Synthesis and Characterization of Carbon Nanotube Hydroxypropyl Methylcellulose Composites

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Abstract. In tissue engineering especially, aqueous injectable, untouched gel-forming systems, possessing variety of advantages has been an attention seeker for the industry when compared to scaffolds. In-situ gel forming matrix can be introduced easily to the defect sites through needle, because of which surgical implantation can be removed first. Secondly, the ease of conformity upon introducing on the surroundings, and introducing easily on cells, and can be introduced as therapeutic agents and growth factors by simple mixing, without any afflict about residual solvents commonly used in scaffolds, when combined. For which, Multi-walled Carbon Nano-tubes has been acid functionalized which then covalently grafted on Hydroxypropyl methylcellulose (HPMC) by the Oxidized Carbon Nano-tubes, to form acyl-chlorinated carbon nano-tubes which has been firstly reacted with thionyl chloride and later dispersed in HPMC to form composite material, MWCNTs – HPMC, several time has been washed multitudinous to eliminate not reacted materials. FT-IR, TGA, SEM and TEM are used for the characterization of the composites, and which shows that it exhibits enhanced thermal stability.

Keywords: CNT, MWCNTs, HPMC, FT-IR, TGA, SEM and TEM

1. Introduction
Composites having at least one of the phases shows dimensions in the nanometer range (1 nm = 10^-9 m) are termed as Nano-composites [1]. They are superior materials show surprising property mixes and remarkable design prospects with an expected yearly growth rate of about 25% and quickest demand to be in engineering plastics and elastomers, their latent capacity is striking to the point that they are valuable in a few regions extending from bundling to biomedical application [2]. Mechanical properties of graphene have revealed that it plays an important role in the improvement in the overall properties of polymer nano-composites which can be used in the different areas of applications [3]. These days, nano-composites offer new innovation and business open doors for all segments of industry, notwithstanding being environmental friendly [4]. According to matrix materials present in the case of micro-composites, nano-composite materials can be further classified into the following three different categories. They are (a) Ceramic Matrix Nano-composites (CMNC); (b) Metal Matrix Nano-composites (MMNC) and (c) Polymer Matrix Nano-composites (PMNC).

Since early 90’s, the study of nano-composite system along with those reinforced with CNTs has been an area of interest, but are having only few reviews and paper publications on CMNC. Dispersion of only 1.0% AFMWCNTs in the matrix improved the Young’s modulus and tensile strength of carbon fiber/epoxy composites by 49% and 52%, respectively. Similarly, the ILSS and flexural strength improved by 37% and 38%, respectively [5-8] and MMNC [9]. However, considering PMNC,
processing aspects, conducting and biodegradable polymer-based systems [10-12], fiber reinforced [4, 6] morphology/property/structure aspects [5, 11-13], along with the various uses, their applications, and perspectives, including pivotal opportunities and obstacles in developing structural and functional fiber nano-composites [12, 14]. In this researcher study about using grey relational analysis, Multi-objective optimization design of die-sinking electric discharge machine (EDM) machining parameter for CNT-reinforced carbon fiber nano-composite [15]. Some of the properties such as lightweight, ductile nature and ease of production, make the Polymer materials used extensively in industry. On the other hand, decenniums of research passed, potential as package of biomedical applications of CNTs are yet less known, which results in gigantic obstacles and chances that can be expected for the system. These are based on the following:

- CNTs with minimal defects,
- Research is flourishing in CNT-related areas,
- Due to hollow nature, heterogenic materials embracing biological molecules, can be filled in CNTs [16],
- Nano-reinforcements with biodegradable polymers helps significantly in designing environmental friendly ‘green materials’ for subsequent applications etc.

