

Synthesis and characterization of Conducting Polymers Multi Walled carbon Nanotube-Chitosan composites Coupled with Poly (Metachloroaniline)

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Abstract: In this research work, Carbon nanotubes (CNTs) 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 CNTs usually form stabilized bundles due to Van der Waals interactions, are extremely difficult to disperse and align in a polymer matrix. The biggest issues in the preparation of CNT reinforced composites reside in efficient dispersion of CNTs into a polymer matrix, the assessment of the dispersion and the alignment and control of the CNTs in the matrix. There are several methods for the dispersion of nanotubes in the polymer matrix such as solution mixing, melt mixing, electrospinning, in-situ polymerization and chemical functionalization of the carbon nanotubes, etc. These methods and preparation of high performance CNT-polymer composites are described in this review. A critical comparison of various CNT functionalization methods is given. In particular, CNT functionalization using click chemistry and the preparation of CNT composites employing hyperbranched polymers are stressed as potential techniques to achieve good CNT dispersion. In addition, discussions on mechanical, thermal, electrical, electrochemical and optical properties and applications of polymer/CNT composites included.

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

INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1], they have received much attention for their many potential applications, such as nanoelectronic and photovoltaic devices superconductors electromechanical actuators electrochemical capacitors nanowires and nanocomposite materials. Carbon nanotubes may be classified as single-walled carbon nanotubes (SWNTs), double-walled carbon nanotubes (DWNTs) or multi-walled carbon nanotubes (MWNTs). SWNT and DWNT comprise cylinders of one or two (concentric), respectively, graphene sheets, whereas MWNT consists several concentric cylindrical shells of graphene sheets. CNTs are synthesized in a variety of ways, such as arc discharge laser ablation high pressure carbon monoxide (HiPCO) and chemical vapor deposition (CVD). CNTs exhibit excellent mechanical, electrical, thermal and magnetic properties. The exact magnitude of these properties depends on the diameter and chirality of the nanotubes and whether they are single-walled, double-walled or multi-walled form [2].

Experimental Details

Material: Metachloroaniline 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 thionyl chloride 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 H₂SO₄:HNO₃ (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) [4].

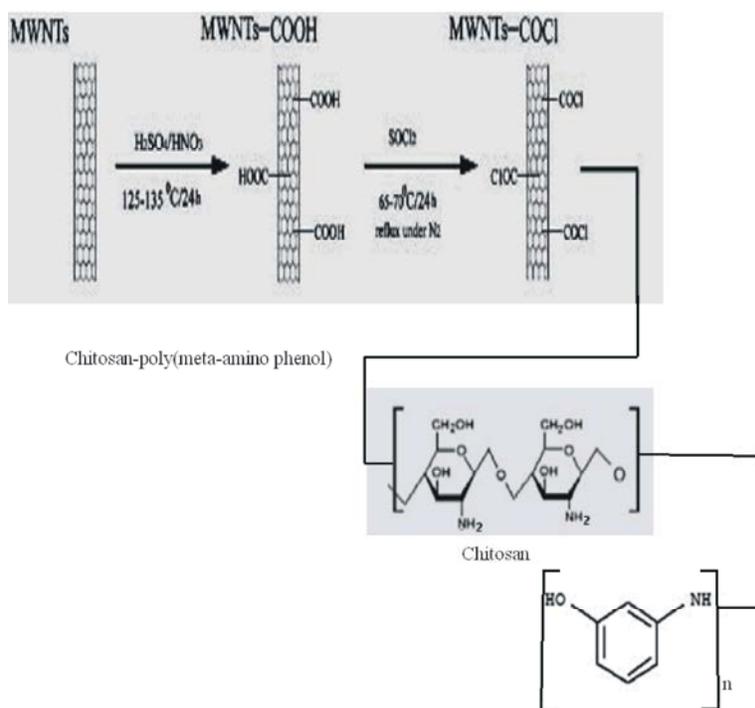


Fig. 1: Structure of MWCNT-CO.-CH.poly(m-chloroaniline)

Synthesis of MWCNT-COCl: The MWCNT was treated with thionyl chloride (-SOCl_2) for 24h at 60-75. This results corroborated the successful carboxylation of MWCNTs. Subsequently, upon reacting with thionyl chloride (-SOCl_2), the -COOH was transformed into acyl chloride functional groups and the distinctive stretching vibration of -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[5].

