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Functionalization of Multi-Walled Carbon Nanotubes with Poly(2-ethyl-2-oxazoline)

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Summary: Multi-walled carbon nanotubes (MWCNTs) were successfully functionalized with water-soluble poly(2-ethyl-2-oxazoline) (PEOX) through a polymer wrapping process. Pristine MWCNTs were first treated with nitric acid (HNO_3) at 120 °C for 24 hours. The resulting carboxylated MWCNTs were then mixed with 10 wt.% PEOX in ethanol, followed by sonication using a horn-type sonicator for 30 min and stirring at room temperature for 24 hours. Thereafter, unreacted free polymer was washed out repeatedly by centrifugation with an excess amount of ethanol. Scanning electron microscopy exhibited that the diameter of MWCNTs increased approximately by 10 nm after the functionalization of MWCNT with PEOX. Thermogravimetric analysis showed that approximately 15 wt.% polymer was incorporated in the functionalized MWCNTs. The functionalized MWCNTs gave excellent and stable dispersion in water as well as other organic solvents such as ethanol and DMF.

Keywords: dispersion; functionalization; multi-walled carbon nanotubes; poly(2-ethyl-2-oxazoline); water-soluble polymer

Introduction

Carbon nanotubes (CNTs) are arrangements of carbon hexagons that form themselves into tubes.[1] Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) have unique physical, chemical, thermal, and mechanical properties,[2] which allow them to be used in various applications such as field emitters,[3] field-effect transistors,[4] scanning-probe tips,[5] sensors[6] and composites.[7] However, the applications of CNTs have been impeded by their poor solubility in solvents and polymers, which originated from strong van der Waals attractions among CNTs. Therefore, functionalization of CNTs is generally prerequiste to further applications.

The functionalization of CNTs can be categorized into covalent and non-covalent functionalization, according to the nature of the interaction between CNTs and functional groups. Polymers having hydroxyl or amino moieties were often used for the amidation or esterification reactions with CNTs that contain COOH groups. For example, Lin et al.[8] treated SWCNTs and MWCNTs with HNO_3 to generate COOH groups on the CNTs, which were then functionalized with poly(vinyl alcohol) (PVA) through carbodiimide-activated esterification reaction. The PVA-functionalized CNTs were soluble in water and dimethyl sulfoxide (DMSO) at moderate temperature. Jung et al.[9] reported the covalent functionalization of SWCNTs with poly (ethylene glycol) (PEG). The carboxylated SWCNTs were converted to acyl chloride groups in the presence of benzene/THF solvent mixture, which were then reacted with PEG. About 18 wt.% of PEG was

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grafted onto SWCNTs. Riggs et al.[10] functionalized SWCNTs and MWCNTs with poly(propionylethylenimine-*co*-ethylenimine) (PPEI-EI). The carboxylated CNTs were refluxed in thionyl chloride ($SOCl_2$) to give acyl chlorides functionality before the reaction with PPEI-EI. Both the PPEI-EI functionalized SWCNTs and MWCNTs were luminescent and soluble in various solvents including water. Zhang et al.[11] solubilized MWCNTs in chitosan solutions that contain reactive amino and hydroxyl functional groups. The non-covalent interaction between MWCNTs and chitosan offers straightforward methods for manipulation, purification, and modification of MWCNTs.

In this study, we chose non-covalent functionalization of MWCNTs with poly (2-ethyl-2-oxazoline) (PEOX) to render them soluble in water and organic solvents. PEOX possesses amide groups in its structure and is non-ionic, amorphous, and water-soluble thermoplastic polymer (Figure 1).

Experimental Part

Materials

Multi-walled carbon nanotubes (MWCNTs, > 95 vol.% purity) prepared by chemical vapor deposition were purchased from Iljin Nanotech Co. Ltd. Poly(2-ethyl-2-oxazoline) (PEOX, Mw = 50,000, Aldrich), HNO_3 (assay 60–64%, Duksan), ethanol (assay 94.8–95.8%, Duksan), tetrahydrofuran (THF, assay min. 99.5%, Duksan), and N,N-dimethylformamide (DMF, assay > 99.0%, DC Chemical) were used without further purification.

