

STUDY THE GRAFTING OF POLYLACTIC ACID AND ITS COPOLYMER WITH 12-HYDROXY STEARIC ACID ON THE SURFACE OF MWCNT BY ^{13}C CP/MAS AND AFM

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ABSTRACT

The purpose of this study to study the structure property relationship of grafted material on MWCNT, the determination of NMR nuclei spin-lattice (T_1) and spin-spin (T_2) relaxation times suggest that the broaden signals are associated with diamagnetic species namely the nanotube attached polymer moieties. the AFM image of PLA oligomer grafted MWCNTs and topography patterns comprised of height from 0-250 nm and the side lengths ranging from 0.0 to 7.7 μm . Surface patches are formed randomly distributed employing that the presence of side chain hanged at 12-position in the copolymer grafted on MWCNTs.

INTRODUCTION

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 polymer wrapping and "pi-pi" stacking on the surface of carbon nanotubes due to non covalent functionalization methods are difficult to correlate quantitatively 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.¹⁻⁵ The molecular motion of PLLA in blend films were also investigated by solid state ^{13}C CP/MAS NMR. On the basis of the result of relaxation times, it was found that the molecular motion of PLLA100 and PLLA/gelatin blends increased when compared with that of original PLLA.⁶

Poly (lactic acid) (PLA) matrix and acetylated microfibrillated cellulose (MFC) as reinforcing agent. The acetylation of MFC was confirmed by FTIR and (^{13}C) CP-MAS NMR spectroscopies.⁷⁻⁸ The grafted co-polymers based on a polylactide backbone (PLA) to complex DNA. Since atomic force microscopy (AFM), is a powerful tool for semi-quantitative

and qualitative measurements on molecular shape and distribution AFM comparative studies on cationic salen grafted PLA (CS-PLA) and on Schiff's base grafted PLA (SBPLA), on non-oriented or oriented polymer films. Then we used the same method to study the complex of DNA with CS-PLA.⁹ The self assembly of PLA enantiomers have been studied at the nanometer scale using atomic force microscopy. At first, the conformation of D and L PLA macromolecules in dilute regime and the initial state of aggregation of both enantiomers were successively observed and compared with the aggregation of PLLA/PDLA blends. Our results points out differences in the aggregates structure between the homo-aggregates of each enantiomers and the 3 Dimensional stereocomplexes formed with racemic mixture of D and L entities. On the one hand, D or L PLA chains, which adopt a rigid conformation in dilute regime, form gradually aggregates that tend to grow from a nucleation center. On the other hand, stereocomplexes have a non-compact structure and are elongated with height variations within the fibrils that support the side by side aggregation of D and L helical structures to form thicker fibrils.¹⁰⁻¹¹

Experimental

Grafting of PLA and PLA-Co-12 hydroxy stearic acid: The surface bound carboxylic groups on MWCNTs was used as template and L-lactic acid, L-lactic polymers 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 catalyst (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. Similar methodology was adopted to attach L-lactic acid-co-12-hydroxyl stearic acid to MWCNTs through ester linkage. Poly (L-lactic acid, $\bar{M}_n = 14,000$) was prepared in our laboratory by dehydropolycondensation method and also used. Poly (L-lactic acid) was also grafted on functionalized carbon nanotubes by dehydropolycondensation method.¹²⁻¹³

Characterization

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 tetramethyl silane ((CH₃)₄Si). 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.

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). 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

¹³C Cross Polarization /Magic Angle Spinning (¹³C CP/MAS): Figure 1 a shows ¹³C CP/MAS of grafted PLA where as Figure 1 b shows ¹³C CP/MAS of PLA starting from L-lactic acid. The ¹³C resonance appeared at approximately 17, 70 and 170 ppm corresponds to the methyl, methane and carbonyl carbon respectively in the polymer. ¹³C NMR signals of PLA become very broad upon the attachment of MWCNTs via the esterification of nanotube bound carboxylic acid. Results from the determination of NMR nuclei spin-lattice (T₁) and spin-spin (T₂) relaxation times suggest that the broaden signals are associated with diamagnetic species namely the nanotube attached polymer moieties.¹⁴ Similar line broadening appeared in case of grafted PLA oligomers in comparison with PLA oligomers.

