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Quantitative analysis of carbon nanotube cross-linking reactions

Yong-O Im*, Sung-Hyun Lee*, Sung-Uk Yu, Jaegeun Lee***,†, and Kun-Hong Lee***

*Department of Chemical Engineering, Pohang University of Science and Technology,
77, Cheongam-ro, Nam-gu, Pohang, Gyeongsangbuk-do 37673, Korea
**Department of Organic Materials & Fiber Engineering, Chonbuk National University,
567 Baekje-daero, Deokjin-gu, Jeonju-si, Jellabuk-do 54896, Korea
***Carbon Convergence Materials Research Center, Korea Institute of Science and Technology,
92, Chudong-ro, Bongdong-eup, Wanju-gun, Jeollabuk-do 55324, Korea
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Abstract−Covalent cross-linking of carbon nanotubes (CNTs) is a useful way of transferring the unique properties of individual CNTs to macroscopic structures for a wide variety of applications. For elaborate engineering of the cross-linking reaction of CNTs, quantitative analysis of cross-linking reaction is imperative. We report here a universally applicable method to quantitatively analyze the cross-linking of CNTs by esterification. To distinguish the cross-linking reaction from the one-side reaction, where only one end of the linker reacts with a CNT, mass and molar balances were established based on thermogravimetric analysis data. This analysis revealed that approximately one in five linkers was involved in the cross-linking reaction. Qualitative characterizations such as Fourier transform infrared and Raman spectroscopy were also used to confirm the cross-linking reaction.

Keywords: Carbon Nanotubes, Cross-linking Reaction, Quantiative Analysis

INTRODUCTION

Chemical modification of carbon nanotubes (CNTs) is a promising approach that takes advantage of the excellent mechanical and electrical properties of individual CNTs [1-3]. Among the various types of chemical modification, cross-linking of CNTs, which forms covalent bonds between CNTs, is a useful way of transferring the unique properties of individual CNTs to macroscopic structures for an extensive range of applications [4]. For example, it was reported that the cross-linking of CNTs improved the tensile strength of CNT fibers [5,6] and buckypaper [7-9]. Furthermore, the cross-linking reaction can be used to control the dispersion of CNTs [10,11], enhance electrical properties [12], and reinforce polymers through the formation of complex structures [13,14].

To cross-link individual CNTs, molecules called "linkers" are usually used. Linkers have chemically active sites at each end that can form covalent bonds with the sidewall of CNTs. When both ends of the linker react with a CNT, the linker connects two individual CNTs and a cross-linking reaction is completed. If a reaction does not occur at each end of the linker, the cross-linking reaction is not successful.

Processes of confirming cross-linking reactions remain quite difficult. Basically, a chemical reaction should be confirmed by qualitative analyses. For example, Fourier transform infrared (FT-IR) spectroscopy reveals the presence of various functional groups, and thus the chemical reaction for cross-linking of CNTs can be confirmed. Raman spectroscopy can also be used to examine the cross-linking reaction of CNTs. As Raman spectroscopy can be used to observe the graphitic features of a carbon material, alteration of the graphitic structure of CNTs because of chemical modification of the CNT surface can be detected.

However, for elaborate engineering of the cross-linking reaction, quantitative studies must be accompanied by qualitative analyses. The number of cross-links between CNTs is directly related to mechanical properties of cross-linked CNTs in macroscopic applications such as buckypaper and CNT fiber. The mechanical properties of buckypaper and CNT fiber are determined by load transfer between individual CNTs. Cross-linking reaction supports weak shear interaction between CNTs by introducing covalent bonding resulting in an improvement of load transfer. Therefore, quantitative analysis that observes the number of cross-links is required for delicate applications of the cross-linking reaction.

