

Polymer adsorption in the grafting reactions of hydroxyl terminal polymers with multi-walled carbon nanotubes

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Abstract

Melt stirring of non-functional polymers such as poly(ethylene oxide) dimethylether (PEO–Me) and polystyrene (PS–H) with multiwalled carbon nanotubes (MWNTs) in the absence of solvent for 48 h induced a substantial amount of polymer adsorption on the MWNTs. The chloroform extraction of the reaction products using centrifugation yielded black colored solutions exhibiting UV absorbance corresponding to the presence of MWNTs. The adsorption of polymer was confirmed on the surfaces of solvent washed residual and recovered MWNTs from the reactions using thermogravimetric analysis (TGA) and FT-IR spectroscopy. Covalent grafting reactions carried out using hydroxyl-terminated PEO–OH and PS–OH with acid chloride containing MWNTs under identical melt stirring condition produced similar results. The presence of polymer on the residual and recovered MWNTs irrespective of the nature of the terminal groups indicates that the adsorption of polymers poses a problem in accurately determining the grafting efficiency. FT IR spectra of the PEO-*g*-MWNTs shows a substantial shift in CH stretching vibrations indicating a plausible weak intermolecular interaction with π electrons of the MWNTs.

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1. Introduction

Surface modification of carbon nanotubes (CNTs) has attracted significant interest recently [1–12]. Several strategies have been used for the functionalization of CNTs through covalent and non-covalent reactions with organic molecules, including polymers, to circumvent the dispersion problem. Covalent functionalization through post chemical reactions and non-covalent functionalization through intermolecular interactions have been attempted to suppress van der Waals forces bundling up the individual CNTs. The covalent functionalization strategy mostly exploits nanotube bound carboxylic acids in amidation or esterification reaction with amine or hydroxyl containing polymer or organic molecules [1,2,8,9,13].

Haddon and co-workers [1] produced soluble single walled nanotubes (SWNTs) by attaching octadecyl moieties via amide linkages. Subsequently, Sun and co-workers [7,9,13] performed esterification of the surface bound carboxylic acids with various oligomeric and polymeric compounds containing terminal hydroxyl groups for the functionalization of SWNTs and MWNTs. They found, through microscopic and spectroscopic analyses, that the polymer fraction after extraction contained an appreciable amount of polymer-grafted carbon nanotubes. Recently, we and others [11,12,14–16] have used the ‘grafting-from’ strategy to grow polymers from SWNTs and MWNTs and produced polymer grafted nanotubes which are dispersible in organic solvents.

The efficiency of polymer grafting reactions on carbon nanotubes varies widely depending on the reaction condition. The quantification of covalently attached polymer and non-covalently adsorbed polymer during grafting reaction is an outstanding issue that needs to be addressed thoroughly. In this paper we describe the problems

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associated with the grafting reactions of hydroxyl terminal polymers with carboxylic acid groups on MWNTs due to concomitant non-covalent polymer adsorption. The MWNTs from the grafting reactions were extracted with chloroform along with the polymer and separated as residual and recovered polymer-*g*-MWNTs after removing free polymers. The results were compared with control experiments carried out under similar condition using non-functional polymers.

2. Experimental section

Solvents such as chloroform (CHCl₃) and dichloromethane (Aldrich) were HPLC grade solvents and used as received. Distilled toluene was stored over a small amount of oligostyryllithium on a vacuum line. Poly(ethylene oxide) dimethylether (PEO–Me, $M_n=2000$ g/mol, $M_w/M_n=1.11$) and hydroxyl terminated poly(ethylene oxide) (PEO–OH, $M_n=2000$ g/mol, $M_w/M_n=1.10$) were obtained from Aldrich. The polystyrene (PS–H, $M_n=2500$ g/mol, $M_w/M_n=1.05$) and hydroxyl terminated polystyrene (PS–OH, $M_n=2000$ g/mol, $M_w/M_n=1.09$) were synthesized using standard living anionic polymerization under high vacuum [17]. Secondary butyllithium (*s*BuLi) was prepared using *sec*-butyl chloride and lithium metal in cyclohexane. 3-*tert*-Butyldimethylsilyloxy-1-propyllithium (FMC corporation, USA) was used as initiator to prepare hydroxyl-protected polystyrene. The hydroxyl-terminated polystyrene was obtained after the hydrolysis of the protecting groups present at one of the chain terminus. The hydrolysis was done using tetrabutylammonium fluoride (1 M in THF) for 24 h at room temperature.