Figure 2 A and A' show the ¹³C CP/MAS NMR spectra of grafted copolymer (L-lactic acid-co-12 hydroxyl stearic acid) on MWCNTs surface and copolymer respectively. As expected, the solution NMR resonances are narrower than the solid- state NMR resonances. The ¹³C resonances at approximately 17, 70 and 170 ppm corresponds respectively to the methyl, methane and carbonyl carbon in the polymer. The line broadening of methyl, methane and carbonyl groups increased when the copolymer grafted on the surface of MWCNTs. The line broadening suggested the formation of new crystallites, which is likely to be induced in the proximity of MWCNTs. Experiments were performed to compare the cross-polarization efficiency for the crystalline and amorphous domains in the polymer. They were assumed to be identical with in the errors in the NMR measurements.

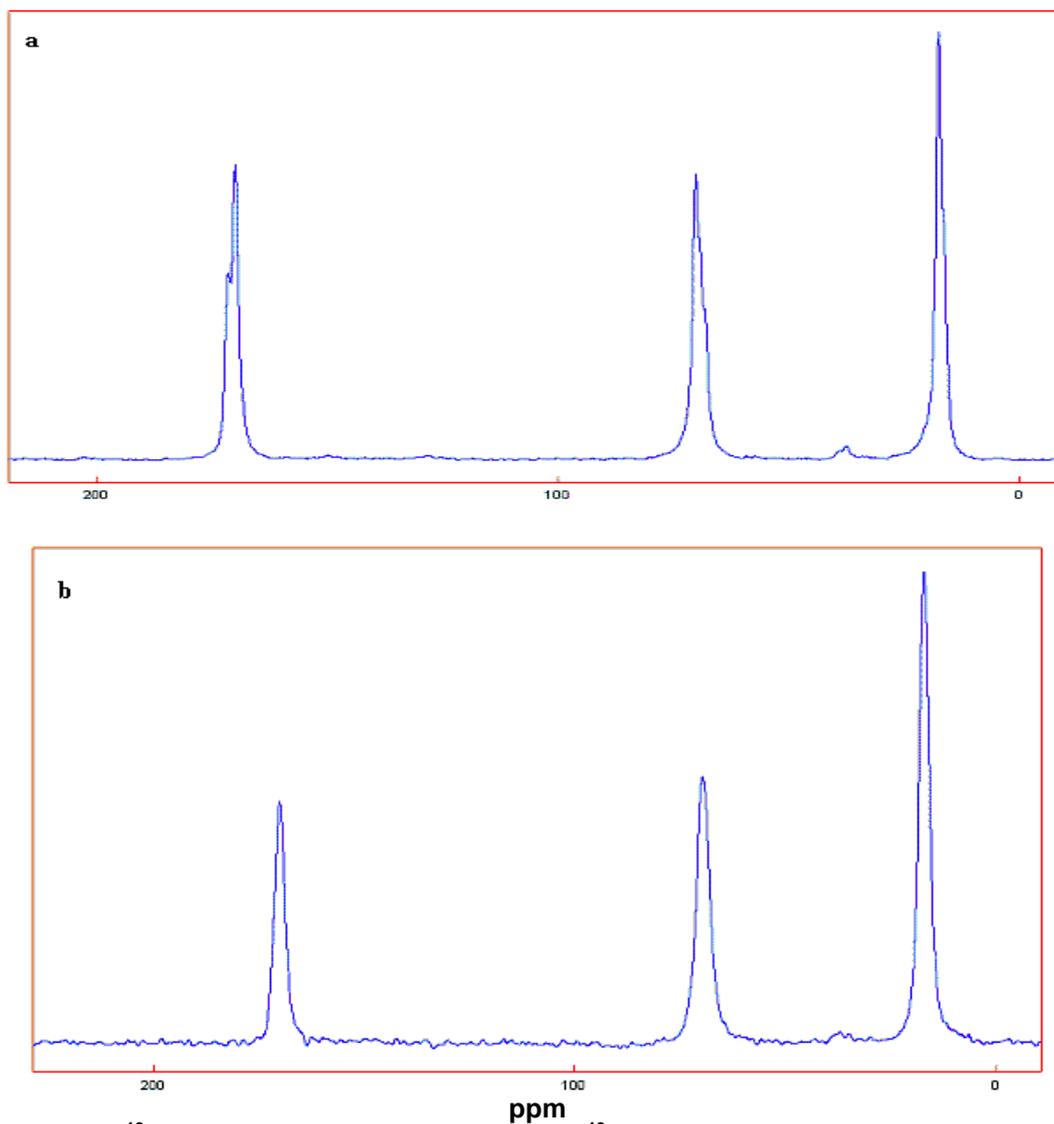
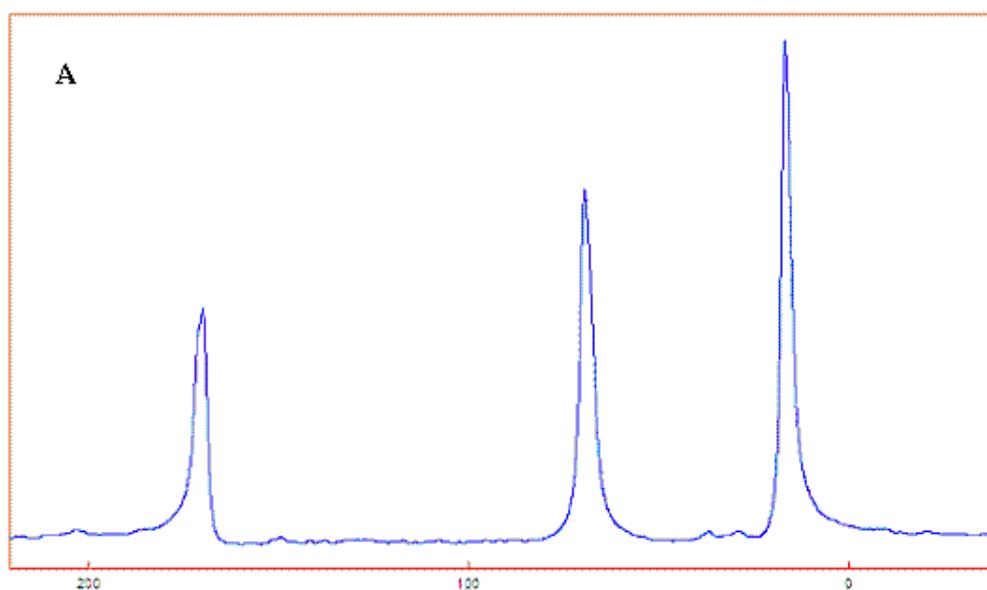


