In this work copolymer of L-lactic acid and 12-hydroxy stearic acid is grafted on to multiwalled carbon nanotubes (MWCNTs) using dehydropolycondensation techniques. In order to introduce functional groups, MWCNTs were functionalized. The functionalized MWCNTs were reacted with copolymers through insitu polymerization. The attachment of copolymer (L-lactic acid-co-12-hydroxystearic acid) chains to the MWCNTs were confirmed by FTIR, TGA, scanning electron microscopy (SEM), transmission electron microscopy (TEM).

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.1-5 The carbon nanotubes are classified as SWNTs, DWNTs and MWNTs depending upon number of rolled sheets and are conducting or semi conducting depending upon the chirality of the tubes. The CNTs can be dispersed in the polymer matrix by a variety of techniques, such as direct mixing, insitu polymerization, solution blending and also melt blending. Carbon nanotubes particularly MWCNTs have diameter in the range of 2-60 nm for the innermost tubular layer and in additional thickness of 0.7 nm for every extra layer. The covalent grafting of organic or polymeric molecules on to the MWCNTs has been accomplished by the “grafting to” technique by using esterification and amidation reactions.1 However the loss in conformational entropy of the polymer significantly suppresses chains from diffusing to and reacting with carboxylic acid sites of MWCNTs, which leads to insufficient grafting. The polymer wrapping and “pi-pi” stacking on the surface of carbon nanotubes due to non covalent functionalization methods are difficult to correlate quantitively with properties due to the presence of excess polymer chains from covalently attached surface functional groups by using the “grafting from” method is the best way to produce polymer brushes on any surface.

Sun and coworkers showed that esterification of carboxylic acid can also be applied to functionalize and solubilize nonotubes of any length.1, 6-7 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.7 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.8 obtained Young's modulus of 0.45±0.23 TPa, tensile strength of 1.72±0.64 GPa, and strain (12 %).9 high electrical conductivity (0.1 S.cm-1)10 and high aspect ratio.

Biocompatible polymers such as poly caprolactone, chitosan and poly lactide have also much attention because of their biomedical applications for example, and electric field is known to stimulate the healing of various tissues. In case of bone fracture healing, the use of an electric field was based on the observation that, when a bone was subjected to mechanical load (stress) deformation of bone (strain) is normally...
accompanied by an electrical signal bearing the strain characteristics.
Methodology for chemical modification of CNT with polymer can be classified in to ‘grafting to’ and ‘grafting from’ methods. “Grafting to” means that polymer first prepared and then linked through a covalent bond to the surface of CNT, ‘grafting from method’ means polymerization of monomers on the surface through functional groups.

In this study, we highlight copolymer of L-lactic acid and 12-hydroxy stearic acid grafted on to multiwalled carbon nanotubes (MWCNTs) using dehydropolycondensation techniques. In order to introduce functional groups, MWCNTs were functionalized. The functionalized MWCNTs were reacted with copolymers through insitu polymerization. The attachment of copolymer (L-lactic acid-co-12-hydroxy stearic acid) chains to the MWCNTs were confirmed by FT-IR, TGA, scanning electron microscopy (SEM), transmission electron microscopy (TEM).

EXPERIMENTAL
Materials: The MWCNTs used in this study were synthesized by thermal chemical vapour deposition (CVD) method. The purity of the pristine MWCNTs was > 95 %. L-lactic acid (88% aqueous solution) was purchased from PURAC, USA. 12-hydroxy stearic acid was purchased from Aldrich Sigma, tin chloride dihydrate from Aldrich Sigma, xylene 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 HNO₃ and 1M H₂SO₄ 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 Elmer). 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
FT-IR: IR spectra were recorded as KBr pellets, on Perkin-Elmer Infrared Spectrometer Model 16PC FT-IR, using sodium chloride optics. IR bands are expressed in frequency (cm⁻¹).

Molecular weight determination: Molecular weights (relative, Mₙ and Mₘ) and polydispersity (Mₚ/Mₙ) were determined with respect to polystyrene standards by size exclusion chromatography on a Thermo Finnigan Spectra Series AS300 machine at 25 °C by eluting PLA solutions of 10 mg/mL concentration in CHCl₃, with toluene as internal standard, through a series of five µ-Styragel columns of pore sizes 10², 10³, 10⁴ 500, and 100 Å respectively, and length 30 cm each. CHCl₃ was used as the mobile phase (flow rate 1 mL/min) and a refractive index detector (Spectra Series RI-150) was used for detection of different molecular weight fractions. Molecular weights were calculated with respect to polystyrene calibration.

Thermogravimetric Analysis: Thermal stability was analyzed using Perkin-Elmer TGA-7, by heating the samples from 50–700 °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). We used silicon nitride cantilevers with a nominal spring constant of 0.1 N m⁻¹ and an integrated pyramidal tip whose nominal apex radius was typically equal to 50 nm (Microlever, Thermo Microscopes, and Sunnyvale, CA)

¹³C Cross Polarization/Magic Angle spinning (¹³C CP/MAS): ¹³C CP/MAS NMR spectra were measured with Bruker MSL-300 NMR Spectrometer (75.5 MHz) with ¹³C CP/MAS accessory at room temperature (25 °C). The sample powder (ca. 200 mg) was placed in a cylindrical ceramic rotor and spun at 3 KHz. Contact time and repetition time were 2ms and 5s respectively. Spectral width and data points were 27 KHz and 8 K, respectively. The ¹H field strength was 2mT for both the CP and decoupling processes. The number of accumulations was 160-200. ¹³C Chemical shifts were calibrated indirectly with reference to the higher field
adamantane peak (29.5 ppm relative to tetramethylsilane ((CH$_3$)$_4$Si). The Hartmann-Hann condition was matched using adamantane in each case. The experimental errors for the chemical shifts were within ± 0.1 ppm for broad peaks as described.