In this study, the effects of functionalized graphene as an addition of cross-linked epoxy resin LY 556 were studied using MD simulation. Three different types of cross-linked epoxy systems were used for analysis, of which one has pristine graphene and two have different functional groups (NH2-graphene and COOH graphene) [17]. There are wide varieties of polymer resins supporting a dramatic refinement in their biodegradability. In this context, hydroxyl-propyl methylcellulose (HPMC) was used as matrix material for the nano-composite preparation. Hydro-mellose, short for hydroxyl-propyl methylcellulose (HPMC), is one of the derivatives of cellulose (i.e cellulose ether) and is synthesized from alkali treated cellulose that is reacted with methyl chloride and propylene oxide. They are inert, visco-elastic type semi-synthetic polymers. Their excellent biocompatibility, non-toxicity and bio-reabsorb ability [18] This paper investigated the effect of AF-MGLs on improving the tensile modulus, strength and glass transition temperature of AF-MGL/EpC nano-composites. In this work, AFMGLs were mixed from 0 to 6.0 wt. % in the epoxy matrix [19], make them usable in multifarious areas such as tissue engineering, food additive, textiles, and pharmaceuticals. HPMC in addition is an aqueous soluble polymer used for coating tablets which protects drug intact and allow drug to release as quickly as it reaches the gastric environment [20]. In this paper researcher understanding the modeling and MD simulation of graphene and graphene based polymer nano-composites [21]. Super-strong lightweight CNT structures incorporated into HPMC matrix provides novel approach in designing high performance composite materials possessing higher mechanical and thermal properties. Hybrid composite comprising of AF-MLG and Af- MWCNT (1:1 ratio) fillers with 0, 0.25, 0.50, 1.0 and 2.0 weight percentage in epoxy resin is successfully fabricated by solilication method. Investigation of tensile and flexural properties is performed along with characterization of hybrid composite has been done through SEM, TEM, XRD, FTIR and TGA analysis [22-24]. Although, across nanotube/polymer interface, the atomically smooth graphene surface of nano-tubes result of weak Vander Waal’s interfacial bonding between covalent grafting of CNTs to HPMC, so as to form CNT-HPMC nan0-composites. Especially for controlled release drug delivery, three step methods for synthesizing CNT-HPMC composites have been reported.

2. Experimental

2.1. Materials
MWCNTs (purity, >98%, length, >50 um, diameter, 20-40 nm were synthesized by CVD technique given in the procedure using Fe-Mo/MgO catalyst, prepared by combustion technique. Hydroxy-propyl methylcellulose (Thomas backer, Mumbai), nitric acid, sulphuric acid, and thionyl chloride used in analytical grade reagents as received.
2.2. Instruments and Measurements

E FT-IR (Perkin-Elmer FT-IR spectrometer) in KBr pellets (0.0051 gm of samples with 0.1 gm KBr) Scan No. 36, resolution 2 cm⁻¹ in the range of 400-4000 cm⁻¹ has been utilized for confirming the existence of functional groups in HPMC and its derivatives. Pellets are prepared by using Freeze-dried samples and KBr. Analysis of thermal stability was carried in a Thermo gravimetric analyzer (TGA) SDT Q600 and instruments used for analysis was Universal V4.1D TA. Within the temperature range of 30°C to 800°C runs were carried out and at a constant rate of 20°C/min it consist a ramp. And nitrogen flow rate is being conserved at 60 ml/min. JEOL 2010 microscope has been used to obtain the Scanning Electron Microscope (SEM) images which were operated at 20.0 kV; from a thin film which is being dispersed in an ethanol solvent on a holey carbon grid a SEM image is formed. CM200 Philips microscope was used to perform Transmission Electron Microscopy (TEM) at 200 kV. The sample was grounded in a mortar and suspended in ethanol, Examination is being done in a CM200 Philips microscope for characterization of CNTs by placing the drops on a holey carbon grid.

2.3. Synthesis of MWCNT-HPMC nano-composites

2.3.1. Synthesis and Purification of CNTs

Using combustion method Fe-Mo/MgO catalysts were developed, Fe(NO₃)₃.9H₂O, (NH₄)M₀₇.024.4H₂O and Mg(NO₃)₂.6H₂O stoichiometrically mixed in desired proportions for forming viscous precursors along with on adding calculated amount of PEG 200. To yield 5:0.5:70 (mass ratio), paste like-material is made by dissolving of mixture rigorously. After which it was heated up to 550°C for 10 minutes in a muffle furnace right after transferring it to a quartz boat. Obtained foamy material was then ground to a fine powder after letting the boat to cool at room temperature.

