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Functionalization of multi-walled carbon nanotubes by epoxide ring-opening polymerization

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ABSTRACT

In this study, covalent functionalization of carbon nanotubes (CNTs) was accomplished by surface-initiated epoxide ring-opening polymerization. FT-IR spectra showed that polyether and epoxide group covalently attached to the sidewalls of CNTs. TGA results indicated that the polyether was successfully grown from the CNT surface, with the final products having a polymer weight percentage of ca. 14–74 wt%. The O/C ratio of CNTs increased significantly from 5.1% to 29.8% after surface functionalization of CNTs. SEM and TEM images of functionalized CNTs exhibited that the tubes were enwrapped by polymer chains with thickness of several nanometers, forming core–shell structures with CNTs at the center.

1. Introduction

Since their discovery by Iijima in 1991, carbon nanotubes (CNTs) have attracted extensive attention from researchers due to their outstanding electronic, mechanical, and thermal properties associated with their high aspect ratio and one-dimensional tubular structure [1–4]. On these sthengths, CNTs have tremendous potential for applications in many scientific and technological fields, such as polymeric composites, hydrogen storage, nanoprobes, field electron emitter, chemical sensors, and so on [5–7].

However, their insolubility and weak dispersibility in common solvents and matrices have limited their applications. An effective method to prevent aggregation of nanotubes is functionalization of CNTs. The functionalization of CNTs by polymers may be divided into two categories on the basis of either non-covalent or covalent bonding between the CNTs and polymer [8,9]. Furthermore, covalent attachment of polymers will help to disperse CNTs. Recently, functionalization of single-walled and multi-walled CNTs by ring-opening polymerization was reported. Using this approach, polymer functionalized CNTs have been prepared using ε-caprolactam, *p*-dioxanone, 3-ethyl-3-(hydroxymethyl)oxetane, ε-caprolactone, and L-lactide as monomers [10–14].

In this communication, we briefly report on the functionalization of CNTs by the surface-initiated ring-opening polymerization of epoxides. The structures of functionalized CNTs were characterized by Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopic (TEM) techniques.

2. Experimental section

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) used in this work were purchased from Nano Solution Co. Ltd. of Korea (diameter: 10–25 nm, length: 20–50 μm, degree of purity: >90%). The purification was carried out by using oxidative acid treatment, as in previous studies [15]. Epichlorohydrin, sodium hydroxide, acetone, and ethyl alcohol were purchased from Aldrich Chem. and were used without further purification.

2.2. Functionalization of CNTs

Fifty milligrams of acid treated CNT (A-CNT), 400 mg of epichlorohydrin, and 50 mg of 40% NaOH aqueous solution were placed in a 50 mL round-bottomed flask equipped with a reflux condenser and the mixture was stirred for 3 h at 60, 70, and 80 °C, respectively. The mixture was filtered and the black solid was washed with acetone and deionized water several times. Finally, the product was dried in a vacuum oven at 100 °C for 24 h. The samples prepared are referred to as F60-CNT for reaction

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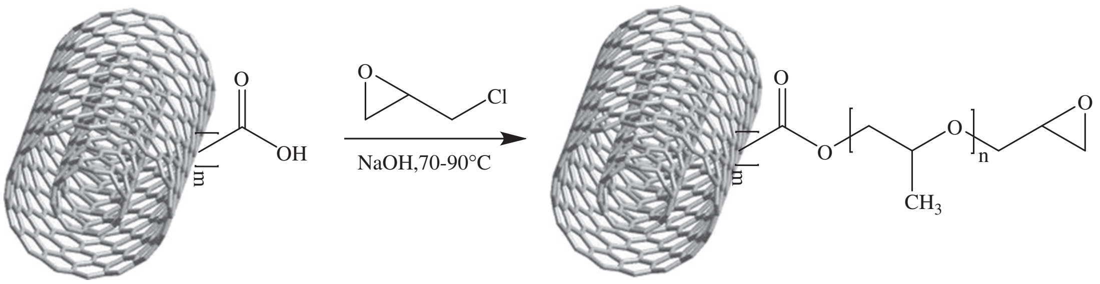

Scheme 1. Procedure for functionalization of CNT by epoxide ring-opening polymerization.

