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Synthesisand Characterization of Conducting Polymers Multi Walled Carbon Nanotube (MWCNT)–Chitosan Composites Coupled with Poly (Para Methoxyaniline)

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Abstract: The present study was carried out by acid functionalized multiwallcarbonnanotubes (MWCNT) covalently grafted to chitosan by first reacting the oxidized carbon nanotubes with thionylchloride to form acylchlorinated carbon nanotubes. Then it was subsequently dispersed in chitosan and covalently grafted to form composites, MWCNT–chitosan which was washed several times to remove unreacted materials. Poly (paramethoxyaniline) is attached with MWCNT which increases electrochemical properties of nanocomposites. This composites 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(paramethoxyaniline) · Multiwalledcarbonnanotube (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 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^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 multiwalled carbon nanotubes (MWNTs) in structural materials such as polymer composites are more feasible

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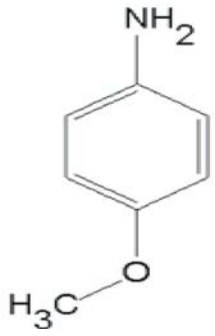

Fig. 1: Structure of para methoxy aniline

MECHANISM

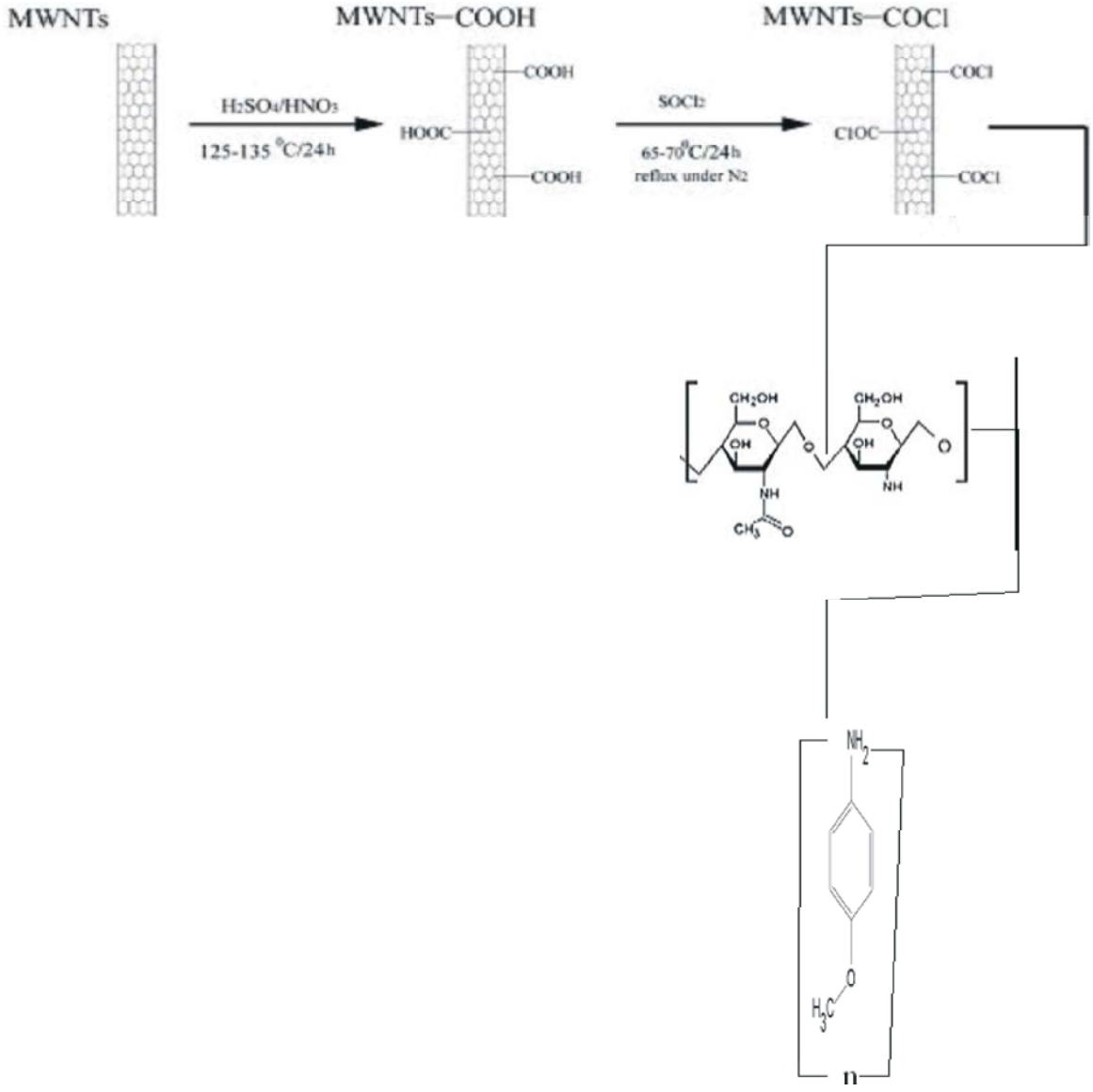

Fig. 2: Structure of Functionization of Poly (Paramethoxyaniline)/C-MWCNT

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].