The MWNTs were provided by NanoLab (Watertown, MA) and were used as received. The MWNTs were obtained through the chemical vapor deposition method and were purified with an HF wash to remove residual catalyst. The resulting product has approximately 1 mol% carboxylic acid groups with respect to the carbon atoms of the MWNTs as determined by titration, X-ray photoelectron spectroscopy (XPS) and promptgamma methods. Extensive oxidative procedures such as refluxing in nitric acid or treating with sulfuric and nitric acid mixture were not used to increase the concentration of acid groups. It was found that the MWNTs yielded a small quantity of iron or iron oxide particles as residue (~4–5 wt%) in the thermogravimetric (TGA) analysis.

2.1. Grafting of hydroxyl terminal polymers with MWNTs in bulk

A typical grafting reaction was performed using hydroxyl-terminated polymers (PEO–OH and PS–OH) as follows: a sample of 500 mg of dried MWNTs was refluxed in 50 ml of thionyl chloride at 70 °C for 24 h. The excess thionyl chloride was removed under vacuum and MWNTs–

COCl were washed with dry THF and stored under nitrogen. A known amount of MWNT–COCl (50 mg, $\sim 4.2 \times 10^{-5}$ mol of –COCl) was placed into a 25 ml flask and a carefully dried PEO–OH (1 g, $\sim 5.0 \times 10^{-4}$ mol of –OH) in toluene (5 ml) was transferred into the flask at room temperature. The solvent was removed under vacuum and the mixture was stirred under nitrogen at 100 °C. After 48 h, 100 ml of CHCl₃ was added and stirred vigorously for 15 h at room temperature. The entire mixture was centrifuged at 7000 rpm and a clear black colored chloroform layer was separated. The residual MWNTs were separated using centrifugation twice more with additional amounts of CHCl₃ (3 × 100 ml). The collected chloroform extracts were concentrated and the polymer-*g*-MWNTs along with the free polymer were precipitated in excess *n*-hexane and dried at 40 °C for 24 h under vacuum (yield = 0.98 g, 98%). The residual MWNTs were washed several times with chloroform and filtered until no polymer was present in the filtrate and dried at 40 °C for 24 h under vacuum. The yield of the residual MWNTs was 38 mg (W_r), which indicated that 24% of the MWNTs on the basis of starting weight (W_s) ($[W_s - W_r]/W_s$) had been functionalized and became soluble. A small amount of precipitated polymer-*g*-MWNTs with free polymer was taken and dissolved in CHCl₃ and filtered using a 0.2 μm teflon membrane. The solvent wash was repeated until no polymer was found in the filtrate. The recovered MWNTs were subjected to TGA and IR analysis.

Similar procedures were used for reacting hydroxyl-terminated polystyrene (PS–OH) with MWNTs–COCl at 150 °C. In a control experiment, the reactions of non-functional polymers such as PS–H and PEO–Me at 150 and 100 °C, respectively, were also carried out as described above.

2.2. Characterization

Thermogravimetric analysis was performed using a TA Instruments TGA 2050 analyzer in air from 30 to 900 °C (10 °C/min). UV–vis spectra were recorded using a Thermo Spectronic's Biomate 5 instrument using dilute solutions of MWNTs and the composite dispersions. FT-IR spectra were recorded using a Bio-Red Win-IR Pro instrument with a resolution of 2 cm⁻¹. KBr was used to prepare sample pellets. Tabletop ultrasonic cleaner (FS-20H, Fisher Scientific) operating at 40 kHz with 80 W ultrasonic power was used. Polymers were characterized using a gel permeation chromatograph (GPC) equipped with an isocratic pump (Knauer K-501), UV detector (Knauer UV-K2501), RI detector (Knauer RI-K2301), and 1 × 100 Å (60 cm), and linear (60 cm) polymer standard service (PSS) SDV gel columns. PSS WinGPC software was used to acquire and analyze the chromatogram. GPC was calibrated with a set of PS and PMMA standards (PSS, Germany).

