

Grafting Vinyl Monomers onto Mwcnt Coupled with Chitosan: II: Graft Copolymerization of Ethyleacrylate onto Chitosan Coupled with Multiwalled Carbon Nano Tube

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Abstract: Multiwalled Carbon Nanotube (MWCNT) was functionalized by oxidation and further treatment with thionyl chloride. The chloro -acetyl derivative of MWCNT was reacted with chitosan to obtain MWCNTCS derivative. The derivatives of MWCNT were characterized by FTIR, SEM and NMR methods. Ethyl acrylate was grafted onto MWCNT-CS by using ceric ammonium nitrate as the initiator. The grafted samples were characterized using FTIR, SEM, TGA methods. Evidence of grafting was confirmed by FTIR spectroscopy. The morphology was evaluated by SEM. The thermal analysis indicated the different stages of the degradation of the grafted copolymer. The antibacterial activities of the grafted polymer was also evaluated.

Key words: MWCNT • Chitosan • Ethyl acrylate • Graft Copolymerization • Antibacterial Activity

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 nonmaterial 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. Recently because of the promising physical, thermal, mechanical and electric properties, 1, 2 carbon nanotubes (CNTs) have attracted extensively scientific interest [2]. Moreover, applications of multiwall carbon nanotubes (MWCNTs) in structural materials such as polymer composites are more feasible with their mass production, which leads to price reduction. Specifically, use of CNTs in polymer/carbon nanotube composites has attracted wide attention. In this sense, it has been reported that the matrix properties can be effectively enhanced via the addition of CNTs in different polymer matrices. 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].

Chitosan is a linear polysaccharide derived from chitin, the second most abundant organic compounds only next to cellulose in the nature. Chitin can be found in the shells of marine invertebrates (crabs, crustaceans, etc.), fungi, insects and yeasts. Depending on the source, it generally functions as an exoskeleton, providing structural integrity, commonly embedded in a matrix of proteins, minerals and at times various other polysaccharides. Chitin is a homopolymer comprised of 2-acetamido-2-deoxy- β -D-glucopyranose units; however, some units exist in the deacetylated form as 2-amino-2-deoxy- β -D-glucopyranose. When chitin is deacetylated to at least 50%, it is referred to as chitosan, in other words this is essentially the N-deacetylated derivative of chitin. Chitosan has many interesting biological and chemical properties. The excellent features such as biocompatibility, ecologically safe biodegradability (degradation products of chitosan are non-toxic, non-immunogenic and no carcinogenic) and low toxicity with versatile biological activities (chitosan has antimicrobial activity and low immunogenicity recommends this biopolymer for applications in biomedicine [4,5]. In addition, chitosan is very efficient for interaction with the anionic solutes including dyes in acidic solutions due to the reactive groups, such as -OH and -NH₂. This property has been widely used for the removal of the water-soluble dyes, as an alternative to the conventional sorbents and flocculants [6, 7]. However, due to inter- and intermolecular H-bonding, chitosan is only soluble in few dilute acid solutions (depending on the molecular weight), which limits its applications. As a result, many attempts have been made in chemical modification of chitosan, aiming at improving its water solubility.

Among these an ideal way is the graft modification of chitosan [8-11] to modify its properties. The main advantage in the grafting efforts is the high degree of functionality of chitosan - the molecule backbone contains two hydroxyl groups and one primary amine group per repeat unit. The active primary amino groups on the molecule being reactive provide sites for the attachment of different side groups employing mild reaction conditions. In this way versatile materials based on chitosan with specific functionality can be obtained. Grafting vinyl monomers onto chitosan [10, 11] is one of the most effective methods to improve the

performances of chitosan without sacrificing its properties and also is a challenging field of research with unlimited future prospects. Vinyl graft copolymerization can be described as the modification of a preexisting polymer chain (trunk polymer). Graft copolymers are synthesized to improve physicochemical properties of synthetic/natural polymers for applications in agriculture, biomedicine and other fields. Different studies have been published on the grafting copolymerization of chitosan with various vinyl monomers like acrylonitrile [12], methyl methacrylate [13], acrylamide [14], acrylic acid [15], using cerium ammonium nitrate as redox initiators. In this context, the present study is focused on the copolymerization of chitosan with different vinyl monomers via surfactant-free emulsion copolymerization (SFEP) using potassium persulfate as initiator. The SFEP technique is one of the most important methods for the synthesis of polymer beads with controlled size. Polymeric colloidal micro- and nanoparticles possessing an extremely large surface area are attractive candidates as carrier vehicles for bioactive substances, such as therapeutic drugs, proteins, genes, or enzymes. For such applications, colloidal particles prepared from biocompatible and biodegradable polymers are desirable. In the present research program, we wish to report the graft copolymerization of ethyle acrylate onto chitosan using ceric ammonium nitrate as the initiator. The grafted polymers were characterized by SEM, FTIR and TGA studies. The antibacterial activities of the grafted samples have been reported.