The most typical quantitative method is thermogravimetric analysis (TGA). The amount of linkers in grafted CNTs can be determined using TGA [7,9,15]. However, it is necessary to distinguish between chemical reactions at both ends of the linker (cross-linking reaction) and reaction at only one side the linker (one-side reaction). In many previous studies, the possibility of one-side reactions was not considered, which inevitably resulted in an overestimation of the yield of the cross-linking reaction. Most recently, De Marco et al. reported a quantitative analysis of the cross-linking reaction and one-side reaction [10]. They synthesized carbon-bonded organogels by reductive coupling between CNT anions and *p*-diiodobenzene, with the loss of iodine during the reaction. The molar ratio between the one-side and cross-linking reactions was derived using TGA and X-ray photoelectron spectroscopy (XPS) to iden-

†To whom correspondence should be addressed.
E-mail: cntagiousjacky@gmail.com

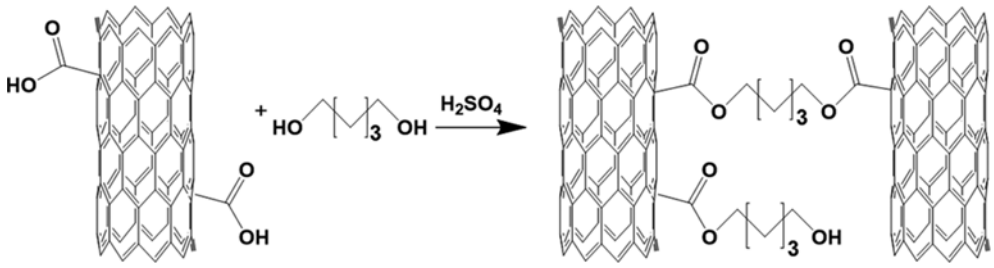

Fig. 1. Esterification reactions between carboxylic acids on the CNT and the alcohol groups of the linker (1,5-pentanediol), resulting in chemical links between individual CNTs. Both cross-linking and one-side reactions are present in the product.

tify the content of iodine atoms, as the amount of remaining iodine atoms corresponds to the amount of one-side reaction. However, this method cannot be applied universally because it relies on the presence of a specific atom. Thus, a more general quantitative method to characterize the cross-linking of CNTs is necessary.

In this work, we present a universal quantitative analysis of the cross-linking reaction of CNTs. An esterification cross-linking reaction was selected for the quantitative analysis. To distinguish the cross-linking reaction from the one-side reaction, mass and mole balances were established based on TGA data, and the molar ratio between the cross-linking reaction and one-side reaction was calculated. Cross-linking was also characterized qualitatively by FT-IR spectroscopy, dispersion analysis, and Raman spectroscopy.

EXPERIMENTAL

MWNT and MWNT-COOH were purchased from Nanostructure & Amorphous Materials Inc. MWNT consists of multiwalled CNTs with lengths of 10-30 μm and 95% purity. MWNT-COOH also consists of multiwalled CNTs with the same length and purity, but also has a carboxylic functional group (3.67-4.05 wt%). 1,5-Pentanediol (97.0%) and sulfuric acid (95.0-98.0%) were purchased from Sigma Aldrich.

CL-MWNT was synthesized by esterification of MWNT-COOH. In a 250 mL round bottom flask, 200 mg of MWNT-COOH, 20 mL of 1,5-pentanediol, and 200 μL of sulfuric acid were mixed, and the mixture were heated at 160 °C for 1 h with stirring. After heating, the mixture was filtered and washed with acetone to remove any remaining linkers, and CL-MWNT powder was dried in an oven at 70 °C.

TGA was carried out from 40 to 850 °C with a ramp of 5 °C/min under an air atmosphere using a Q50 TA thermogravimetric analyzer (TA Instruments, USA) to quantitatively analyze the cross-linking reaction of CNTs. FT-IR spectra were obtained to detect the functional groups on the surface of CNTs using a Cary 670 FT-IR spectrometer (Agilent Technologies, USA). To measure the dispersion of CNTs, a Turbiscan Lab analyzer (Formulaction, France) was used. CNTs (50 mg) were added to 50 mL of ethanol in a vial and sonicated for 30 min. After the sonication, the entire height (~55 mm) of the CNT suspension was scanned for 2 days at 25 °C. The graphitic characteristics of the CNTs were confirmed by Raman spectroscopy (Horiba Jobin-Yvon LabRam Aramis spectrometer, France). The 514 nm line of the Ar-ion excitation source was used, and the scattered light signal was collected using a ×50 microscope objective lens. The chemical bonding states were observed by using XPS (VG ESCALAB250, VG Scientific, UK) with an Al Kα (1486.6 eV) source. The morphologies of the CNTs were determined through field-emission scanning electron microscopy (FE-SEM, Nova Nano-SEM 450, Czech Republic).

