

## Synthesis and Characterization of Conducting Polymers Multi Walled Carbon Nanotube (MWCNT)-Chitosan Composites Coupled with Poly (Ortho-Phenyldiamine)

*Anindita Bassat, Rajashree Chahataray and P.L. Nayak*

Sushilavati Government Womens College, Rourkela, Odisha, India

**Abstract:** In this research work, acid functionalized multiwallcarbonnanotubes (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 (orthophenyle diamine) is attached with MWCNT which increases electrochemical properties of nanocomposites. This composite has been characterized by FTIR, UV-visible spectrum, SEM and TEM, EPR 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 (orthophenyldiamine) • Multi-walledcarbonnanotube (MWCNT) • Nanocomposites • Oxidativepolymerization • Chitosan • SEM • TEM • XRD • UV-visible spectrum • EPR • FTIR

### 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 Carbonnanotube:** 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 multiwall carbon nanotube. Individual nanotubes naturally align themselves into ropes held together by Vander Waals forces. The chemical bonding of nanotubes is composed of  $sp^2$  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 multiwall carbon nanotubes (MWNTs) in structural materials such as polymer composites are more feasible 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 no uniform 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 [3].

## MATERIALS AND METHODS

**Materials:** Orthophenyldiamine 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 per sulfate (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 per sulfate, 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].

### Mechanism

**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 P.H. 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].

**Preparation of Anthranilic Acid /C-MWCNTs Nanocomposites:** 5 wt% c-MWCNTs (based on the weight of Orthophenyldiamine) was dispersed in the solution of 0.015 mol Orthophenyldiamine 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 Orthophenyldiamine/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:** Figure-2 shows the FTIR spectra of MWCNTs and MWCNTs-COOH. All the peaks, characteristic of MWCNTs, 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 MWCNTs-COOH, one appearing around 1721 cm<sup>-1</sup>, arising from the stretching vibration of the C=O group, 1233 and one at 1180 cm<sup>-1</sup>, 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 MWCNTs, the expanded FTIR spectra between 3300 and 3500 cm<sup>-1</sup> was inspected. [7].

In Figure -3 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 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 2θ 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].

