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Grafting of poly alrutitic acid on the surface of MWCNT

Shailesh Kumar Mishra
Department of Chemistry, Ganesh Lal Agrwal College,
Nilamber Pitamber University, Medininagar-India
Email: mishraskdtg@gmail.com

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Abstract: The functionalized MWCNTs were reacted with aleuritic acid, oligomers of aleuritic acid through insitu polymerization. The attachment of PAL homopolymer chains to the MWCNTs were confirmed by FT-IR, TGA, scanning electron microscopy (SEM), transmission electron microscopy (TEM).

(Keywords : Grafting, aleuritic acid, MWCNT)

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 ð-ð 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 nanotubes 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 obtained Young's modulus of 0:45±0:23 TPa , tensile strength of 1:72±0:64 GPa and strain (12 %), high electrical conductivity (0.1 $S.cm^{-1}$) and high aspect ratio.[8-10]

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.

Poly aleuritic acid is the unique biodegradable polymer, which can replace all the conventional plastic so far available as their properties are concerned. At the same time, PAL has been limited to biomedical application as resorbable implant materials, because of its biodegradability and high production cost. Carbon nanotubes have noncreative surfaces and have not been used for dehydropolycondensation of PAL and related copolymers. To our knowledge, dehydropolycondensation of Aleuritic acid and Aleuritic acid oligomers has not been previously attempted, and this is the first report that demonstrates the growth of homopolymers

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.

The grafting of Aleuritic acid ad Aleuritic acid oligomer and to multiwalled carbon nanotubes (MWCNTs) using dehydropolycondensation techniques. The functionalized MWCNTs were reacted Aleuritic acid ad Aleuritic acid oligomer through insitu polymerization. The attachment of PAL homopolymer chains to the MWCNTs were confirmed by FT-IR, TGA, scanning electron microscopy (SEM), transmission electron microscopy.

Experimental

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}).

Thermogravimetric Analysis*:* Thermal stability was analyzed using Perkin-Elmer TGA-7, by heating the samples from 50–700 ^{0}C with a heating rate of 10 ^{0}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.

Results and Discussions

The surface bound carboxylic group on MWCNTs was used as template aleuritic 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 Aleuritic acid was azeotropically dehydrated using equal volume of xylene solvent for 2 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 ^{0}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 ^{0}C for 15 h. Poly aleuritic acid was also grafted on functionalized carbon nanotubes by dehydropolycondensation method. The reaction mixture was washed with

chloroform several times to remove the unbound PLA and filtered under vacuum through 0.22 µm polytetrafuloroethylene (PTFE) membrane to yield corresponding grafted polymers and copolymers.

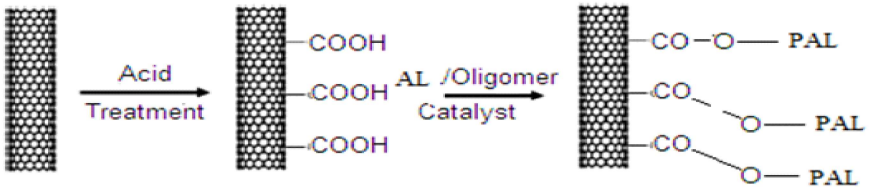


Figure 1: Reaction scheme for grafting of Aleuritic acid and oligomers of Aleuritic acid

FT-IR: Figure 2 shows the FT-IR of PAL without nanotubes. The peak at 1760.73 cm^{-1} is attributed due to carbonyl group and a broad peak around 3500 cm^{-1} is due to –OH stretching. Figure 2b depicts the FT-IR spectra of the grafted PAL-1 and showed an absorption at 2870 cm^{-1} (-CH stretching), 1751cm^{-1} (-C=O stretching).[11] Similarly grafted PLA-2 (Figure 2c) also showed 2876cm^{-1} (-CH stretching) and 1756 (-C=O stretching). It was observed that -CHs frequency of grafted PAL-1 and grafted PAL-2 shifted considerably lower frequency ($\Delta\nu$ = 7 and 1 cm^{-1}) as compared to PAL (Figure 2b). The carbonyl stretching frequency of both grafted PAL-1 and grafted PAL-2 has also shifted to lower frequency ($\Delta\nu$ = 6 and 1 cm^{-1}). The Low frequency shift may be attributed to non-covalent interaction of PAL with MWCNTs.[12] As the residual MWCNTs were thoroughly washed several times with chloroform and dried under vacuum for 40 ^{0}C for 3h, the presence of polymer absorption in the IR spectrum supports the occurrence of a grafting reaction.