RESULTS AND DISCUSSION

Esterification, which is the reaction between a carboxylic acid and an alcohol to form an ester, was used to covalently cross-link individual CNTs. Sulfuric acid acted as a catalyst for the reaction because it absorbs water produced during the reaction, thus preventing the reverse reaction. Ideally, individual CNTs can be connected by a cross-linking reaction because the linker 1,5-pentanediol has an alcohol group on each end of the carbon chain. Unfortunately, some 1,5-pentanediol molecules react with carboxylic acid through a one-side reaction owing to limited accessibility of CNTs to the linker (Fig. 1). The possibility of both the cross-linking and one-side reactions should be considered for accurate quantitative analysis of the cross-linking reaction.

The presence of functional groups on the CNTs was confirmed by FT-IR spectroscopy using the transmission method (KBr pellet), as shown in Fig. 2. The spectra of all three samples (MWNT, MWNT-COOH, and CL-MWNT) have peaks around 1,186 and

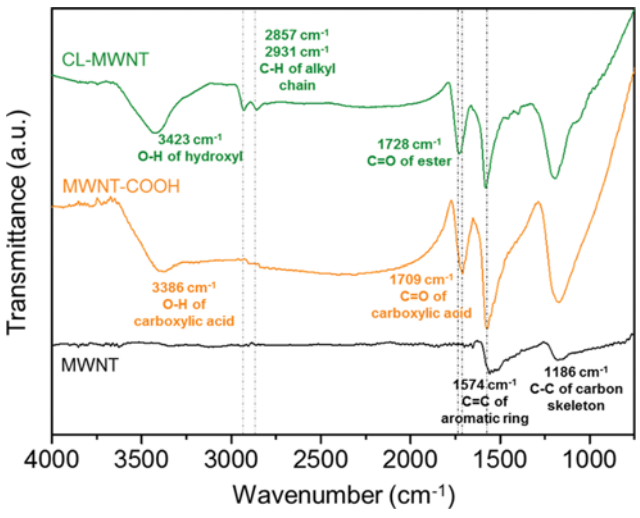

Fig. 2. FT-IR spectra of MWNT (black), MWNT-COOH (orange), and CL-MWNT (green).