Fig. 1: (a) ^{13}C CP/MAS of grafted PLA1 and (b) ^{13}C CP/MAS of PLA without nanotubes



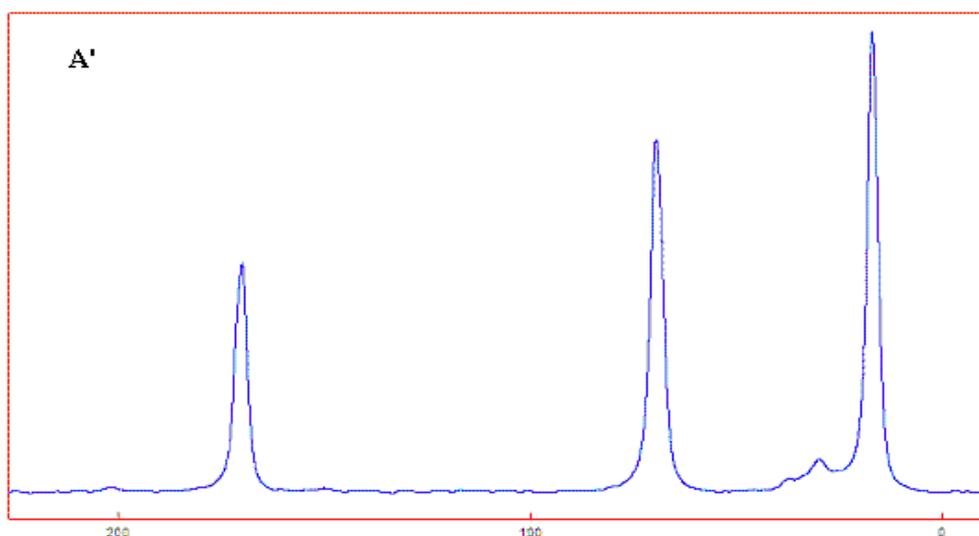


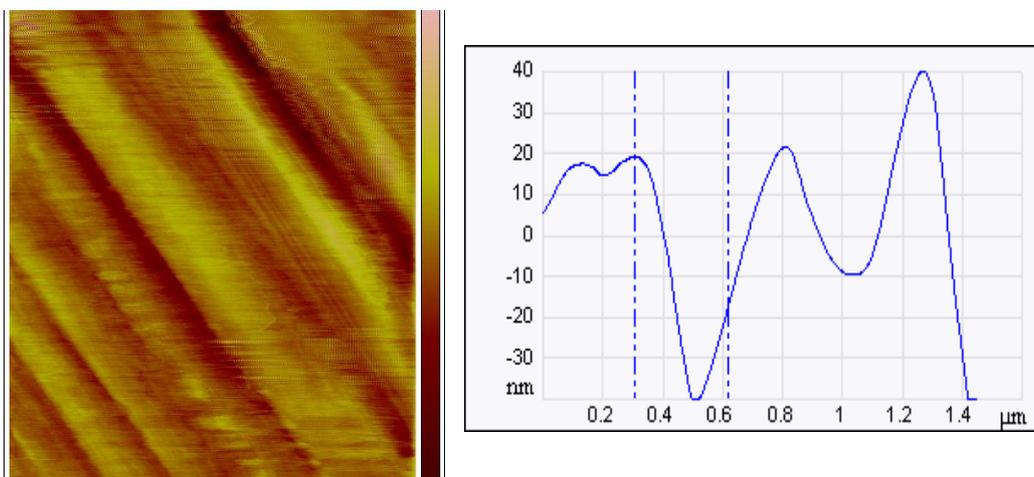
Fig. 2: (A) ^{13}C CP/MAS of grafted copolymer and (A') ^{13}C CP/MAS of copolymer

Atomic Force Microscopy

Figure 3 a shows the AFM image of the L-lactic acid grafted MWCNTs and topographic patterns comprised of variable height ranging from 20-40 nm and side lengths ranging from 0.0 to 1.5 μm . Figure 3 b displays the AFM image of PLA oligomer grafted MWCNTs and topography patterns comprised of height from 0-250 nm and the side lengths ranging from 0.0 to 7.7 μm . These are clearly distinct AFM images observed in case of L-lactic acid grafted MWCNTs, grafting reaction occurred and clearly reflected between the two carbon nanotubes. The PLA grafted on MWCNTs appeared as oval shaped randomly distributed

indicating grafting reaction occurred on the surface of MWCNTs

Figure 4 displays AFM image of the surface of copolymer 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 copolymer grafted on MWCNTs. The random distribution of patches on the surface was maintained and arrangement of the patches was distinctly different considering that the averaged center to outer distance between neighboring patches is approximately 80 nm on a flat surface.