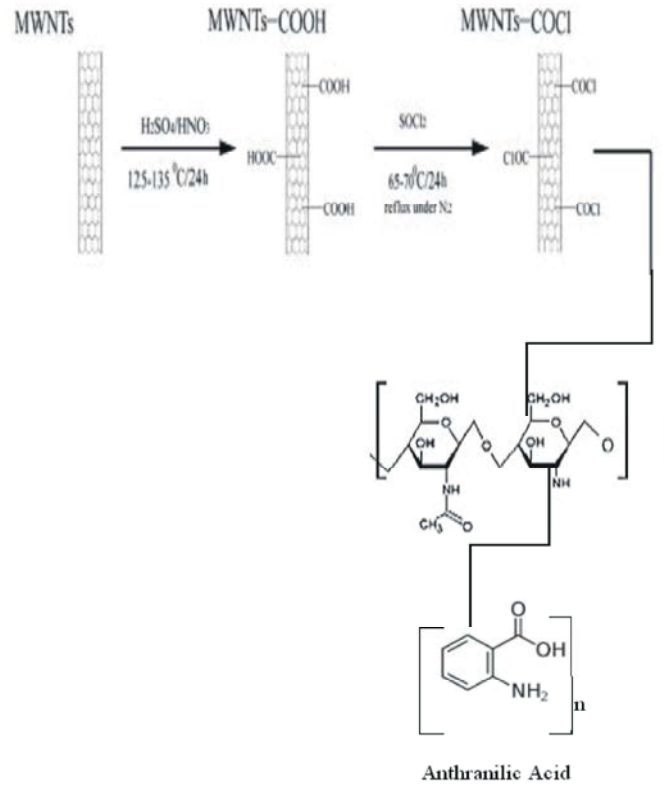


Fig. 1: Structure of Functionalization of Poly (Orthophenyldiamine)/c-mwnt

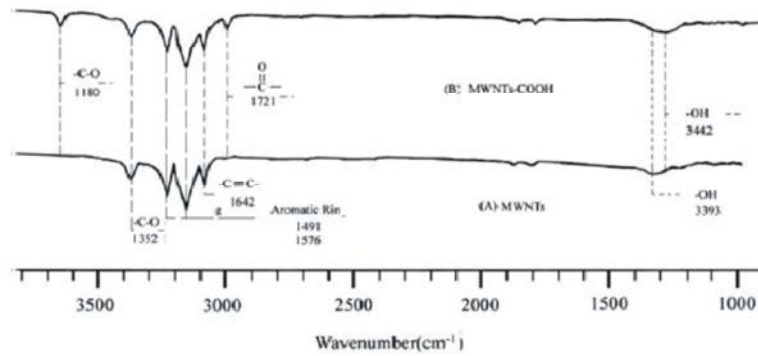


Fig. 2: FTIR spectrum of (A)MWCNT&(B)MWCNT-COOH

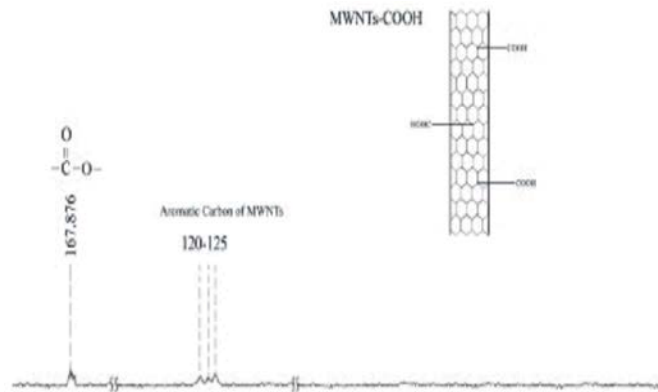


Fig. 3: NMR of MWCNT-COOH

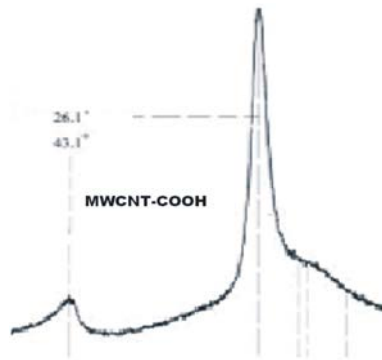


FIG. 4: X-RAY DIFFRACTION OF MWCNT -COOH

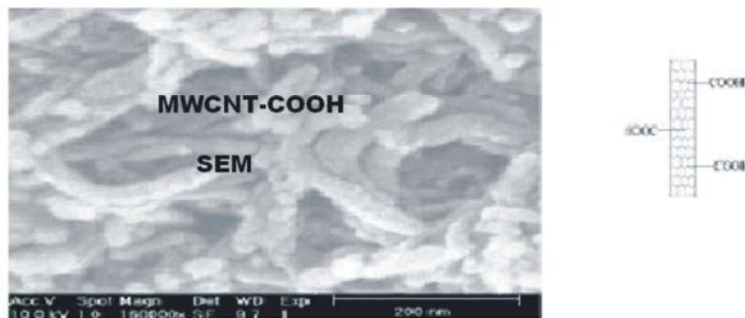


FIG. 5: SEM MICROGRAPH OF MWCNT-COOH

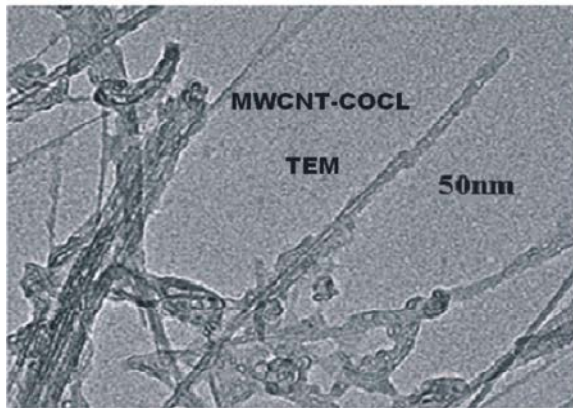


FIG. 6: TEM of MWCNT-COCL



FIG. 7: SEM OF MWCNT-COCL

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 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 samples of MWCNT-COOH (5 wt%) blends, in which the major component forms the matrix and the minor component (MWNTs) 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 CNT. TEM indicated that coatings were clearly visible on the surface of CNTs and that the functionalized MWCNTs had attached to the chitosan surface [13].

