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Electron Beam Irradiation-Enhanced Wettability of Carbon Fibers

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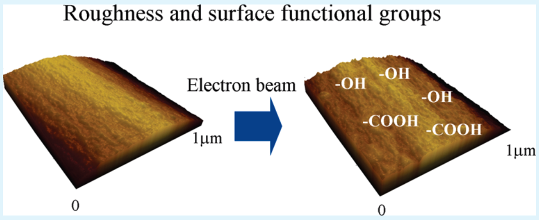
S *Supporting Information*

ABSTRACT: A simple but controllable way of altering the surface nature of carbon fibers, without sacrificing their intrinsic mechanical properties, is demonstrated using electron beam irradiation. Such treatment leads to physically improved roughness as well as chemically introduced hydrophilic oxygen-containing functional groups on the surface of carbon fibers that are essential for assuring an efficient stress transfer from carbon fibers to a polymer matrix.



KEYWORDS: carbon fiber, electron beam, hydrophilicity, wettability, composite

INTRODUCTION

Carbon fibers exhibit unique mechanical, physical and chemical properties including high tensile strength, modulus, and thermal resistance that make them commercially useful in the fabrication of lightweight but tough sporting goods, aircraft, and vehicles.[1,2] However, carbon fibers consisting of highly crystalline graphitic basal planes have poor wettability with a polymer matrix (e.g., epoxy and phenol resins) because of their hydrophobic nature. Such fibers have a low interfacial bonding strength with the polymer matrix, thereby resulting in low reliability in the mechanical performance of carbon-fiber-reinforced plastics.[3−5] Thus, to fully exploit the intrinsically high mechanical characteristics of carbon fibers in composite materials, the problem of the poor wettability of carbon fibers with regard to a polymer matrix should be solved. To date, several methods of modifying the surface of carbon fibers (e.g., chemical modification and thermal treatment)[6−11] have been examined. Unfortunately, such methods have been reported to give rise to a substantial deterioration in the mechanical strength of carbon fibers. Thus, an effective way of introducing chemically active functional groups as well as improving the surface roughness of carbon fibers in a controllable fashion, while maintaining the mechanical strength of the carbon fibers, is critically needed.

Here, we have adopted electron beam irradiation as a modification tool for altering the surface properties of carbon fibers, because such an eco-friendly tool has successfully been used for altering the morphology of carbon particles[12] as well as a cross-linking agent between bundled single-walled carbon nanotubes and between adjacent walls of multi-walled carbon nanotubes.[13,14] Here, using electron beam irradiation, carbon fibers with highly enhanced wettability have been produced, without any deterioration of their mechanical strength, by introducing chemically active polar functional groups as well as by improving the physical roughness of their surface, which is essential for assuring a strong bonding strength between the fibers and the polymer matrix as well as an efficient stress transfer from the polymer matrix to the fibers.

EXPERIMENTAL SECTION

In this study, we have used carbon fibers (Toray Industries, 12K) as starting materials. The sizing material (approximately 1.0 wt %) on the carbon fibers was completely removed using acetone as a washing agent at room temperature. The surface modification was carried out by exposing carbon fibers (1 cm (width) × 10 cm (length)) to an electron linear accelerator under atmospheric conditions (Korea Atomic Energy Research Institute) using a potential of 1.0 MeV and 1 mA. The dose for each of the samples was varied in the range of 100−300 kGy by changing the irradiation time. The surface morphology of the electron-beam-irradiated carbon fibers was observed using scanning electron microscopy (SEM, S-4700, Hitachi, 15 kV) and atomic force microscopy (AFM, Nanoscope-III, Digital Instrument). The chemical state of the surface was examined by X-ray photoelectron spectroscopy (XPS) with a VG Scientific ESCALAB250 spectrometer equipped with a monochromatized AlK_{α} X-ray source (15 mA, 14 kV). The pressure during the analysis was maintained in the range of 1×10^{-9} to 1×10^{-10} Pa. The surface chemical composition of carbon fibers was calculated from the ratio of the area under the corresponding element with respect to the total of C 1s signal. The sampling depth was less than 5 nm. The surface functionality of the carbon fiber was examined by