MATERIALS AND METHODS

Materials: Chitosan (CS) (Degree of Deactivation = 95% determined by ¹H-NMR and Molecular Weight 13.45 × 10⁴ Da) was purchased from India Sea Foods, Kerela, India. Ethyl Acrylate and other chemicals were used as analytical grade and purchased from Sigma Aldrich Company. 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 per sulfate, 85% lactic acid solution, sulfuric acid, nitric acid and thinly 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 [4].

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

Synthesis of MWCNT-COCL from MWCNT-COOH: The MWCNT-COOH was treated with thionyl chloride ($-\text{SOCl}_2$) for 24h at 60-75°C. Subsequently, upon reacting with thionyl chloride ($-\text{SOCl}_2$), the COOH was transformed into acyl chloride functional groups MWCNT-COCL

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.

Graft Copolymerization: MWCNT-chitosan powder (2gm) was dissolved in 100 ml of acetic acid solution (2%, v/v). After MWCNT-chitosan was dissolved, the solutions were filtered with cheesecloth by vacuum aspiration to remove foam and any undissolved impurities. The ceric ammonium nitrate in 0.5 M nitric acid solution was then loaded into the reactor under continuous stirring. Then a known weight of ethyl acrylate (EA) monomer was also injected into the reactor. The reaction was assumed to have started at the moment the monomer was injected. The grafting reaction was carried out under nitrogen atmosphere in a 500 ml, four-necked flask equipped with a reflux condenser, a stirrer, dropping funnel and a gas inlet system immersed in a constant temperature water bath.

In atypical reaction, The grafting reaction was carried out for varying time intervals (1–4 h). The zero time of the reaction was at the time of monomer addition. After completion of the reaction, the reaction mixture was immediately poured into methanol in the ratio of 1: 5 of material to liquor for precipitation. The precipitated product was recovered by centrifugation and washed with pure methanol (2×50 ml). The crude copolymer thus obtained was dried till constant weight under vacuum (7.6 mm Hg) for 24 h at 100°C. The dried product was extracted with dimethyl formamide for 48 h and washed with methanol to remove the homopolymer. The grafted MWCNT - chitosan-EA) was dried to a constant weight

The process of grafting is depicted in Fig. 1.

Characterization

Ftir Analysis: Figure 2 shows the FTIR spectra of

MWCNTs and MWCNTs-COOH. All the peaks, characteristic of MWNTs, at 1600–1450 cm^{-1} (aromatic ring), 1352 cm^{-1} (C=O), 3393 cm^{-1} (OH) and 1642 cm^{-1} appear in both spectra. Closer inspection revealed two unique peaks in the spectrum of MWCNT-COOH, one appearing around 1721 cm^{-1} , arising from the stretching vibration of the C=O group 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 evaluated [8].

NMR Studies: The NMR data in Figure 3 shows that the peak is seen shifted to 167.876 ppm because of the removal of NH 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 [9].

X-RAY Diffraction: 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 [10].

This Fig. 5 shows the SEM photo of MWCNTs-COOH is the result of insufficient dispersion and poor interfacial adhesion between filler and matrix [11].

This Figure 6 shows the TEM indicated that the coatings were clearly visible on the surface of MWCNT-COOH and 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 [12].

Sem Studies of MWCNT-COCL: This Fig. 7 shows the morphology of the MWCNT -COCL, 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 [13].