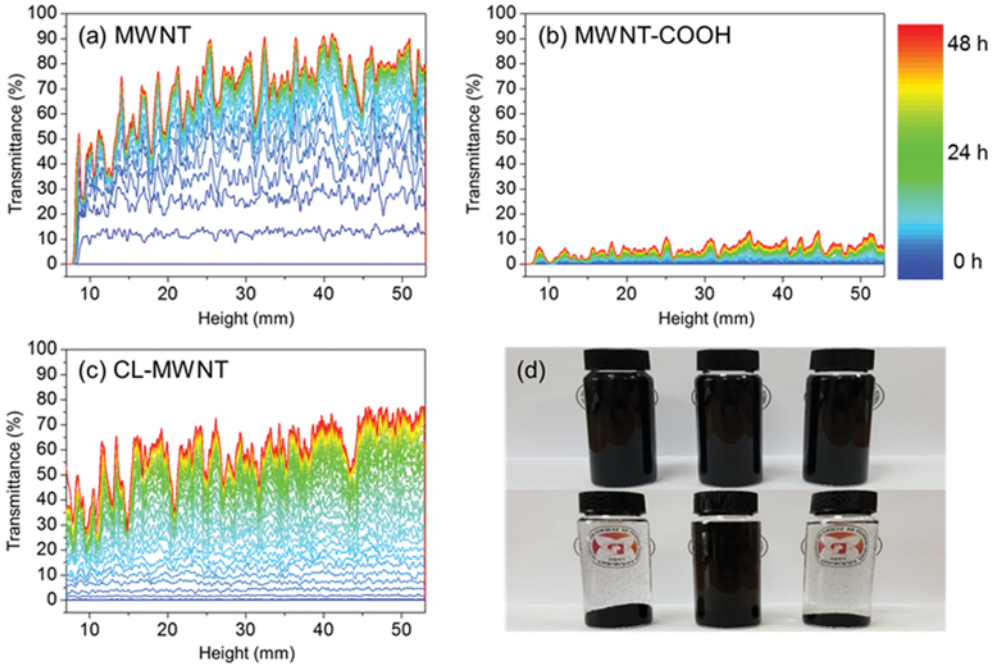

Fig. 3. Dispersion analyses for (a) MWNT, (b) MWNT-COOH, and (c) CL-MWNT by Turbiscan. All three samples were dispersed in ethanol by sonication. These data are represented as a function of time (0-48 h) and sample height (7-53 mm). (d) Pictures of MWNT (left), MWNT-COOH (middle), and CL-MWNT (right) as-dispersed in ethanol (top) and 16 h after dispersion (bottom).

1,574 cm^{-1}, which are assigned to C-C stretching vibrations from the carbon skeleton [16] and C=C stretching vibrations from the aromatic rings [17], respectively. The carboxylic acid of MWNT-COOH results in C=O and O-H stretching vibrations at 1,709 and 3,386 cm^{-1}, respectively, which are not observed in the MWNT spectrum. After esterification, as shown in Fig. 1, the carboxylic group is transformed into an ester group. Both these functional groups have C=O stretching vibrations; however, the peak is shifted slightly from 1,709 cm^{-1} [18] to 1,728 cm^{-1} [19] owing to differences in the vibration mode of carboxylic acids and esters. In addition, the peaks at 2,857 and 2,931 cm^{-1} originated from the stretching vibration of C-H in the alkyl chain [20] of 1,5-pentanediol, which was used as the linker. These changes in the FT-IR spectra indicate that the carboxylic acids of MWNT-COOH were successfully transformed to esters by the cross-linking reaction. Both MWNT-COOH and CL-MWNT exhibit O-H stretching, as shown by the broad band around 3,400 cm^{-1}. In the case of MWNT-COOH, this band originates from carboxylic groups. A complete cross-linking reaction would eliminate all the carboxylic groups, but an O-H peak remains in the CL-MWNT spectrum. This peak originates from hydroxyl groups of one-side reacted linkers.

The transmittance of the CNT dispersions was evaluated to assess the influence of the surface state of the CNTs on their dispersion in solvent. The dispersion of CNTs in solvent is influenced by the affinity between the CNT and the solvent. CNTs are barely dispersed in most solvents. To overcome this dispersion limitation, there have been many studies on the functionalization of CNT surfaces to achieve dispersion of CNTs in various solvents [21,22]. Turbiscan can be used to measure the transmittance of the dispersion every hour and evaluate the dispersion of a material in solvent. After the same amounts (50 mg) of MWNT, MWNT-COOH, and CL-MWNT were added to 50 mL of ethanol and sonicated for 30 min, the transmittance of the entire height of the dispersion was scanned for two days (Fig. 3). Owing to the affinity of the carboxylic groups for ethanol, the transmittance of the MWNT-COOH dispersion did not increase significantly over time, which indicated that the MWNT-COOH dispersion was maintained. However, the transmittance of the MWNT dispersion increased significantly, as MWNT was poorly dispersed in ethanol. The transmittance of the CL-MWNT dispersion was between those of MWNT and MWNT-COOH at the same point of time. When ethanol is used as the solvent, the dispersion ability is mainly proportional to the number of carboxylic or hydroxyl groups on the surface of the CNTs. The cross-linking reaction consumes two carboxylic acids, whereas one hydroxyl group on the 1,5-pentanediol chain is retained following the one-side reaction and only one carboxylic acid is consumed. Thus, the transmittance result for the CL-MWNT dispersion indicates that the cross-linking and one-side reactions occurred simultaneously, which coincides with the FT-IR results. Photographs of the CNT dispersions after 16 h also show that the amount of sunken powders in CL-MWNT dispersions is in between those in MWNT and MWNT-COOH dispersions. This indicates that the degree of the dispersion of CL-MWNT is also between those of MWNT and MWNT-COOH (Fig. 3(d)).

