Technical and scientific contributions

An XPS study on defluorination of fluorinated MWCNTs by electron beam irradiation

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Abstract

In this study, we investigated to elucidate clearly the E-beam effect on fluorinated MWCNTs and their defluorination properties. A new carbon material which has a unique surface property was made from Multi-Walled Carbon Nano Tubes (MWCNTs) using a fluorination and defluorination. Fluorinated MWCNTs were prepared by direct thermal fluorination method at 373 K. Defluorination of fluorinated MWCNTs was carried out by electron beam irradiation. The surface properties of all MWCNTs were studied by XPS using a non-monochromatic (Al Kα) source. The C1s core level spectra of MWCNTs were deconvoluted to several Pseudo-Voigt functions (sum of Gaussian-Lorentzian functions). As the results of XPS, the C-F covalent bonding concentration increased after fluorination. Whereas the C-F covalent bonding concentration decreased by electron beam irradiation as same as before fluorination. The carbon-fluorine bondings can be broken by electron beam irradiation. However, the nitrogen adsorption isotherms of MWCNTs at 77 K suggest that the pore structure of fluorinated MWCNTs was changed, and the changed pore structure was maintained after defluorination.

Key words; MWCNT; Fluorination; Defluorination; Electron beam irradiation

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1. Introduction

A novel allotrope of carbon, carbon nanotubes are unique nanostructures with remarkable electronic and mechanical properties (Berber et al., 2000). However, the lack of solubility and the difficult manipulation in any solvents have imposed great limitations to the use of CNT. Indeed, as-produced CNT are insoluble in all organic solvents and aqueous solutions. They can be dispersed in some solvents by sonication, but precipitation immediately occurs when this process is interrupted. On the other hand, it has been demonstrated that CNT can interact with different classes of compounds. The formation of molecular complexes allows a better processing of CNT toward the fabrication of innovative nanodevices. In addition, CNT can undergo chemical reactions that make them more soluble for their integration into inorganic, organic, and biological systems (Tasis et al., 2006). Therefore, in order to improve dispersibility and reactivity, an attempt to induce functional groups on the surface of CNTs was gone on (Tasis et al., 2006). Among these methods, the fluorination of carbon nanotubes have only been developed in order to modify the structural and electronic properties of the tubular structures (Hamwi et al., 1997; Tressaud et al., 2002). The strongest electronegativity of F\(^-\) ion leads to strong bonding between fluorine and other elements (Lee, 2007).

Up to now, epoxy resin-based CNT composites have been also extensively investigated in view of their potential applications in the electronics, aerospace and automotive industries (Ma et al., 2008, and...
Wang et al. (2008). The effect of an electron beam (E-beam) and g-ray irradiation on the curing of epoxy resins composite was investigated (Nho et al., 2004). There has been a considerable development about the E-beam curing advanced composites for the use of aerospace and other industries (Saunders et al., 2000). The E-beam curing of composites offers many advantages compared with conventional thermal curing (Janke et al., 1999).

Although numerous studies about the carbon/fluorine system and the properties of CNTs carried out to improve their application by world wide research groups, a study of defluorination on CNTs is still fresh ground. Especially, there are few papers reported about the relationship between the pore structure and surface functional groups of MWCNTs (Hattori et al., 2007). Therefore, it is important to study the effect of surface characteristics of fluorinated CNT cured by E-beam in N₂ and air atmosphere.

In the present study, we investigated to elucidate clearly the E-beam effect on fluorinated MWCNTs and their defluorination properties. Also, we report and discuss the results obtain by X-ray photoelectron spectroscopy (XPS) analysis and nitrogen adsorption isotherms at 77 K of the fluorinated and defluorinated MWCNTs by electron beam irradiation.

2. Experimental

2.1. Materials
MWCNTs were obtained from NK CNT Co., Korea. It was grown by the vapor growth method using acetylene (C₂H₂) as carbon source and ironpentacarbonyl (Fe(CO)₅) as catalyst and purified by chemical and thermal treatment. The nanotubes are under 20 \( \mu \text{m} \) long, and outer and inner diameters are 60-80 nm and 30-50 nm, respectively. Fluorine gas used for oxyfluorination, were supplied by Messer Grieheim GmbH (99.8%). Oxygen (99.999%) and argon (99.999%) gas were also used.