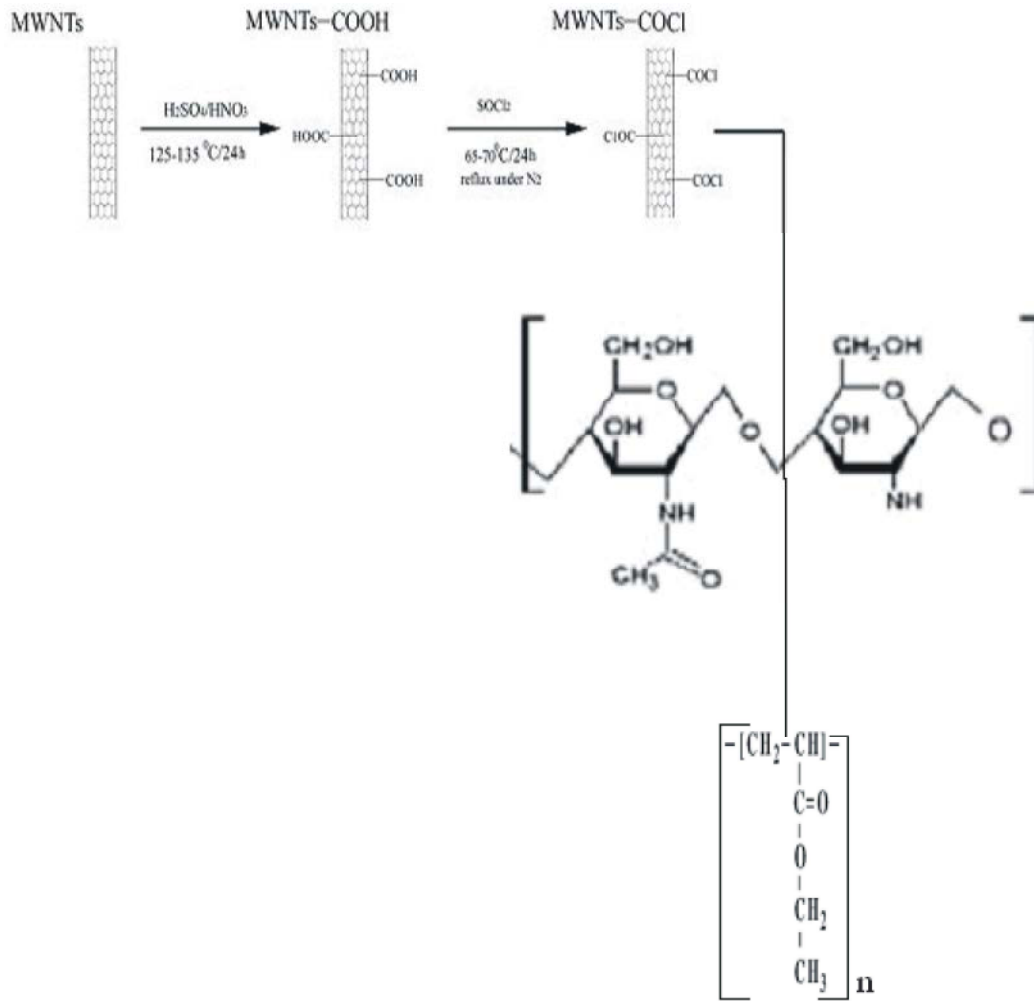


Fig. 1: Grafting Ethyle Acrylate onto MWCNT- Chitosan

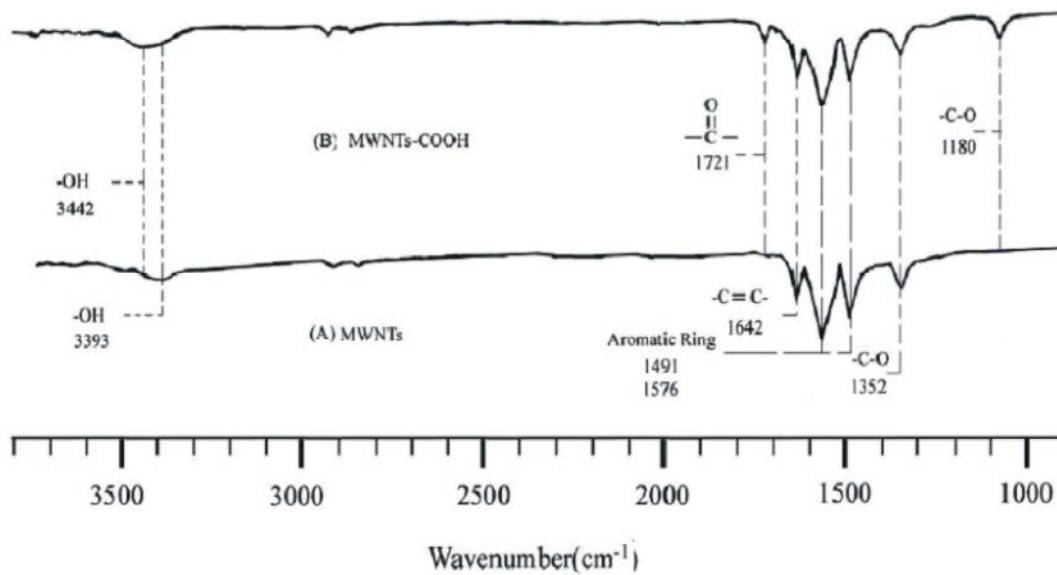


Fig. 2: Ftir Spectrum of (A) MWCNT& (B) MWCNT-COOH

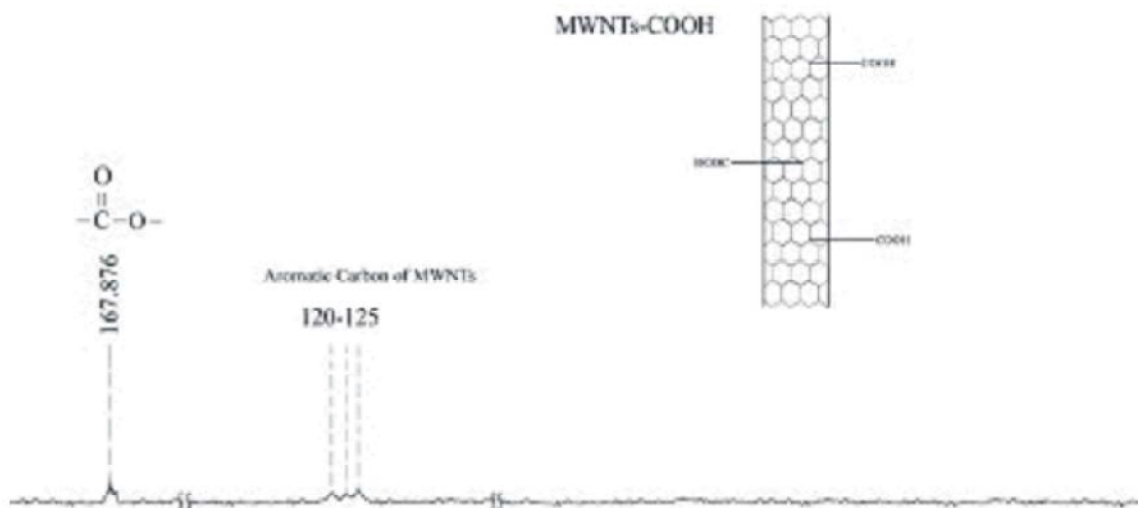


Fig. 3: NMR of MWCNT-COOH

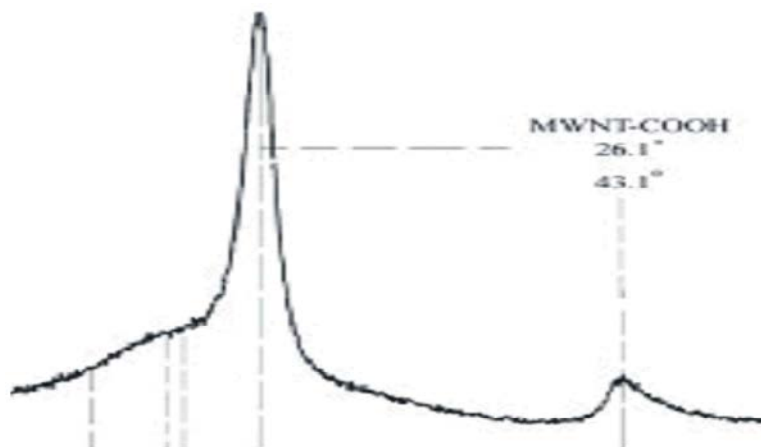


Fig. 4: X-RAY Diffraction of MWCNT -COOH

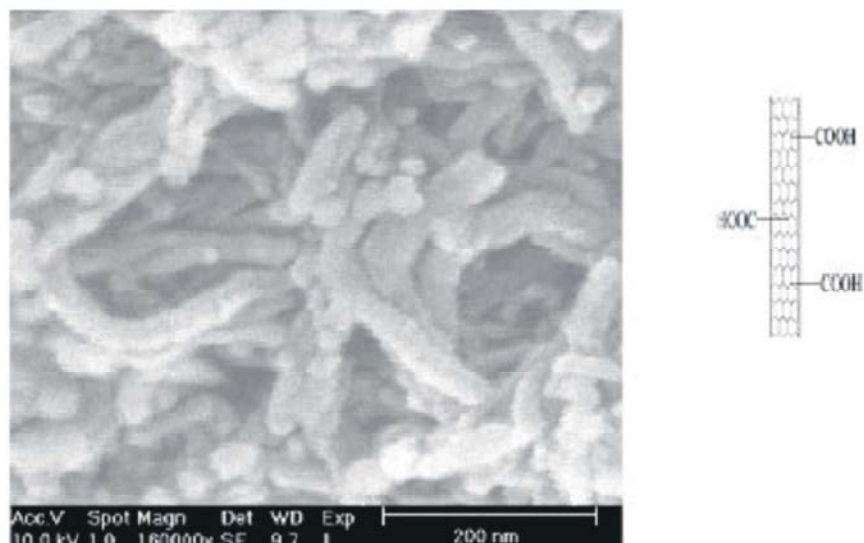


