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Study on the Functionalization of Multi-Walled Carbon Nanotube with Monoamine Terminated Poly(ethylene oxide)

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Summary: Through the introduction of carboxylic acid or thionyl chloride groups in multi-walled carbon nanotubes (MWNT-COOH or MWNT-COCl) and amine group in poly(ethylene oxide) (PEO-NH_2), complexation of MWNT with PEO was successfully performed, yielding MWNT/PEO complex having approximately 40 wt.% of PEO. The MWNT/PEO complexes exhibited excellent dispersibility in solvents including water, ethanol and DMF. From SEM observation, the increases in the diameter of the nanotubes were observed. The presence of PEO on the nanotube surface was also confirmed through EDX and FT-IR. The effects of different functionality on MWNTs (–COOH vs. –COCl) and different molecular weight of PEOs (1000 g/mol vs. 2000 g/mol) were not so prominent.

Keywords: dispersion; functionalization; multi-walled carbon nanotube; poly(ethylene oxide); water-soluble polymer

Introduction

Carbon nanotubes (CNTs) have been one of the most attractive objects to study owing to their unique properties. Outstanding mechanical, thermal and electrical properties come from their carbon structures allow them to be used in various applications such as field emission displays,[1] sensors,[2] transistors[3] and polymer composites.[4–7] However, agglomeration and entanglement of CNTs originated from their high aspect ratio and attractive van-deer Waals interactions have been an obstacle for their practical uses.

For the last few years, this problem has encouraged many researchers to investigate methods that enhance the dispersion and solubility of CNTs. Various polymers were applied to CNTs to yield CNT/polymer complexes, which exhibit better dispersion in polymer matrix and enhance the properties of the polymer composite such as tensile strength, electrical conductivity, solubility and so on. Since poly(ethylene oxide) (PEO) is a representative hydrophilic polymer having good solubility in many solvents and polymers, multi-walled carbon nanotube (MWNT) complexed with PEO has been attractive filler in various polymer composites. Goh et al. suggested MWNT/poly(methyl methacrylate) composite, where amine terminated PEO (PEO-NH_2) acted as a compatibilizer.[8] The terminal amine groups of PEO-NH_2 ionically interacted with carboxylic acid groups on MWNTs, while PEO chain formed miscible entanglements with poly(methyl methacrylate) matrix. Adding the modified MWNTs to poly(methyl methacrylate) matrix increased the storage modulus of the composites. Sun et al. employed diamine terminated PEO for the solubilization of pristine and purified single-walled carbon nanotubes (SWNTs).[9] Haddon et al. and Sano et al. also reported the PEO grafted SWNT.[10,11] Recently, Basiuk

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et al. suggested the possibility of direct functionalization of MWNTs with hydrocarbons having amine functional groups.[12] In this paper, studies on the complexation of MWNTs with monoamine terminated PEOs according to different functionalities of MWNTs and reaction conditions are reported. PEO having methyl chain end was also employed to verify the effect of amine functionality.

Experimental Part

Materials

Multi-walled carbon nanotubes (MWNTs) were synthesized by chemical vapor deposition method and purchased from Iljin nanotech co.. Monoamine terminated poly (ethylene oxide) with molecular weight of 1000 g/mol (PEO-NH_2-1000, [PO]/[EO] = 3/19) and 2000 g/mol (PEO-NH_2-2000, [PO]/[EO] = 10/31) were obtained from Huntsman. Dimethyl terminated poly(ethylene oxide) with molecular weight of 1000 g/mol (PEO-CH_3-1000) and 2000 g/mol (PEO-CH_3-2000) were purchased from Aldrich. Sodium hydroxide (NaOH) was also purchased from Aldrich. Sulfuric acid (96%) and Nitric acid (64–66%) were purchased from Duksan. Tetrahydrofuran (THF) and thionyl chloride ($SOCl_2$) were purchased from Samchun.

