

Grafting Vinyl Monomers onto MWCNT Coupled with Chitosan III: Graft Copolymerization of Methyl Methacrylate onto Chitosan Coupled with Multiwalled Carbon Nano Tube

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Abstract: In the present paper, the vinyl monomer methyl methacrylate(MMA) was grafted onto chitosan-MWCNT-COCL.Acid functionalized with multiwalled carbonnanotubes (MWCNT) were covalently grafted to chitosan by first reacting the oxidized carbon nanotubes with thionyl chloride to form acylchlorinated 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. The grafted samples were characterized using FTIR, SEM, TEM, TGA methods. In this study chitosan has been graft copolymerised with methyl methacrylate (MMA) and the properties of the graft copolymer has been studied. This paper focuses on the synthesis and physico- chemical characterisation of MMA- grafted chitosan copolymer. 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 and antifungal activities of the grafted Vinyl Monomer MMA were also investigated.

Key words: MWCNT • Chitosan (cs) • Methyl Methylacrylate (MMA) • Graft Copolymerization
• Antibacterial • Antifungal

INTRODUCTION

Structure of Carbonnanoubes: Carbon nanotubes are allotropes of carbon with cylindrical structure. these are useful for nanotechnology, electronics, optics and other fields of material science and technology [1]. 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 sp² 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.

Structure of Chitosan: Chitosan or P-(1, 4)-2-amino-2-deoxy-D-glucosei, a hydrophobic biopolymer obtained industrially by hydrolyzing the amino acetyl groups of chitin, which is the main component of shells of crab, shrimp and krill, by an alkaline treatment. The structure of chitosan is shown in Figure 1[3].

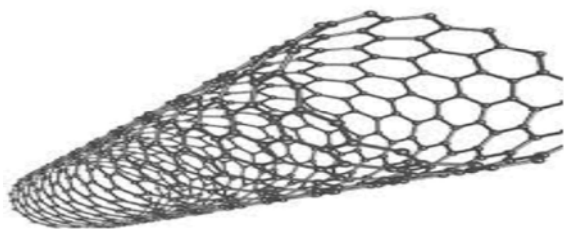


Fig. 1: STRUCTURE OF CARBON NANOTUBE

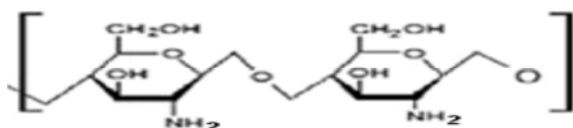


Fig. 2: Structure of chitosan

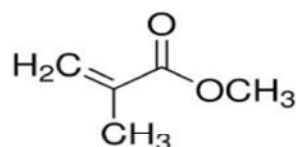


Fig. 3: STRUCTURE OF METHYL METHAACRYLATE

Structure of Methyl Methacrylate (MMA): Methyl methacrylate (MMA) is an organic compound with the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$. This colourless liquid, the methyl ester of methacrylic acid (MAA) is a monomer produced on a large scale for the production of poly (methyl methacrylate) (PMMA) [4].

MATERIALS AND METHODS

Materials: Multi-walled CNT (90% purification) used in this MWCNTs. Subsequently, upon reacting with thionyl study was purchased from Cheap Tubes (USA, 10-20 nm diameter 0. Chitosan (CS) (Degree of Deactivation = 95% determined by $^1\text{H-NMR}$ and Molecular Weight 13.45×10^4 Da) was purchased from India Sea Foods, Kerela, India. Methyl MethaAcrylate(MMA) 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 [5].

Methods

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).

Synthesis of MWCNT-COCL from MWCNT-COOH:

The MWCNT was treated with thionyl chloride ($-\text{SOCl}_2$) for 24h at 60-75. This results corroborated the successful carboxylation of MWCNTs. Subsequently, upon reacting with thionyl chloride ($-\text{SOCl}_2$), the $-\text{COOH}$ was transformed into acyl chloride functional groups and the distinctive stretching vibration of $-\text{COCl}$ should have been observed [6].

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 [7].

Graft Copolymerization: A chitosan aqueous solution of 2 wt % was prepared by dissolving 20 g of chitosan powder in 1000 mL of acetic acid solution (1%, v/v). After 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 Methyl Acrylate 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 [8]. In atypical reaction, Chitosan (0.006-0.025 mol; 1-4 g) was dispersed in a definite volume of water with constant stirring and bubbling of a slow stream of nitrogen for 30 min at the desired temperature (20-400C) [9]. After 30 min, a freshly prepared 10 mL solution of CAN (0.02-0.06 mol, 0.11-0.33 g) in nitric acid (0.1-0.4N) was added and stirred for 10 min. Nitrogen gas was continuously passed through the reaction mixture and AN (0.091-0.152 mol, 6-10 mL) was added. In all the reactions, total volume of the reaction was kept constant. 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.