Fig. 5: SEM Micrograph of MWCNT-COOH

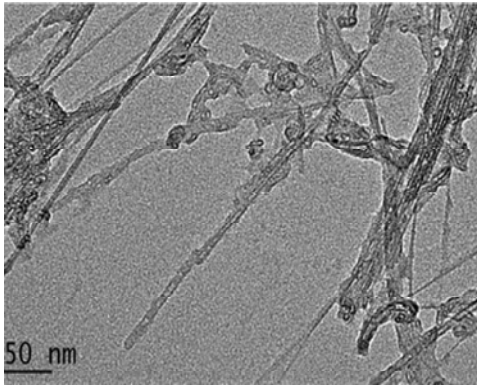


Fig. 6: TEM of MWCNT-COCL

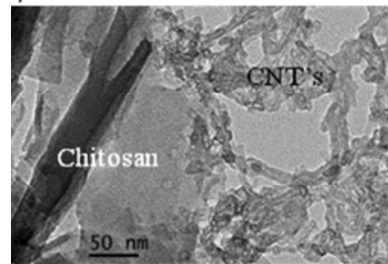


Fig. 8: TEM OF MWCNT-CHITOSAN

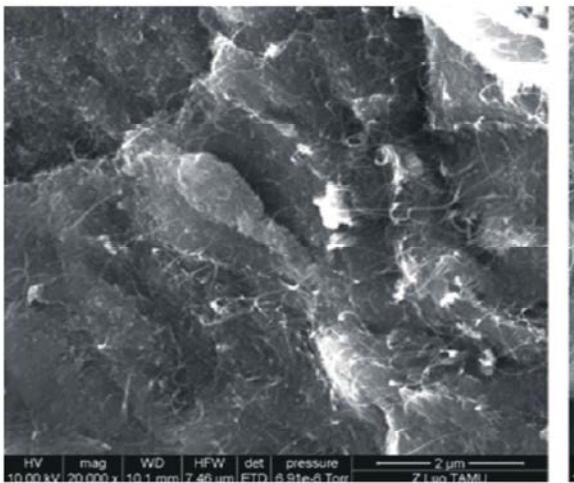


Fig. 7: SEM OF MWCNT-COCL

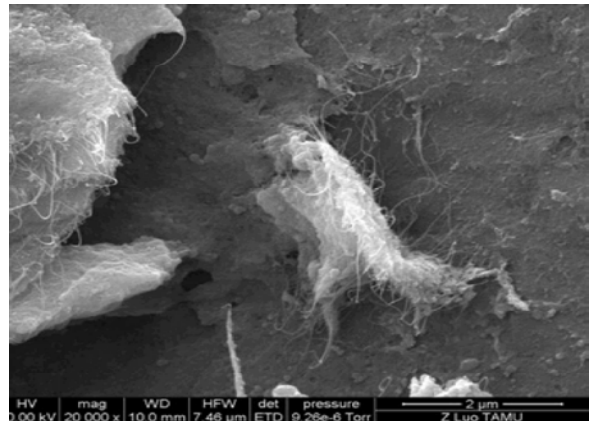


Fig. 9: SEM OF MWCNT-CHITOSAN

Transmission Electron Microscope (Tem) of MWCNT-Chitosan: In Fig. 8, the TEM indicated that coatings were clearly visible on the surface of CNTs and that the functionalized MWCNTs had attached to the chitosan surface [14].

Sem Studies of MWCNT-Chitosan: SEM (Fig. 9) 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 [15].

TGA Analysis: Thermo gravimetric analysis (Fig. 10) 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 [16]. 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.