200 mg of Fe-Mo/MgO catalyst was consistently circulated in a quartz boat and was embedded into the center of the quartz tube while the N2 gas (99.9% purity) flow was kept up for 30 min at a flow rate of 140 ml/min. The temperature of the reaction was fixed at 800°C. Hence, acetylene gas (99.99% purity) was then passed at a rate of 60 ml/min for 30 min through the reaction chamber while N2 gas flow rate was kept up at 140ml/min. The furnace was permitted to cool to ambient temperature under a N2 atm. The sample was collected as black powder from the quartz boat. The samples were filtered by 2 stages: (I) Dipped in 36% HCl and afterward ultrasonically vibrated for 30 min, which dodges the impact of MgO support. The supernatant fluid was emptied by centrifugation. (ii) The solid was dried via air oxidation at 500°C to dispose of the amorphous carbon.

Carbon deposit before and after purification was analyzed from the following formula:

\[
\text{Carbon yield} = \left( \frac{\text{wt loss by carbon oxidation}}{\text{% of residue after oxidation}} \right) \times 100\%
\]

The purity of the CNTs prepared in this technique is approximately 98.6%.

2.3.2. Preparation of CNT hydro-mellose composites

To yield carboxylic acid functionalized MWCNTS (CNT-COOH) CNTs were oxidized with a 3:1 H₂SO₄:HNO₃ for a whole day (24 hours). On reaction with thionyl chloride at 750°C for 24 hours while refluxing, formyl chloride (CNT-COCI) has been obtained from the carboxylic acid group. Thionyl chlorinated MWCNTs (20 mg) after solicitation for a time period of 20 minutes in hydroxyl-propyl methylcellulose solution (40 mg in 0.2 M aqueous NaCl, 40 ml) and at room temperature it has been stirred for 16 hours. For the removal of unbound HPMC, by the process of ultracentrifugation, the modified MWCNTs were collected and washed with purified water and for obtaining MWCNT-HPMC composites drying has been done at room temperature.

3. Results And Discussion

3.1. FT-IR analysis

Infrared (IR) spectroscopy is a widely used method for characterization of chemical bonds. On comparing the IR spectra of CNTs taken before and after functionalization will appear, if pristine bonds were created. The spectra were taken from purified CNTs and functionalized CNTs (CNT-COOH, CNT-COCI and CNT-HPMC composites) samples were pressed in pellets with KBr powder.
(Fig. 1). In comparison with IR spectra of decontaminated and acid oxidized CNTs [Fig. 1(a) and (b)], the peak at 3370 cm⁻¹ because of intermolecular H-bonded O–H stretch before oxidation with acids shows a less intense absorption, then it becomes very broad and more intense absorption peak in Fig. 1(b)). The small and less intense peak at 1623 cm⁻¹ is correlated with the absorption frequency of the olefinic (C=C–C=C) double bond in conjugation with carbonyl group.

![Figure 1. FT-IR spectra of (a) purified CNT, (b) CNT-COOH, (c) CNT-COCI and (d) CNT-HPMC composite](image)

O-H bending deforms in -COOH groups, as a result of which peak has been identified at 1385 cm⁻¹. Therefore, it proves that the C=C groups in CNTs are disappeared and they are readily bonded with carboxylic acid (-COOH) groups. Furthermore, in Fig. 1 (a), the more intense and very sharp peak seen at 2363 cm⁻¹ is because of non terminal C=C stretching present CNT framework. This peak is completely disappeared in the FT-IR spectrum of CNT-COOH. Therefore, it proves that the C=C groups in CNTs are disappeared and they are readily bonded with carboxylic acid (-COOH) groups and hydroxyl (-OH) groups. Because functionalization, the generation of -OH and -COOH groups on CNTs is confirmed. Furthermore, it shows that KMnO₄ is capable of opening the n-bonds of MWNTs. The presence of -Cl group with -C=0 has been credited by 1657 cm⁻¹ and the wide locale between 850–550 cm⁻¹ because of C-Cl extending vibration demonstrates the presence of -COCl after thionyl chloride treatment with CNT-COOH (Fig. 1(c)]. In the CNT-HPMC, the 3451 cm⁻¹ peak is more widen, because of broad hydrogen bonding, and an inconspicuous energy shift in the -C=O stretched to 1599 cm⁻¹. Peaks inferable from B (1,4) glycosidic bonds and C-O-C extended vibration was changed to 1124 cm⁻¹, respectively (Fig. 1(d)].