Purification and Functionalization of MWNTs

Pristine MWNT (AP-MWNT) was purified and carboxylated through acid treatment.[13] AP-MWNT (2.0 g) was placed in round bottom flask, followed by the addition of sulfuric acid (96%, 50 mL) and nitric acid (64–66% 17 mL) mixture (3/1 = v/v). The reactant was sonicated in bath type sonicator (Branson 5510) at 40 Hz for 10 min. The reaction flask was then removed from the sonicator and put into an oil bath equipped with reflux condenser. Gas came out from the reactor was neutralized in NaOH/water solution. The mixture was further reacted at gradually increased reaction temperature from 90 to 130 °C for 3 hour under vigorous stirring (300 rpm). The mixture was then diluted with excess amount of deionized water, followed by filtration through 0.45 μm PVDF membrane (hydrophilic, Millipore) to separate the solid components. The washing procedure was repeated until the pH of the filtrated solution reached approximately 7. The obtained solid product was then washed repeatedly with 200 mL of acetone. Finally, the solid product was washed with THF two times and dried under vacuum at 60 °C for 24 hour, yielding MWNT with carboxyl functional group (MWNT-COOH).

The carboxyl group on MWNT was converted to acyl chloride group through a reaction employing excess amount of $SOCl_2$ (MWNT-COCl).[13] Into a reaction flask equipped with reflux condenser was added 1.0 g of MWNT-COOH and 30 mL of $SOCl_2$. The mixture was then reacted at 65–70 °C for 24 hours under vigorous stirring (300 rpm). After cooled down to room temperature, the mixture was washed four times with THF. During washing procedure, the solid product was separated from the THF solution through centrifugation at 14 000 rpm for 1 hour. The final solid product was then dried under vacuum at 60 °C for 24 hours.

Preparation of MWNT/PEO Complex

MWNT/PEO complexes were prepared through a melt mixing process in a round bottom flask. 0.1 g of MWNTs and 1.7 g of PEO were added to the flask, followed by a vigorous mixing under nitrogen at 140 °C for 24 hours. After the reaction, the mixture was washed four times with excess amount of ethanol. The solid product was separated from the solution through centrifugation at 14 000 rpm for 1 hour. The final solid product was dried under vacuum at 60 °C for 24 hours.[9]

Analysis

Morphology of MWNT/polymer complex was observed using FE-SEM (Field Emission Scanning Electron Microscope, Hitachi S-4700). The amount of polymer and oxygen elemental distribution in MWNT/polymer complex was determined by thermogravimetry analysis (TGA, STA S-1500, Scinco) and energy dispersive x-ray analysis (EDX, Horiba 7200-H). Functionality of MWNT/PEO complex was characterized by Fourier Transform-Infrared Spectroscopy (FT-IR, Thermo, Nicolet 380, ATR)

Dispersibility of MWNTs in Solvents

The dispersibility of MWNTs in various solvents was tested employing water, ethanol, DMF (N,N-dimethylformamide) and hexane. 0.5 mg of samples were dispersed in 10 mL of solvents through sonication for one and half hours. The stability of the dispersion was observed at 0 hour, 24 hours, 48 hours and 72 hours.

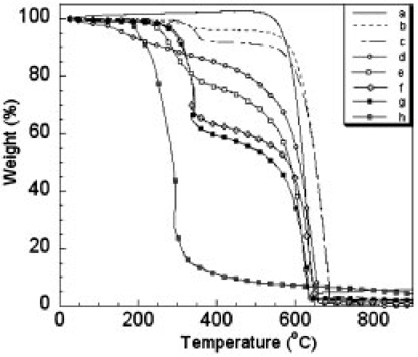


Figure 1.
Thermogravimetry analysis (TGA) curves of AP-MWNT, MWNT-COCl, PEO-NH_2 and various MWNT/PEO complexes; AP-MWNT (a), AP-MWNT/PEO-CH_3 (b), AP-MWNT/PEO-NH_2 (c), MWNT-COCl (d), MWNT-COCl/PEO-CH_3 (e), MWNT-COOH/PEO-NH_2 (f), MWNT-COCl/PEO-NH_2 (g), PEO-NH_2 (h). The molecular weight of PEO was 2000 g/mol.