Although the FT-IR spectroscopy and dispersion analyses proved that the CNTs were successfully cross-linked with some linkers only reacted at one end, no quantitative information was obtained. To obtain quantitative information about the CNT samples, TGA was carried out. The TGA spectra of MWNT, MWNT-COOH, and CL-MWNT are presented in Fig. 4. The weight of CL-MWNT

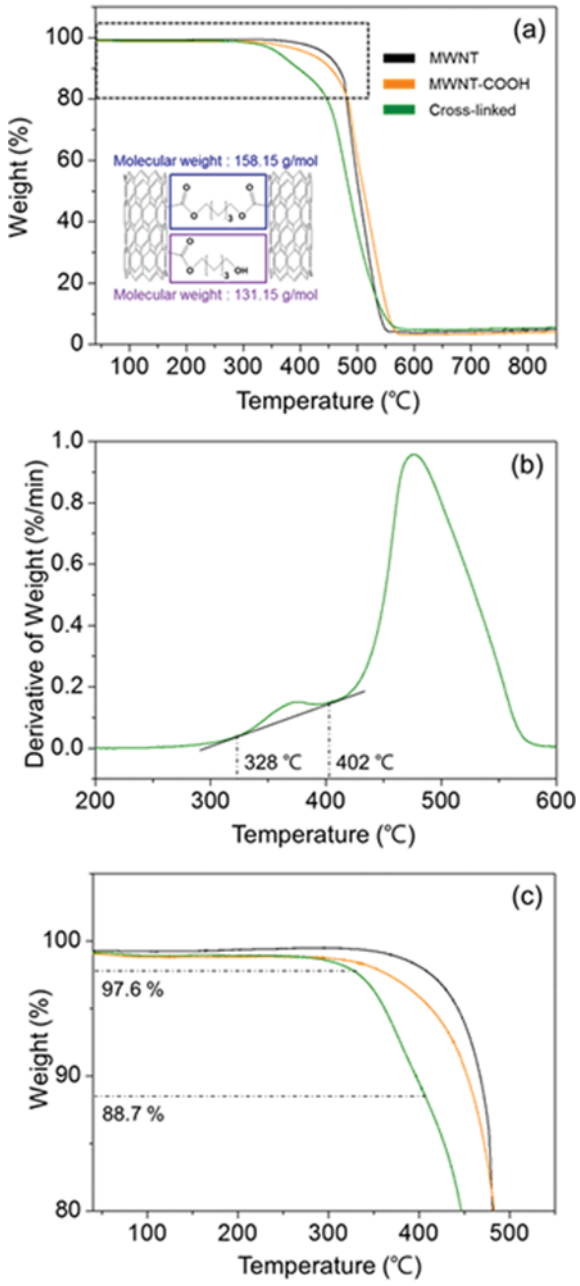

Fig. 4. (a) TGA curves of MWNT (black), MWNT-COOH (orange) and CL-MWNT (green), and (b) derivative of the CL-MWNT weight loss curve. The tangent line of the left peak in the derivative curve is indicated. (c) Enlarged image of (a) shows a weight loss of 8.9% assigned to the total amount of linkers.

began to decrease at a lower temperature than that of MWNT or MWNT-COOH. This different behavior is due to the presence of linkers bonded to the CNTs in CL-MWNT. The bond order of the carbon-carbon CNT structure is 1.5 owing to the resonance structures of the CNTs, whereas that of the linker is 1. As dissociation energy is related to bond order, the linkers were dissociated at lower temperature than the CNTs. Considering that that the boiling point of 1,5-pentanediol is 285 °C, the fact that the weight percentage of CL-MWNT did not decrease until 300 °C indicates that any unreacted linkers that were physisorbed on the surface of CNTs were completely removed during the filtration step. The derivative of the weight loss curve gives the temperature range for the dissociation of a specific material. The tangent line of the derivative curve of CL-MWNT indicates that the linkers in CL-MWNT were dissociated in the temperature range of 328-402 °C (Fig. 4(b)). This temperature range corresponds to a weight loss of 8.9% (from 97.6% to 88.7%), as shown in Fig. 4(c).