Preparation of METACHLOROANILINE/C-MWCNTS NANOCOMPOSITES: 5 wt% *c*-MWCNTs (based on the weight of metachloroaniline) was dispersed in the solution of 0.015 mol metachloroaniline 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 metachloroaniline /c-

MWCNTs nanocomposite. The purification and drying procedures were the same as those for the synthesis of the bare polymer[6].

Characterization

FTIR Analysis: Figure 1 shows the FTIR spectra of MWCNTs and MWCNTs-COOH. All the peaks, characteristic of MWCNTs, at 1600-1450 cm^{-1} (aromatic ring), 1352 cm^{-1} (-C-O), 3393 cm^{-1} (-OH) and 1642 cm^{-1} (-C=C-), appear in both spectra. Closer inspection revealed two unique peaks in the spectrum of MWCNTs-COOH, one appearing around 1721 cm^{-1} , arising from the stretching vibration of the C=O group, 12,33 and one at 1180 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 MWCNTs, the expanded FTIR spectra between 3300 and 3500 cm^{-1} was inspected [7].

NMR Studies: In Figure 2 (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].

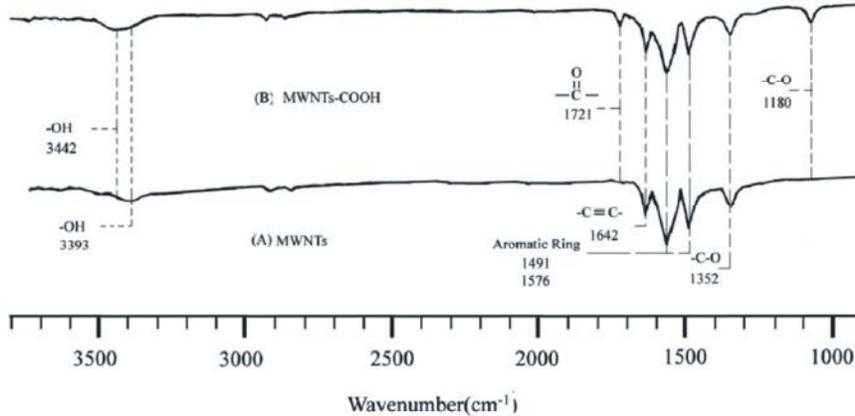


Fig. 1: FTIR spectrum of (A)MWCNT and (B)MWCNT-COOH