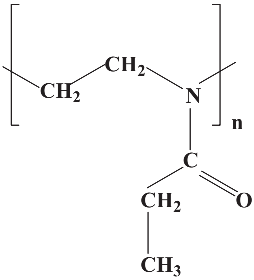

Figure 1.
Chemical structure of poly(2-ethyl-2-oxazoline) (PEOX).

Functionalization and Dispersion Procedures

MWCNTs were treated with 3 M or 9 M HNO_3 at 120 °C for 24 hours, followed by dilution and washing with an excess amount of deionized water. Solid product was separated from solvent through filtration using a hydrophilic polyvinylidene fluoride (PVDF) membrane with 0.45 μm pores. The resulting carboxylated MWCNTs were further reacted with 10 wt.% of PEOX in ethanol. The weight ratio of MWCNT and PEOX in the reactant was kept at 1/50. The mixture was sonicated using a horn-type sonicator for 30 min, followed by stirring at room temperature for 24 hours. Unreacted free polymer was removed from the mixture through washing procedures employing an excessive amount of ethanol. Solid product was collected through centrifugation at 17,000 r.p.m. for 1 hour at each step. The washing procedure was repeated until no further PEOX was removed from the product, as confirmed by thermogravimetric analysis (TGA). The functionalized MWCNT-PEOX was dried under vacuum at 60 °C for 24 hours. To evaluate the dispersibility of CNTs, pristine MWCNT (AP-MWCNT) and MWCNT-PEOX samples were dissolved in water, ethanol, THF, and DMF at the concentration of 50 μg/mL. The experimental procedure is summarized in Figure 2.

Characterization

Thermogravimetric analysis (TGA) was performed by using Scinco STA S-1500 Simultaneous Thermal Analyzer under air at the heating rate of 10 °C/min. Fourier Transform-Infrared Spectroscopy (FT-IR) spectra were recorded with Nicolet 380 spectroscopy equipped with attenuated total reflection (ATR) accessory. Scanning electron microscope (SEM) observations were carried out by using Hitachi S-4700 SEM system.

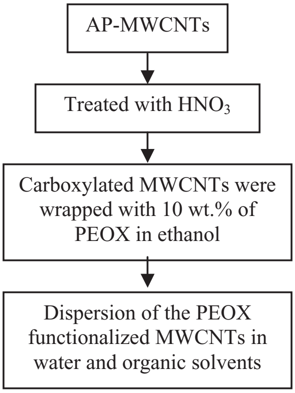

Figure 2.
Experimental procedures for functionalization and dispersion of MWCNTs.

Results and Discussion

Figure 3 shows TGA curves of PEOX, AP-MWCNT, MWCNTs treated with 3 M of HNO_3, MWCNTs treated with 9 M of HNO_3, and MWCNT-PEOX complexes. PEOX and AP-MWCNTs decomposed near 400 °C and 600 °C, respectively. The MWCNTs treated with 3 M or 9 M of HNO_3 seemed to afford ~1 wt.% or ~3 wt.% of COOH groups, respectively, which were inferred from their weight losses at ~400 °C. This clearly indicates that more concentrated acid generated a larger amout of COOH functional groups on tubes. TGA data also revealed that the HNO_3-treated MWCNTs started to decompose at a lower temperature than the AP-MWCNTs probably due to the presence of COOH defects on tubes. Interestingly, the decomposition temperature for MWCNT (9 M HNO_3) near 650 °C was shifted up by 20 °C, which was attributed to heavier bundling of CNTs by the presence of functional groups.

When the 3 M and 9 M HNO_3-treated MWCNTs were employed, the contents of PEOX in the MWCNT-PEOX samples were ~8 and ~15 wt.%, respectively, as determined by their weight losses around 400 °C in Figure 3. The presence of PEOX in the MWCNT-PEOX complex was also confirmed by FT-IR, as supported by the development of characteristic C=O stretching bands near 1635 cm^{-1} for PEOX. The content of PEOX was much higher when the 9 M HNO_3-treated MWCNTs were used, probably due to the presence of a higher concentration of COOH groups on MWCNTs.

