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Amine functionalization of carbon nanotubes for the preparation of CNT based polylactide composites- A comparative study

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Abstract

This work describes a comparison between two chemical functionalization strategies for the amine functionalization of multi walled CNTs. In the first procedure, the CNTs are functionalized in direct amination process that avoids the use of strong acids or acid chloride unlike the conventional functionalization methods whereas the second method is a two step procedure involving mild acid treatment followed by amidation. Both procedures allow not only to control of amine content on the CNT surface but also to obtain remarkable degree of fictionalization. The functionalization of CNTs is confirmed by analytical techniques like scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The modified CNTs with optimum amine content are used to prepare Polylactide (PLA) /CNT nanocomposites with improved properties through solution casting method.

Keywords: CNTs, amine functionalization, PLA/CNT composite, thermal and mechanical properties

1. Introduction

Carbon nanotubes (CNTs) and the novel carbon based nanomaterials have been the subject of world wide research interest in recent years. They are proven to have unique electronic, mechanical, and physical properties.[1,2] However, the limited solubility of CNTs in most organic solvents limits their chemical manipulation, quantitative characterization, and wide application. In recent years, there has been much interest in preparing homogeneous dispersions/solutions of CNTs, suitable for processing into thin films and composites exploiting the unrivalled properties of CNTs. The main routes consist of end and/or sidewall functionalization, use of surfactants with sonication or high-shear mixing [3-6] polymer wrapping of nanotubes [7-10] and protonation by superacids.[11] Among all the methods, grafting of CNT surface

with amines has been widely investigated in preparing soluble CNTs. Wong et al. reported modification multi walled carbon nanotubes (MWCNTs) via amide bond formation between carboxyl functional groups bonded to the open ends of MWCNTs and amines.[12] Chen et al.[13] have demonstrated that full-length single walled carbon nanotubes (SWCNTs) can be solubilized in common organic solvents by noncovalent (ionic) functionalization of the carboxylic acid groups by using octadecyl amine (ODA). They found that the same dissolution process applied to arc-produced MWCNTs, average length < 1 μm), only gave rise to very unstable suspensions in organic solvents which were visually scattering. It has been shown by Qin et al. [14] that by modifying Haddon's method using two Soxhlet extractors, large quantities of solubilized MWCNTs could be prepared. However, the conventional approach of amine functionalization is tedious with a typical reaction time of 4-8 days which involves steps such as carboxylation, acyl chlorination followed by amidation. Although these methods are quite successful, they often indicate chopping of the tubes into smaller pieces (may be due to oxidative induced cutting during refluxing with concentrated acid and acid chloride for a long time) thus partly losing the high aspect ratio of CNTs (length/diameter). For the structural applications such as nanotube-based composites and copolymers, full-length MWCNTs are preferred because of their high aspect ratio. Hence incorporation of pristine nanotubes without losing the structural integrity and homogeneously dispersing them in polymer matrix still remains a challenging issue.

The motivation for the current work is to develop simple strategies for the amine functionalization of MWCNTs (referred as CNTs throughout the text) that improves their dispersion in a Polylactide (PLA) matrix. The work is focused on single and two step hexadecyl amine (HDA) functionalization of CNTs where the amine content on

CNT surface is successfully controlled by varying the reaction time. For a comparison, conventional amine functionalization which involves concentrated acid and thionyl chloride treatment was also performed. The effectiveness of functionalization procedures were analyzed using scanning (SEM), Fourier-transform infrared (FTIR) and X-ray photoelectron (XPS) spectroscopies. The composite properties were investigated by SEM and thermogravimetric analyses (TGA).

2. Experimental

2.1 Amine functionalization of CNTs

The CNTs used in this study were purchased from Sigma Aldrich with more than 95% purity (inner diameter-10 nm, outer diameter-20nm, length-0.5 to 500 μm). Hexadecylamine (HDA), chloroform, ethanol and HNO_3 were purchased from Sigma-Aldrich and used as received.

In a single-step procedure, 0.2 g of CNTs were refluxed with 1 g of HDA in a round bottomed flask at an optimized temperature of 180 °C in an oil bath. The degree of amine functionalization was controlled by varying the reaction time. The excess of HDA was removed by washing with ethanol several times. The solid was collected by Nylon membrane filtration (0.45 μm pore size), and dried at 110°C overnight (referred to as CNTs-1).