Based on the data from the TGA loss curve, the ratio of the cross-linking reaction and one-side reaction was quantitatively calculated. The molecular weights of the linkers obtained from the cross-linking reaction (Fig. 4(a), blue box) and one-side reaction (Fig. 4(a), purple box) are 158.15 and 131.15 g/mol, respectively. The average carboxylic acid group content in MWNT-COOH is 3.85 wt%, with a molecular weight of 45.02 g/mol. First, the sum of the weight percentage of the linker involved in the cross-linking reaction (M_{CL}) and that in the one-side reaction (M_O) is the total weight percentage of reacted linkers (M_{tot}), which is 8.9 wt% from previously mentioned TGA data, by mass balance. Second, the number of carboxylic acids in the CNTs (N_{tot}) should be equal to the number of carboxylic acids consumed by the cross-linking reaction (N_{CL}) and the one-side reaction (N_O) based on mole balance. As the cross-linking reaction uses two carboxylic acids and the one-side reaction uses one carboxylic acid, the following equations are established:

$$M_{CL}+M_O=M_{tot} \tag{1}$$

$$2\times N_{CL}+N_O=N_{tot} \tag{2}$$

From the molar mass of the linkers obtained from the cross-linking and one-side reactions:

$$\frac{M_{CL}}{158.15\ \text{g/mol}}=N_{CL} \tag{3}$$

$$\frac{M_O}{131.15\ \text{g/mol}}=N_O \tag{4}$$

The amount of carboxylic acid groups in mole units on the surface of the CNTs is calculated by using the following equation:

$$N_{tot}=\frac{(100-M_{tot})\times 0.0385}{45.02\ \text{g/mol}} \tag{5}$$

These equations give M_{CL} of 2.0 wt% and M_O of 6.9 wt%. The molar ratio of linkers from the one-side reaction to those from the cross-linking reaction (N_O to N_{CL}) is 4.2, which means that about one of every five 1,5-pentanediol molecules is involved in a successful cross-linking reaction. This quantitative analysis can be confirmed using XPS data (Fig. S1). As shown in Fig. 1, the cross-linking reaction does not change the number of oxygen atoms, as one equivalent of water is eliminated from each cross-linking reaction. However, the number of oxygen atoms increases when only one-side of the linker reacts, owing to the unreacted oxygen atom at the other end of the chain. The atomic percentage of oxygen atoms clearly increased after the cross-linking reaction from 6.31% in MWNT-COOH to 8.93% in CL-MWNT (Table 1).

The graphitic features of MWNT, MWNT-COOH, and CL-MWNT were detected using Raman spectroscopy (Fig. 5). In Raman

Table 1. Atomic composition of MWNT, MWNT-COOH, and CL-MWNT

	Carbon (%)	Oxygen (%)
MWNT	95.72	4.28
MWNT-COOH	93.69	6.31
CL-MWNT	91.07	8.93

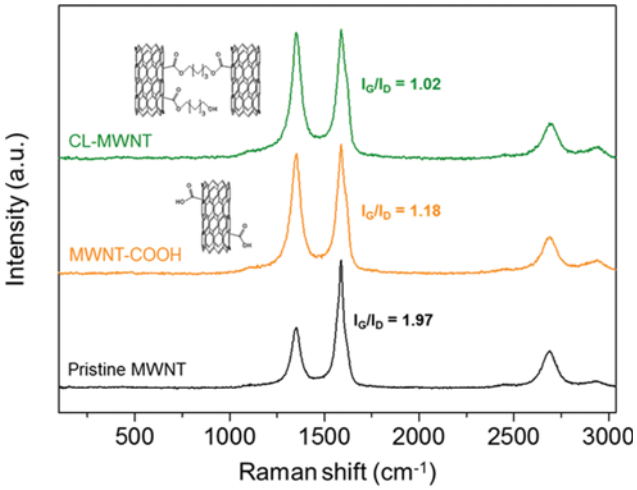

Fig. 5. Raman spectra of pristine MWNT (black), MWNT-COOH (orange), and CL-MWNT (green). The G/D ratio of MWNT-COOH was lower than that of MWNT owing to the functional groups on the CNTs, whereas the G/D ratio of CL-MWNT was similar to that of MWNT-COOH.