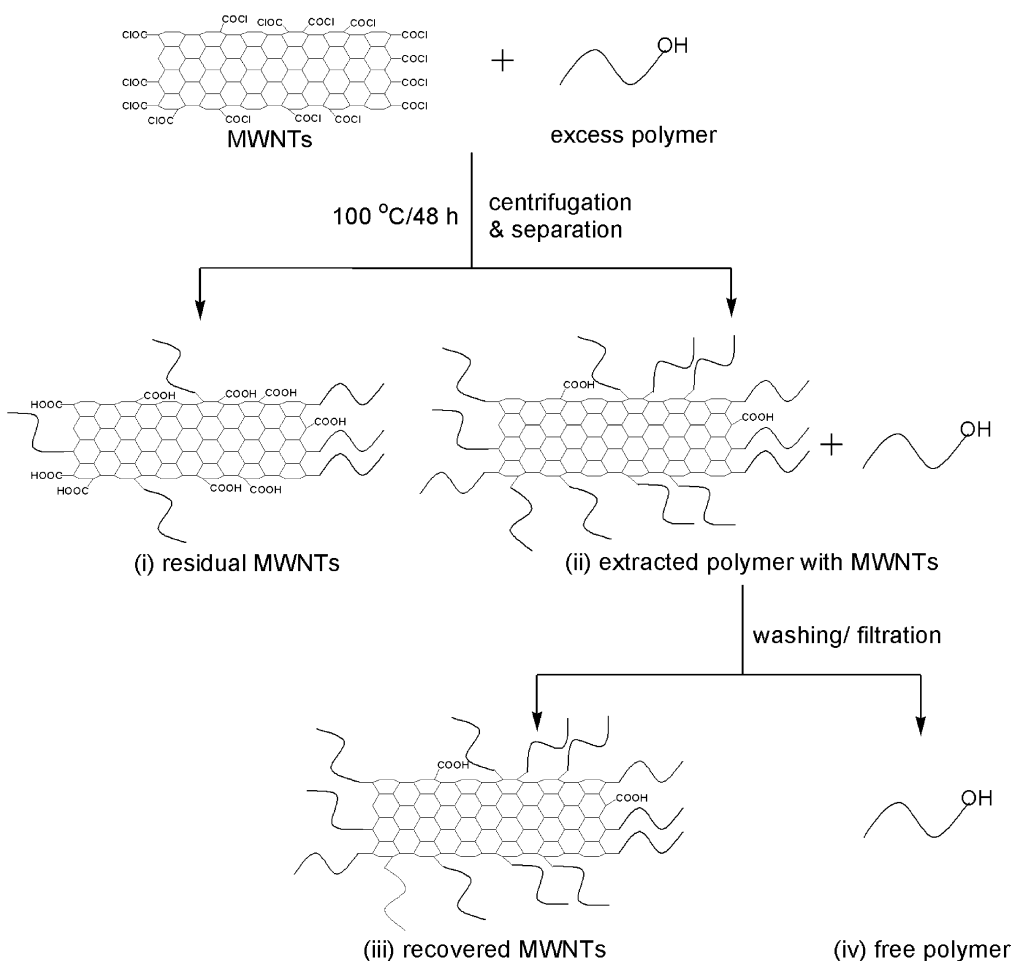
3. Results and discussion

3.1. Covalent functionalization of MWNTs using esterification reaction of terminal hydroxyl containing polymers in the melt condition

Grafting reactions of hydroxyl terminated poly(ethylene oxide) (PEO–OH, $M_n = 2000$ g/mol, and $M_w/M_n = 1.10$) and polystyrene (PS–OH, $M_n = 2000$ g/mol, and $M_w/M_n = 1.09$) with thionyl chloride treated MWNTs were performed in melt at 100 and 150 °C, respectively for 48 h. The reactions were carried out with excess polymer that is the ratio of hydroxyl functional groups with respect to the carboxylic acid groups of the MWNTs was kept in all reactions above 1. Scheme 1 shows the reaction and the following work-up procedure leading to the separation of various products. The soluble portion of the reaction mixture after the reaction was extracted in chloroform several times using centrifugation to remove residual MWNTs (Scheme 1, (i)). A large amount of tubes were collected as residual MWNTs. The chloroform extracts looked black in color indicating the presence of MWNTs in the reactions carried out using both PEO–OH

and PS–OH polymers. The extracted polymer with MWNTs solution was concentrated and precipitated. The precipitated polymer (Scheme 1, (ii)) was slightly gray in color in both the reactions. As these reactions were done with excess polymer, the extracted grayish polymer contains a large amount of free polymer. In an attempt to remove the free polymer, the extracted grayish polymer was dissolved in, and washed with chloroform (in the case of PEO reactions) or THF (in the case of PS reactions) and filtered using 0.2 μm teflon membrane to recover the MWNTs that contain only covalently grafted polymer (Scheme 1, (iii)). The recovered MWNTs from the teflon membrane were washed thoroughly with CHCl_3 and THF until the filtrate showed absence of polymer by precipitation with a non-solvent.