In a two-step functionalization procedure, pure CNTs were oxidized by refluxing with 5M HNO_3 (10 ml/0.1 g) for 1 h filtered, washed and dried 110°C overnight (referred to as O-CNTs). The oxidized MWCNTs (0.2 g) were then refluxed with 2 g of HDA at an optimized temperature of 120 °C by varying the reaction time. The solution was filtered, washed with ethanol to remove excess HDA dried at 110°C overnight (referred to as CNTs-2).

The weight percentage of HDA in the functionalized samples calculated from gravimetric analysis using the equation; [15] Weight % of HDA = (Weight of HDA in the sample/Weight of the sample) × 100. The functionalized CNTs thus obtained were sonicated in 100 ml chloroform for 30 min to obtain a black solution which was used for the PLA-CNT composite preparation.

2.2 Preparation of PLA/CNT Composite

PLA/CNT composites containing 1.5 wt% of functionalized CNTs (CNTs-1 and CNTs-2) were prepared by using a solution-blending film casting method. A known amount of PLA was first dissolved in a minimum amount of chloroform at 50°C. 100 ml of CNT solution in chloroform containing a predetermined amount of amine functionalized CNTs was sonicated with chloroform solution of PLA in an ultrasonic bath for 2h. The mixture was then cast on a glass petri dish and kept at room temperature for a day to evaporate the solvent which resulted in black composite film. The composite film was subsequently dried at 70°C under vacuum for 2 days. A neat PLA film, in the absence of CNTs, was also prepared by using the same technique. Dried neat PLA and PLA/CNT composite films were chopped into pieces and compression moulded by pressing under 2 MPa pressure at 180°C for 10 min. These compression moulded films were used for the various characterizations.

2.3 Sample Characterization

The surface morphology of the solid samples and composite film was studied by a Leo 1525 FE-SEM using 6 kV accelerating voltage. All the powder samples were sputter coated with carbon to avoid charging. The nanocomposite sample was fractured in liquid nitrogen and then coated with carbon. FTIR spectra were measured in transmittance mode by a Perkin Elmer Spectrum 100 FT-IR spectrometer (diamond crystal mode). XPS analyses were performed on a Kratos Axis Ultra device, with a

monochromatic Al X-ray source (1486.6 eV). Survey spectra were acquired at 160 eV and region spectra at 20 eV pass energies. Thermal property of the samples was investigated by TG analysis using a Q500 TGA instrument. The samples were heated in platinum crucibles under the air flow of 50 ml min^{-1}. The dynamic measurement was between ambient and 1000º C with a ramp rate of 10 º C min^{-1}.

3. Results and Discussion

The functionalized CNTs were black powders. The weight percentage of HDA in the CNTs-1 and CNTs-2 samples calculated from gravimetric analysis (refer Table 1) suggested that the grafting of HDA chains on CNTs increases with increase in reaction time. Xu et al. [16] reported similar results on a series of ODA grafted CNTs prepared by a three step procedure including acyl chlorination. Of the CNTs functionalized by two different procedures for the same time period, CNTs-1 showed higher amine content which may be due to the high reaction temperature.

Table 1. Correlation of weight % of HDA loaded on MWCNTS with reaction time

Time/h	**Amine content/ wt%**	
	CNTs-1	CNTs-2
3	10.3	2.8
6	24.8	6.9
12	52.4	12.2
24	61.5	21.7
92	89.7	51.4

Since preliminary studies showed a detrimental effect of higher amine content (> 35 wt% in CNTs) on the composite properties (results not given here) we chose CNTs with amine content in the range 20-25 % (refer Table 1) for further investigations. So from now on, unless otherwise specified, CNTs-1 and CNTs-2 refer to CNTs functionalized for 6 and 24 h in a single and double step procedures respectively.