2.2. Fluorination of MWCNTs

Fluorination apparatus consist of reactor, vacuum-pump and buffer-tank connected gas cylinders. The MWCNTs loaded on nickel boat in reactor and were degassed at 473 K. Fluorination was carried out at 373 K for 10 min after introduction of fluorine gas to 1 bar. The details have been described elsewhere (Lee et al., 2003).

2.3. Defluorination of MWCNTs

Defluorination of MWCNTs was directly carried out by E-Beam irradiation. Fluorinated MWCNTs were radiated using electron beam accelerator (ELV-4, EB tech Co. Korea). The experimental parameters
were as follows: energy, 1MeV; current, 2.5 mA. E-beams were irradiated at a dose rate 7500 kGy/h in atmosphere.

2.4. Surface properties of MMCNTs

Raman measurements were made in backscattering geometry with a JY LabRam HR fitted with a liquid-nitrogen cooled CCD detector. The spectra were collected under ambient conditions using the 514.5nm line of an Ar⁺ ion laser. The surface properties and pore structures of MWCNTs used in this study, were investigated by MultiLab 2000 spectrometer (Thermo electron corporation, England) and ASAP 2020 (Micromeritics Ins. Corp.), respectively.

3. Results and Discussion

Fig. 1 showed XPS spectra of MWCNTs investigated in this study. The survey spectra in the 0-1000 eV of bonding energy range were investigated to identify the elements on the surface of samples and perform a quantitative analysis. As-received MWCNTs and fluorinated MWCNTs were shown almost similar peak’s shapes. All of the survey spectra of MWCNTs showed distinct carbon and oxygen peaks at around 285.0 eV and 533 eV, respectively. And F1s peak was also found fluorinated MWCNTs around
688 eV. The C1s atomic concentrations of MWCNTs used in this study, were 95.39 at% (as-received MWCNTs), 66.96 at% (fluorinated MWCNTs) and 93.68 at% (defluorinated MWCNTs), respectively. And also, The F1s atomic concentrations of MWCNTs used in this study, were 0 at% (as-received MWCNTs), 28.41 at% (fluorinated MWCNTs) and 1.49 at% (defluorinated MWCNTs), respectively. These results suggested that the carbon-fluorine bondings which were formed by fluorination could be removed by electron beam irradiation.

Fig. 2 showed the C1s and F1s spectra of as-received MWCNTs, fluorinated MWCNTs and defluorinated MWCNTs, respectively. As you can see in this Fig. 2, the both C1s spectra of as-received MWCNTs and defluorinated MWCNTs by E-beam irradiation showed peaks centered at 285 eV. These shapes were also originated from sp² carbon. And the shoulder peaks at 286-288 eV were due to carbon atoms bonded to oxygen atoms. After fluorination, this sp² peak shape largely changed and its intensity became broader and significantly reduced. A variety of news peak also appeared at 289.0 (nearly covalent C–F) and 292.0 (covalent CF₂, CF₃), assigned to carbon-fluorine bonding, respectively. These peaks at high binding energy side indicated the existence of various carbon species bonded to fluorine. The C1s peaks observed at 291.2–294.6 eV were ascribed to sp³ hybridized carbon atoms with covalent C–F bonds, which were similar to those in the covalent compounds, graphite fluorides, (CF)n and (C₂F)n (Lee, 2007).

The F1s spectrum of fluorinated MWCNTs showed that carbon fluorine bonding at 688.0 eV (Hamwi et al., 1997; Nanse et al., 1997; Nanse et al., 1997). As shown in this Fig., in contrast with the C
1s spectra, the F 1s spectra showed symmetric shape. On the other hand, the carbon-fluorine covalent bonding of fluorinated MWCNTs was almost removed after electron beam irradiation. These results suggested that the sp² carbons are recovered and reformed by electron beam irradiation.