The residual MWNTs (Scheme 1, (i)), the extracted grayish polymer with MWNTs (Scheme 1, (ii)) and the recovered MWNTs after removing free polymer (Scheme 1, (iii)) were dried under vacuum for 40 °C for 6 h and subjected to thermogravimetric analysis (TGA), infrared (IR) and ultraviolet (UV) spectroscopic analyses. The results are summarized in Table 1. Examination of these



Scheme 1. Grafting reaction of hydroxyl terminal polymer with MWNTs–COCl and its various products. Only grafted chains are shown and the contribution of co-adsorbed chains has not been shown for clarity.

Table 1
TGA of the grafting reaction products of a single hydroxyl group functionalized polymers and non-functionalized polymers with MWNTs in bulk

Run	Polymer	[R-OH]/[car-bon] _{MWNT-COCl} ^a R = PEO or PS 10 ²	Time, h/temperature, °C	Residual MWNTs ^b		Soluble portion extracted in CHCl ₃ ^c				
				% of polymer ^d	% of MWNT	Grafting efficiency ^e (%)	Precipitated ^c composite % of polymer	% of MWNT ^f	Recovered ^d MWNTs % of polymer	% of MWNT ^f
1	PEO-OH _{2K}	11.90	48/100	7.6	92.4	4.6	98.9	1.1	14.2	85.8
2	PEO-OH _{2K}	43.10	48/100	8.5	91.5	5.1	99.1	0.9	8.5	91.5
3	PEO-Me _{2K}	44.50	48/100	7.0	93.0	4.2	99.6	0.4	53.8	46.2
4	PS-OH _{2K}	32.00	48/150	10.7	89.3	6.4	97.8	2.2	–	–
5	PS-H _{2.5K}	23.10	48/150	4.9	95.1	2.9	98.0	2.0	0.1	89.9

^a Mole fraction of OH or H-terminated polymer to carbon.

^b Residual MWNTs, settled in centrifugation, containing MWNT-g-polymer and non-grafted tubes were washed several times with THF and methylene chloride to remove the soluble partially grafted MWNTs and the excess PMMA-OH.

^c Precipitated from the filtrate containing partially grafted MWNTs and the excess polymer.

^d Recovered soluble extracts redissolved in CHCl₃, washed and filtered using a 0.2 μm teflon membrane to remove excess polymer.

^e Grafting efficiency = (moles of polymer present on the MWNTs/mol of COOH groups present in MWNTs) × 100.

^f Calculated from the weight loss curve of thermogram.

samples revealed that all of the different fractions of MWNTs contain grafted polymer (PEO-g-MWNTs or PS-g-MWNTs).

However, the percentage of grafted polymer varies significantly in both the residual and recovered MWNTs. The TGA analysis showed that the residual MWNTs contain 7–11 wt% of grafted polymer (PEO or PS) (Fig. 1(A) (i)). The FT-IR spectra of the residual MWNTs showed absorptions at frequencies centered at 2919 cm⁻¹ (CH-stretching), 1453 cm⁻¹ (CH-bending), 1118 cm⁻¹ (CH-bending) corresponding to the PEO indicating the presence of grafted PEO on the MWNTs (PEO-g-MWNTs) (Fig. 1(B) (i)). Similarly the residual MWNTs obtained from the PS-OH reaction were showing 2922 cm⁻¹ (CHs), 1452 cm⁻¹ (CHb and Arbr), and 1102 cm⁻¹ (CHr) indicating the presence of grafted PS on the MWNTs (PS-g-MWNTs). As these MWNTs are thoroughly washed with CHCl₃ several times and dried under vacuum for 40 °C for 6 h, the presence of polymer absorbance supports the occurrence of the grafting reaction.