Figs. 1 a & b show the FTIR spectra of pure, functionalized MWCNTs from two different procedures and the corresponding PLA/CNT composites. The characteristic IR bands for CNTs are located between 1900 and 2100 cm^{-1} which are essentially the same for oxidized and functionalized CNTs indicating the preservation of graphite structure of CNTs even after oxidation and functionalization. The bands at 1740 cm^{-1} in the spectrum of O- CNTs (refer Fig. 1b) correspond to the C=O groups on the CNT surface formed during nitric acid oxidation. The spectral features of amine functionalized samples in CNTs-1 and CNTs-2, i.e. peaks around 2954–2850 cm^{-1} (stretching vibrations of the alkyl chain), 1500-1600 cm^{-1}(stretching vibrations of the amide) clearly indicate the incorporation of HDA to the CNT surface.[17-19] The FTIR spectrum of PLA/CNT composite shows all the typical peaks of PLA at 1700-1760 and 500-1500 cm^{-1}, [20, 21] while retaining those for HDA and CNTs. This confirms the presence of functionalized CNTs in the polymer matrix. In the case of CNTs-2, the characteristic peak for CNTs is shifted to higher wavenumber which is due to the covalent nature of the functionalization leading to amide formation. No such peak shift is observed in the case of CNTs-1 (refer Fig.1a) indicating that the HDA chains are adsorbed on the CNT surface without forming any covalent bonds.