Results and Discussion

In this study, three different kinds of MWNTs with various surface functionality (AP-MWNT, MWNT-COOH and MWNT-COCl) and four different kinds of PEO with various chain end functionality and molecular weight (PEO-NH_2-1000, PEO-NH_2-2000, PEO-CH_3-1000, PEO-CH_3-2000) were employed to cover different combinations of complexation reactions (Table 1).

The composition of MWNT-COOH and MWNT/PEO complexes were determined through thermogravimetry analysis (TGA) as shown in Figure 1. The weight loss near 700 °C represents the decomposition of MWNT (Figure 1a), while that near 300 °C represents the decomposition of PEO (Figure 1h). The composition of MWNTs was determined by relative amount of weight loss at each temperature. The content of PEO in AP-MWNT/PEO-CH_3 was only ~3% (Figure 1b), indicating insufficient complexation of MWNT with PEO. This probably originated from the absence of functional group on PEO and MWNT. Introduction of polar functional groups either in PEO (PEO-NH_2, Figure 1c) or MWNT (MWNT-COCl, Figure 1e) improves the complexation reaction, resulting in higher content of PEO in the complexes (~7% of PEO for AP-MWNT/PEO-NH_2 and ~20% of PEO for MWNT-COCl/PEO-CH_3). Better complexation was observed when functionalized MWNT was employed (MWNT-COCl/PEO-CH_3, Figure 1e), probably because polar repeating unit of PEO may afford polar-polar interaction with the COCl functional groups on MWNT.

Table 1.
Multi-walled carbon nanotubes (MWNTs) and poly(ethylene oxide)s (PEOs) employed in this study for different reaction pairs.

	PEO-NH_2-1000	PEO-NH_2-2000	PEO-CH_3-1000	PEO-CH_3-2000
AP-MWNT	X[a]	O[b]	X	O
MWNT-COOH	O	O	X	X
MWNT-COCl	O	O	O	O

[a] Symbol "**X**" indicates the reaction pair that is not covered in this study;
[b] Symbol "O" indicates the reaction pair that is covered in this study.

When reactive functional groups were introduced both in MWNT (MWNT-COOH or MWNT-COCl) and PEO (PEO-NH_2), the MWNT/PEO-NH_2 complexes contained almost 40% of PEO (Figure 1f and 1g). This clearly indicates better reactivity of functionalized MWNTs such as MWNT-COOH and MWNT-COCl with PEO-NH_2 owing to the presence of reactive groups. Interestingly, no distinct difference between MWNT-COOH and MWNT-COCl for the complexation was noticed (Figure 1f and 1g), indicating similar reactivity of MWNT-COOH and MWNT-COCl against PEO-NH_2s. Goh *et al.* also reported that PEO-NH_2s may interact ionically with carboxylic group on MWNT (MWNT-COOH), while MWNT-COCl may form covalent bond through the reaction with NH_2 on PEO.[8] Scheme 1 illustrates the complexation of MWNT-COOH and MWNT-COCl with PEO-NH_2.[14]

Figure 2 shows the dispersibility of MWNTs and MWNT/PEO-NH_2 complexes in water. Pristine MWNT (AP-MWNT, Figure 2a) and MWNT-COCl (Figure 2b) sediment almost completely, which suggest no specific affinity exist between MWNTs and water. However, MWNT-COOH (Figure 2d) and MWNT/PEO-NH_2 complexes (Figure 2c and 2e) exhibited stable dark solution even after 3 days, probably because –COOH and PEO on MWNTs have high affinity with water. Once PEO-NH_2s were complexed with MWNTs, no specific difference of the complexes originated from MWNT-COCl and MWNT-COOH was observed (Figure 2c and 2e).