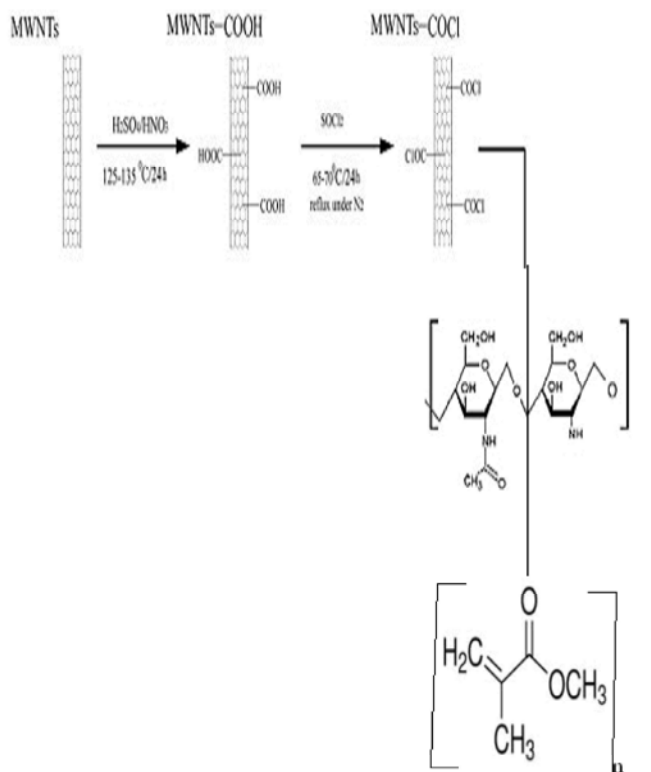


Fig. 4: GRAFTING OF METHYL METHAACRYLATE ON MWCNT- CHITOSAN

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 400C. The dried product was extracted with dimethyl formamide for 48 h and washed with methanol to remove the homopolymer (polyacrylonitrile). The grafted Chitosan (Chitosan-g-MA) was dried to a constant weight [10].

Mechanism: The mechanism of graft-copolymerization onto chitosan is depicted in Fig. 4.

Characterization

Ftir Analysis: Figure 5 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 [11].

NMR Studies: In Figure 6, 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 [12].

X-Ray Diffraction: In this Fig 7 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 [13].

In this Figure 8 shows 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 [14].