spectra, the G-band, which is detected at 1,590 cm^{-1}, corresponds to the sp^2 carbons of graphitic structures, whereas the D-band, which is detected at 1,350 cm^{-1}, corresponds to sp^3 carbons in disordered structures [23]. Generally, the ratio of the intensities of these two bands, I_G/I_D, indicates the extent of CNT functionalization, as functionalization destroys sp^2 carbon bonding. The I_G/I_D ratio of MWNT-COOH was lower than that of MWNT as a result of functionalization. Moreover, the I_G/I_D ratio of CL-MWNT was almost the same as that of MWNT-COOH. Since the esterification reaction does not increase the number of sp^3 carbons on the wall of CNTs, the overall number of sp^3 carbons was not changed after the reaction, which led to unaltered I_G/I_D ratio of CL-MWNT. The slightly decreased I_G/I_D of CL-MWNT may be attributed to the incorporation of linker which is composed of sp^3 carbons.

CONCLUSION

The cross-linking of CNTs by esterification was confirmed qualitatively and quantitatively. Qualitative analyses such as FT-IR spectroscopy, dispersion analysis, and Raman spectroscopy indicated that individual CNTs were covalently connected through ester bonds. Furthermore, the quantitative ratio of cross-linking reactions to one-side reactions was calculated by using mass and molar balances based on TGA data. The quantitative analysis developed in this work is expected to be applicable to various kinds of cross-linking reactions and will enable more elaborate engineering of the cross-linking reaction.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Quantitative analysis of carbon nanotube cross-linking reactions

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*Department of Chemical Engineering, Pohang University of Science and Technology,
77, Cheongam-ro, Nam-gu, Pohang, Gyeongsangbuk-do 37673, Korea
**Department of Organic Materials & Fiber Engineering, Chonbuk National University,
567 Baekje-daero, Deokjin-gu, Jeonju-si, Jellabuk-do 54896, Korea
***Carbon Convergence Materials Research Center, Korea Institute of Science and Technology,
92, Chudong-ro, Bongdong-eup, Wanju-gun, Jeollabuk-do 55324, Korea
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Even in the MWNT sample, oxygen components are present in the CNTs owing to the partial oxidation of CNTs under ambient conditions. The oxygen contents from partial oxidation were determined from the XPS spectra. Basically, the esterification reaction does not introduce any new types of atom, other than carbon and oxygen; thus, the overall spectra of MWNT-COOH and CL-MWNT are similar.

The morphologies of the CNTs were observed using SEM. The CNTs of CL-MWNT were more aggregated than those of MWNT and MWNT-COOH. The reaction of the 1,5-pentanediol linker with CNTs brought the CNTs closer together, resulting in the aggregation of CNTs in CL-MWNT.

The weight loss curve derivatives for MWNT and MWNT-COOH had similar trends. After the decomposition of the linkers the weight loss curve derivative for CL-MWNT also showed an increase around 420 °C, indicating that the CNTs in all three samples were decomposed in the same temperature range.

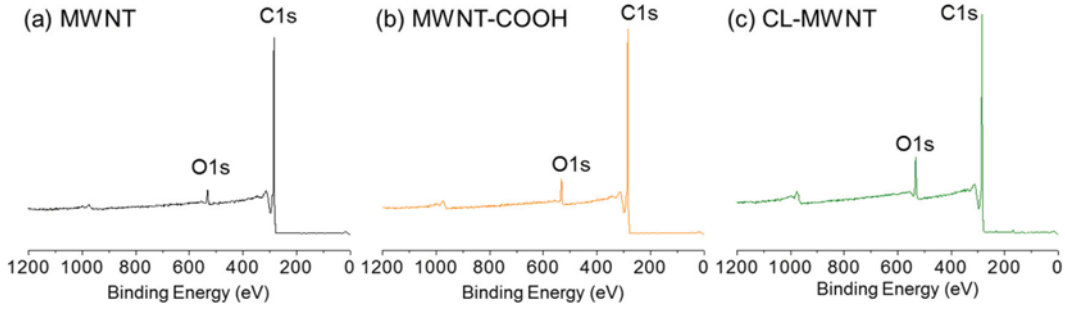

Fig. S1. XPS spectra of (a) MWNT, (b) MWNT-COOH, and (c) CL-MWNT.