A dilute solution of the extracted grayish polymer in both PEO-OH and PS-OH reactions (Table 1, run 1, 2 and 4) exhibits UV–vis absorbance decreasing monotonously from 250 to 900 nm, which supports the presence of soluble grafted MWNTs (Fig. 6(A)). Although, the extracted

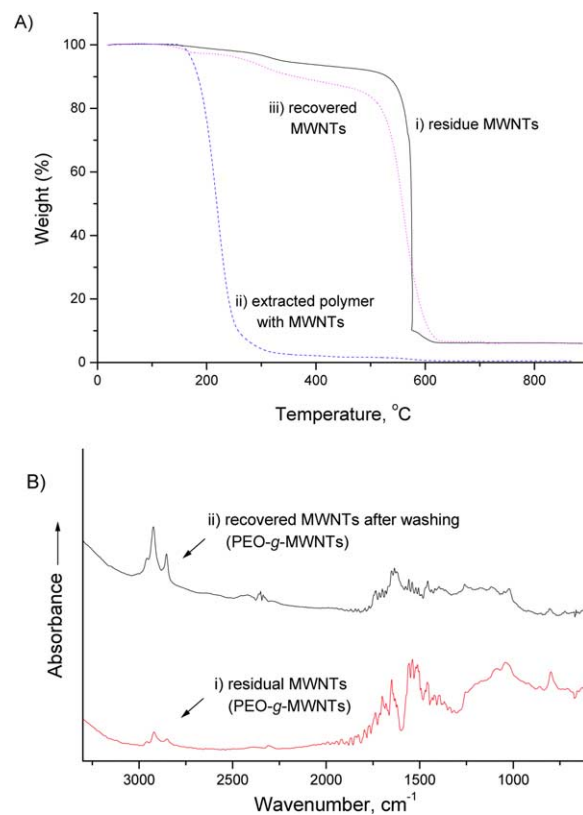


Fig. 1. (A) TGA of residual MWNTs (i), extracted MWNTs with polymer (ii) and recovered MWNTs after washing (iii) in the grafting reactions of hydroxyl terminated PEO and (B) IR spectra of residual MWNTs (i) and recovered MWNTs after washing, PEO-g-MWNTs (ii).

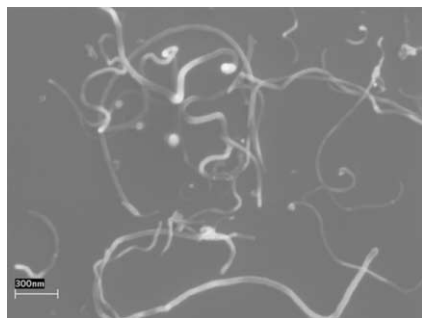


Fig. 2. SEM of the residual PEO-g-MWNTs obtained from the reaction of PEO-OH with MWNT-COCl. The sample was dispersed in chloroform and a drop dried on silica.

polymer solution looked grayish, it contained only a small portion (0.4–2.5 wt%) of MWNTs as evidenced from the TGA analysis of the precipitated polymer (Fig. 1(A) (ii)). The TGA analysis of the recovered MWNTs after removing the free polymer by washing procedures showed that they contain more grafted polymer than the residual MWNTs (14 wt%) (Table 1, run 1, Fig. 1(A) (iii)). FT-IR of the recovered MWNTs shows peaks corresponding to the PEO supporting the presence of grafted PEO (Fig. 1(B) (ii)). This suggests that the amount of polymer grafted MWNTs extractable in CHCl_3 could depend on the number of polymeric chains grafted on the nanotubes. Higher weight percentage of polymer in the recovered PEO-g-MWNTs might correspond to higher functionalization or enhanced grafting. The residual PEO-g-MWNTs are soluble in CHCl_3 after a few minutes of sonication and the dispersed tubes are seen in SEM analysis (Fig. 2).

3.2. Problem associated with the quantification of polymer grafting: adsorption of polymer on to MWNTs

Control experiments were carried out under similar condition employed for grafting reactions using polymers without hydroxyl functionality to study the effect of polymer coating or wrapping. Polymers such as poly(ethylene oxide) having both of the chain ends terminated with methoxy groups (PEO-Me) and polystyrene (PS-H) terminated with a proton were mixed with MWNTs-COOH and kept stirring at 100 and 150 °C, respectively, under N_2 for 48 h. Since these non-functional polymers are chain-end capped with a hydrogen or methyl group, they do not react with the acid groups present in the MWNTs. Nonetheless, the reaction mixture extracted in CHCl_3 using centrifugation was black in color indicating some of the MWNTs became soluble along with the polymer (Fig. 3). The extracted MWNTs with excess polymer were collected by precipitation. They were apparently black in color due to the presence of MWNTs (Fig. 4). The presence of MWNTs in these samples can be clearly seen from SEM analysis of the solid samples (Fig. 5). This gives a direct evidence for the adsorption-induced dissolution of MWNTs by polymers.

