

# Synthesis and Characterization of Novel Hybrid Polyoxazoline-Grafted Multiwalled Carbon Nanotubes

Jong-Hwan Jeon, Seung-Hwa Lee, Jung-Hyurk Lim, Kyung-Min Kim

Department of Polymer Science and Engineering, Chungju National University, Chungju, Chungbuk 380-702, Korea

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**ABSTRACT:** The novel hybrid polyoxazoline-grafted multiwalled carbon nanotubes (POZO-grafted MWNTs) were synthesized by the reaction of partially hydrolyzed polyoxazolines (Hydrolyzed-POZO) and MWNTs having carboxylic acid groups (MWNT-COOH) in the presence of DCC as a condensing agent. Hydrolyzed-POZO (degree of hydrolysis, 20.2 mol % by  $^1\text{H-NMR}$ ) were produced from the hydrolysis of polyoxazolines in an aqueous NaOH solution at reflux for 72 h. MWNT-COOH were prepared by acid treatment of pristine MWNTs. The composition, structure, thermal property, and surface morphology of the novel hybrid POZO-grafted MWNTs were fully characterized by FT-IR, Raman,  $^1\text{H-NMR}$ , DSC, TGA, SEM, and TEM. The obtained POZO-grafted MWNTs are well solu-

ble in various organic solvents and water. It was observed that the glass transition temperature ( $T_g$ ) of POZO-grafted MWNTs was lower than that of Hydrolyzed-POZO due to the absence of hydrogen bonding interactions between Hydrolyzed-POZO itself caused by the incorporation with MWNTs. It was also found that Hydrolyzed-POZO was homogeneously attached to the surfaces of MWNTs through the "grafting-to" method. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2937–2943, 2010

**Key words:** 2-Methyl-2-oxazoline; polyoxazoline; hydrolyzed polyoxazoline; multiwalled carbon nanotubes (MWNTs); polyoxazoline-grafted MWNTs

## INTRODUCTION

Polyoxazoline prepared by ring-opening polymerization of 2-methyl-2-oxazoline is highly hydrophilic and well compatible with several commodity organic polymers. It should be also noted that this polymerization proceeds in a living manner, i.e., without chain transfer or terminating reactions, which makes it possible to control the molecular weight of the polymer, to obtain the monodispersed polymer and also to design various functional polymers with different macromolecular architectures.

The polymerization of 2-substituted 2-oxazolines has been intensively studied by several research groups since the 1960s and is reviewed.<sup>1–3</sup> These monomers can be polymerized through cationic ring-opening polymerization producing polyoxazolines. This polymerization occurs through a "living"

form and consequently it is very attractive for the elaboration of different macromolecular architectures. For example, block, graft copolymers, and non-ionic hydrogels have been synthesized.<sup>1–6</sup> Moreover, it is possible to obtain hydrophilic or hydrophobic polymers depending on the kind of 2-substituent group on the oxazoline ring. Hydrogels are soft materials with interesting properties, which can be used in such differing fields as, for example, medicine, agriculture, domestic, civil engineering, etc. An important property of these materials is that they swell significantly in water and other polar solvents.

Carbon nanotubes (CNTs) are noted for their outstanding electrical, mechanical, and thermal properties. However, the practical uses of pristine CNTs are impeded by their aggregation properties and their insolubilities in organic solvents or water. To increase solubility and reduce the tendency of aggregation, CNTs are often functionalized with organic moieties and polymers.<sup>7–11</sup> Polymer-grafted CNTs are highly effective reinforcing fillers for polymers.<sup>12–22</sup> When the polymer grafted onto CNTs is the same as or miscible with the matrix polymer, stress can be effectively transferred from the matrix to CNTs which results in significant improvements in the mechanical properties of the matrix polymer. CNTs can be functionalized covalently or non-covalently with various polymers. Non-covalent interactions such as  $\pi$ - $\pi$  interaction,  $\pi$ -cation interaction, and ionic interaction between CNTs and polymers

Correspondence to: K.-M. Kim (kkmkim@chungju.ac.kr).