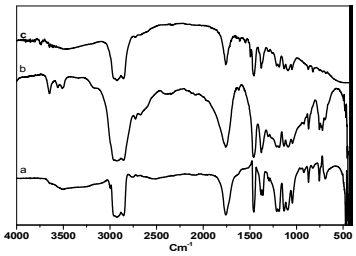


Figure 2: FT- IR spectra of (a) PAL with out nanotube, (b) PAL-1 and (c) PAL-2.

Thermogravimetric analysis: TGA provides a measure of the degree of functionalization. The relative content of grafted PAL-1 and PAL-2 was investigated by TGA. The PAL grafted MWCNTs were pyrolyzed from 50 to 700 ^{0}C at rate of 10^{0}C/ min under an nitrogen atmosphere. After 5 min at 700 ^{0}C, the weight percentage curve leveled up at 286 ^{0}C (Figure 3 b). The weight loss was determined to be 90 % (Figure 3 b) of PAL-1. In controlled experiment all of the bulk PAL (typically by‘M_n =5000) was lost below 300 ^{0}C (Figure 3 a) suggesting that the entire PAL component of PAL grafted MWCNTs sample was lost during the TGA analysis. The weight loss percentage in case PAL-2 was 12 %. The temperature derivative percentage weight loss curve showed two main weight loss peaks. According to the heating profile the first weight loss occurred at 146 ^{0}C and the second at 236 ^{0}C. Cleavage of the polymer chain from sidewall of the carbon nanotubes would account for this observation since it is not possible to determine the molecular weight of the polymer chain grafted on to the MWCNTs.

It is very essential to mention here that the work-procedure in this investigation involves washing and removal of free polymer using filtration in order to characterize unambiguously the grafting reaction. The amount of polymer present on the tubes (4-8 %) is considerably lower than the amount of precursor acid groups on the MWNTS. Low level of grafting was observed when equimolar or higher amounts of PAL

oligomers were used. It appears that the reaction of high molecular weight PAL polymer chain ends with active sites of the nanotubes is hindered because of the entropy constraints of the polymer. It is also difficult to ascertain the extent of polymer wrapping or coating contributing to the grafting efficiency.[12, 13-15]

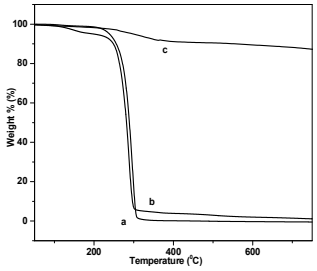
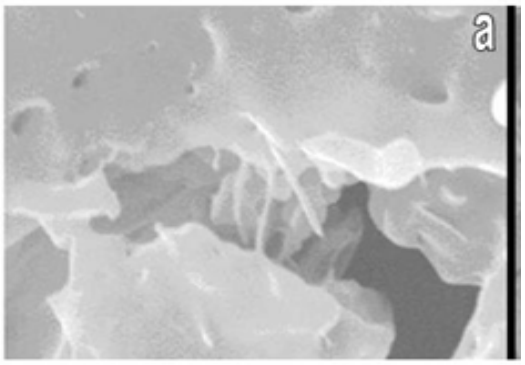


Figure 3: TGA curve of PAL, (b) TGA curve of PAL-1 and (c) TGA curve of PAL-2.

Scanning electron microscopy: SEM images of grafted PAL-1-MWCNTs of these materials were illustrated in Figure 4a. These images demonstrate a low MWCNTs content. The Figure 4b (PAL-2) also showed high content of MWCNTs because PAL chain is anchored to the surface of MWCNTs and the polymer chain arranged in a particular configuration. Finally, the PAL in the grafted polymers and copolymers remain semicrystalline, as indicated from FTIR studies (-CH_3 (920.6 cm^{-1}, C=O stretching (1750-1789 cm^{-1} and C-H stretching modes (2880-3005 cm^{-1}) and also confirmed α-helical structure.[10]