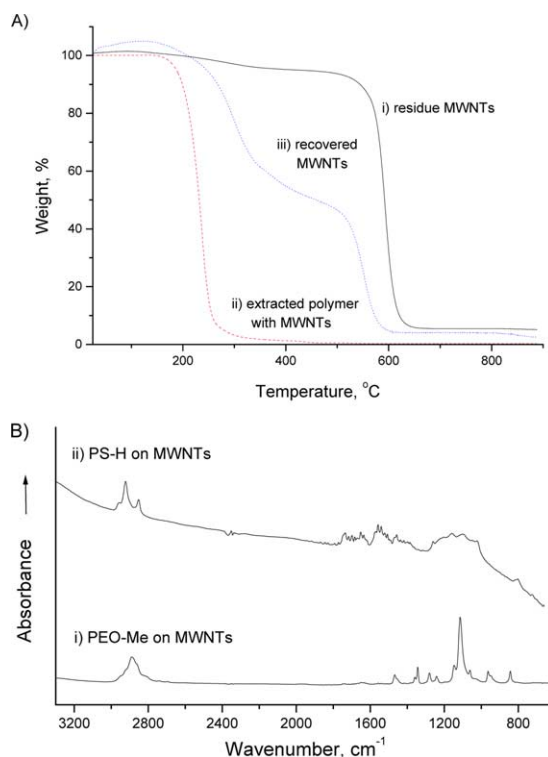


Fig. 3. (A) TGA of residual MWNTs (i), extracted MWNTs (ii) and recovered MWNTs after washing (iii) MWNTs from the PEO-Me reaction and (B) IR spectra of recovered MWNTs after washing showing adsorption of methyl and proton terminated PEO-Me (i) and PS-H (ii) respectively.

The UV-vis spectrum of the chloroform solutions of these samples has a strong absorption from 300 to 900 nm supporting the presence of MWNTs (Fig. 6(B)). Both of these polymers (PEO-Me and PS-H) have no absorption from 300 to 900 nm. The intensities of the absorption vary in all the cases in spite of the fact that the same concentration ($[\text{polymer}]_0 = 1 \text{ mg/ml}$) was used. This indicates that the extractable amount of MWNTs through polymer adsorption is not consistent in every reaction under stirring using teflon coated magnetic stir bar. The apparent solubility of the MWNTs shows clearly the presence of polymer coating or wrapping through adsorption.

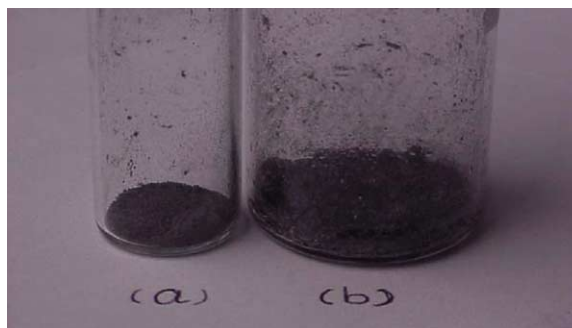


Fig. 4. Vials containing precipitated non-functional polymers from chloroform extraction (a) extracted PEO-Me with MWNTs (reaction 3, Table 1) and (b) extracted PS-H with MWNTs (reaction 5, Table 1).

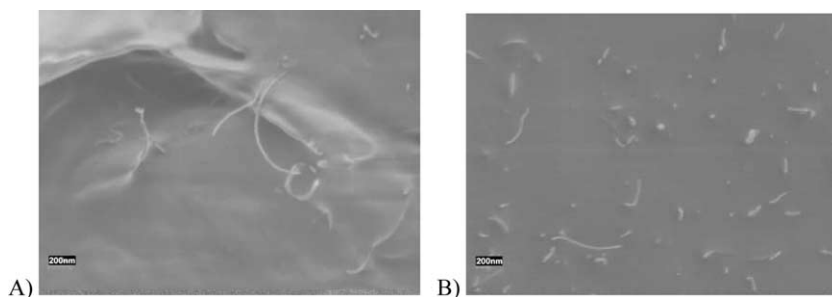


Fig. 5. SEM of precipitated polymer samples (solid) from the chloroform extraction of non-functional polymers in blank experiments with MWNTs. (A) PEO-OMe and (B) PS-H samples (shown in Fig. 4) showing the presence of carbon nanotubes.

