

## **Covalent Attachment of 12-Hydroxy Stearic acid on the Surface of CNT**

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**ABSTRACT:** 12-hydroxy stearic acid is grafted on to multiwalled carbon nanotubes (MWCNTs) using melt condensation techniques. The functionalized MWCNTs were reacted with homopolymers through insitu polymerization. The attachment of 12-hydroxystearic acid homopolymer chains to the MWCNTs were confirmed by thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), *transmission electron microscopy (TEM)* and *atomic force microscopy (AFM)*.

*Keywords: Grafting; MWCNT; Melt condensation; 12-HSA; Polymer; Biodegradable*

### **INTRODUCTION**

The functionalization of carbon nanotubes (CNTs) and covalent grafting using monomers and polymers has attracted much recent attention for their potential application. The surface modification of carbon nanotubes has mainly been focused to enhance their chemical compatibility and dissolution properties.<sup>1-5</sup> Sun and coworkers showed that esterification of carboxylic acid can also be applied to functionalize and solubilize nanotubes of any length.<sup>1,6-7</sup> An advantage with ester linkages is that they can be facilely difunctionalized via acid or base- catalyzed hydrolysis, allowing the recovery of carbon nanotubes from the soluble samples.<sup>7</sup> There is now ample experimental evidence for the conclusion that the nanotubes bound carboxylic acid are the site to attach a variety of functional groups for the solubilization of both shortened and full-length carbon nanotubes.

Carbon nanotubes are considered to be ideal reinforcing agent for high strength polymer composite, because of their tremendous mechanical strength (Pan et al.<sup>8</sup> obtained Young's modulus of  $0.45 \pm 0.23$  TPa, tensile strength of  $1.72 \pm 0.64$  GPa, strain (12 %) <sup>9</sup>, high electrical conductivity ( $0.1 \text{ S.cm}^{-1}$ )<sup>10</sup> and high aspect ratio.

## EXPERIMENTAL

*Materials:* The MWCNTs used in this study were synthesized by thermal chemical vapour deposition (CVD) method. The purity of the pristine MWCNTs, 12-hydroxy stearic acid was purchased from Aldrich Sigma, tin chloride dihydrate from Aldrich Sigma and chloroform from SD Fine Chemicals (India).

*Purification of MWCNTs:* To eliminate the impurity in the MWCNTs such as metallic catalyst, they were treated in a mixture of 3 M HNO<sub>3</sub> and 1M H<sub>2</sub>SO<sub>4</sub> at 60 °C for 12 h, followed by refluxing in 5 M HCl at 120 °C for 6 h. The purity of acid treated MWCNTs was measured to be 99 % using TGA (TGA-7 Perkin Emmler). These acid treatments are known to introduce carboxylic and hydroxylic functional groups onto the surface. The functionalized MWCNTs (FMWCNTs) were filtered and washed with large amount of water and then vacuum dried at room temperature overnight.

## CHARACTERIZATION

*Thermogravimetric Analysis:* Thermal stability was analyzed using Perkin-Elmer TGA-7, by heating the samples from 50–800 °C with a heating rate of 10 °C/min under nitrogen atmosphere with a flow rate 20 mL/min.

*Scanning Electron Micrograph (SEM):* SEM was taken on a gold-coated surface of polymer sample after careful washing and drying by using a Leica Cambridge Stereo scan Model 440.

*Transmission Electron Microscopy (TEM):* Samples solution in DMF after sonication for TEM imaging were made on copper grids were kept overnight on filter paper for drying. TEM imaging was done using a JEOL 1200EX electron microscope operating at an accelerating voltage of 80 kV-120 kV. Images were captured using charged couple detector camera and viewed using Gatan Digital Micrograph software.

*Atomic Force Microscopy:* AFM experiments were conducted with a PicoSPM equipped with a fluid cell and an environmental chamber (Molecular Imaging, Phoenix, AZ) and controlled by a Nanoscope III electronics (Digital Instruments, Santa Barbara ,CA). Silicon nitride cantilevers with a nominal spring constant of 0.1 N m<sup>-1</sup> and an integrated pyramidal tip whose nominal apex radius was typically equal to 50 nm (Microlever, Thermo Microscopes, and Sunnyvale, CA). All AFM measurements were performed in

either nitrogen atmosphere or water rather than in air to eliminate or at least significantly reduce capillary forces.