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enable the absorption of polymers onto the CNTs surfaces.<sup>23–27</sup> Also, CNTs can be functionalized covalently with polymers by “grafting-to” and “grafting-from” methods.<sup>28–35</sup>

In this article, new hybrid polyoxazoline-grafted MWNTs (POZO-grafted MWNTs) were synthesized by the reaction of partially hydrolyzed polyoxazoline (Hydrolyzed-POZO) and MWNT-COOH in the presence of DCC as a condensing agent via the “grafting to” method. The obtained POZO-grafted MWNTs are well soluble in various organic solvents and water because of the good attachment of POZO to the surfaces of MWNTs. It was found that Hydrolyzed-POZO were uniformly deposited and distributed on the surfaces of MWNTs, confirmed by SEM and TEM images. Our final goal is to fabricate the homogeneous hybrid materials with the obtained POZO-grafted MWNTs utilizing the sol-gel reaction of tetramethoxysilane (TMOS). It is really interesting to note that POZO-grafted MWNTs are homogeneously dispersed in the silica matrix via hydrogen bonding interactions between POZO-grafted MWNTs and the residual silanol groups of silica gel. The results of the homogeneous hybrid materials with the obtained POZO-grafted MWNTs utilizing the sol-gel reaction of TMOS will be reported soon in the other literature.

## EXPERIMENTAL SECTION

### Materials

All solvents and reagents were used as supplied except for the following materials. *N, N*-Dimethylformamide (DMF) was distilled from CaH<sub>2</sub> under reduced pressure. Acetone was distilled from anhydrous potassium carbonate under nitrogen. 1, 2-Dichloroethane was distilled from P<sub>2</sub>O<sub>5</sub> under nitrogen. Acetonitrile was distilled from CaH<sub>2</sub> under nitrogen. Methyl *p*-toluenesulfonate was distilled under reduced pressure. 2-Methyl-2-oxazoline was distilled from potassium hydroxide. Tetrahydrofuran (THF) was distilled from LiAlH<sub>4</sub> under nitrogen. Pristine MWNTs were obtained from the Iljin Nanotech (diameter: 10–20 nm, length: 10–50 μm, >90 vol % of purity). Polycarbonate membrane (pore size: 0.2 μm) was obtained from the Whatman International. *N, N'*-Dicyclohexylcarbodiimide (99%) (DCC) was purchased from Aldrich. Nitric acid (HNO<sub>3</sub>) (60%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (98%), sodium hydroxide (NaOH), and all solvents were purchased from Aldrich.

### Measurements

Raman spectrophotometer (NRS-3200, JASCO) was used to confirm and characterize MWNT-COOH,

which was formed after chemical modification of pristine MWNTs under acidic condition. <sup>1</sup>H-NMR spectra were obtained on a 400MHz AVANVE 400FT-NMR (BRUKER) spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a FTS-6000 (BIO-RAD) spectrometer. The thermal behavior was examined by differential scanning calorimetry (DSC) (DSC 2010, TA Instruments) and thermogravimetric analysis (TGA) (TGA S-1000, SCINCO) under nitrogen atmospheres, respectively. The morphologies and structures of hybrid POZO-grafted MWNTs were observed by scanning electron microscopy (SEM) (JSM-6700, JEOL) and field emission scanning microscopy (FE-TEM) (Technai G2 F30).

### Acid treatment of pristine MWNTs (1)

Typically, 6.0 g of crude MWNTs, 50 mL of 60% HNO<sub>3</sub>, and 150 mL of H<sub>2</sub>SO<sub>4</sub> were added into a 500 mL flask equipped with a condenser with vigorous stirring. The flask was immersed in a sonication bath (40 kHz) for 90 min. The mixture was then stirred at 90°C for 4 h. During this period, densely brown gas was collected and treated with an aqueous NaOH solution connected to the condenser by a plastic tube. After cooling to room temperature, the reaction mixture was diluted with 800 mL of deionized water and then vacuum-filtered through a 0.2 μm polycarbonate filter paper. The dispersion, filtering, and washing steps were repeated until the pH of the filtrate was reached to 7 (at least four cycles were required). The filtered solid was washed with ca. 100 mL of acetone and THF at 5 times to remove the water from the sample and dried under vacuum for 24 h at 60°C.

### Synthesis of polyoxazoline (POZO) (2)

As a typical procedure, the mixture of 2-methyl-2-oxazoline (5 mL, 58 mmol), methyl *p*-toluenesulfonate (0.09 mL, 0.48 mmol), and acetonitrile (50 mL) were placed in a 100 mL glass flask and sealed under nitrogen, which was then heated at 75°C for 72 h. The resulting polyoxazoline was isolated by precipitating into diethyl ether. The white precipitate was collected by filtration and dried in vacuum (3.83 g, 77%).  $M_n = 1603$ ,  $M_w/M_n = 1.185$ , polystyrene standard; eluent, CHCl<sub>3</sub>. <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>): δ 3.46 ppm (strong, 2H), 2.11 ppm (strong, 3H).