The extracted MWNTs with excess polymer had 0.4 wt% (Fig. 3(A) (ii)) and 2 wt% MWNTs in PEO-Me and PS-H reactions, respectively. Moreover, the recovered MWNTs after removing free polymer by several solvent wash and filtration showed the presence of a large amount of polymer, 53.8 wt% in the case of PEO-Me (Fig. 3(A) (iii)) and 10.1 wt% in the case of PS-H. The amount of polymer coated on the recovered MWNTs is not consistent with any other reactions (Table 1). We believe that it depends on the physical forces generated in the stirring process, which is difficult to keep constant in very reaction using a simple teflon stir-bar. The amount of adsorbed polymer is high in

some cases, largely due the influence of experimental conditions affecting physisorption. However, it is clear that the adsorption of polymer exists concomitantly in covalent grafting reactions carried out with hydroxyl-terminated polymers. The FT-IR spectrum of the recovered MWNTs after washing with solvent shows absorption signals corresponding to the non-functional polymers supporting the presence of polymer adsorption (Fig. 3(B)). This result is in accordance with Dai and co-workers [18,19] who have used PEO as adsorbent to introduce biomolecular recognition of SWNTs.

The residual MWNTs (insoluble in CHCl_3 by simple extraction) were washed with CHCl_3 or THF several times until no polymer was present in the filtrate. The residual MWNTs, after a thorough washing and drying, showed 7 wt% polymer in the case of PEO-Me (Fig. 3(A) (i)) and 4.9 wt% polymer in the case of PS-H (Table 1, run 3 and 5). The presence of non-functional polymers in the residual MWNTs could be attributed to polymer coating or wrapping of bundled nanotubes during stirring in molten polymer. It should be mentioned that the residual and recovered MWNTs are subjected to a thorough washing procedure to remove free polymer. The presence of such a large amount of non-functional polymer on the MWNTs, however, inconsistent the amounts are, in these reactions is entirely due to polymer coating or wrapping around the tubes through non-covalent interactions.

The FT-IR analysis of the PEO-OH grafting reaction products shows evidence for a weak molecular interaction between the PEO's methylene groups and the MWNTs. The symmetric and asymmetric stretching frequencies of the methylene groups are centered at 2887 cm^{-1} in a neat PEO-OH, which shifts to 2919 cm^{-1} in the washed residual MWNTs (PEO-g-MWNTs) (Fig. 7 (ii)). A similar frequency shifts was also observed in the PEO present on the recovered MWNTs after removing non-interacting polymers (Fig. 7 (iv)). It is known that a weak bonding involving CH groups with other donor molecules would shift the frequencies of CH vibrations [20]. A substantial frequency shift, $\Delta\nu = 35\text{ cm}^{-1}$, of observed in the residual and recovered MWNTs is attributed to the presence of a weak non-covalent interactions involving CH groups of the PEO with the MWNTs. Such a non-covalent interaction involving

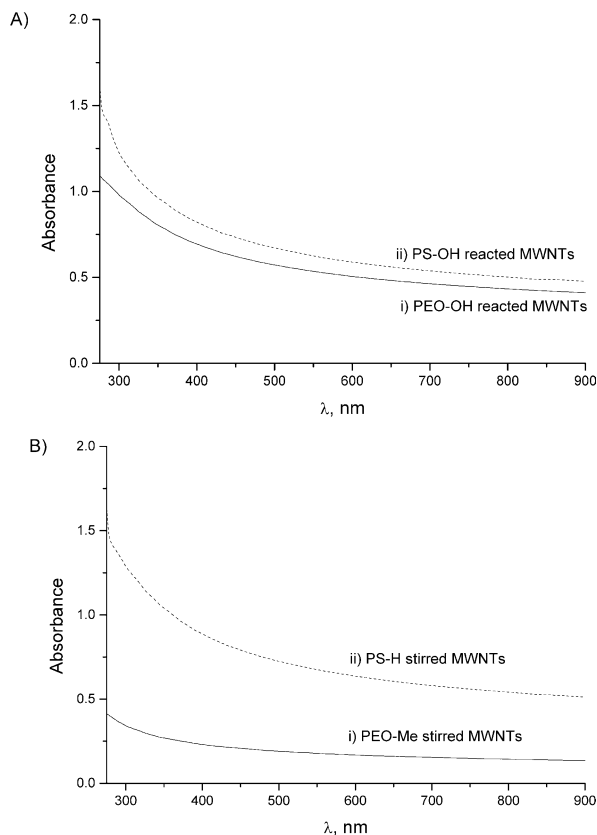


Fig. 6. UV-vis spectra of chloroform extracted-polymer (1 mg/ml) showing absorption due to the presence of dissolved MWNT (A) hydroxyl functionalized polymer reactions with MWNTs-COCl and (B) hydrogen or methyl group terminated polymer reactions with MWNTs-COOH.