Para Methoxy Aniline: It is a black liquid. It is a brown Crystals.It is yellow to brown, Crystalline solid with an amine-like odor.It is stable, flammable, incompatible with acids, acid chlorides, acid anhydrides, chloroformates, strong oxidizing agents, alkaline materials, aldehydes, ketones, nitrates. It is extremely toxic. It is a strong oxidizing agent.

Experimental Details

Materials: Parmethoxyaniline was purchased from Aldrich. Multiwalled 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].

Oxidation of MWCNTS: Typically, MWCNTs were reacted with Nitric Acid and distilled water (3:1) was refluxed for 24 hours at 75°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 (-$SOCL_2$) 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 [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 ◎ 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 Paramethoxyaniline/C-MWCNTs Nano Composites: 5 wt% of c-MWCNTs (based on the weight of poly (paramethoxyaniline) was dispersed in the solution of 0•015 mol poly (paramethoxyaniline) 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 Muck 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 poly (paramethoxyaniline) /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 3 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} (__C¼C__), appear in both spectra. Closer inspection revealed two unique peaks in the spectrum of MWNTs–COOH, one appearing around 1721 cm^{-1}, arising from the stretching vibration of the C¼O group, 12,33 and one at 1180 cm^{-1}, arising from the stretching vibration of the C¼O 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 cm^{-1} was inspected [7].

The Figure 4 shows that MWCNTs–COOH 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].