a

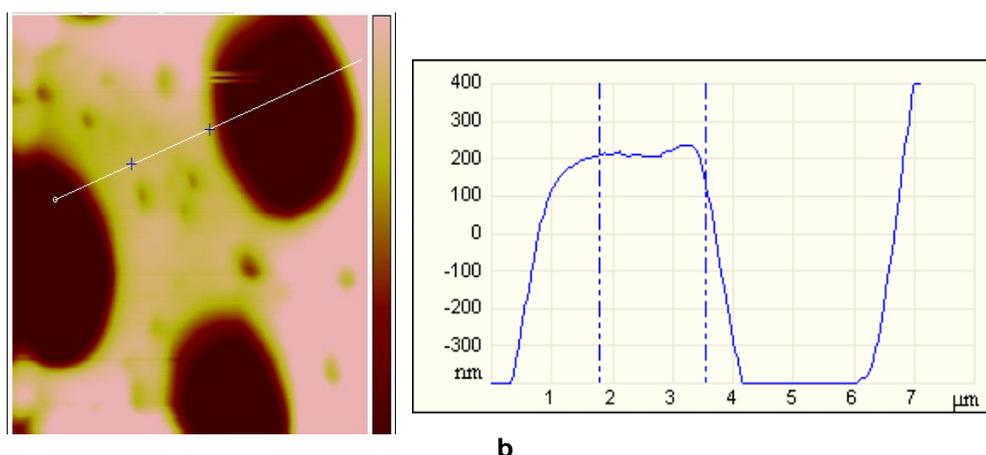


Fig. 3: AFM of grafted materials (a) PLA-1 and (b) PLA-2

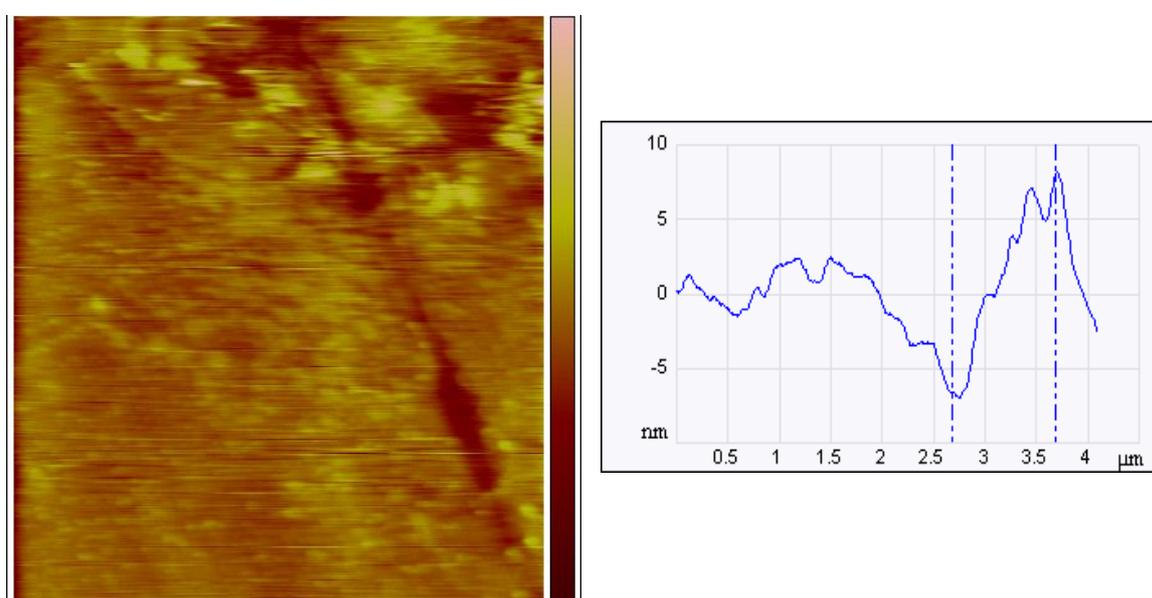


Fig. 4: AFM images of copolymer grafted on MWCNTs

CONCLUSION

The appearance of a shoulder of the melting endothermic peak on the second heating cycle suggested the formation of new crystallites, which is likely to be induced in the proximity of MWCNTs and also strongly supported by ^{13}C CP/MAS NMR study. A smooth surface was detected by AFM for grafted homopolymers. Such microstructure would account for the homogeneous distribution of MWCNTs and improve mechanical and electrical properties of the polymer. Such microstructure would account for the homogeneous distribution of MWCNTs and improve mechanical and electrical properties of the polymer.

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REFERENCES

1. (a) Chen J, Hamon MA, Hu H, Chen Y, Rao and Eklund PC AM. Haddon, R. C. Science 1998;282:95. (b) Sun YP, Fu K, Lin Y and Huang W. Acc Chem Res. 2002;35:1096.
2. Star JF, Stoddart D, Steuerman M, Diehl A, Boukai EW, Wong X, Yang SW, Chung H, Choi J and Heath R. Angew Chem. 2001;113:1771-1775; Angew Chem Int. 2001;40:1721-1725.