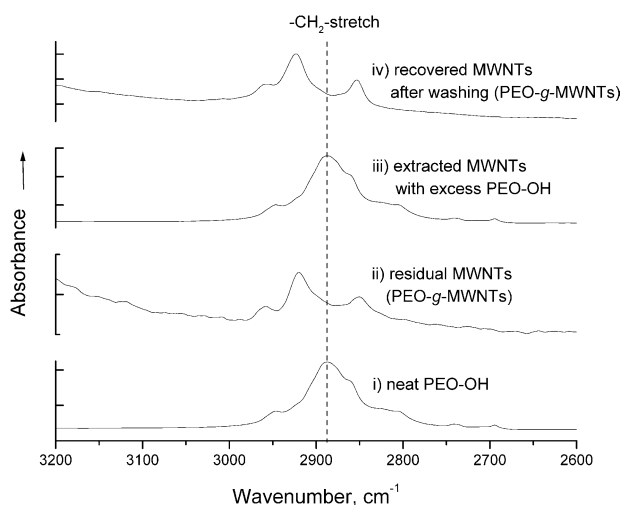


Fig. 7. FT-IR frequency shifts of asymmetric and symmetric CH_2 stretching in the washed PEO-g-MWNTs (in KBr pellet); (i) neat PEO, (ii) residual MWNT (PEO-g-MWNTs), (iii) extracted MWNTs containing excess PEO-OH, and (iv) extracted MWNTs after washing (PEO-g-MWNTs).

π - π stacking of polymers or organic molecules with carbon nanotubes has been reported by Stoddart [4], Dai [21] and co-workers, and others [21–23]. However, the non-covalent interaction involving CH groups of the polymer with the MWNTs appears to be independent of the nature of polymer as polymers containing ether linkages as well as aromatic pendants both show tendency to coat the tubes.

The results of the grafting reactions done with hydroxyl-terminated polymers indicate that the grafting efficiencies are low in the residual MWNTs (Table 1). The polydisperse nature of MWNTs (in terms of their functionality as well as their length) results in a heterogeneous grafting reaction that produces multiple distributions of polymer-g-MWNTs, some of which are soluble during extraction in CHCl_3 and some are not. The control experiments carried out with non-functional polymers support the existence of molecular interactions between the MWNTs and the polymers. These results suggest that it is difficult to ascertain the extent of polymer wrapping or coating contributing to the grafting efficiency in the functionalization reaction done under melt-stirring condition.

It is widely reported that the grafting hydroxyl or amine terminated polymeric or small molecules with acid chloride functionalized CNTs proceeds with excellent efficiencies. However, the concomitant contribution of non-covalent molecular interactions to the grafting efficiency has not been discussed. Nevertheless, Haddon and co-workers [24] have showed that the weight percent of octadecylamine present after the functionalization reaction with SWNTs (~ 64 wt%) was much higher than the actual acid functionality. Sun and co-workers [6,7] have performed several grafting reactions of hydroxyl containing polymers with acid chloride functionalized tubes and reported very high grafting efficiencies. It is important to note that in all these procedures the reagents were vigorously stirred with

tubes at high temperatures for long period of time in the absence of solvent. These conditions provide sufficient shear force to induce molecular interaction leading to a partial coating of organic molecules through non-covalent interaction on electron rich surface of the CNTs.

4. Conclusions

The grafting reaction carried out using hydroxyl terminated PEO and PS with MWNTs under melt stirring condition produced extractable and non-extractable PEO-g-MWNTs or PS-g-MWNTs with different weight percent of polymer in it. The determination of the actual weight percentage of polymer chains that are covalently connected to the MWNTs is difficult as a substantial amount of polymer coating on the MWNTs was observed under identical reaction condition with the methyl terminated PEO-Me, and the hydrogen terminated PS-H. Characterization of a thoroughly solvent washed residual and extractable MWNTs by TGA and FT-IR shows up to ~ 5 –50 wt% non-functional polymer adsorbed on the MWNTs. A considerable shift in the CH vibrations ($\Delta\nu$ 35 cm^{-1}) was seen in the PEO-g-MWNTs indicating the presence of molecular interaction with MWNTs.

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