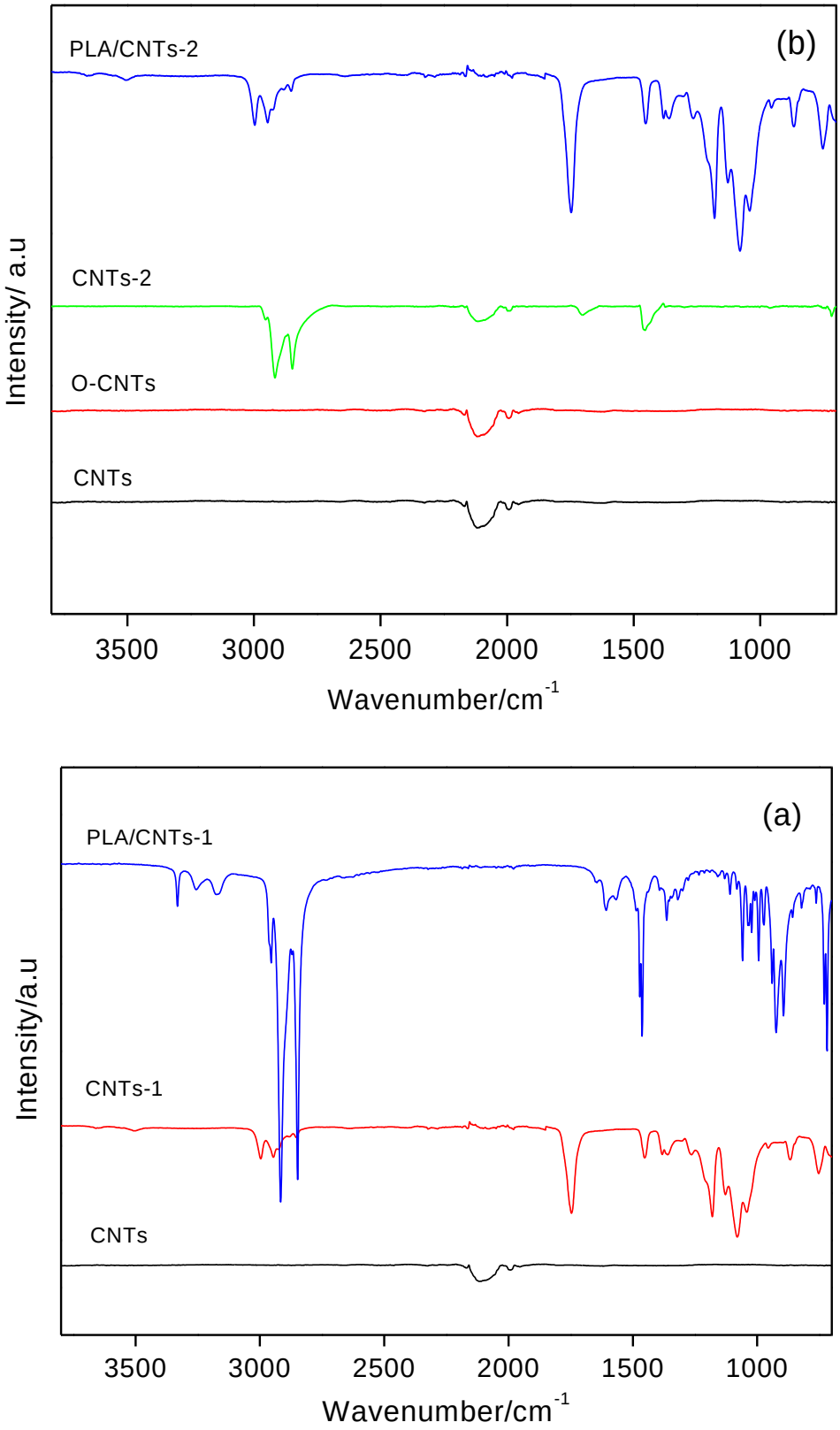

Fig.1. FTIR spectra of pure, oxidized and amine functionalized CNTs and corresponding composite samples (a) one-step and (b) two-step functionalization

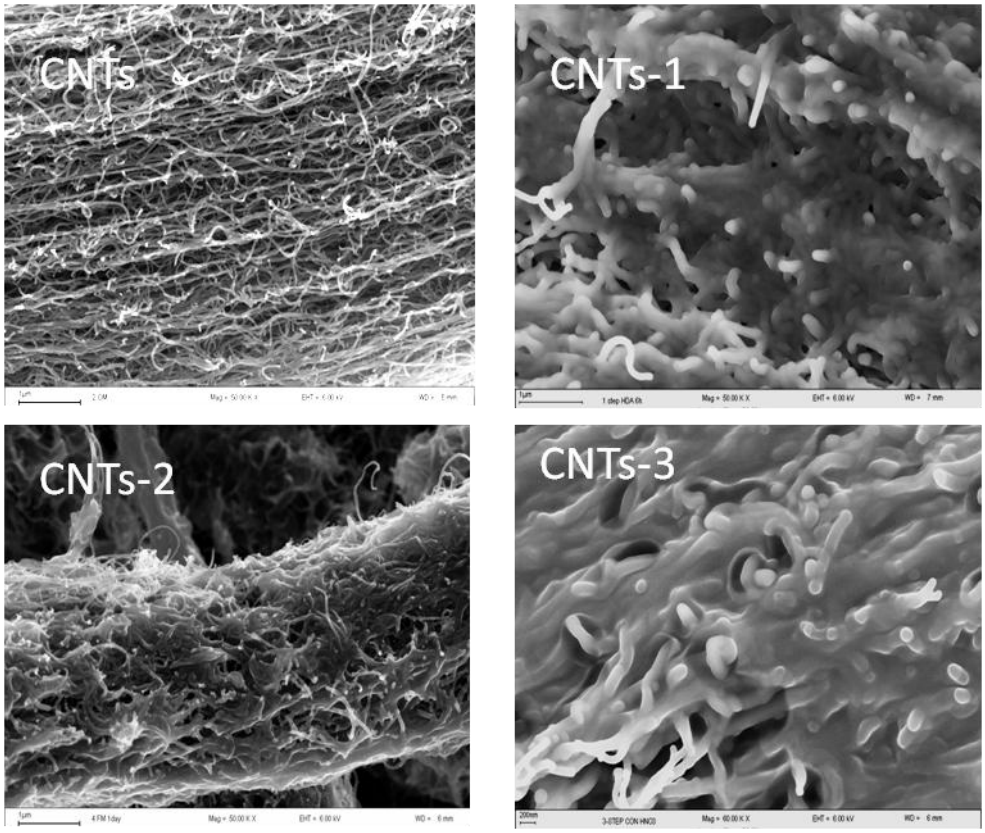

Fig. 2. SEM images of pure (CNTs) and amine functionalized CNT samples. CNTs-1, 2, 3 represent CNTs functionalized by one, two and three step procedures respectively.