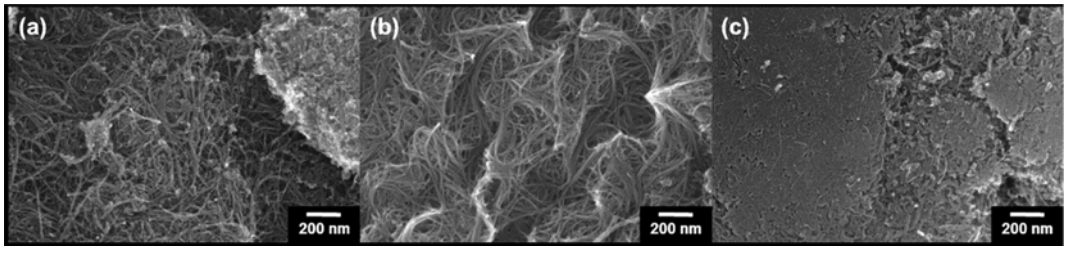

Fig. S2. SEM images of (a) MWNT, (b) MWNT-COOH, and (c) CL-MWNT.

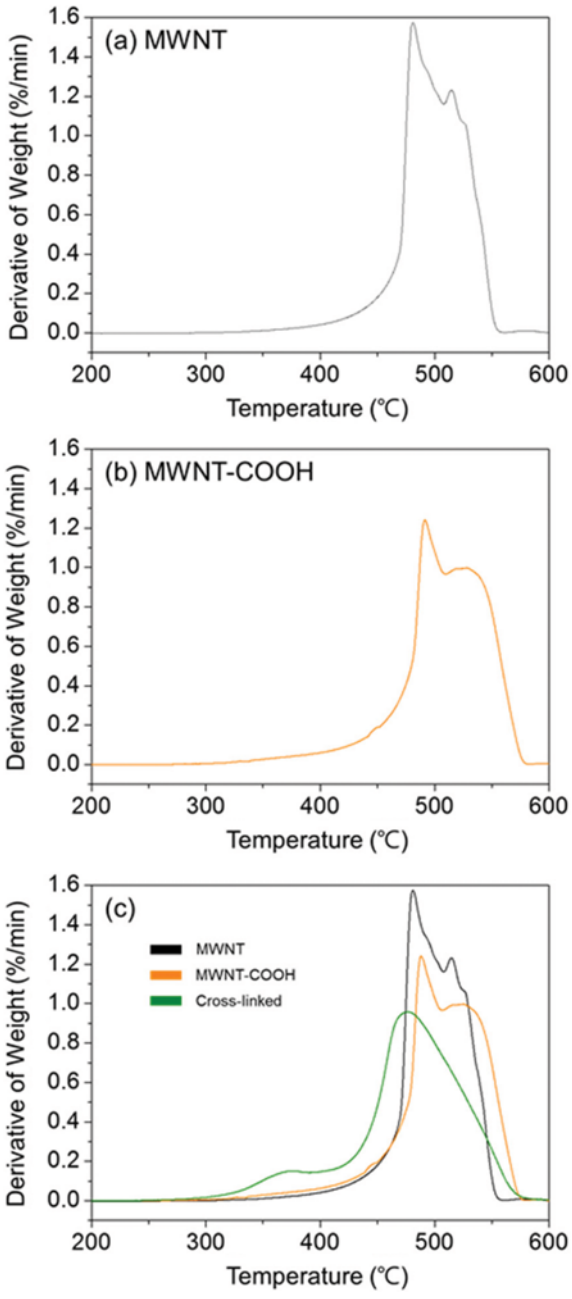

Fig. S3. Weight loss curve derivatives for (a) MWNT and (b) MWNT-COOH. (c) Comparison of weight loss curve derivatives.