### Synthesis of partially hydrolyzed polyoxazoline (hydrolyzed-POZO) (3)

A typical procedure was as follows. POZO (2) (2.0 g) was dissolved in 50 mL of aqueous NaOH (0.18 g, 4.6 mmol) solution and stirred at reflux for 72 h. Water was removed by evaporation under reduced

pressure. Concentrated solution was dissolved in methanol and precipitated into diethyl ether. The white precipitate was collected by filtration, washed well with diethyl ether, and dried in vacuum. The degree of hydrolysis was determined by  $^1\text{H-NMR}$  spectrum (20.2 mol % hydrolyzed).  $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ):  $\delta$  3.46 ppm (strong, 2H), 2.6–2.8 ppm (broad, 2H), 2.11 ppm (strong, 3H).

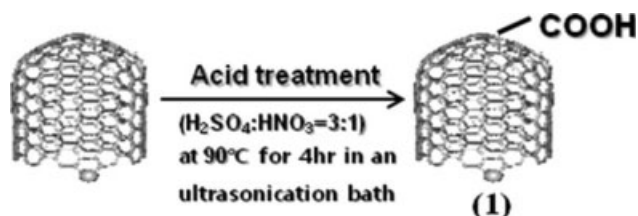
### Synthesis of polyoxazoline-grafted MWNTs (POZO-grafted MWNTs)

MWNT-COOH (1) (0.1 g), dry 1, 2-dichloroethane (40 mL), and freshly distilled DMF (12 mL) were placed in a 100 mL glass flask and the mixture was sonicated for 30 min. Then Hydrolyzed-POZO (3) (1.0 g) was added to this solution under dry nitrogen and stirred at room temperature for 2 h. To this solution dicyclohexylcarbodiimide (DCC) (0.78 g, 3.76 mmol) was added. After the mixture was stirred for 72 h and the reaction mixture was diluted with 100 mL of cosolvent (1, 2-dichloroethane: DMF = 3 : 1). The diluted mixture was sonicated for 20 min, and filtered through a 0.2  $\mu\text{m}$  polycarbonate membrane. The solid was repeatedly washed with 1, 2-dichloroethane and DMF to remove unreacted Hydrolyzed-POZO. The purified product was dried under vacuum as a black solid.

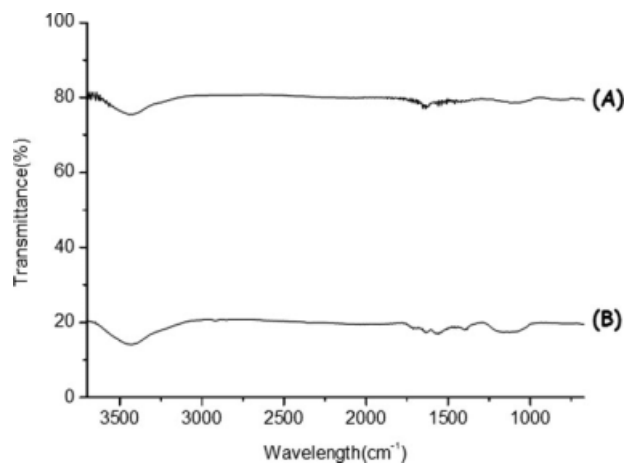
## RESULTS AND DISCUSSION

The modification of pristine MWNTs to MWNT-COOH is outlined in Scheme 1. Figure 1 shows the FT-IR spectra of pristine MWNTs and MWNT-COOH. The spectrum of the pristine MWNTs shows a C=C stretching peak at  $1632\text{ cm}^{-1}$ . It, however, shows no discernable peak, indicating the formation of carboxylic acids or defects after purification. The C=C stretching peaks, which indicate graphite structure of MWNTs, are observed in the MWNT-COOH as well. After acid treatment, MWNT-COOH show a C=O stretching peak from the COOH group at  $1714\text{ cm}^{-1}$  and a very broad O-H stretching peak between  $3200$  and  $3600\text{ cm}^{-1}$ .