The degree of surface functionalization of CNTs was studied by SEM analysis and the results are given in Fig.2. No visual difference between pure and oxidized CNTs was observed indicating that the acid treatment is non-destructive in nature (results not shown here). The SEM image of CNTs-1 show considerable amount of amine on the CNT surface when compared to CNTs-2 which is in agreement with the gravimetric analysis results for the amine content (refer Table 1). For a comparison, SEM analysis was done on CNTs that are functionalized in a conventional three step procedure (referred to as CNTs-3) which involved CNT oxidation with concentrated HNO_3, refluxing with thionyl chloride for 8h followed by treatment with amine for 92 h. CNTs-1 and CNTs-3 are observed to have similar surface morphologies showing that

the single step procedure is as effective as the three step procedure in functionalizing the CNT surface.

To find out the nature of bonding between the HDA chains with the outer graphene layer of the CNTs, XPS analyses was done. Fig. 3a represents the XPS spectra of CNTs and CNTs-1 samples. The appearance of 'N 1s' peak at 400 eV, in CNTs-1indicate the presence of amine groups on the CNT surface. The weak 'O 1s' and 'O KLL' peaks present in this case may be attributed to the presence of surface adsorbed oxygen in the sample. The characteristic 'C 1s' peak of CNTs-1 remains almost at the same position as that of CNTs, confirming that there is no covalent bond formation. On the other hand, the presence of covalently bonded amine groups on CNTs-2 could be identified by comparing the XPS spectra of CNTs, O-CNTs and CNTs-2 (refer Fig. 3b). The typical peaks observed were C1s at 284.05 eV, O1s around 527.7 and N1s at 395.6 eV for CNTs-2.[22-24] Moreover, the C1s lines of O-CNTs and CNTs-2 are significantly shifted to lower binding energy values (~ 5 eV) indicating successful amide formation on CNT surface.