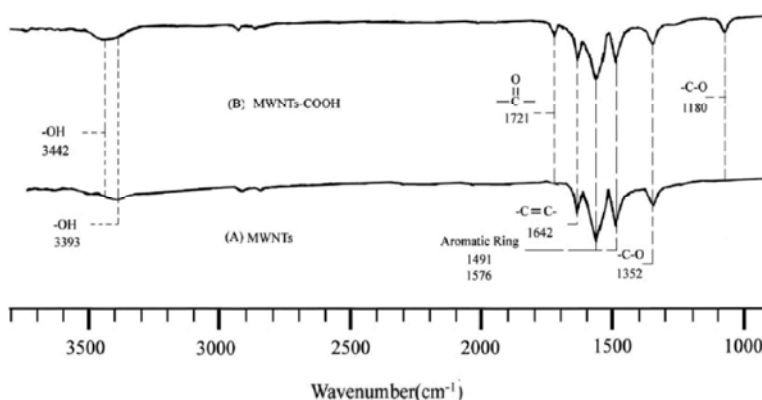


Fig. 5: FTIR spectrum of (A) MWCNT (B) MWCNT-COOH

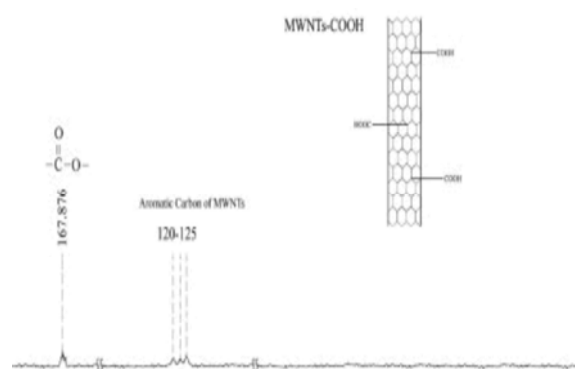


Fig. 6: NMR of MWCNT-COOH

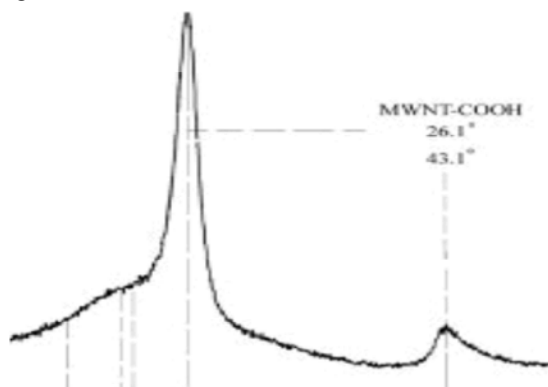


Fig. 7: X-RAY DIFFRACTION OF MWCNT -COOH

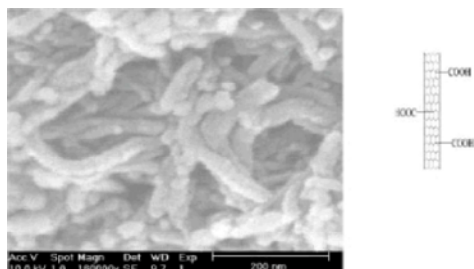


Fig. 8: SEM MICROGRAPH OF MWCNT-COOH

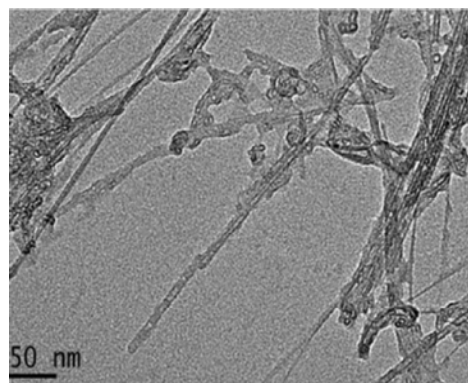


Fig. 9: TEM of MWCNT-COCL

Transmission Electron Microscope Studies of MWCNT-COCL: In this Figure-9 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 [15].

SEM Studies of MWCNT-COCL: The Fig 10 shows 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.

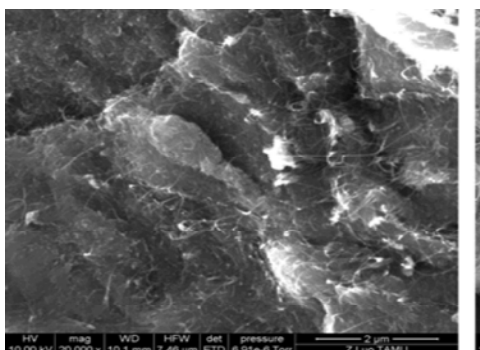


Fig. 10: SEM OF MWCNT-COCL

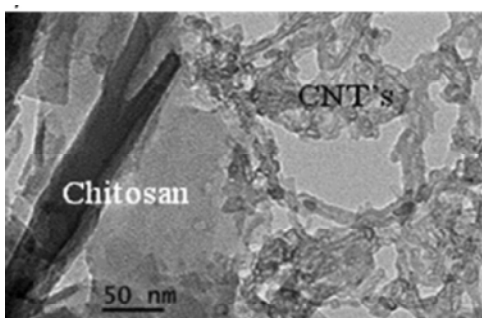


Fig. 11: TEM OF MWCNT-CHITOSAN

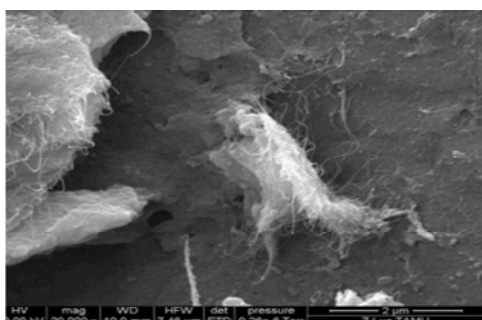


Fig. 12: SEM of MWCNT-CHITOSAN

Transmission Electron Microscope (TEM) of MWCNT-CHITOSAN: The Fig 11 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.

SEM Studies of MWCNT-CHITOSAN: The Fig 12 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 [15].

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.

TGA Analysis: In the Fig 13 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. 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.