Raman spectroscopy is a powerful tool used to characterize the functionalized CNTs. The typical Raman spectra for the MWNTs consist of two quite



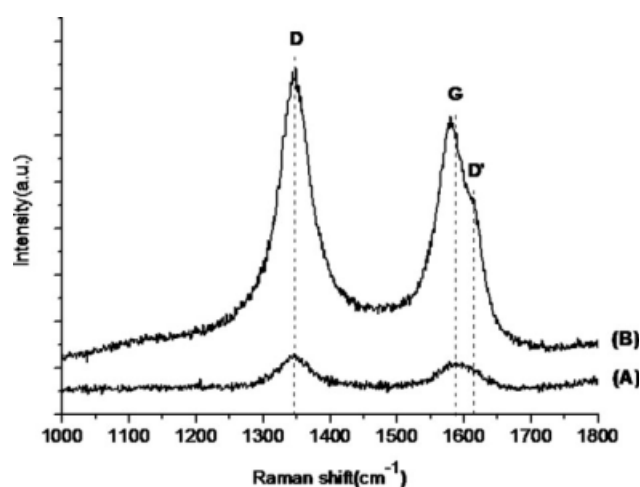
**Scheme 1** Chemical modifications of the pristine MWNTs.



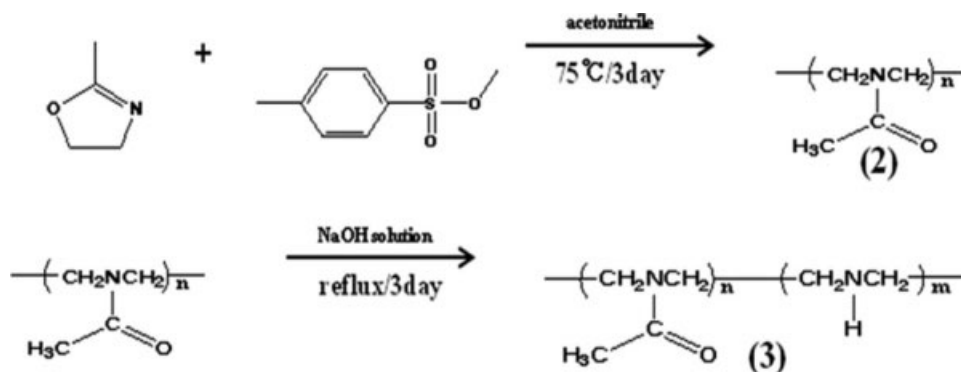
**Figure 1** FT-IR spectra of (A) pristine MWNTs and (B) MWNT-COOH with KBr.

sharp modes, the G band around  $1580\text{ cm}^{-1}$  and the D band around  $1350\text{ cm}^{-1}$  accompanied by an additional D' band as shoulder to the G band at crystalline graphite carbon in MWNTs, whereas the D band is originated from the disorder induced features. The presence of the D' band at  $1612\text{ cm}^{-1}$  is affected by the disorder in MWNTs, which can be barely observable in pristine MWNTs but is clearly detectable after the functionalization of MWNTs. As shown in Figure 2(A), the D and G band of pristine MWNTs show at nearly  $1350\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$ , respectively. After acid treatment of MWNTs, the G band was shifted to  $1571\text{ cm}^{-1}$  and D' band was observed at  $1612\text{ cm}^{-1}$ , indicating an increase in defects along the MWNT body.

The preparation of Hydrolyzed-POZO is represented in Scheme 2. Ring-opening polymerization of 2-methyl-2-oxazoline was carried out in the presence of methyl *p*-toluenesulfonate as an initiator. The partial hydrolysis of polyoxazoline was carried out in aqueous sodium hydroxide solution to form partially



**Figure 2** Raman spectra of (A) pristine MWNTs and (B) MWNT-COOH on slide glass.



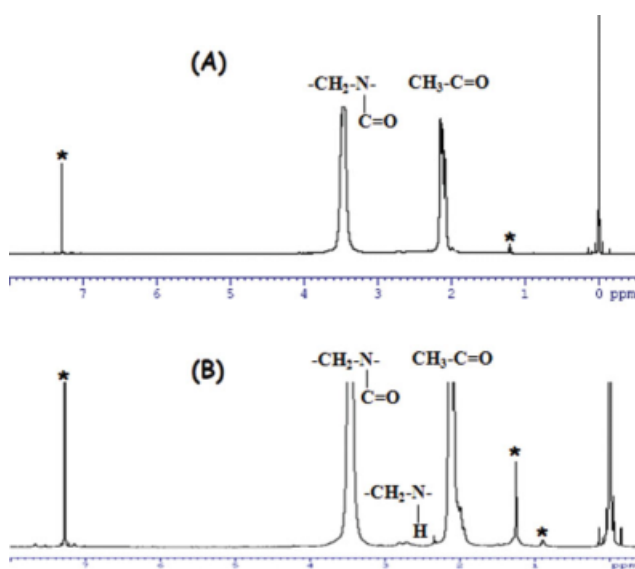
Scheme 2 Synthesis of hydrolyzed-POZO.