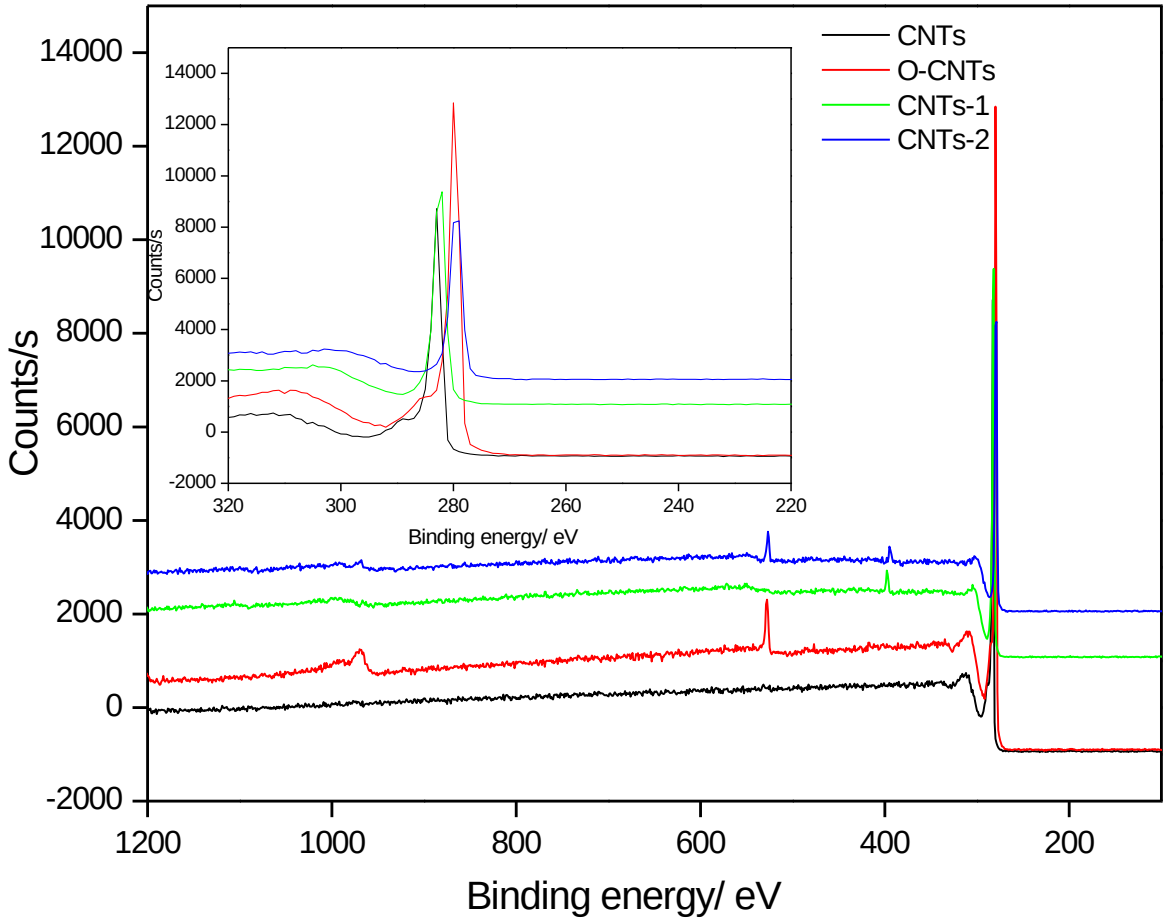

Fig. 3. XPS scans of pure, oxidized and amine functionalized CNT samples. CNTs-1 and 2 represent CNTs functionalized by one and two step procedures respectively.

The PLA-CNT composite films were prepared with 1.5 wt% of functionalized CNTs (CNTs-1and CNTs-2). These films were subjected to TGA to measure their thermal stability and the resulting curves are shown in Fig. 4.