Wrapping MWCNTs by water-soluble polymer is a general phonomenon, driven largely by a thermodynamic force to eliminiate the hydrophobic interface between the tubes and their aqueous medium.[12] In addition, Furtado et al.[13] indicated that

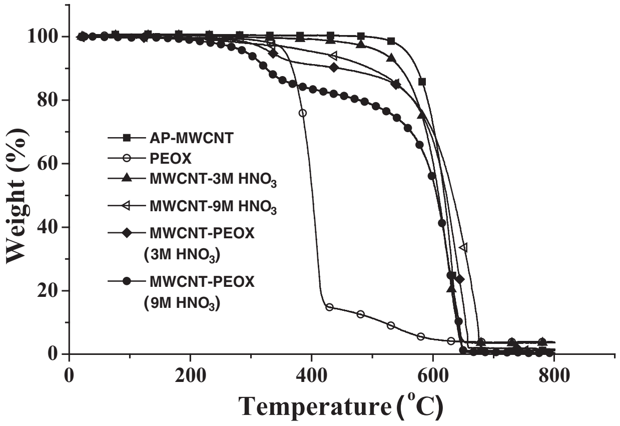

Figure 3.
TGA curves of PEOX, AP-MWCNTs, MWCNTs treated with differenct concentrations of HNO_3, and MWCNTs functionilized with PEOX.

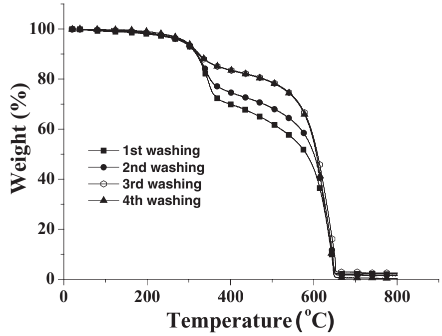

Figure 4.
TGA curves of the MWCNT-PEOX complexes after different number of washing cycles using an excess amount of ethanol.

functionalization of SWCNTs with oxygen moieties improved debundling of SWCNTs in amide solvents, likely resulting from stronger interaction between the functional groups on SWCNTs and solvents. These results indicate that, as observed in this study, the polymer wrapping process is a spontaneous reaction and more amount of polar-polar interaction between COOH groups on MWCNTs and amide groups in PEOX facilitates the formation of the MWCNT-PEOX complex.

The MWCNT-PEOX complex was stable even in the presence of hydrophilic solvent such as ethanol, as confirmed by repeated washing cycles (Figure 4). The amount of PEOX, which was initially 26 wt.% in the MWCNT-PEOX complex, was reduced to 15 wt.% after the 3rd washing cycle, because free PEOX was washed out during the process. However, no further reduction on the content of PEOX was observed during the 4th washing, suggesting the formation of stable MWCNT-PEOX complexes with little free polymer.

Figure 5 presents SEM images and diameter distributions of the AP-MWCNTs and the MWCNT-PEOX. Compared with those of the AP-MWCNTs (Figure 5c), the diameters of the MWCNT-PEOXs increased as much as ~10 nm (Figure 5d). The increment in the diameters was attributed to the presence of PEOX on MWCNTs, which again confirms the formation of the MWCNT-PEOX complex.