## RESULT AND DISCUSSION

The surface bound carboxylic groups on MWCNTs was used as template, 12-hydroxy stearic acid were attached to the MWCNTs through ester linkage using dehydropolycondensation method. Using a silylated R.B flask, requisite amount of 12-hydroxy stearic acid and functionalized multiwalled carbon nanotube (FMWCNTs) and catalyst (tin chloride dihydrate 0.2 wt %) were added followed by heating the reaction mixture slowly. The reaction was allowed to proceed at a temperature of 145 °C for 20 h under vacuum. The reaction mixture was washed with chloroform several times to remove the unbound homopolymer filtered under vacuum through 0.22 μm polytetrafluoroethylene (PTFE) membrane to yield corresponding grafted homopolymers.

*Grafting of homopolymer on the surface of MWCNTs:* The grafting of homopolymer was carried out by taking silylated three-neck flask. The reaction mixture was cooled up to 50 °C and 5 mol % of 12-hydroxystearic acid, FMWCNTs and tin chloride dihydarte were added in to it.

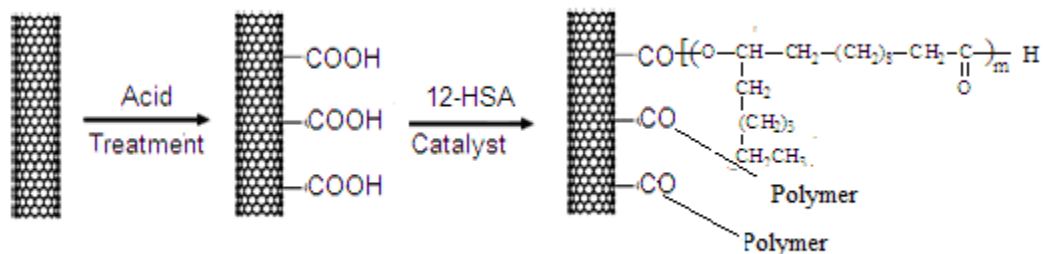


Figure-1: In situ grafting of 12-hydroxy stearic acid on the surface of MWCNTs.

*Thermo gravimetric analysis:* The homo polymer- grafted MWCNTs were pyrolyzed under an atmosphere of nitrogen and shown in figure 2. The homopolymer began to degrade around 220 °C and complete degradation occurred around 415 °C. After 800 °C , the weight percentage curve leveled at % (figure 2). The weight loss was determined to

be 45.43 %. TGA curve of homopolymer, degradation began around 135 °C and completed at 415 °C.

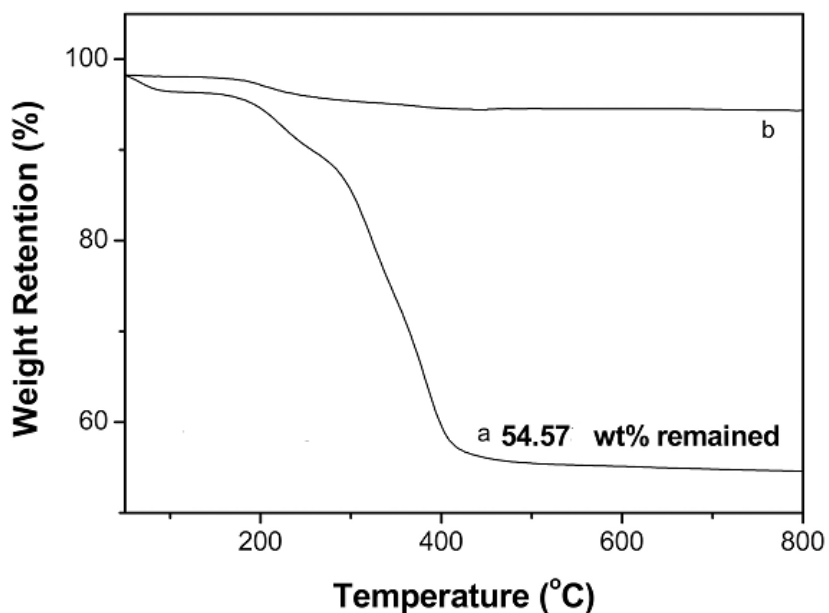


Figure 2: (a) TGA curves of grafted homopolymer and (b) TGA curve of FMWCNT.