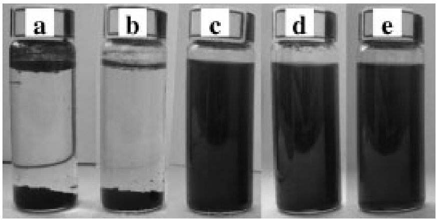
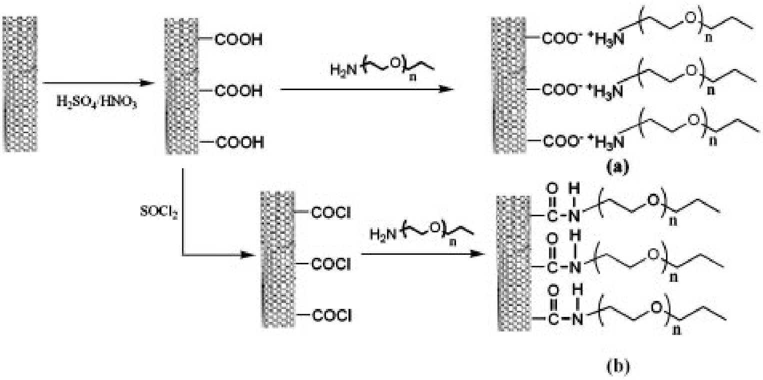


Figure 2.
Dispersibility of MWNTs and MWNT/PEO complexes in water; AP-MWNT (a), MWNT-COCl (b), MWNT-COCl/PEO-NH_2 (c), MWNT-COOH (d), MWNT-COOH/PEO-NH_2 (e). The molecular weight of PEO was 2000 g/mol.

The improved dispersibility of MWNT in the presence of PEO was also observed in washing/centrifugation procedure employing ethanol as a solvent. MWNT-COOH/PEO-NH_2 and MWNT-COCl/PEO-NH_2 exhibited incomplete sedimentation of nanotubes even under vigorous centrifugation process, affording not only solid precipitates but also black supernatant solution. This indicates that MWNTs were very effectively complexed with PEO-NH_2s, which enhanced the dispersibility of the complex in ethanol solution. In this study, practically only the sedimented samples were collected and employed in further experiments. Interestingly, MWNTs reacted



Scheme 1.
Preparation of MWNT/PEO-NH_2 complexes and specific interaction of PEO-NH_2 with MWNTs through ionic bond (a, MWNT-COOH/PEO-NH_2) and covalent bond (b, MWNT-COCl/PEO-NH_2).[14]

with PEO-CH_3s were almost completely sedimented during centrifugation process and exhibited transparent supernatant solution. This clearly indicates that very weak specific interaction exists between PEO-CH_3 and MWNTs, resulting in unstable MWNT/PEO-CH_3 complex. MWNT/PEO-NH_2 complexes also exhibited excellent and stable dispersion in DMF.

The complexation of MWNT with PEO was also confirmed through morphological analysis employing scanning electron microscope (SEM). Compared with the diameter of AP-MWNT (Figure 3a), no distinct increase in the diameter of the nanotubes was observed for MWNT-COCl/PEO-CH_3 (Figure 3b). The observation is in consistence with the result from compositional analysis (TGA), where only ~20% of PEO was complexed with MWNT (Figure 1e). For MWNT-COCl/PEO-NH_2 (Figure 3c) and MWNT-COOH/PEO-NH_2 (Figure 3d), where approximately 40% of PEOs were complexed with MWNTs (Figure 1f and 1g), the increase in the diameter of the nanotubes were prominent.

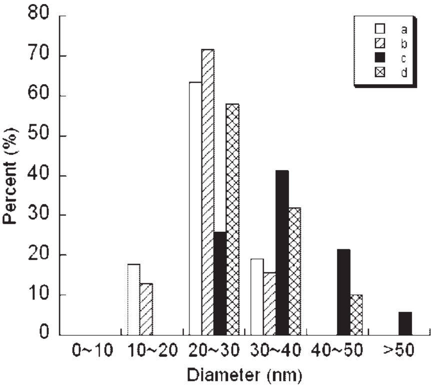


Figure 4.
Diameter distribution of carbon nanotubes for AP-MWNT and MWNT/PEO complexes; AP-MWNT (a, average diameter = 26.0 nm), MWNT-COCl/PEO-CH_3 (b, average diameter = 26.3 nm), MWNT-COCl/PEO-NH_2 (c, average diameter = 35.9 nm), MWNT-COOH/PEO-NH_2 (d, average diameter = 30.7 nm). The molecular weight of PEO was 2000 g/mol.