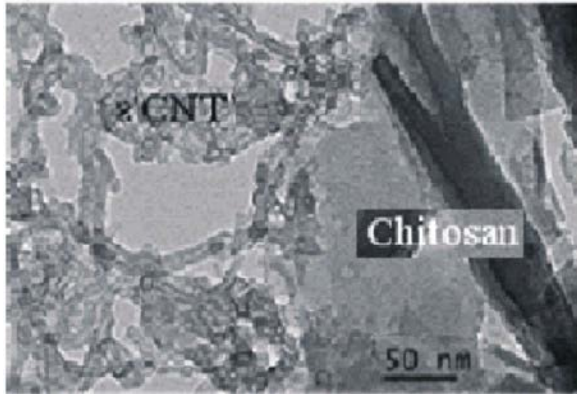


FIG. 8: TEM OF MWCNT-CHITOSAN

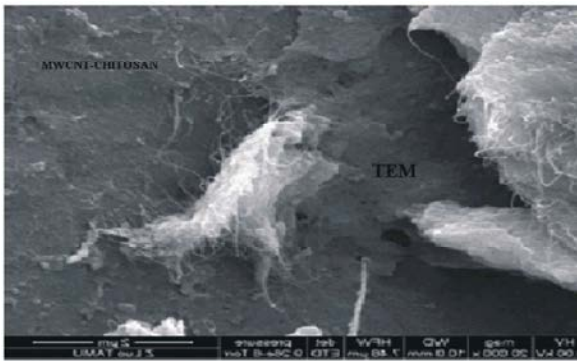


FIG. 9: SEM OF MWCNT-CHITOSAN

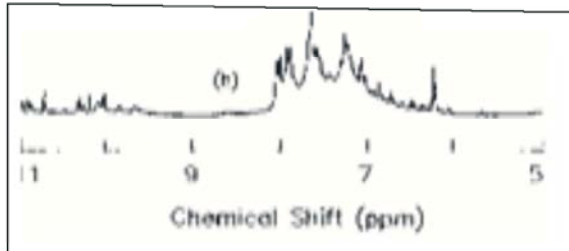


Fig. 10: NMR of poly (Orthophenyldiamine)/c-MWCNT

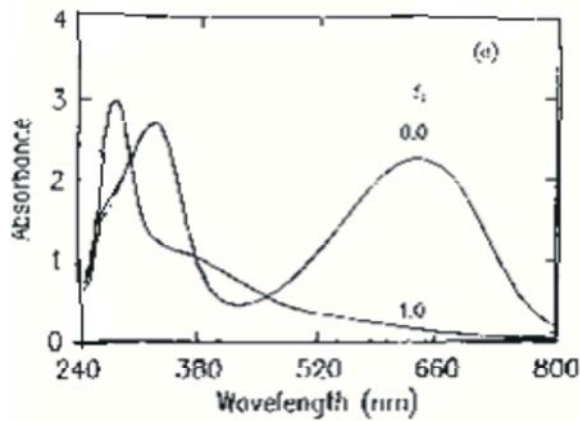


Fig. 11: UV-Visible spectrum of poly (Orthophenyldiamine)/ c-MWCNT

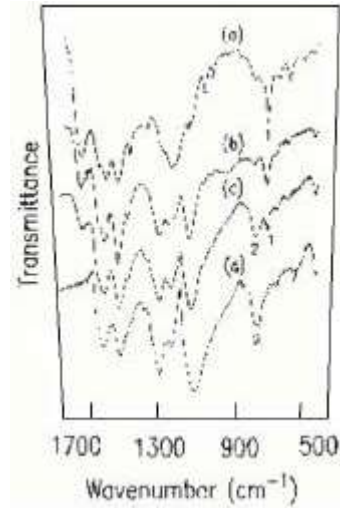


Fig. 12: FTIR spectrum of poly(Orthophenyldiamine)-c-MWCNT

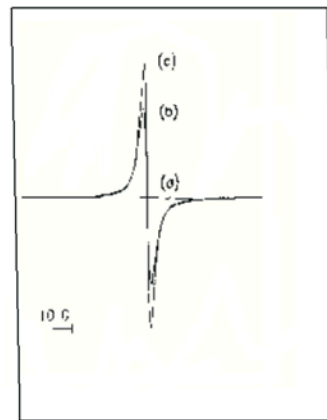


Fig. 13: EPR spectrum of Poly (Orthophenyldiamine)

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].

The HNMR spectra for all the PAA copolymer dissolved in DMSO- $d_6$  are all quite similar and resemble the spectra for PAA(0.5) shown in the above Figure-10. The signal for the carboxylic acid proton appears at 9.6-10.9 ppm. The  $^{12}C$  NMR spectra of the copolymers and of poly (Orthophenyldiamine)/DMSO- $d_6$  show several peaks between 90 and 180 ppm; however, the poor resolution of the spectra did not provide structural information [15-18].

FTIR spectrum for poly(Orthophenyldiamine) in Figure-1 shows strong bands for the  $C=O$  stretching at  $1694\text{cm}^{-1}$  and  $C-N$  stretching at  $1205\text{cm}^{-1}$ . The vibrational

modes of the benzene rings appear between 1600 and 1450 cm<sup>-1</sup>. In addition the band appearing at 758 cm<sup>-1</sup> probably corresponds to the C-H out of the plane bending vibrational of the 1,2,3- trisubstituted benzene rings [19].

The EPR spectra for the copolymers indicate a decrease in the number of spins/grams with increasing anthranilic acid content. Orthophenyldiamine itself shows no EPR signal [20].

### CONCLUSION

C-Multiwall carbon nanotubes with Poly (Orthophenyldiamine) exhibit excellent mechanical, electrical and magnetic properties as well as nanometer scale diameter and high aspect ratio, which make them an ideal reinforcing agent for high strength polymer composites. However, since MWCNTs usually form stabilized bundles due to Vander Waals interaction are extremely difficult to disperse and align in a polymer matrix. FTIR, EPR, SEM, TEM, X-ray diffraction of the composites was studied. Future work will focus on the bioactivity studies both in simulated body fluid to establish apatite forming ability especially if envisioned for application in bone tissue engineering.

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