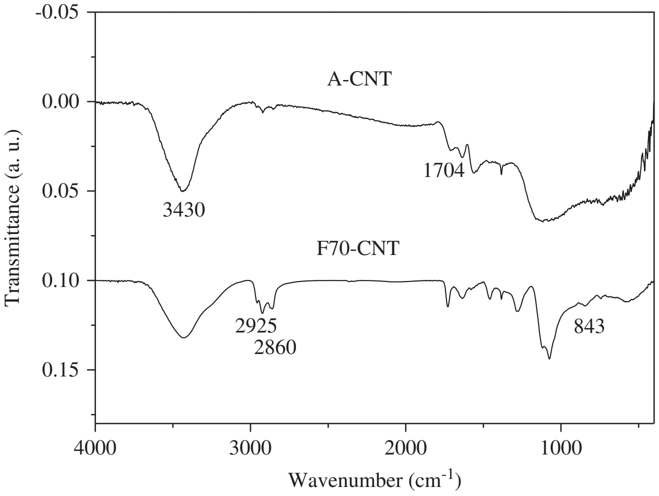

Fig. 1. FT-IR spectra of A-CNT and F70-CNT.

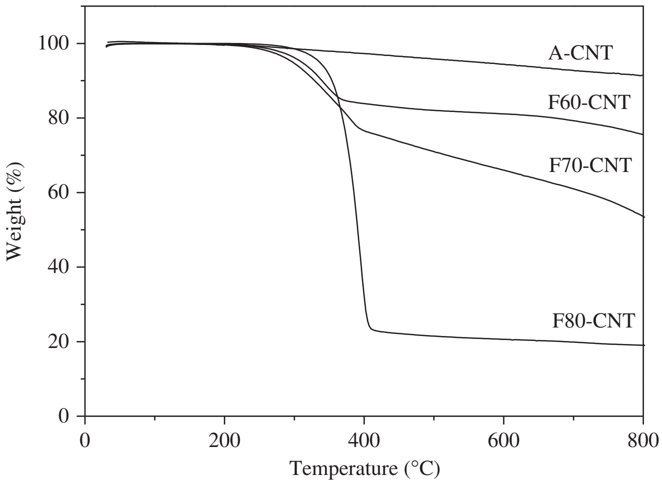

Fig. 2. TGA thermograms of A-CNT, F60-CNT, F70-CNT, and F80-CNT.

temperature of 60 °C, F70-CNT for reaction temperature of 70 °C, and F80-CNT for reaction temperature of 80 °C, respectively.

2.3. *Characterization and measurements*

Fourier transform infrared (FT-IR) spectra were recorded with a Bio-Rad Co. digilab FTS-165 spectrometer by using KBr pellets. TGA data were obtained with a NETZSCH TG 209 F3 analyzer at a heating rate of 10 °C min^{-1} from 30 to 850 °C under a nitrogen atmosphere. Scanning electron microscope images were obtained from a FE-SEM S-4300/HITACHI microscope. Elemental composition of CNTs before and after surface modification was measured using an elemental analyzer (CE EA-1110). Transmission electron microscopy photographs were obtained using Field Emission-Transmission Electron Microscopy (FE-TEM, JEM2100/JEOL) with an accelerating voltage of 200 kV.

3. Results and discussion

Scheme 1 illustrates the procedure for functionalization of CNTs by epoxide ring-opening polymerization. CNTs were purified using a mixture of concentrated H_2SO_4 and HNO_3 (3:1). They were then functionalized by epoxide ring-opening polymerization using sodium hydroxide as a catalyst. After the functionalization step, the product was washed thoroughly with acetone and deionized water, and filtered to remove acetone or deionized water-soluble substances. The functionalization of CNTs was confirmed by FT-IR, TGA, SEM, and TEM.