In the Figure 14(a) shows that methyl methacrylate (MMA) was dispersed onto chitosan/MWCNT surface. In the Figure-11(b). there is sufficient deposition of methyl methacrylate on to the chitosan/MWCNT matrix. In the above figure there is a clearly distinguished between grafted and ungrafted chitosan [16].

X-Ray Diffraction: This Figure 15 reveals that IR spectrum of the grafted chitosan -MMA matrix showed a broad peak at 3422.8 cm^{-1} due to bonded -OH group and at 2918.8 , 1653.5 and 1058.7 cm^{-1} arising from -CH₂, C-C and C-O stretching respectively.

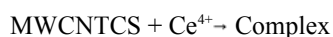
Mechanism of Grafting:

Initiation:

- Direct oxidation



Formation of Complex:



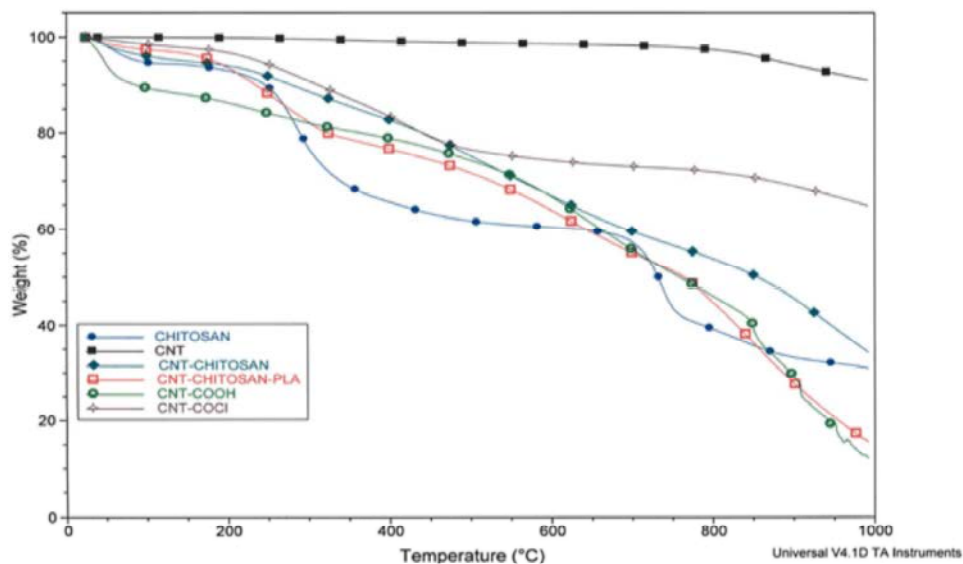


Fig. 13: TGA ANALYSIS OF MWCNT, MWCNT - COOH, MWCNT-COCL, MWCNT - CHITOSAN

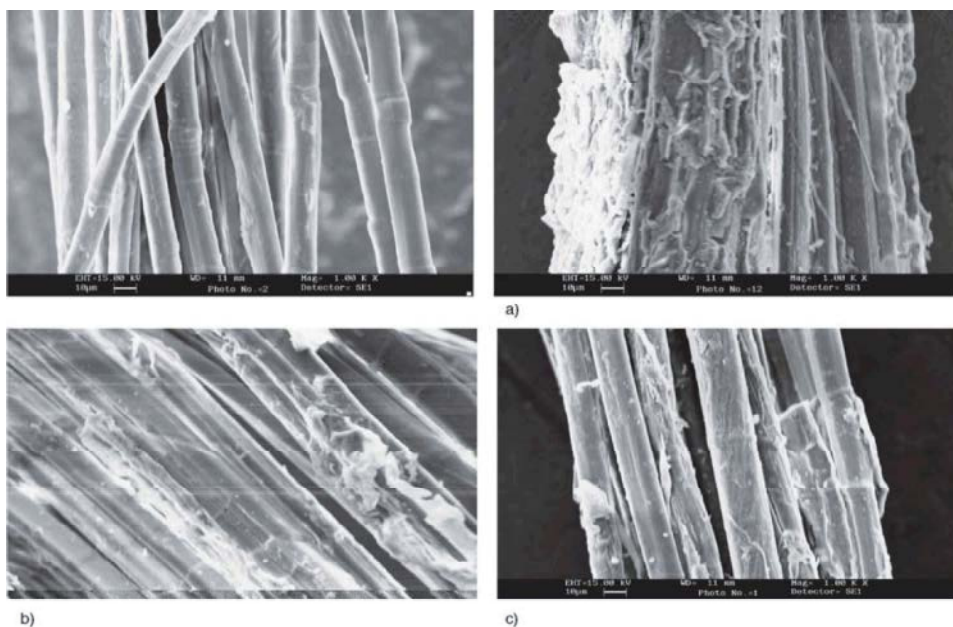


Fig. 14: SEM of methyl methacrylate onto chitosan/MWCNT

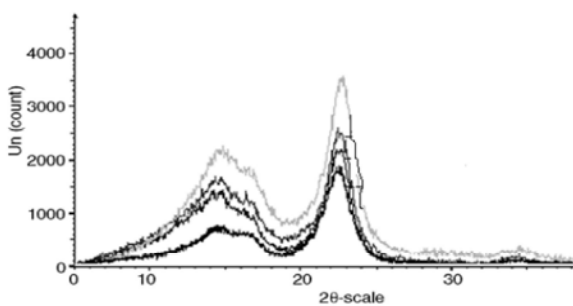


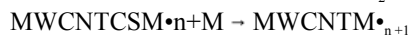
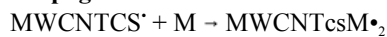
Fig. 15: x-ray diffraction of MWCNT/chitosan-MMA



where CS is chitosan

CS^{\bullet} is chitosan chain radical, M is Vinyl monomer

Propagation:



Where $\text{MWCNTCSM}^{\bullet_n}$ is the propagating chain

Termination: $\text{MWCNTCSM}\cdot\text{n} + \text{p}\cdot \rightarrow \text{MWCNTCSMn+p}$
where p indicates all the propagating chain,

$\text{P} = \text{MWCNTCS}\cdot + \text{Mn}$

$\text{M}\cdot\text{n}$ is the chain radical

Chain Transfer: $\text{MWCNTCSM}\cdot\text{n} + \text{ce}^{4+} \rightarrow \text{MWCNTCSMn} + \text{Ce}^{3+} + \text{H}^+$

The monomer conversation was found to be between 70 & 80% after 2 hours of reaction at 60°C. The grafting efficiency is increased with the increasing of chitosan molecules & only took part in the graft copolymerization. The experimental results indicate that chitosan molecules used not only took part in the graft copolymerization but also used as a surfactant providing stability of the dispersed particles.

Anti Bacterial Activities of Grafted MMA ONTO