3.2. Electron imaging analysis

Investigation morphology and sizes of the purified and functionalized CNTs has been done by scanning electron microscopy. SEM image of purified CNTs (Fig. 2(a)] portrays that the uniform orientation of CNTs without any noticeable defects. The nano-tubes show up as straight rods with their sizes shifting between 20 - 41 nm in diameters and a few micrometers long; however some bent tubes can likewise be seen.

SEM was also used to investigate the carbon nano-tube sample after modification with -COOH, -COCI and HPMC. As shown in Fig. 2(b) the morphology of carbon nano-tubes after oxidation with acids is preserved. Some destruction was observed, which means carbon nano-tubes are broken by the strong acids. Presence of CNTs in micron length in fig.2c and the bonding with hydro-melllose (HPMC) of functionalized CNTs in fig.2d can be identified by the SEM of CNT-COCI, and distinct agglomeration of CNTs can be observed at the surface texture of the CNT-HPMC, within the regions of HPMC it has been cloistered, more hydrophobic phase likely.
Figure 2. SEM images of (a) purified MWNTs, (b) CNT-COOH, (c) CNT-COCl and (d) CNT-HPMC composite

On comparing the TEM (Fig. 3b) of the coating of HPMC on CNTs and CNT-COCl, it can be seen clearly that coating on CNTs are quite visible. A substantial examination that functionalized CNTs has joined to the surface of HPMC.

Figure 3. TEM micrographs of (a) CNT-COCl and (b) CNT-g-HPMC

3.3. Thermal Analysis

Fig.4. portrays the thermal behaviour of CNT and CNT-HPMC composites. As-blended CNTs, at 800°C, weight reduction demonstrated was under 1%, which demonstrates the defect-less and immaculateness of the nanotubes. The acid oxidation of CNTs which presents -COOH functional groups made more deformities. It demonstrated a complete weight reduction of about half at 800°C. All things considered, corrosive oxidation utilizing concentrated H2SO4/HNO3 blends additionally prompted cutting of CNTs and the production of more deformities in their destinations. At 800°C it is obviously seen that the weight reduction is half. Beneath 450°C, Two particular weight misfortunes can appear in the thermal analysis of pure HPMC. In HPMC the 20% weight reduction found can be credited to methyl and propyl side groups. Subsequently, it very well may be seen that the thermal
stability of HPMC has been upgraded within the sight of CNTs. Oxidative expulsion of glycosidic linkage has been credited and between 600 to 800°C the second weight reduction happened.

![TGA analysis](image)

**Figure 4.** TGA analysis

4. Conclusion
The limitations of CNT-based system had been eliminated and a highly effective drug delivery system has been developed and is based on the functionalized MWCNTs. Covalent functionalization of CNT-HPMC had been used to obtain nanotubes. Thermal properties had been enhanced by the incorporation of CNTs in HPMC. Confirmatory analysis had been done by FTIR, SEM, and TEM of the bonding of CNTs and HPMC. In further research scopes the reduction in toxicity which helps in reducing side-effects in the patient and the amount of drug to be applied can be controlled for the application in drug delivery. In addition HPMC groups attachments on the caps and walls of MWNTs opens up the path of studying or innovate the way of raw MWNTs to more derivatives. And variety of applications in medical fields can be obtained by manipulating CNT materials.

5. References

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