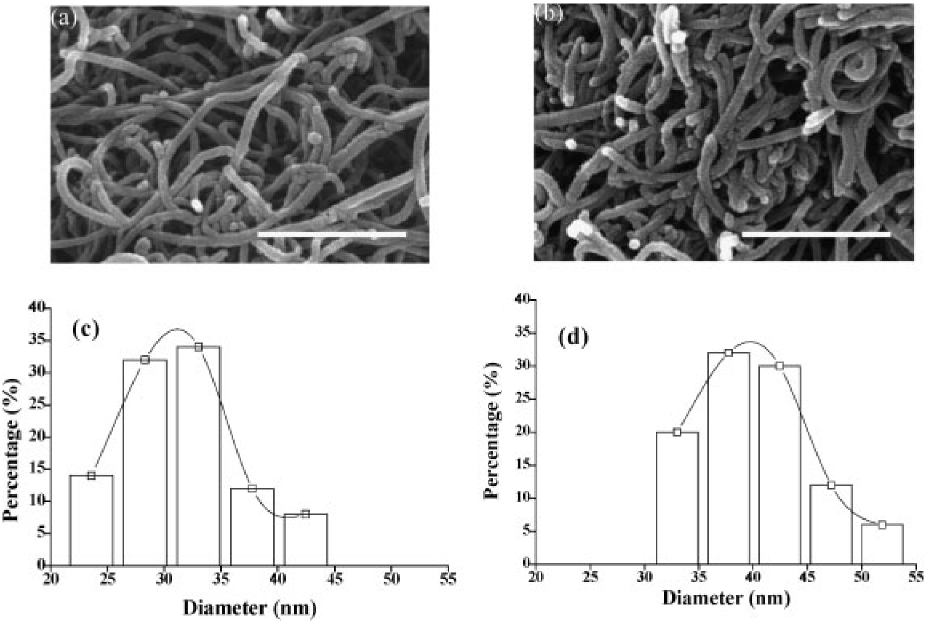

Figure 5.
SEM images of AP-MWCNT (a), MWCNT-PEOX (b), and the diameter distributions of AP-MWCNTs (c) and MWCNT-PEOXs (d). Typically 50 tubes were considered for each sample to analyse their diameter distribution.

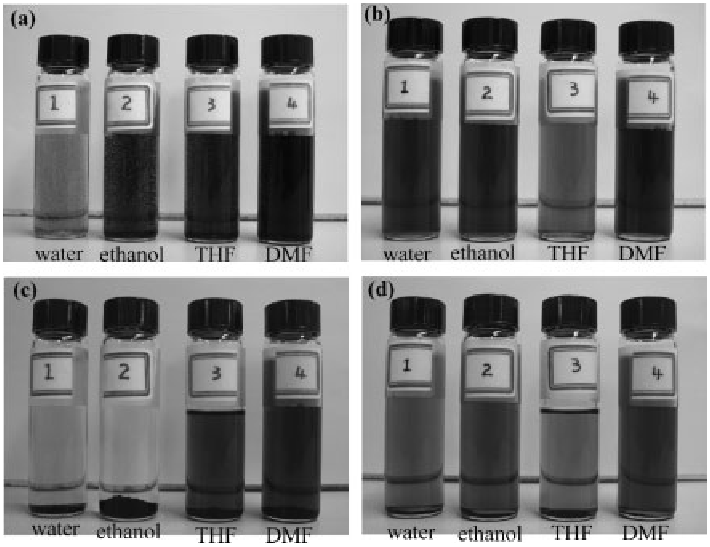

Figure 6.
Dispersibility of AP-MWCNTs and MWCNT-PEOX in water, ethanol, THF, and DMF: AP-MWCNT at 0 hour (a), MWCNT-PEOX at 0 hour (b), AP-MWCNT after 672 hours (c), and MWCNT-PEOX after 672 hours (d).

The dispersibility of the AP-MWCNTs and the MWCNT-PEOXs in various solvents were evaluated 672 hours after the ultrasonic dispersion (Figure 6). The AP-MWCNTs were well dispersed in DMF and THF to afford homogeneous black solutions after an extended settlement over 672 hours (Figure 6c). The AP-MWCNTs, however, were not dispersed in water and ethanol, as noticed by immediate precipitation of CNTs (Figure 6a and 6c), indicating poor solubility of the AP-MWCNTs in water and ethanol. It is to be noted that the MWCNT-PEOX exhibited homogeneous dispersion in water and ethanol even after 672 hours (Figure 6b and 6d). The result clearly indicates that the MWCNT-PEOX complex was successfully formed, where PEOX improved the solubility of the complex in hydrophilic solvents. The MWCNT-PEOX was also homogeneously dispersed in THF and DMF (Figure 6b and 6d).

Conclusion

The MWCNT-PEOX complex was successfully prepared by incorporating carboxylic acid functional groups in MWCNTs and then engaging a simple wrapping process of PEOX polymer. Upon introducing carboxylic acid groups in MWCNTs, a higher concentration of HNO_3 brought more amount of COOH groups to MWCNTs. The content of PEOX in the MWCNT-PEOX was higher when a greater amount of COOH groups was introduced in MWCNTs. Compared with those of AP-MWCNTs, the diameters of the MWCNT-PEOX increased as much as $\sim$10 nm, indicating the successful formation of complex. Unlike pristine MWCNTs (AP-MWCNTs), which were not soluble in water and ethanol, the MWCNT-PEOX exhibited homogeneous and stable dispersion in water and ethanol, which again confirms the successful formation of the complex. The MWCNT-PEOX was also homogeneously dispersed in THF and DMF.

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