Fig. 1 shows FT-IR spectra of A-CNT and F70-CNT. In the FT-IR spectrum of A-CNT, the broad band at 3430 cm^{-1} and the slightly less intense band at 1704 cm^{-1} are attributed to the surface OH groups and C=O stretching vibration of CNTs, respectively. After functionalization of CNTs, new peaks appeared at wave numbers of 2860 and 2925 cm^{-1}, corresponding to the aliphatic C–H stretching vibrations. The bands at 843 and 1274 cm^{-1} are assigned to the asymmetrical C–O–C and the symmetrical epoxide ring. The FT-IR results verify that the polyether chains and the epoxide groups are covalently attached to the CNTs [11,14,16].

Table 1
Thermal stability of CNT samples obtained from TGA thermograms.

Sample	T_{d5} (°C)	Weight loss at 560 °C
A-CNT	560.0	5.0
F60-CNT	310.4	18.5
F70-CNT	297.6	32.1
F80-CNT	336.0	79.1

The amount of the polymer grafted to the CNTs was estimated by TGA, and the results are shown in Fig. 2. Thermal stability factors can be determined from the TGA thermograms [17,18]. The initial decomposing temperature (the temperature of 5% weight loss, T_{d5}) of the A-CNT is 560 °C, which indicates that the acid treated CNTs are thermally stable up to this temperature, as shown in Table 1. If the mass loss of the A-CNT at 560 °C is used as a reference, the mass of functionalized CNTs at 560 °C is 81.5, 67.9, and 20.9 wt%, respectively, indicating polymer content of 13.5, 27.1, and 74.1 wt% for F60-CNT, F70-CNT, and F80-CNT, respectively [10,13,19]. The amount of grafted polymer varied from 14 to 74 wt% as the reaction temperature was increased from 60 to 80 °C.

The elemental compositions of A-CNT and F70-CNT are summarized in Table 2. The O/C ratio of A-CNT increased significantly from 5.1% to 29.8% after surface functionalization, which indicated that the attachment of oxygen-containing groups on CNT surface [20].

The morphology of the A-CNT and F80-CNT after through washing with ethyl alcohol was observed by using SEM, and the results are exhibited in Fig. 3. As can be seen in the figure, the functionalized CNTs appear to be thicker compared to the A-CNT. As shown in Fig. 3(a), the A-CNT exhibits smooth textures on the surface of tubes. In contrast, the functionalized CNTs show rough surfaces, indicating the attachment of organic moieties on their surfaces, as shown in Fig. 3(b) and (c) [11–13,21].

Table 2
Elemental composition of CNTs.

Element (at%)	C	O	O/C (%)
A-CNT	92.0	5.1	5.5
F70-CNT	62.0	29.8	48.1

Fig. 4 shows typical TEM images of the A-CNT and F80-CNT. In the TEM images of the A-CNT (Fig. 4(a) and (b)), the tube surface is relatively smooth and clean and is covered with a thin phase. After the functionalization process, the tubes are enwrapped by polymer chains with thickness of several nanometers, forming a core–shell structure with CNTs at the center. Additionally, the boundary between the tube and the polymer layer is distinct, as shown in Fig. 4(c) and (d) [10,12,14,22]. The thickness of the polymer shell shown in Fig. 4(c) and (d) is ca. 2–5 nm.