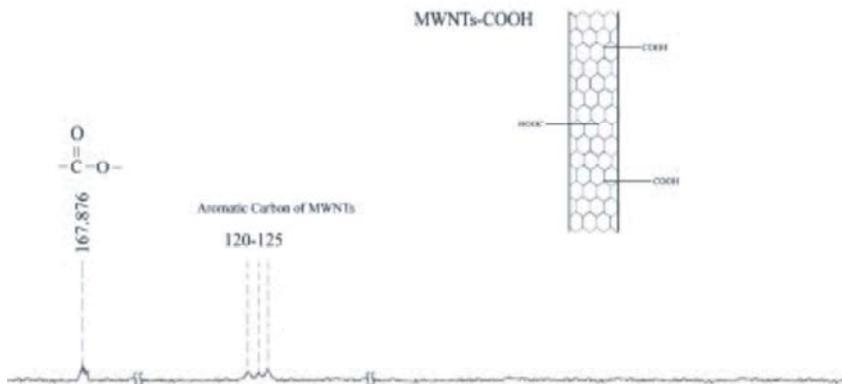


Fig. 2: NMR of MWCNT-COOH

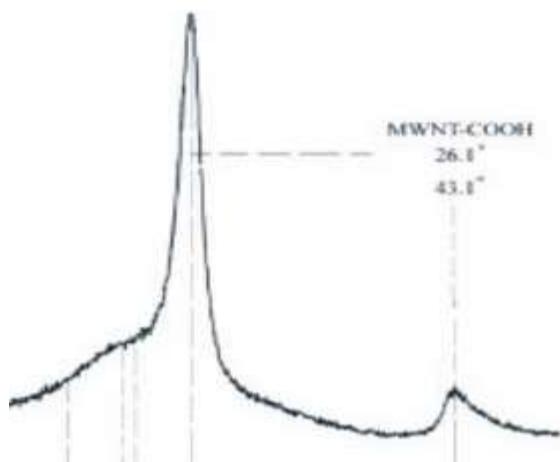


Fig. 3: X-RAY DIFFRACTION OF MWCNT-COOH

X-RAY Diffraction: In this fig-3 shows X-ray diffraction was used to examine the crystalline structures of pure MWCNT-COOH, because there is a peak at about at $2\theta \frac{1}{4}$ 26.18 and 43.18 in the spectrum of MWCNTs-COOH was observed [9].



Fig. 4: SEM MICROGRAPH OF MWCNT-COOH

Scanning Electron Microscope (SEM) Studies of MWCNT-COOH: 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].

Transmission Electron Microscope Studies of MWCNT-COOH: In this Figure shows that TEM indicated that the coatings were clearly visible on the surface of

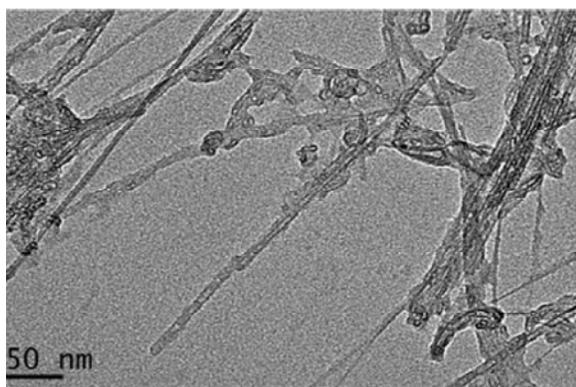


Fig. 5: TEM of MWCNT-COCL

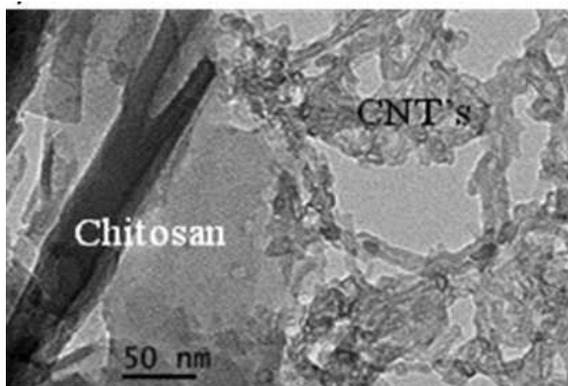


Fig. 7: TEM OF MWCNT-CHITOSAN

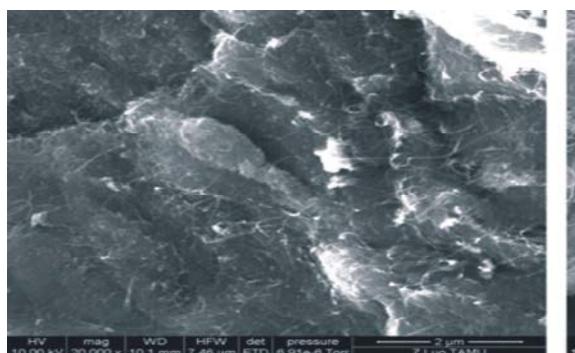


Fig. 6: SEM OF MWCNT-COCL

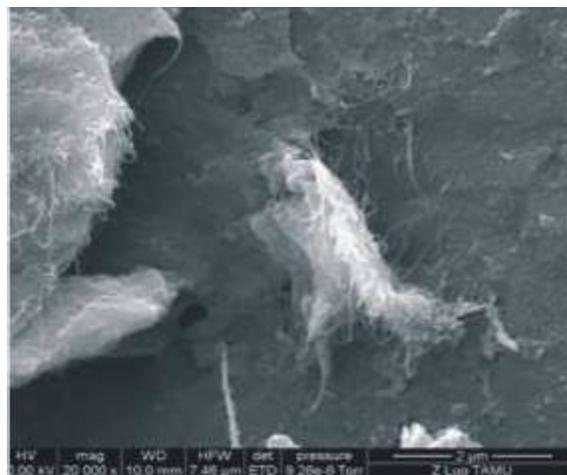


Fig. 8: SEM of MWCNT-CHITOSAN

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 [12]. 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[13]