hydrolyzed polyoxazoline. The degree of hydrolysis was controlled by the concentration of sodium hydroxide and also by the reaction time, which was successfully determined by  $^1\text{H-NMR}$ . Figure 3 illustrates the  $^1\text{H-NMR}$  spectra of polyoxazoline before and after the alkaline hydrolysis. The secondary amino protons ( $\delta$  2.8) of the partially hydrolyzed polyoxazoline were observed in Figure 3(B). From the integral ratio between the methylene protons adjacent to secondary amino group ( $\delta$  2.8) and those adjacent to acetamide group ( $\delta$  2.1), the degree of hydrolysis was determined to be 20.2 mol %.

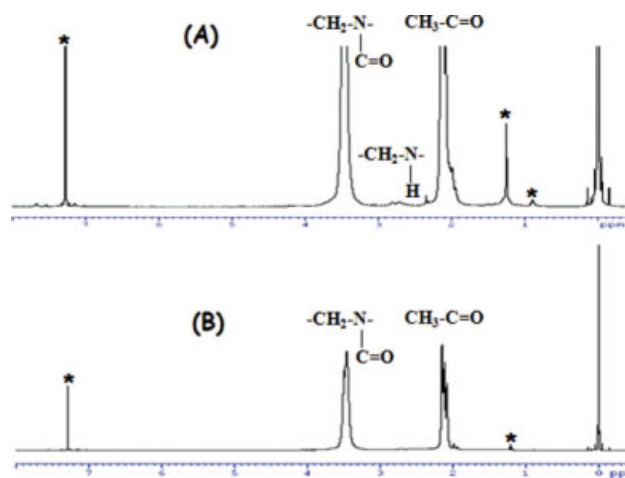
The fabrication of novel hybrid POZO-grafted MWNTs is shown Scheme 3. Figure 4 illustrates the  $^1\text{H-NMR}$  spectra of Hydrolyzed-POZO (A) (degree of hydrolysis, 20.2 mol % by  $^1\text{H-NMR}$ ) and POZO-grafted MWNTs (B). The peak of the methylene protons adjacent to the secondary amino group ( $\delta$  2.8) disappeared completely. It was confirmed that there

was successful reaction between secondary amino group of Hydrolyzed-POZO and carboxylic acid group of MWNT-COOH.

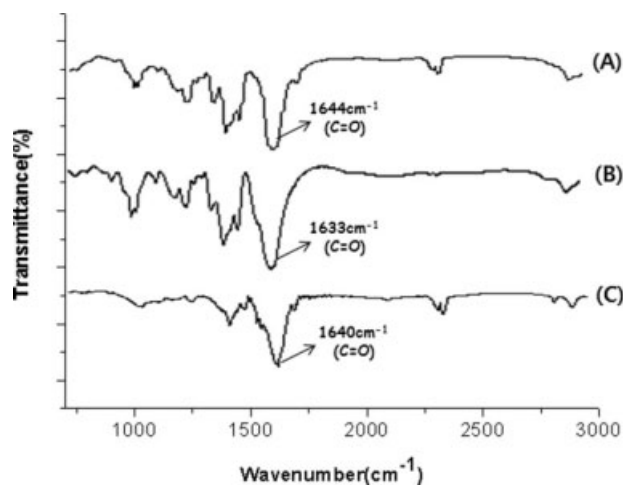
FT-IR measurement was also conducted to confirm the successful fabrication of POZO-grafted MWNTs by the reaction of Hydrolyzed-POZO and MWNT-COOH in the presence of DCC as a condensing agent. Figure 5 shows FT-IR spectra of POZO, Hydrolyzed-POZO, and POZO-grafted MWNTs. The amide carbonyl peaks of POZO were observed at  $1644\text{ cm}^{-1}$  as shown in Figure 5(A). Figure 5(B) shows the shift ( $1633\text{ cm}^{-1}$ ) of amide carbonyl peaks caused by hydrogen bonding interactions between secondary amino group and carbonyl group of acetamide in Hydrolyzed-POZO. But, after the reaction of Hydrolyzed-POZO and MWNT-COOH, the amide carbonyl peaks of POZO-grafted MWNTs were almost shifted back to their original positions. This reason might be ascribed to the disappearance of hydrogen bonding interactions by the reaction of Hydrolyzed-POZO and MWNT-COOH.