Scanning Electron Micrograph of Chitosan/MWCNT-EA: The scanning electron microscope picture of grafted chitosan/MWCNT-CS-EA is shown in the Figure 11. It clearly exhibits the polysaccharide nature having varied particle sizes with rough surface. Even the polysaccharide seems completely scattered along with larger particles. A change in contour of the polysaccharide on grafting and the thick polymeric coating of ethyl acrylate on their surface along with grafting of ethyl acrylate such that all the gap between polysaccharide particles have been closed indicate the effect of grafting. It can be seen that individual polysaccharide molecules of Chitosan/MWCNT-CH--EA have joined through these surface coatings during grafting process.

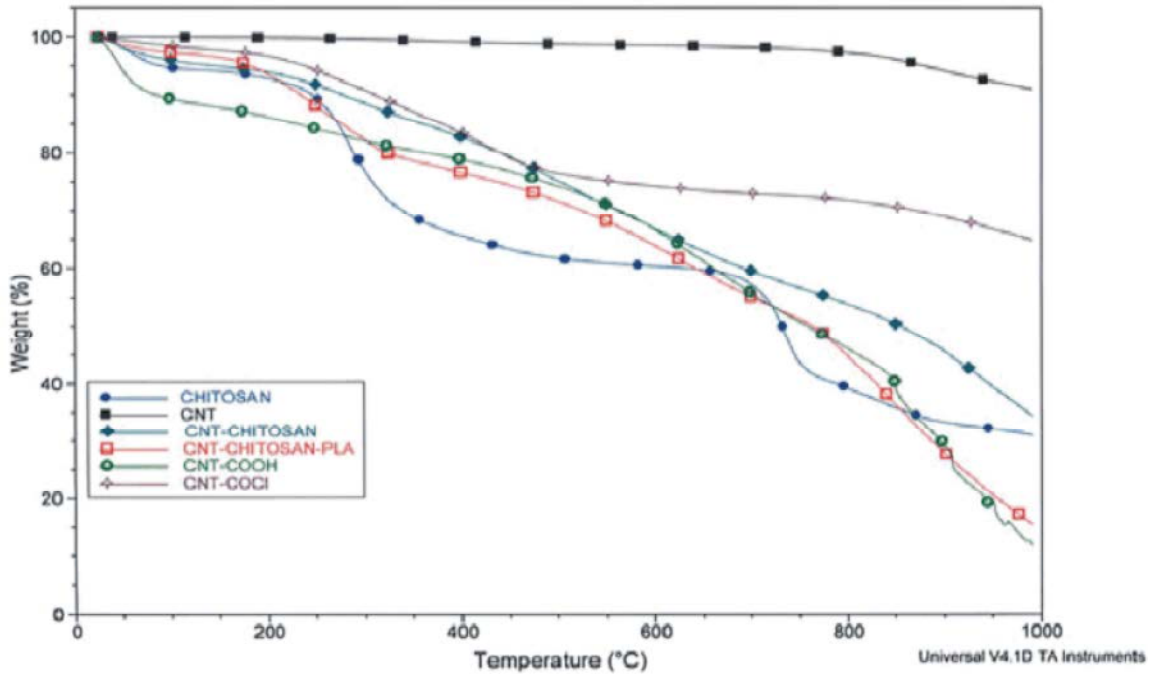


Fig. 10: TGA Analysis of MWCNT, MWCNT-COOH, MWCNT-COCL, MWCNT-CHITOSAN

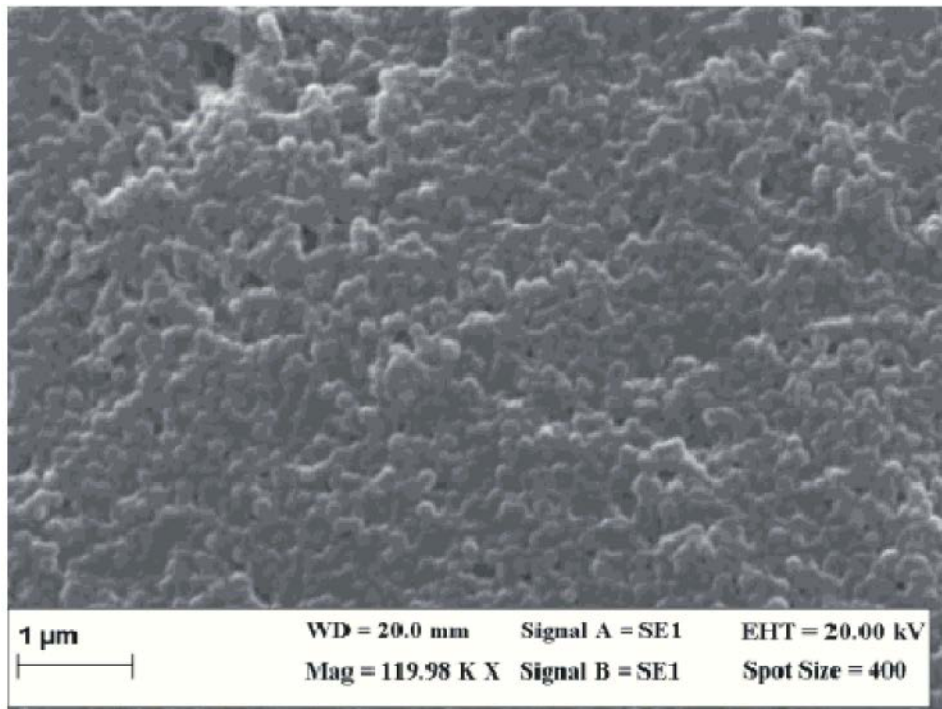


Fig. 11: Scanning Electron Micrograph of Grafted CHITOSAN/MWCNT-EA

X-RAY Diffraction Studies: The Figure 12 shows the change of CS/MWCNT-EA structure after graft copolymerization was investigated by X-ray diffraction. The XRD patterns of CS/MWCNT-EA. CS/MWCNT-EA