Transmission Electron Microscope (TEM) of MWCNT-CHITOSAN: 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.

Sem Studies of MWCNT-CHITOSAN: SEM was performed to assess the morphology of theMWCNTs 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.

The UV-vis spectra of metachloroaniline and metachloroaniline/MWCNT are shown in Fig 2. The first absorption band appears in the region of 238-389nm is assigned to the π - π^* 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- π^* transition, which correspond to non-bonding lone pair electron transitions of hetero atoms like nitrogen and oxygen respectively. Metachloroaniline/ 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 π -conjugated backbone of the polymer by the addition of an emulsifier

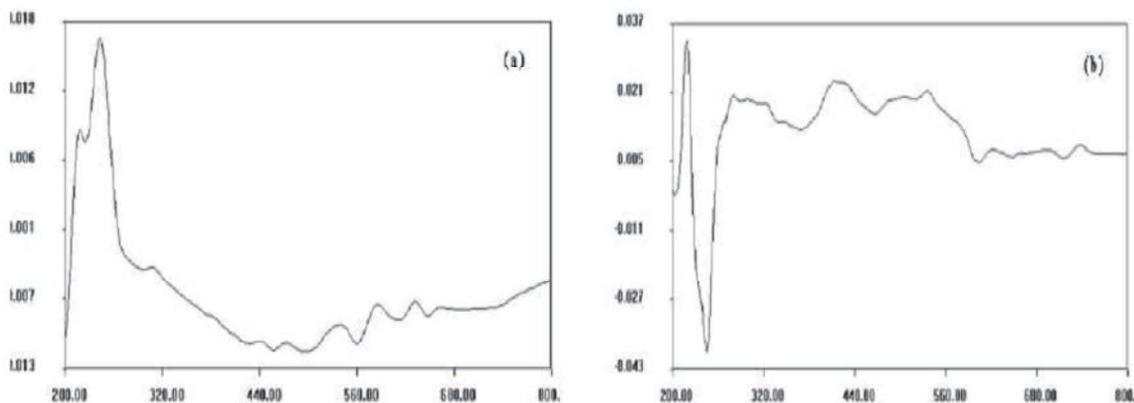


Fig. 8: UV-Vis absorption spectrum of metachloroaniline/MWCNTs

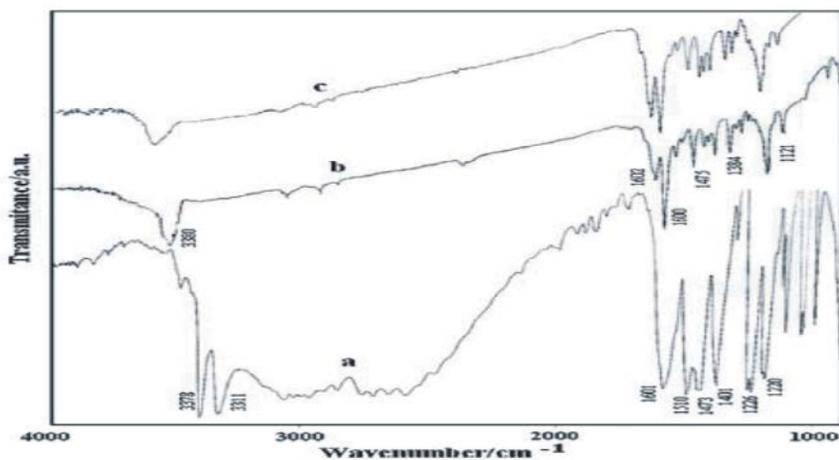


Fig. 9: FTIR spectrum of METACHLOROANILINE/c-MWCNT

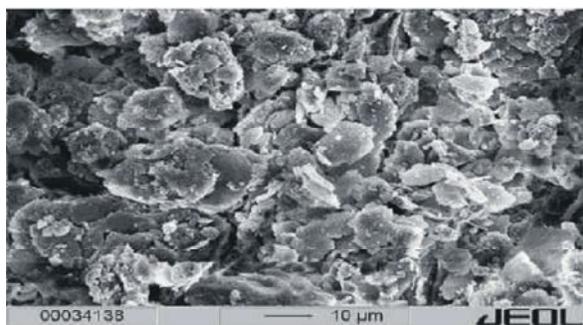


Fig. 10: SEM of META CHLOROANILINE/c-MWCNT

MWCNTs. The observation of polaron bands is consistent with a high degree of doping and good solubility of the polymer nano compound [14].

The FTIR peaks for pure show the broad peaks at 3450 cm^{-1} due to the stretching vibration-OH superimposed on-NH stretching band and broaden due to interhydrogen bonds of polysaccharides. The 1656 cm^{-1}