**Figure 3**  $^1\text{H-NMR}$  (400MHz) spectra of (A) POZO and (B) Hydrolyzed-POZO (degree of hydrolysis, 20.2 mol %) in  $\text{CDCl}_3$ . Asterisks show the peaks due to solvents. [Colour figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

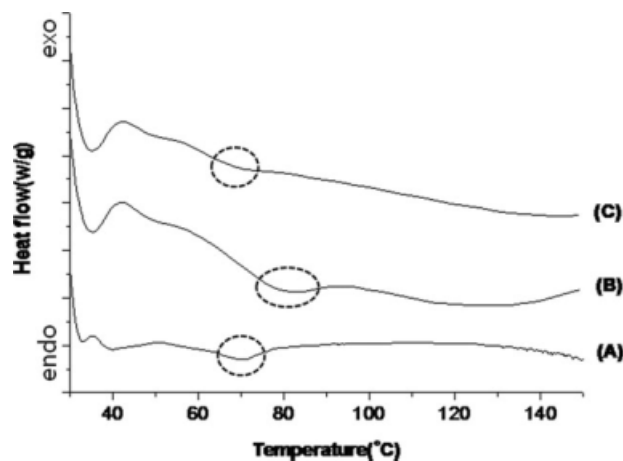


**Figure 4**  $^1\text{H-NMR}$  (400MHz) spectra of (A) Hydrolyzed-POZO (degree of hydrolysis, 20.2 mol %) and (B) POZO-grafted MWNTs in  $\text{CDCl}_3$ . Asterisks show the peaks due to solvents. [Colour figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

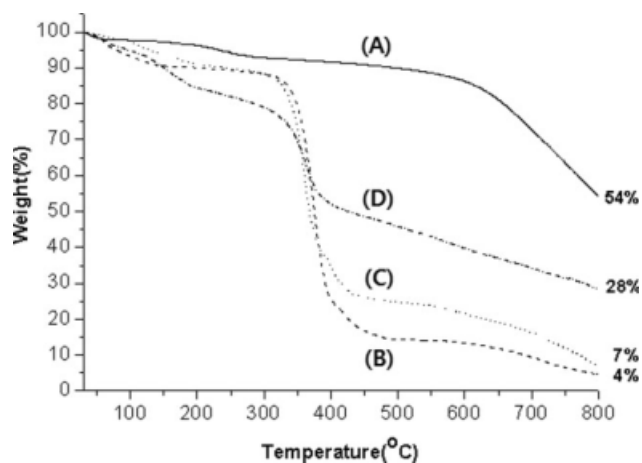


**Figure 5** FT-IR spectra of (A) POZO, (B) Hydrolyzed-POZO, and (C) POZO-grafted MWNTs with KBr.

Figure 6 represents DSC thermograms of POZO, Hydrolyzed-POZO, and POZO-grafted MWNTs. Hydrolyzed-POZO [Fig. 6(B)] shows an increase in glass transition temperature ( $T_g$ ) compared to that of POZO [Fig. 6(A)]. This can be attributed to the reduction of segmental mobility of Hydrolyzed-POZO, which is caused by hydrogen bonding interactions between secondary amino group and carbonyl group of acetamide in Hydrolyzed-POZO. From Figure 6(C), it was observed that  $T_g$  of POZO-grafted MWNTs decreased after the reaction of Hydrolyzed-POZO and POZO-grafted MWNTs. This result is due to the absence of hydrogen bonding interactions between Hydrolyzed-POZO itself caused by the homogeneous incorporation with MWNTs. This result also suggests that the bulky carbon nanotubes prevent Hydrolyzed-POZO from aggregating each other.



**Figure 6** DSC thermograms of (A) POZO, (B) Hydrolyzed-POZO, and (C) POZO-grafted MWNTs with a heating rate of 10°C/min in nitrogen atmosphere.