shows distinct crystalline peak at around 2θ : 20.00, 30.00, 35.00. The characteristic reflection at $2\theta = 20.00$ corresponds to the orthorhombic crystal structure of chitosan. The CS/MWCNT-EA crystallinity is linked to the great number

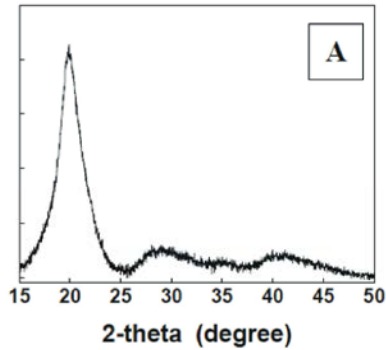


Fig. 12: X-RAY Diffraction Studies of CS/MWCNT-EA

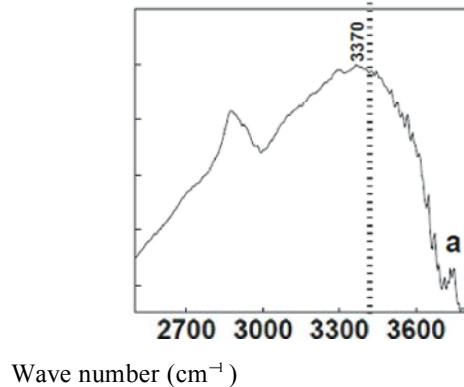
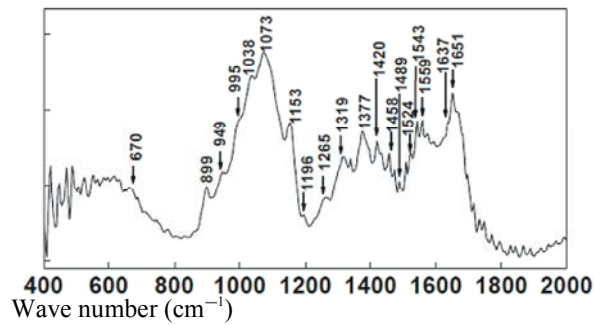


Fig. 13: Ftir of Studies of CS/MWCNT-Ethyle Acrylate

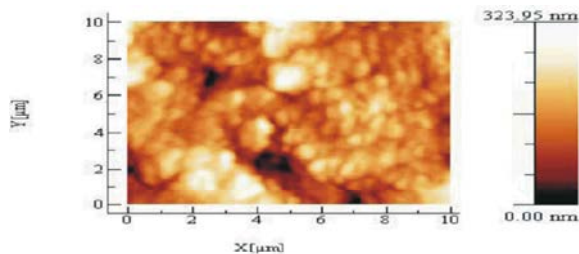


Fig. 14: AFM of CHITOSAN/MWCNT-Ethyle Acrylate

of -OH and -NH₂ groups presented in its structure. These groups can form stronger inter- and intra- molecular H-bonds which lead to a certain regularity of the CS/MWCNT-EA structure and have as result the

appearance of crystalline regions. The graft copolymers XRD patterns CS-Ethyl vacillate exhibit broader and weaker peaks at 2θ = 20.00, implying that these materials were almost amorphous. Thus, the XRD result reveals that the ethyl acrylate chains can interfere with CS ordered packing, most probably by a steric effect which alters the H-bonding.