attributed to the presence of acetylunit with-C=O stretching; 1579 cm^{-1} attributed to N-H bending, the 1376 cm^{-1} attributed to-CH₃ symmetrical angular deformation; 1153 cm^{-1} attributed to β (1,4) glycosidic bonds; and 1091 cm^{-1} attributed to C-O-C stretching vibration.

The morphology of the synthesized metachloroaniline nano compound was measured by SEM and is shown in Fig-10. From the figure it was evident that the morphology of the resultant nano compound is flakes in shape. This confirms that the synthesized meta chloroaniline / MWCNTs falls under the category of nano compound.

The size of the synthesized poly metachloroaniline nano compound measured by transition electron microscopy is given in fig 11. 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 PPAP/MWCNTs falls under the category of nano compound.



Fig. 11: TEM Image of METACHLOROANILINE/ c-MWCNTs

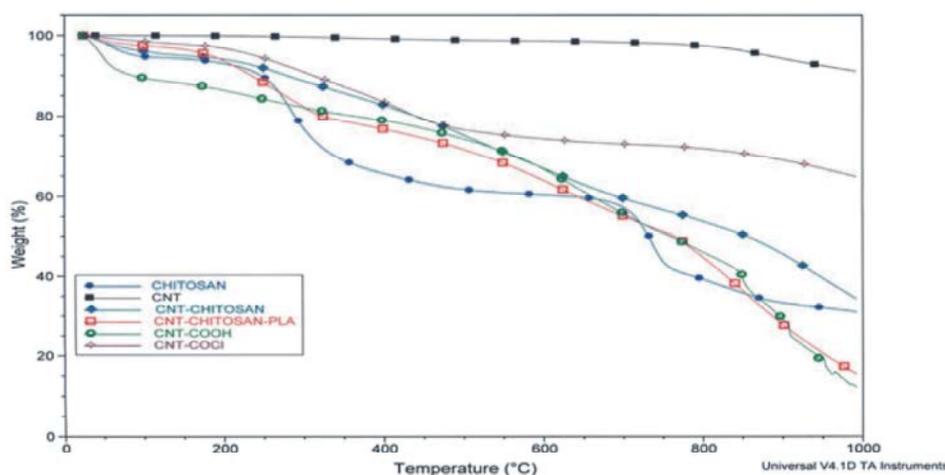


Fig. 12: TGA ANALYSIS OF MWCNT, MWCNT-COOH, MWCNT-COCL, MWCNT-CHITOSAN

Thermogravimetric analysis showed a total weight loss of about 50% at 800 °C. It is most likely that acid oxidation using concentrated HNO₃/H₂SO₄ 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.[22] 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 [23]. 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. [24] The second weight loss occurred between 600 and 800 °C and may be attributed to oxidative removal of the glycosidic linkage [15].

CONCLUSION

Serials of raw MWCNTs and amino-functionalized MWCNTs contained epoxy resin 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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