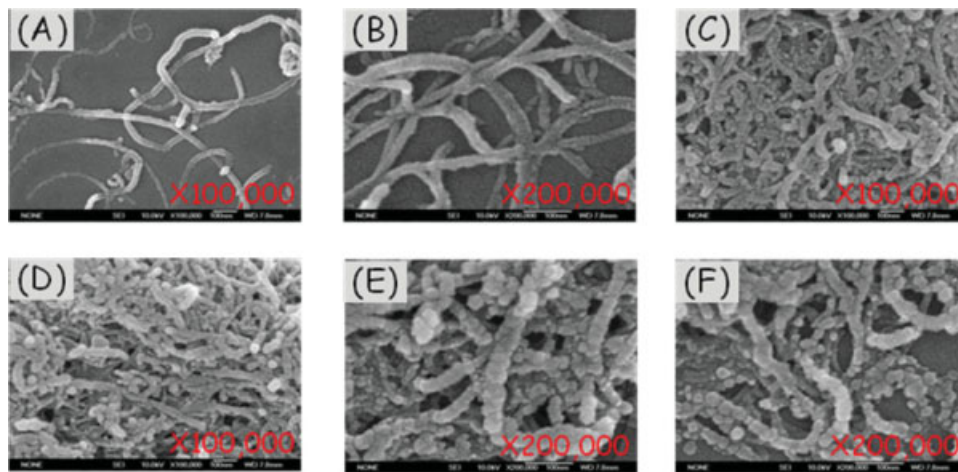
**Figure 7** TGA thermograms of (A) MWNT-COOH, (B) POZO, (C) Hydrolyzed-POZO, and (D) POZO-grafted MWNTs with a heating rate of 10°C/min in nitrogen atmosphere.

To compare the thermal stability of MWNT-COOH, POZO, Hydrolyzed-POZO, and POZO-grafted MWNTs, thermal analysis was carried out by TGA measurements as shown in Figure 7. The residual content of MWNT-COOH was 54% as shown in Figure 7(A). Figure 7(B,C) show the difference from the weight of the residue between POZO (ca. 4 wt %) and Hydrolyzed-POZO (ca. 7 wt %). This can be attributed to the aggregation of Hydrolyzed-POZO, which is caused by hydrogen bonding interactions. The weight (ca. 28 wt %) of the residue obtained from POZO-grafted MWNTs is larger than that (ca. 7 wt %) obtained from Hydrolyzed-POZO as shown in Figure 7(D). This result suggests that Hydrolyzed-POZO is well-deposited on the surface of MWNT-COOH.

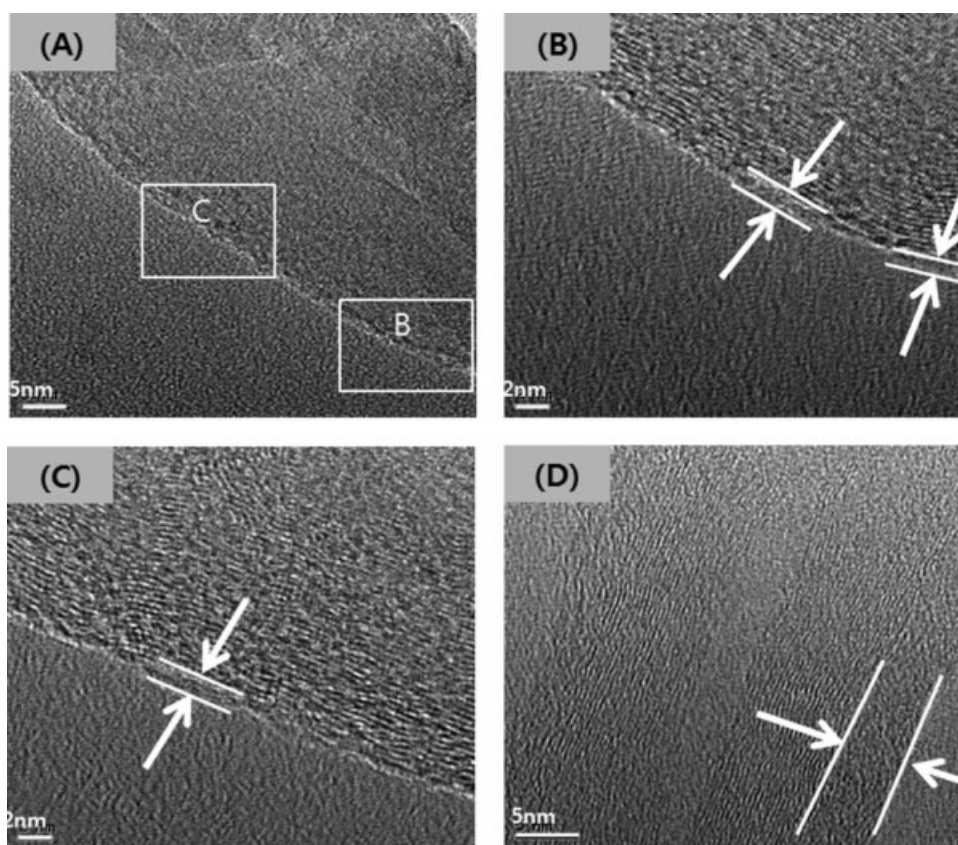
All the aforementioned characterizations effectively demonstrate that Hydrolyzed-POZO was covalently grafted onto the MWNTs. Measurements of SEM and TEM microscopy could provide further direct evidence for the preparation of POZO-grafted MWNTs. Thus, SEM and TEM images of the POZO-grafted MWNTs are shown in Figures 8 and 9.