The average diameter and diameter distribution of carbon nanotubes were determined through image analysis on SEM images (Figure 4). Diameter distribution data of MWNT-COCl/PEO-NH_2 (Figure 4c) and MWNT-COOH/PEO-NH_2 (Figure 4d) clearly exhibited the presence of carbon nanotubes with bigger diameter, compared with those of AP-MWNT (Figure 4a) and MWNT-COCl/PEO-CH_3 (Figure 4b). The average diameter of MWNT-COCl/PEO-NH_2 and MWNT-COOH/PEO-NH_2 were 35.9 nm and 30.7 nm, respectively, which is clearly higher than that of AP-MWNT (26.0 nm) and MWNT-COCl/PEO-CH_3 (26.3 nm).

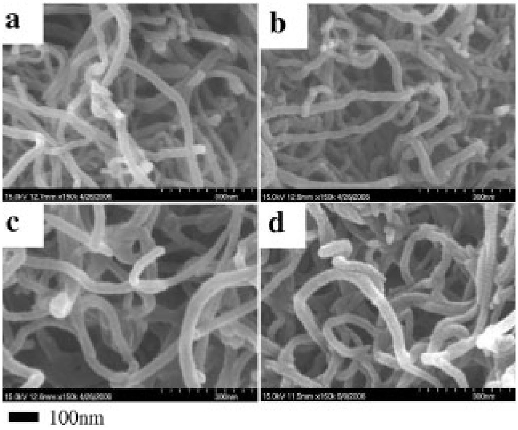


Figure 3.
Scanning electron microscope (SEM) images of AP-MWNT (a), MWNT-COCl/PEO-CH_3 (b), MWNT-COCl/PEO-NH_2 (c) and MWNT-COOH/PEO-NH_2 (d). The molecular weight of PEO was 2000 g/mol.

The increase in the diameter of carbon nanotubes of MWNT/PEO-NH_2 complexes were attributed to the presence of PEOs on the surface of carbon nanotubes, as confirmed by energy dispersive x-ray analysis (EDX, Figure 5). Whiter dots in the images indicate the presence of oxygen element at relatively higher concentration. As contrasted with black background, the presence of oxygen elements originated from PEO on the surface of carbon nanotubes was clearly observed (Figure 5c and 5d). MWNT-COOH also exhibited higher concentration of oxygen on the surface of carbon nanotubes, probably due to the presence of –COOH functional group (Figure 5a). However, no selective presence of oxygen on carbon nanotubes was observed for MWNT-COCl/PEO-CH_3 (Figure 5b). This supports the observation from SEM (Figure 3b and 4b) and TGA (Figure 1e), where the concentration of PEO was low and no distinct increase in the diameter of carbon nanotube was observed.

The presences of PEO in MWNT/PEO-NH_2 complexes were also checked by Fourier Transform-Infrared Spectroscopy (FT-IR). Although the signal was not clear, both MWNT-COCl/PEO-NH_2 (Figure 6a) and MWNT-COOH/PEO-NH_2 (Figure 6b) exhibited characteristic peak from PEO at 2900 cm^{-1} (–CH_2–) and