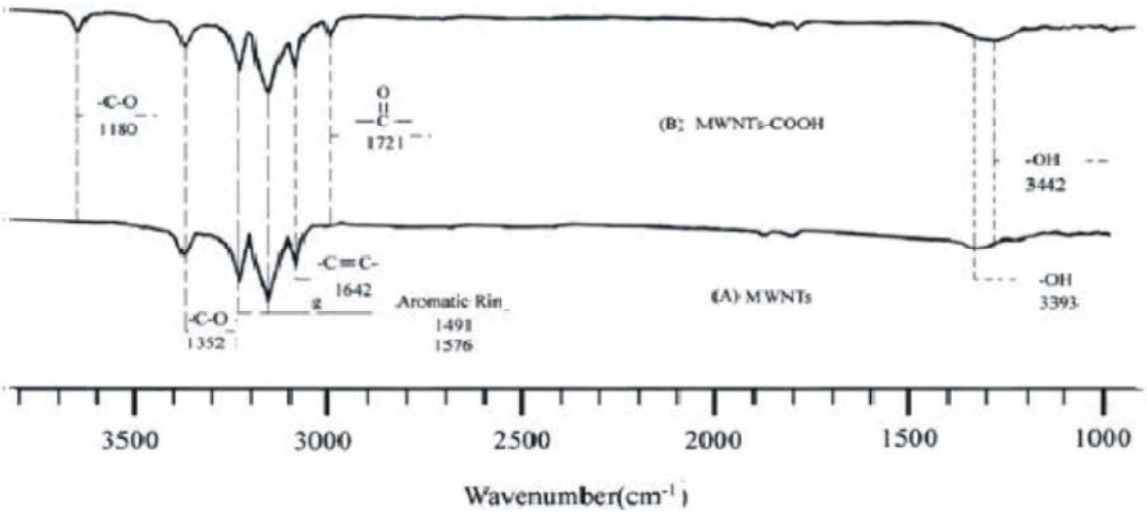

Fig. 3: FTIR spectrum of (A) MWCNT&(B) MWCNT-COOH

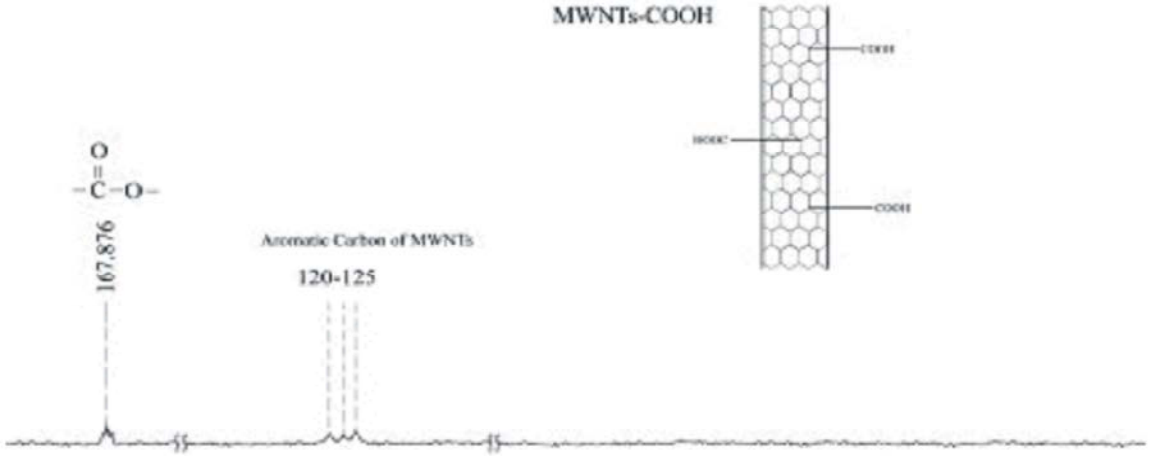

Fig. 4: NMR of MWCNT-COOH

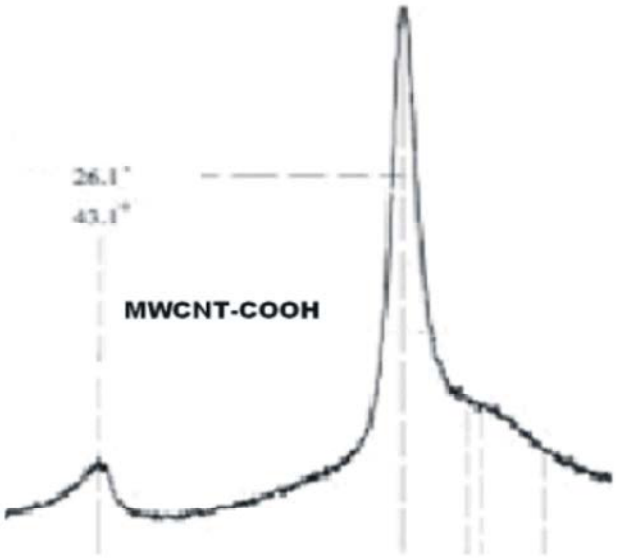

Fig. 5: X-RAY DIFFRACTION OF MWCNT –COOH

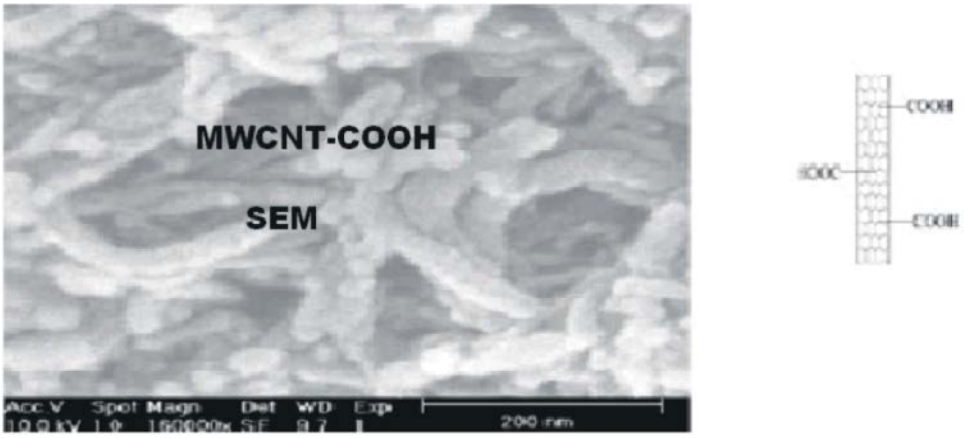

Fig. 6: Sem Micrograph of MWCNT-COOH

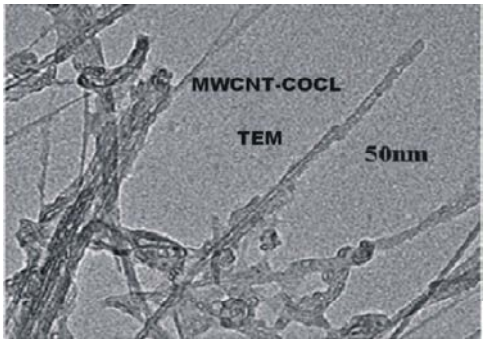

Fig. 7: Tem of MWCNT-COCL

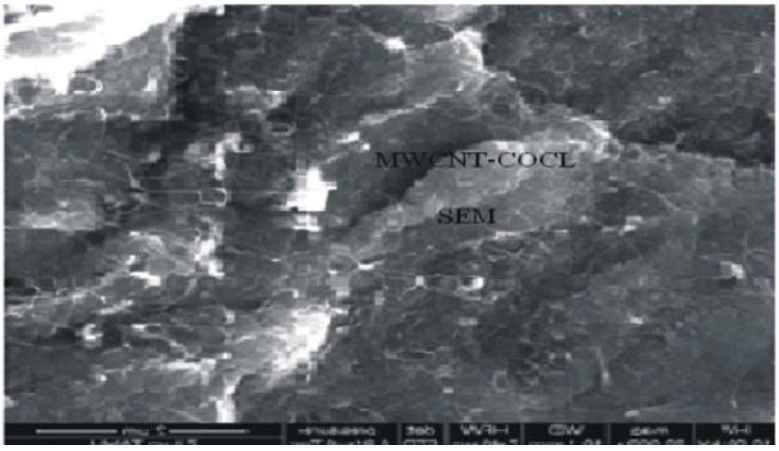

Fig. 8: Sem of MWCNT-COCL

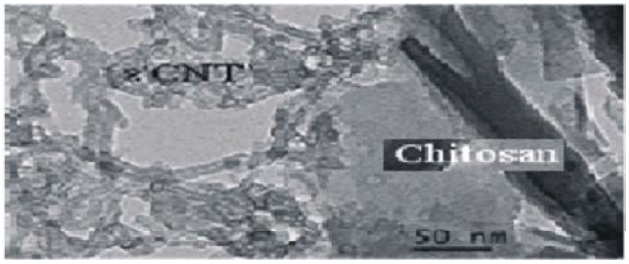

Fig. 9: Tem of MWCNT-CHITOSAN

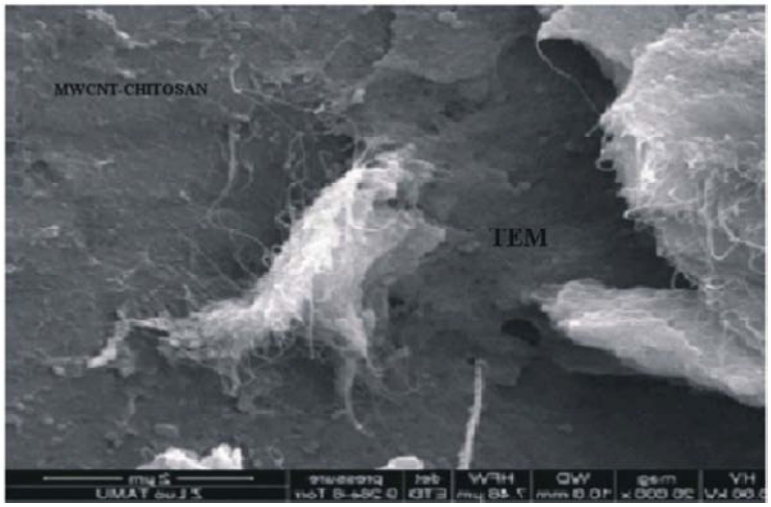

Fig. 10: Sem of MWCNT-CHITOSAN

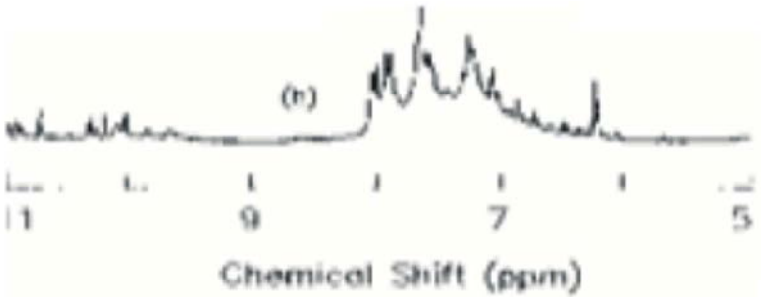

Fig. 11: NMR of poly (para methoxyaniline)/c-MWCNT

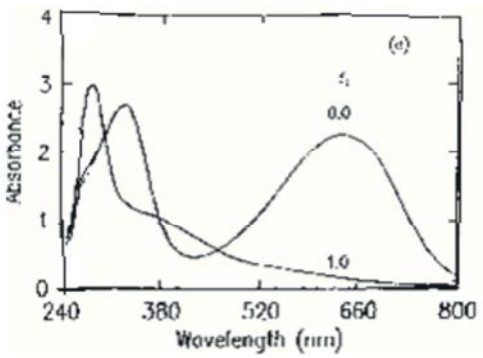

Fig. 12: UV-Visible spectrum of poly (paramethoxyaniline)/c-MWCNT

This Fig. 5 shows that the X-ray diffraction was used to examine the crystalline structures of pure MWCNT-COOH, because there is a peak at about at 2y ¼ 26.18 and 43.18 in the spectrum of MWCNTs–COOH was observed [9].

