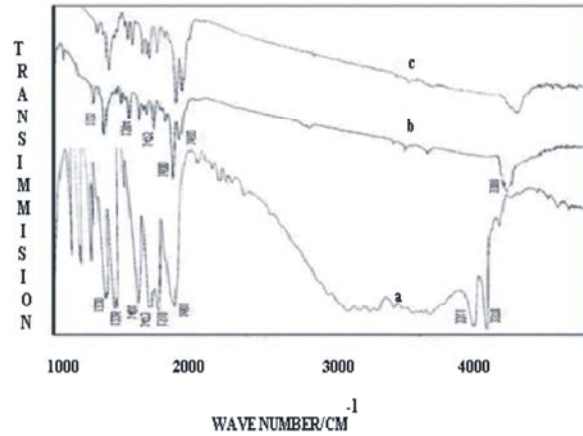


Fig. 12: FTIR Spectra of MWCNT-CH-PT

samples of MWCNT-COOH (5 wt %) blends, in which the major component forms the matrix and the minor component (MWCNTs) the dispersed phase [10].

**Transmission Electron Microscope (Tem) of MWCNT-Chitosan:** TEM was used to give an indication of the attachment of chitosan and eventually chitosan



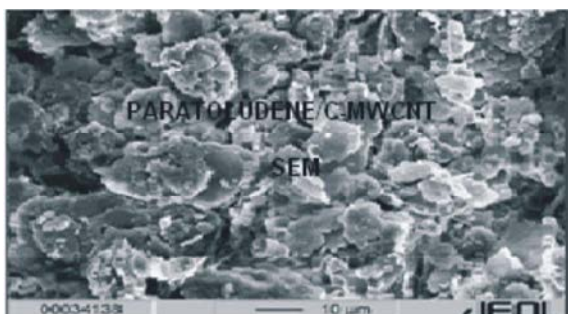


Fig. 13: SEM of Paratoludene\C-mwcnt

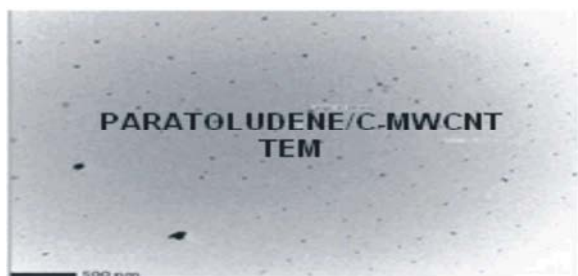


Fig. 14: TEM Image of Paratoludene\C-mwcnts

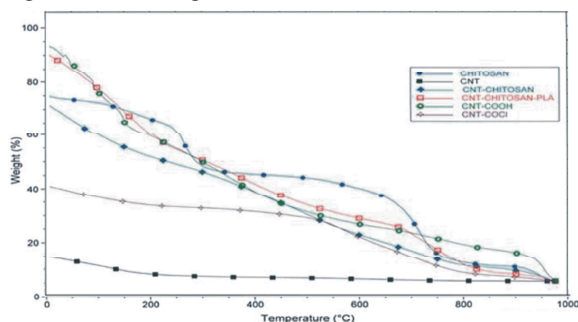


Fig. 16: TGA Analysis If Mwcnt, Mwcnt-cooh, Mwcnt-cocl, Mwcnt-chitosan

to the functionalized CNT. TEM indicated that coatings were clearly visible on the surface of CNTs and that the functionalized MWCNTs had attached to the chitosan surface [11].

**SEM Studies of MWCNT-Chitosan:** 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 [12].

**UV-Visible Spectrophotometer:** The UV-vis spectra of Paratoludene and Paratoludene /MWCNT are shown in Fig 8. The first absorption band appears in the region of 238-389nm is assigned to the  $\pi - \pi^*$  transition of the

benzoid ring. It is related to the extent of conjugation between the phenyl rings along the polymer chain. The absorption band at 589 and 632nm was believed to be  $n - \pi^*$  transition, which correspond to non-bonding lone pair electron transitions of hetero atoms like nitrogen and oxygen respectively. Paratoludene/ MWCNTs additionally has other two peaks around 468 and 740nm are assigned to the polaron transitions. From the UV-vis spectral characterization, it is clear that some polarons are obtained in the  $\pi$  - conjugated backbone of the polymer by the addition of an emulsifier MWCNTs. The observation of polaron bands is consistent with a high degree of doping and good solubility of the polymer nano compound[13].

**FTIR Analysis:** The 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 interhydrogen bonds of polysaccharides. The  $1656 \text{ cm}^{-1}$  attributed to the presence of acetylunit with -CfO stretching;  $1579 \text{ cm}^{-1}$  attributed to N-H bending, the  $1376 \text{ cm}^{-1}$  attributed to -CH<sub>3</sub> symmetrical 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.

**Sem Analysis:** The morphology of the synthesized paratoludene nano compound was measured by SEM and is shown in Fig 6. From the figure it was evident that the morphology of the resultant nano compound is flakes in shape. This confirms that the synthesized paratoludene / MWCNTs falls under the category of nano compound [14].

**TEM:** The size of the synthesized poly(paratoludene) nano compound measured by transition electron microscopy is given in fig 6. 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 paratoludene\MWCNTs falls under the category of nano compound.

**TGA Analysis:** Thermogravimetric analysis showed a total weight loss of about 50% at  $800^\circ\text{C}$ . It is most likely that acid oxidation using concentrated  $\text{HNO}_3/\text{H}_2\text{SO}_4$  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  $800^\circ\text{C}$  is observed [19]. The thermal analysis of pure chitosan shows two distinct weight losses, below  $450^\circ\text{C}$ , 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. 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 [15].

## CONCLUSION

Series of raw MWCNTs and amino-functionalized MWCNT- chitosan-paratuidine composites were prepared. The MWCNTs were dispersed in the matrix using ultrasonication and high-mixing technique. The findings highlighted below may contribute to our understanding of the functionalization mechanisms of amino-functionalized MWCNTs. FTIR, SEM, TEM, X-ray diffraction and TGA analysis confirm the bonding of the carbon nanotubes and the chitosan.

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