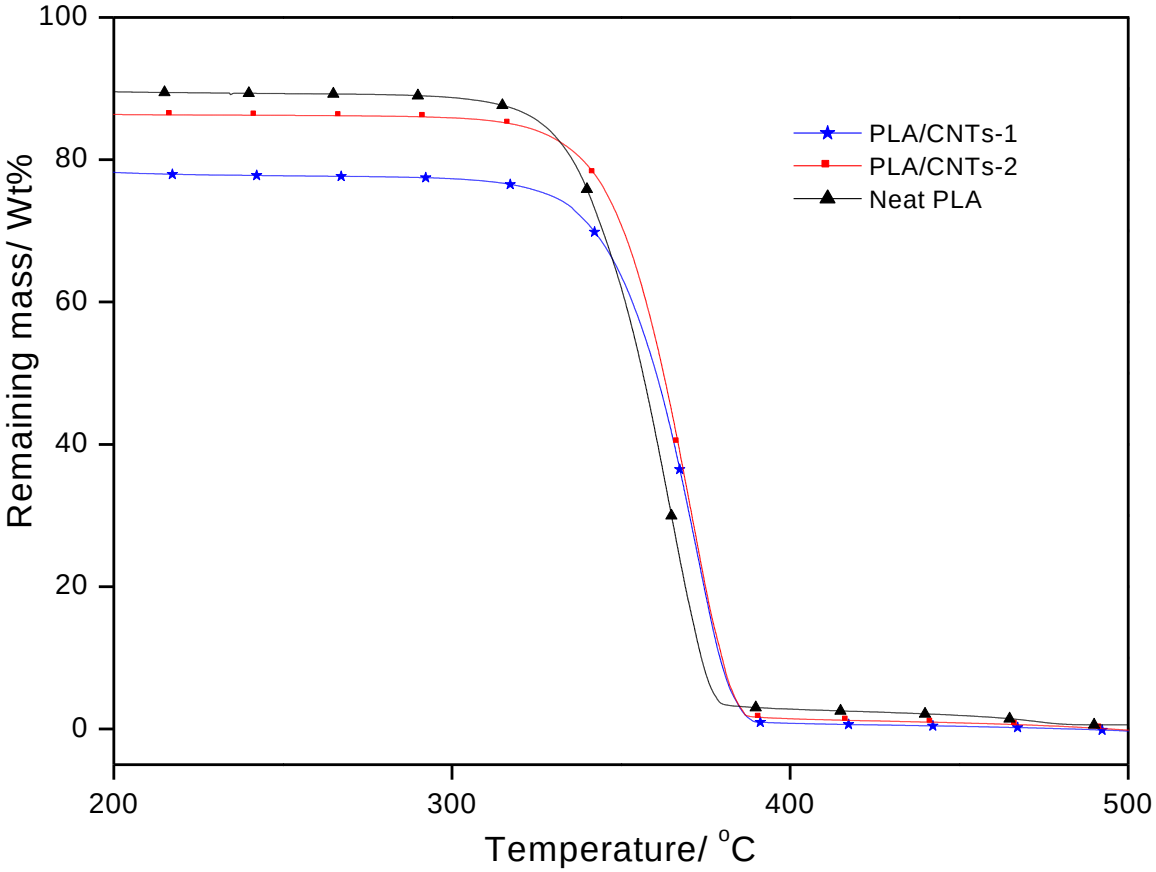

Fig. 4 TGA curves for pure PLA and PLA-CNT composites

The onset of degradation temperature as measured from the intersection of the tangent of the initial point and inflection point is the same for both PLA and nanocomposite films. The PLA/CNT composites showed higher thermal stability when compared to the neat PLA which may be due to the homogenously distributed CNTs in the PLA and good interfacial interaction of CNTs with the polymer matrix. CNTs-2 are found to be slightly better in enhancing the thermal properties of the neat polymer which can be attributed to the presence of surface oxygen functionality on the CNTs which make them more compatible with PLA polymer.

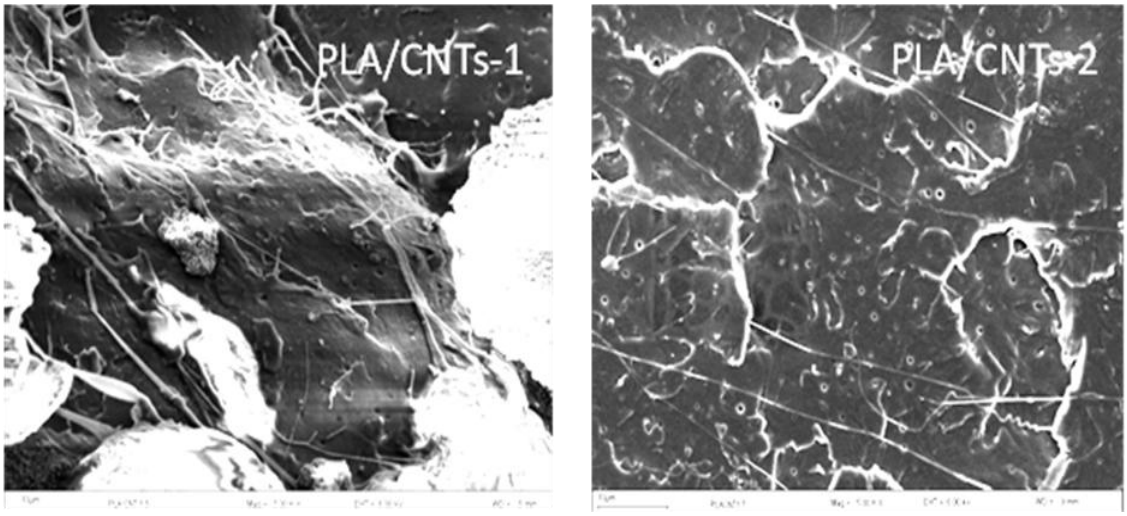

Fig. 5. SEM images of fractured surface for PLA/CNT composites with 1.5 wt% of CNTs-1 and CNTs-2.

Fig.5 presents the SEM images of a typical fractured surface of the PLA-CNT nanocomposite films containing CNTs-1 and CNTs-2. It is evident that the CNTs nicely distributed within the PLA matrix and offer good interfacial interaction. The long filament like morphology represents individual CNTs with preserved morphology. Therefore, solution mixing is found to be an efficient method to disperse individual CNTs by enhancing the interfacial adhesion with the PLA matrix. Such nicely distributed CNTs lead to enhanced thermal properties as revealed by TGA results.

4. Conclusions

In conclusion, amine functionalized CNTs were prepared by using two simple procedures. In both methods, the functionalized solids showed gradual grafting of HDA chains on CNT surface with increase in reaction time. Functionalization was demonstrated by FTIR, SEM, and XPS analyses. Single step functionalization showed advantages over the two-step procedure in reducing the reaction time. XPS results indicated the formation of covalent bond through amide groups in the case of two step

functionalization whereas the amine groups were just physisorbed on the CNT surface in one step functionalization. Solution mixing process resulted in a nice dispersion of CNTs with preserved aspect ratio within PLA matrix. The polymer nanocomposite thus prepared showed improved thermal properties when compared to the neat PLA.

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