FTIR

Ftir Studies: Figure 13 shows the FTIR spectra of the graft copolymers in comparison with those of the homopolymers and parent chitosan. The FTIR spectrum of CS (Figure 8) showed features of amide groups: amide I, amide II and amide III bands at 1651, 1524 and 1319 cm⁻¹, respectively. The absorption band located at 1651 cm⁻¹ linked to the acetamide group (-NHCOCH₃) confirms the partial degree of deacetylation of CS. The intense band at 3370 cm⁻¹ is attributed to the overlapping of O-H and N-H stretching vibrations, as well as to intermolecular H-bonds within the polysaccharide. The absorption bands at 1153 cm⁻¹ (anti-symmetric stretching of the C-O-C Bridge), 1073 cm⁻¹ and 1038 cm⁻¹ (skeletal vibrations C-O stretching) are characteristic absorption bands for chitosan polysaccharide structure.

Atomic Force Microscope (AFM): The AFM report of grafted chitosan is shown in the Figure 14. It gives the information which is based on the homopolymers latexes are formed by spherical particles having average diameter ~ 450 nm and ~ 250 nm also confirmed by AFM images. The optical images of graft copolymers: suggest an agglomeration process, this being emphasized mostly in the case of CS/MWCNT-ethyl acrylate sample leading to larger aggregates formation. The hypothesis is sustained by the AFM images.

Mechanism of Grafting Ethyle Acrylate onto MWCNT-CS:

Production of Free Radical: Oxidation:



Initiation:



Propagation:

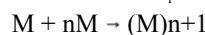
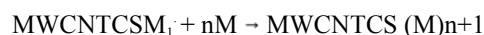




Fig. 15: Anti Bacterial Activities of Grafted CHITOSAN/MWCNT-EA

Termination:

$MWCNTCS (M)_{n+1} + Ce \rightarrow CS (M)_{n+1} + Ce^{3+}$ (Graft Copolymer)

$(M)_{n+1} + Ce^{4+} \rightarrow (M)_{n+1} + Ce^{3+}$ (Homopolymer)

Chain Transfer:

$MWCNTCS (M)_n + Ce^{4+} \rightarrow MWCNTCS (M)_n + Ce^{3+} + H^+$

$CS (M)_n + M \rightarrow CS (M)_n + M$

(Where MWCNTCH, m, CH(M)_{n+1} and (M)_{n+1} represent MWCNTchitosan, Ethyl Acrylate, the graftcopolymer and homopolymer, respectively).

Antibacterial Activities of Grafting Compound: A preliminary study has been carried out to compare the antibacterial activity of grafted chitosan hydrochloride film samples with that of chitosan. Grafted chitosan were efficient in inhibiting the against *Escherichia coli*, *Klebsiella*, *B.cereus*, *E.coli*, *Pseudomonas*. Figure 15 is a photo of a Petri dish showing the zones of inhibition. The highest zone of growth of inhibition occurs at a concentration of 100m %, while the lowest zone of growth inhibition occurs at a concentration of 6.25 %. The antibacterial profile of essential grafting compound of chitosan-ethyl acrylate was studied. Like essential grafting compound was found to be effective against all the four bacteria *B. cereus*, *E. coli*, *klebsiella*, *Pseudomonas*. All the bacteria, tested were inhibited at 100%, 50%, 25 %, 12.5 & 6.25% concentration of essential grafting compound along with control. The result of zone of inhibition after 24 hr was reported in. The essential grafting sample was found to be sensitive against *B.cereus*. The minimum inhibitory concentration was found to be 25% while for essential grafting sample, minimum inhibitory concentration was found to be 12.5%. The zone of inhibition of essential grafting sample for

E. coli with control was 12.60 mm. The essential grafting sample was found to be resistant to bacterium. The zone of inhibition for *Pseudomonas* with control was 11.45 mm. The grafting sample was found to be sensitive against *Pseudomonas*. The minimum inhibitory concentration was found to be 25 %.

CONCLUSIONS

Multiwalled carbon nanotube(MWCNT) was functionalized by oxidation to get the MWCNT-COOH derivative which was treated with thionyl chloride to produce MWCNT-COCL. The thionyl derivative was reacted with chitosan to get MWCNT-CS. Derivative. The MWCNT-CS derivative was grafted onto ethyl acrylate. The grafted polymer composite was characterized by FTIR, SEM, TEM and AFM technique. The antibacterial properties of the grafted polymer was also evaluated.

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