The surface morphology of MWNT-COOH and POZO-grafted MWNTs can be explored by SEM. Figure 8(A,B) present a typical SEM image of the MWNT-COOH, showing a very clean surface for all the tubes. The direct evidence of the deposition of Hydrolyzed-POZO on the surface of MWNT-COOH was given by Figure 8(C-F). It can be seen that Hydrolyzed-POZO with spherical structures are well anchored onto the external walls of MWNT-COOH. Clearly, the surface of MWNT-COOH was uniformly covered with a certain amount of Hydrolyzed-POZO.

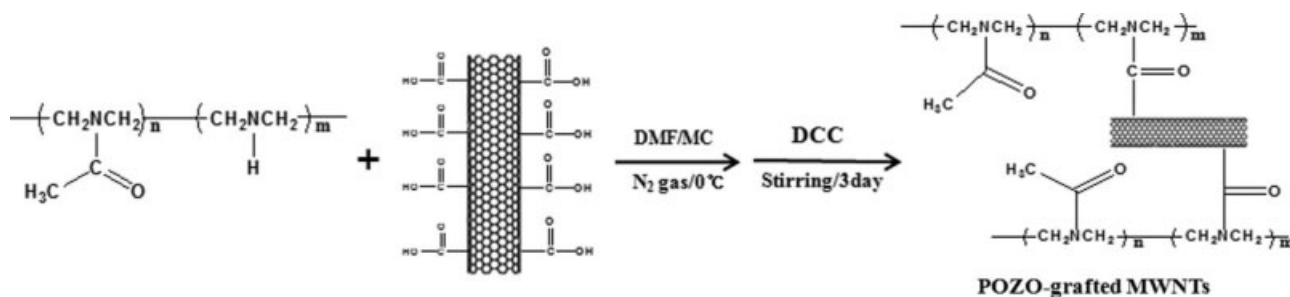
For TEM observation, the sample of POZO-grafted MWNTs was prepared by redispersing in methanol



**Figure 8** FE-SEM images of (A and B) MWNT-COOH and (C-F) POZO-grafted MWNTs on Si-wafer. [Colour figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 9** FE-TEM images of (A and D) an individual POZO-grafted MWNTs and (B and C) magnification of the area specified by the dashed square in (A) on copper grids.



**Scheme 3** Schematic illustration of the preparation of POZO-grafted MWNTs.

and the solution was dropped onto a carbon-coated copper grids and then drying under vacuum. Direct structural characterization of an individual POZO-grafted MWNTs were realized by Field Emission Transmission Electron Microscopy (FE-TEM) and POZO-grafted MWNTs image is presented in Figure 9(A). Figure 9(B,C) are the magnification of the area specified by a dashed square in Figure 9(A). From the images, POZO-grafted MWNTs exhibits an amorphous polymer layer which is Hydrolyzed-POZO with a thickness at 1–2 nm along the outer walls of the MWNTs. In addition, amorphous polymer layer of POZO-grafted MWNTs is clearly observed as shown in Figure 9(D). This result confirms that Hydrolyzed-POZO is homogeneously deposited onto the surface of MWNT-COOH.

### CONCLUSIONS

In summary, we have developed a new approach for novel hybrid POZO-grafted MWNTs. The novel hybrid POZO-grafted MWNTs was fabricated by the reaction of Hydrolyzed-POZO and MWNT-COOH in the presence of DCC as a condensing agent.  $^1\text{H-NMR}$  and FT-IR analysis indicated that the degree of hydrolysis of POZO was 20.2 mol % and POZO-grafted MWNTs were successfully prepared through the “grafting-to” method, respectively. From DSC measurement, it was observed that  $T_g$  of POZO-grafted MWNTs decreased compared to that of Hydrolyzed-POZO. The SEM and TEM images of POZO-grafted MWNTs show that partially Hydrolyzed-POZO was uniformly and homogeneously attached to the surface of MWNT-COOH.

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