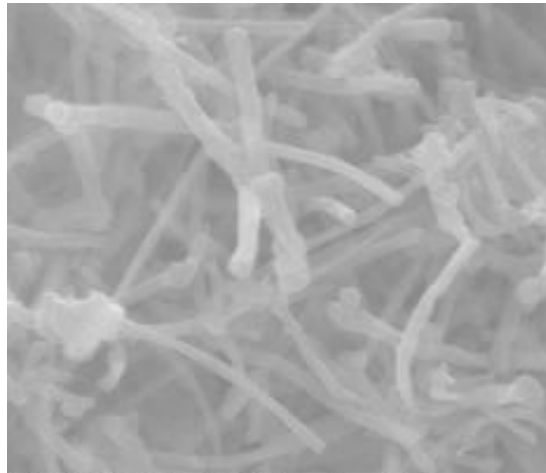


Figure 3: SEM of grafted homopolymer of 12-HSA on MWCNTs.

*Scanning electron microscopy:* Figure 3 shows the SEM image of grafted homopolymer (12-HSA). The images provided evidence of chemical linkage between homopolymer and MWCNTs. It is clearly evident from spectral analysis that the homopolymer molecules were grafted on the surface of MWCNTs during dehydropolycondensation.

These images demonstrated high MWCNTs content, for the material samples showed good dispersibility in chloroform, dichloromethane and acetone.

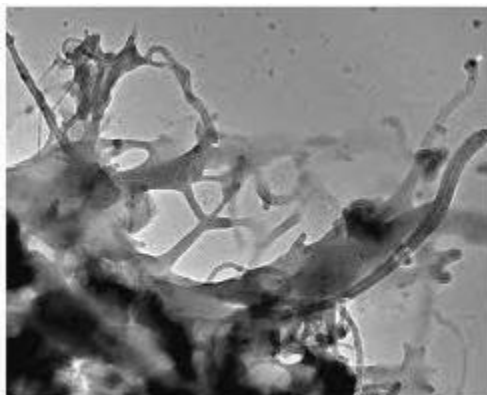


Figure 4: TEM of grafted homopolymer on MWCNTs.

*Transmission electron microscopy:* Transmission electron microscopy was used to directly image of grafted homopolymer on MWCNTs. The TGA traces indicates that the grafted homopolymer content was approximately 45.43%. TEM images provide confirmation of unbundling of grafted homopolymer on MWCNTs

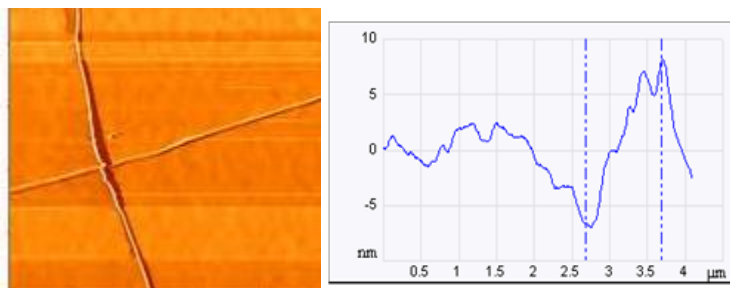


Figure 5: AFM images of homopolymer grafted on MWCNTs.

*Atomic Force Microscopy:* Figure 5 displays AFM image of the surface of homopolymer grafted MWCNTs formed on the topographic patterns comprised of 10 nm in height and side length ranging from 0.5 nm to 4 μm. Surface patches are formed randomly distributed employing that the presence of side chain hanged at 12-position in the homopolymer grafted on MWCNTs.

## CONCLUSION

Homopolymer of 12-HSA have been successfully grafted on the surface of MWCNTs by melt-polycondensation and thoroughly characterized. The maximum level of grafting was observed as 45.43 wt %. In principle, this insitu dehydropolycondensation is feasible for

a wide range of biocompatible and biodegradable monomers (aliphatic hydroxyl carboxylic acid). Such microstructure would account for the homogeneous distribution of MWCNTs and improve mechanical and electrical properties of the polymer.

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