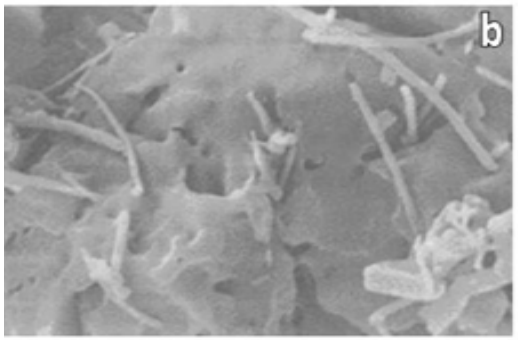
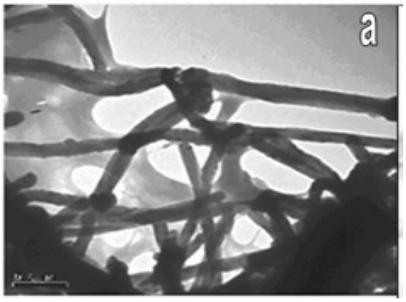


Figure 4: (a) SEM images of PAL-1 and (b) SEM images of PAL-2.

Transmission electron microscopy: TEM images provide conformation for the unbundling of the PAL grafted MWCNTs Figure 5a. The nanotube exhibits a morphology that can be attributed to the polymer that grafted on to the MWCNTs. Figure 5b shows that PAL oligomers are also grafted on to the surface of MWCNTs. However, the chemical attachment points on the MWCNTs are less in comparison with grafted PAL-1.



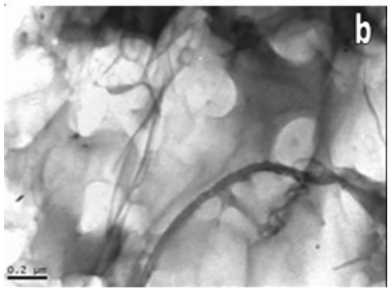


Figure 5: (a) TEM image of PAL-1 and (b) TEM image of PAL-2

Conclusion

In conclusion, monomer and oligomers 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 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.

References

1. (a) J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, R. C Haddon, *Science* 282, 95(1998) (b) Y.P.Sun, K. Fu, Y. Lin, W.Huang, *Acc. Chem. Res* **, 35**, 1096 (2002)
2. J. F. Star, D. Stoddart, M. Steuerman, A. Diehl, E. W. Boukai, X. Wong, S.W. Yang, H. Chung, J. Choi, R. Health, *Angew. Chem.*, **113**, 1771(2001)
3. V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* , **124**, 6804 (2002)
4. C. A. Dyke, J. M. Tour, *Nano. Lett.* **3**, 1215 (2003).
5. (a) G. Viswanathan, N. Chakrapani, H. Yang, B. Wei, H. Chung, K. Cho, C. Y. Ryu, P. M. Ajayan, *J. Am. Chem. Soc* , **125**, 9258 (2003). (b) S. Banerjee, M. G. C. Kahn, S. S. Wong, *Chem. Eur. J* , 9, 1898 (2003)
6. J. E. Riggs, Z. Guo, D. L. Carroll, Y. P. Sun, *J. Am. Chem. Soc* , **122**, 5879 (2000)
7. K. Fu, W. Huang, Y. Lin, L. A. Riddle, D. L. Carroll, Y.P. Sun, *Nano. Lett.* **1**, 439 (2001)
8. Z. W. Pan, S. S. Xie, L. Lu, B. H. Chang, L. F. Sun, W. Y. Zhou, G. Wang, D. L. Zhang, *Appl . Phy. Lett.* **74**, 3152 (1999)
9. M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, R. S. Ruoff, *Science* , **287**, 637 (2000)
10. D. Zhang, M.A. Kandadai, J. Cech, S. Roth, S. A. Curren, *J. Phys. Chem. B*. **110**, 12910 (2006).
11. M.A. Hamon, H. Hui, P. Bhowmik, H. M. E. Itkis, R. C. Haddon, *Applied Physics A Materials Science and Processing* ,**74**, 332 (2001)
12. Y. Lin, M. A. Rao, B. Sadanadan, E. A. Kenik, Y.P. Sun, *J. Phys. Chem. B,* **106**, 1294 (2002)
13. X. Chen, X. Chen, M. Lin, W. Zhong, X. Z. Chen, *Macromolecular Chemistry and Physics*, 208, 964 (2007)
14. D. E. Hill, Y. Lin, A. M. Rao, F. L. Allard, Y.P. Sun, *Macromolecules* **35**, 9466 (2002,)
15. W. Huang, S. Fernando, L. F. Allard Y.P. Sun, *Nano. Lett.*, **3**, 565 (2003)

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