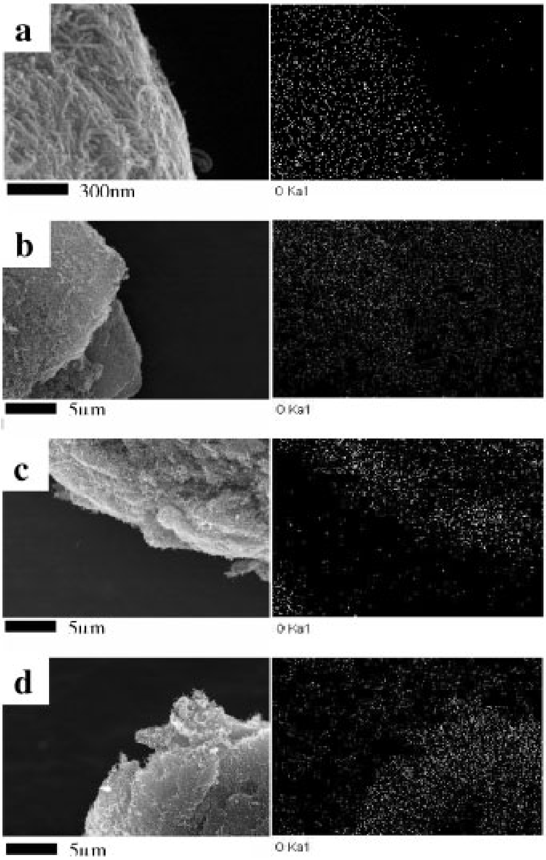


Figure 5.
Scanning electron microscope (SEM) and energy dispersive x-ray analysis (EDX) images of oxygen for MWNT-COOH (a), MNWT-COCl/PEO-CH_3 (b), MWNT-COCl/PEO-NH_2 (c), MWNT-COOH/PEO-NH_2 (d). Whiter dot indicates the presence of oxygen element at relatively higher concentration. The molecular weight of PEO was 2000 g/mol.

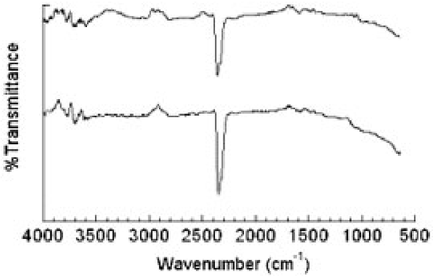


Figure 6.
Fourier Transform-Infrared Spectroscopy (FT-IR) graph of MWNT-COCl/PEO-NH_2 (a) and MWNT-COOH/PEO-NH_2 (b).

1100 cm^{-1} (C–O–C), which suggest the presence of PEO.

The effect of molecular weight of PEO was checked employing PEOs with different molecular weight, 1000 g/mol (PEO-1000) and 2000 g/mol (PEO-2000) (Table 1). The average diameter of MWNT/PEO complexes employing PEO-1000 was slightly lower than that employing PEO-2000 at the same reaction condition. TGA analysis exhibited that the content of PEO in MWNT/PEO-1000 complex was approximately 10% less than that in MWNT/PEO-2000. However, overall, the behavior of PEO-1000 and PEO-2000 were almost identical, indicating the effect of the molecular weight of PEO is almost negligible.

Conclusion

Through the introduction of reactive functional groups in MWNT (MWNT-COOH or MWNT-COCl) and PEO (PEO-NH_2), the complexation of MWNT with PEO was successfully performed, resulting in MWNT/PEO complexes having approximately 40 wt.% of PEO. No distinct difference between MWNT-COOH and MWNT-COCl for the complexation reaction was noticed, indicating similar reactivity of MWNT-COOH and MWNT-COCl against PEO-NH_2s. The MWNT/PEO-NH_2 complexes exhibited excellent dispersibility in solvents including water, ethanol and DMF. From SEM observation, the increases in the diameter of the nanotubes originated from the complexation were observed. The presence of PEO on the nanotube surface was confirmed through EDX and FT-IR analysis, which also support the successful complexation. The effect of the molecular weight of PEO was checked employing PEOs having different molecular weight. However, the behavior of PEO-1000 (molecular weight = 1000 g/mol) and PEO-2000 (molecular weight = 2000 g/mol) were almost identical, indicating the effect of molecular weight of PEO is almost negligible.

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