In conclusion, we demonstrated a simple method for functionalization of CNTs by surface-initiated epoxide ring-opening polymerization. FT-IR, TGA, and EA analyses indicated that both

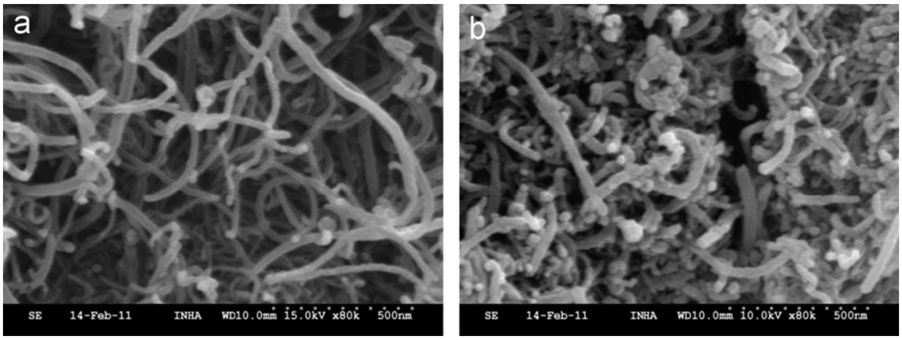

Fig. 3. SEM images of A-CNT (a) and F80-CNT (b).

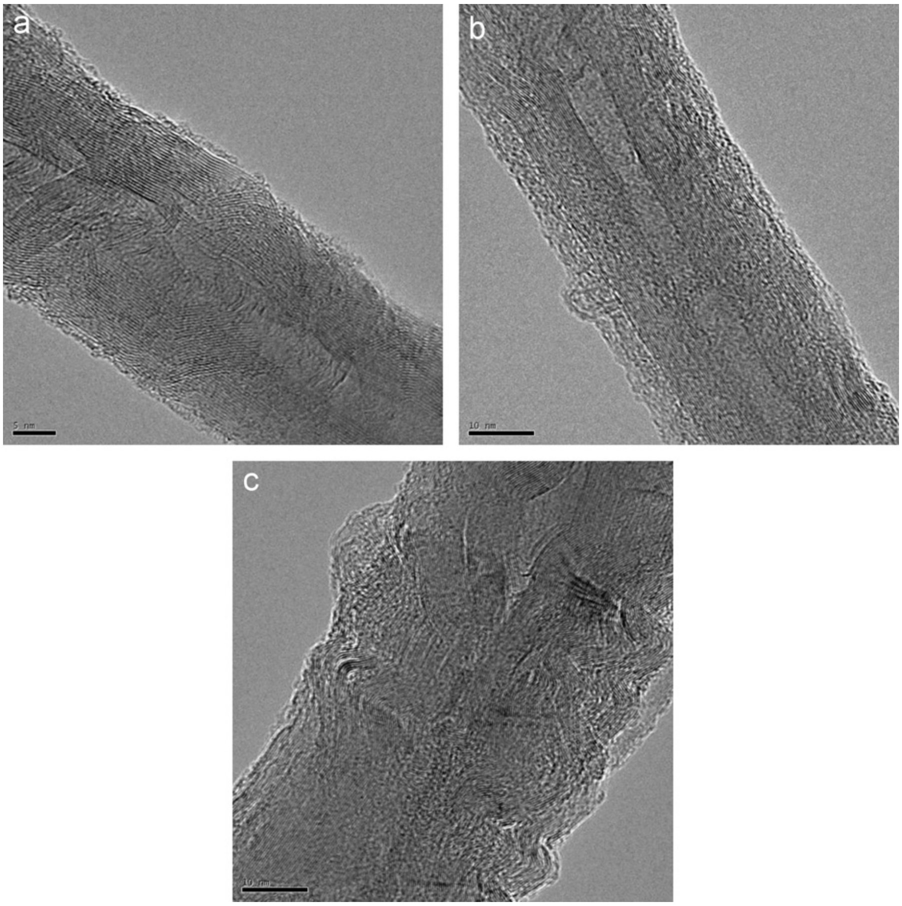

Fig. 4. TEM images of A-CNT (a) and F80-CNT (b, c).

nanotubes and polymers were present within the material isolated from the polymerization reaction. The amount of grafted polymer varied from 14 to 74 wt% with increasing reaction temperature from 60 to 80 °C. Analysis of these structures by SEM and TEM provided further evidence of the formation of polymerized nanotubes, and indicated a core–shell structure with CNTs at the center.

Acknowledgment

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