RESULT AND DISCUSSION
The surface bound carboxylic groups on MWCNTs was used as template and L-lactic acid-co-12-hydroxy stearic acid were attached to the MWCNTs through ester linkage using dehydropolycondensation method. Using a silylated reaction flask equipped with a Dean and Stark type condenser, requisite amount of 88 % L-lactic acid was azeotropically dehydrated using equal volume of xylene solvent for 6 hr using at reflux temperature without any catalyst. After removal of water in the trap of the Dean and Stark condenser, the reaction was cooled at 50 °C. Subsequently functionalized multiwalled carbon nanotube (FMWCNTs) and tin chloride dihydrate 0.2 wt % were added followed by heating the reaction mixture slowly up to the refluxing temperature of the solvent (xylene) under mild stirring. The reaction was allowed to proceed at a temperature of 145 °C for 20 h. The reaction mixture was washed with chloroform several times to remove the unbound copolymer filtered under vacuum through 0.22 µm polytetrafluoroethylene (PTFE) membrane to yield corresponding grafted copolymers.

Grafting of copolymer on the surface of MWCNTs: The grafting of copolymer was carried out by taking silylated three-neck flask reactor L-lactic acid refluxed with xylene for 6 h using Dean stark apparatus. The reaction mixture was cooled up to 50 °C and 5 mol % of 12-hydroxystearic acid, FMWCNTs and tin chloride dihydrate were added in to it. The polymerization reaction was carried out for 20 h under stirring condition under the envelope of dry argon atmosphere (Figure 1).

Molecular weight determination: The blank copolymerization of L-lactic acid and 12-HSA using same method (dehydropolycondensation) without nanotube. Figure 2 show the chromatogram of copolymer, having $M_n = 3400$, $M_w = 8200$ and PDI = 2.4 respectively.

**FT-IR:** Figure 2 a shows the FT-IR of copolymer without nanotube. As is clearly evident, there is an absorption at 3504 cm$^{-1}$ due to the free hydroxyl groups. The characteristic stretching bands of ester group appeared at 1749 cm$^{-1}$ (C=O) $^{11}$ and 1134 cm$^{-1}$ (C-O). The bands at 2997 and 2944 cm$^{-1}$ are due to C-H stretching mode. Figure 3 b shows the IR spectra of MWCNTs grafted copolymer. The characteristic stretching band of carbonyl peak appears at 1726 cm$^{-1}$ (C=O) and 1130 cm$^{-1}$ for C-O stretching. The bands appeared at 2944 and 2863 cm$^{-1}$, which are assigned due to C-H stretching modes. There are more absorptions around 1458, 1377 and 1060 cm$^{-1}$, which can be attributed to the alkyl C-H and C-C bending modes. The peaks appeared in Figure 4 b slightly shifted with respect to copolymer peaks shown in Figure 3 a.

**Thermo gravimetric analysis:** The copolymer-grafted MWCNTs were pyrolyzed under an atmosphere of nitrogen and shown in Figure 3 a. The copolymer began to degrade around 220 °C and complete degradation occurred around 315 °C. After
700 °C, the weight percentage curve leveled at 12% (Figure 3 a). The weight loss was determined to be 88%. Figure 4b displays TGA curve of copolymer, degradation began around 135 °C and completed at 315 °C. Differential TGA curve (Figure 4 a) also confirmed that complete weight loss occurred around 315 °C in the case of copolymer as well as grafted copolymer on the surface of MWCNTs.12-15

Fig. 2: (a) FT-IR of copolymer sample (L-LA-co-12HSA) with out nanotube and (b) FT-IR of grafted copolymer on FMWCNTs.

Fig. 3 A: (a) TGA curves of grafted copolymer and (b) TGA curve of copolymer
Fig. 3 B: (a) DTA curve of grafted materials and (b) DTA curve of copolymer

Fig. 4: SEM of grafted copolymer (L-LA-co-12-HSA) on MWCNTs

Scanning electron microscopy: Figure 4 shows the SEM image of grafted copolymer (L-LA-co-12-HSA). The images provided evidence of chemical linkage between copolymer and MWCNTs. The individual MWCNTs were exfoliated and separated by copolymer molecules. It is clearly evident from spectral analysis that the copolymer 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.

Transmission electron microscopy: Transmission electron microscopy was used to directly image of grafted copolymer on MWCNTs. The TGA traces indicates that the grafted copolymer content in the grafted copolymer was approximately 88%. TEM images provide confirmation of unbundling of grafted copolymer on MWCNTs. The nanotube can
be attributed to copolymer that is grafted on to MWCNTs. These results were supported by spectral data and TGA analysis.

Fig. 5: TEM of grafted copolymer (L-LA-co-12-HSA) on MWCNTs

CONCLUSION
In conclusion, copolymers of L-LA and 12-HSA have been successfully grafted on the surface of MWCNTs by dehydropolycondensation and thoroughly characterized. The maximum level of grafting was observed as 15 wt %. In principle, this in situ 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.

REFERENCES