Chitosan- MWCNT: A preliminary study has been carried out to compare the antibacterial activity of grafted chitosan hydrochloride film samples with that of chitosan. The study was carried out against *P. aeruginosa*, *E. coli*, *B. subtilis* and *S. aureus* using the inhibition zone method. It was observed that grafting improved the antibacterial activity of chitosans. While the inhibition zone diameter for chitosan film ranged between 9 and 11 mm against indicated bacteria, the inhibition zone increased up to 17 mm (against *B. subtilis*) by grafting. Although the difference is not significant, activity of gram-positive bacteria seems to be more pronounced; increase in the inhibition zone diameter is 4 - 5 mm in gram-negative ones whereas it is 5 - 7 mm in gram-positive ones. Grafted samples showed an increasing antibacterial activity as the degree of grafting increased for all of gram-negative and gram positive bacterial; a minimum of 2 mm increase was observed consistently when the grafting percentage increased from 82.5% to 145%. Average film weight (thickness) also affected the degree of antimicrobial activity of both chitosan and grafted chitosan samples. And 3 - 4 mm increase was observed when the average compound weight was increased from 134 to 296. Antibacterial activities of Grafting CS/MA Compound minimal inhibitory concentration (MIC) mg/ml.

Antifungal Activity: Antifungal activities of Grafting compounds Minimal inhibitory concentration (MIC) mg/ml. Further the grafting compound was found to be highly toxic against clinically isolated fungal species.

At a concentration of 50 µg/ml grafting compound revealed a higher antifungal activity against *C. albicans*, *Candida kefyr*, *Aspergillus niger* whereas intermediated activity were showed against *C. tropicalis*, *C. krusei*, *A. flavus*, *A. fumigatus*. The inhibitory activities of the entire grafting compound. The data results were compared with the standard antimicrobics of Ketoconazole (30 mg) and Itraconazole (30 mg).

CONCLUSION

The sized grafting of vinyl monomer MMA onto Chitosan-MWCNT was demonstrated. The antibacterial and antifungal activity of the grafting chitosan was studied. The SEM, TEM, FTIR, TGA OF the MWCNT, MWCNT-COOH, MWCNT-COCL and MWCNT-CHITOSAN was studied. The SEM and X-RAY diffraction of the grafted MMA onto chitosan-MWCNT was studied.

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