This Fig. 6 shows that 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 [9].

This Figure 7 shows that TEM reveals 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.

The Fig. 8 shows that 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. 9 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.

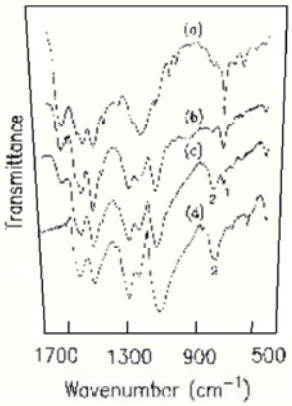

Fig. 13: FTIR sprectumm of (paramethoxyaniline)\c-MWCNT

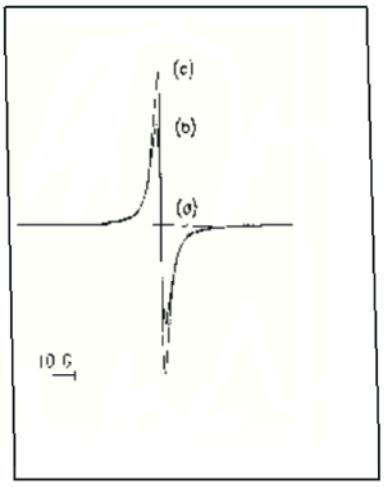

Fig. 14: EPR spectrum of Poly (paramethoxyaniline)

This Fig. 10 shows that 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.

The Fig. 11 shows that NMR spectra for all the poly (paramethoxyaniline) copolymer dissolved in DMSO-d_6 are all quite similar and resemble the spectra for paramethoxyaniline (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 (paramethoxyaniline)/DMSO-d_6) show several peaks between 90 and 180 ppm; however, the poor resolution of the spectra did not provide structural information.

The Figure 12 shows the UV-Visible Spectrum of poly(paramethoxyaniline)/c-MWCNT is analysed with respect to different wave lengths.

FTIR spectrum for poly(paramethoxyaniline) in figure-13 shows the strong bands for the c=o strecting at 1694cm^{-1} and C-N stretching at 1205 cm. The vibrational modes of the benzene rings appear between 1600 and 1450 cm^{-1}. In addiction, the band appearing at 758 cm^{-1} probably corresponds to the C-H out of the plane bending vibrational of the 1,2,3- trisubstitute benzene rings.

The Figure 14 shows that the EPR spectra of poly (paramethoxyanilline) for the copolymers indicate a decrease in the number of spins/grams with increasing anthranilic acid content, Paramethoxyaniline itself shows no EPR signal.

CONCLUSION

C-Multiwalledcarbonnanotubes with Poly (paramethoxyaniline) 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 envision for application in bone tissue engineering.

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