3. Georgakilas V, Kordatos K, Prato M, Guldi DM, Holzinger M and Hirsch A. J Am Chem Soc. 2002;124.
4. Dyke CA and Tour JM. Nano Lett. 2003;3:1215.
5. (a) Viswanathan G, Chakrapani N, Yang H, Wei B, Chung H, Cho, K, Ryu CY and Ajayan PM. J Am Chem Soc. 2003;125:9258. (b) Banerjee S,

- Kahn MGC and Wong SS. Chem Eur. J. 2003;9:1898.
6. Xiaodong Zhao, Wenguang Liu, Kangde. J Appl Polym Sci. 2006;101: 269-276.
 7. Tingaut P, Zimmermann T, Lopez-Suevos F. Biomacromolecules. 8;11(2):454-64 (2010)
 8. Balaji S Selukar, Sharad P Parwe, Kavita K Mohite. Baijayantimala Garnaik. Adv Mat Lett. 2012;3(2):161-171
 9. Véronique Nadeau and Patrice Hildgen* Molecules. 2005;10:105-113
 10. Toshihiro Kasuga, Akiko Obata, Hirotaka Maeda and Larry L Hench. Materials Science Forum (Volumes), , 2007; 53 -543,617-622.
 11. Ashok Narladkar and Eric Balnois. Yves Grohens Macromolecular Symposia, 2006; 241(1):34-44,
 12. Pandey, Asutosh, Kumar and Seluka, Balaji. International Journal of Advances in Pharmacy, Biology and Chemistry (IJAPBC). 2013;2(1):63-67.
 13. Pandey, Asutosh and Kumar International Journal of Advances in Pharmacy, Biology and Chemistry IJAPBC. 2013; 2(1):219-224.
 14. Huang W, Fernando S, Allard LF and Sun YP. Nano Lett. 2003;3:565.