Fig. 3 showed Raman spectra of as-received MWCNTs, fluorinated MWCNTs and defluorinated MWCNTs, respectively. The disordered carbon band (D-band) and graphitized band (G-band) appeared at approximately 1336 and 1582 cm⁻¹, respectively, corresponding to disordered and the ordered graphitic state on the CNTs surface signifying the sp³- and sp²- hybridized carbons, respectively (Kim et al., 2004; Misra et al., 2006). The shape and relative intensity of Raman spectra were changed due to fluorination and defluorination. The ratio of the integrated intensity of D line to that of G line (R = I_D/I_G) depended on the structure of nanotubes (Kastner et al., 1994). On the basis of the Lorentzian peak fitting of these MWCNTs in Fig. 3, the R-value of the integrated intensity (R = I_D/I_G) of as-received MWCNTs was 1.03. After fluorination and defluorination, the R-value slightly increased to 1.09 and 1.18, respectively. The R-value of MWCNTs after fluorination and defluorination by E-beam irradiation were thus increased, indicating the increase of amorphous carbon layers and decrease of graphite structure or elimination of MWCNTs. These results support our BET results.

The textural properties of as received and surface modified MWCNTs were listed in Table 1. It was found that the BET surface area increased from 60 to 99 m²/g after both defluorination and fluorination, whereas the total pore volume recovered after defluorination by E-beam irradiation. The average pore
diameter of as-received MWCNTs had largely decreased after both defluorination and fluorination. These results indicated that newly formed C-F bond had some influence on the blocking or filling of pores on the surface. Thus some mesopores (near to micropore) were probably changed to micropore by sticking some functional groups onto the entrance of the pores, resulting in narrowing of the pore size. These results were agreement with the report by the others (Park and Kim, 2005).

The adsorption isotherms of as-received MWCNTs, fluorinated MWCNTs and defluorinated MWCNTs were also shown in Fig. 4. As shown in this Fig., the adsorption isotherm of as-received MWCNTs was shown almost similar shape with others even though having different specific surface area. The BET specific surface area of MWCNTs were 60 m²/g (as-received MWCNTs), 99 m²/g (fluorinated MWCNTs) and 85 m²/g (defluorinated MWCNTs), respectively. As indicated in Table 1, the specific surface area of MWCNTs increased after fluorination, due to the crack of basal plane of MWCNTs. This pore structure of fluorinated MWCNTs was recovered after defluorination by electron beam irradiation.

Although the textural property of fluorinate MWCNTs was a little decrease through defluorination by E-beam irradiation, we believed that defluorinated MWCNTs can be fully used as reinforcement in epoxy composite.

4. Conclusions

In this paper, the E-beam effect on fluorinated MWCNTs and their defluorination properties is
investigated. Fluorinated MWCNTs are prepared by direct thermal fluorination method at 373 K. Defluorination of fluorinated MWCNTs are carried out by electron beam irradiation. As the results of XPS, the C-F covalent bonding concentration increased after fluorination. Whereas the C-F covalent bonding concentration decreased by electron beam irradiation as same as before fluorination. Namely, the carbon-fluorine bonding which was formed by fluorination were removed by electron beam irradiation.

The R-value of the integrated intensity (R = I_D/I_G) of as-received MWCNTs was 1.03. After fluorination and defluorination, the R-value slightly increased to 1.09 and 1.18, respectively. The R-value of MWCNTs after fluorination and defluorination by E-beam irradiation were thus increased, indicating the increase of amorphous carbon layers and decrease of graphite structure or elimination of MWCNTs.

The adsorption isotherm of as-received MWCNTs was shown almost similar shape with others even though having different specific surface area. However, the nitrogen adsorption isotherms of MWCNTs at 77 K suggest that the pore structure of fluorinated MWCNTs is a little changed, and this pore structure of fluorinated MWCNTs was recovered after defluorination by electron beam irradiation.

Acknowledgements

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References


<table>
<thead>
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<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Micropore volume by DFT (cm³/g)</th>
<th>Average pore diameter (nm)</th>
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<tr>
<td>as-received MWCNTs</td>
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<td>fluorinated MWCNTs</td>
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<td>defluorinated MWCNTs</td>
<td>85</td>
<td>0.168</td>
<td>0.026</td>
<td>7.7</td>
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Fig. 3. Raman spectra of As-received MWCNTs (a), Fluorinated MWCNTs (b) and Defluorinated MWCNTs (c).

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