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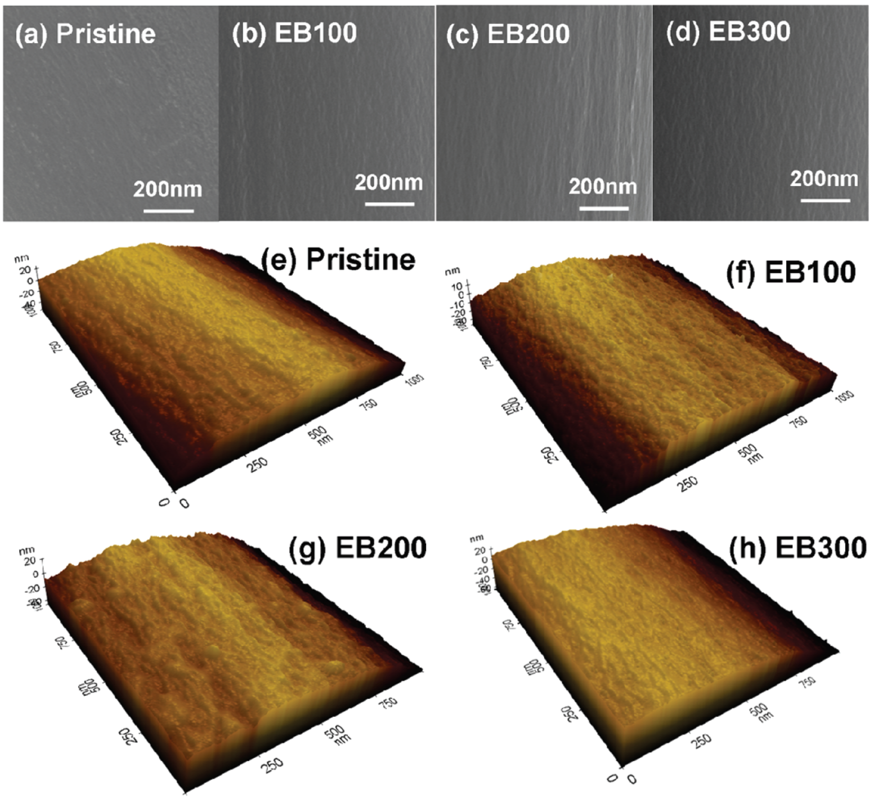

Figure 1. (a−d) FE-SEM and (e−h) AFM images of pristine and electron-beam-irradiated carbon fibers at different doses of irradiation energy. Note that the surface roughness is maximum for carbon fibers that were irradiated at a dose of 200 kGy.

Table 1. Surface Roughness, Chemical Composition, Structural Parameters, Contact Angle, and Tensile Strength for the Pristine and the Electron Beam Irradiated Carbon Fibers, Respectively

		chemical composition[b]						
sample I.D.	surface roughness (nm)[a]	carbon	oxygen	nitrogen	O1s/C1s	R value (I_D/I_G)[c]	cntact angle (deg)[d]	tensile strength (GPa)[e]
pristine	1.77 ± 0.42	85.4±0.5	14.6±0.5		0.17	2.15	91.5±1.25	3.60±1.67
EB100	1.68 ± 0.35	81.2 ± 0.5	18.2 ± 0.5	0.6 ± 0.5	0.22	2.14	85.8 ± 0.75	3.62 ± 1.13
EB200	2.79 ± 0.47	81.0 ± 0.5	18.2 ± 0.5	1.8 ± 0.5	0.22	1.92	82.0 ± 1.55	3.61 ± 0.86
EB300	1.87±0.40	79.6 ± 0.5	18.7 ± 0.5	1.9 ± 0.5	0.23	2.26	77.9 ± 1.62	4.00 ± 1.42

[a] Surface roughness was obtained after flattening the curved AFM image of the pristine and electron beam irradiated carbon fibers. [b] Chemical composition was obtained from XPS data. [c] R value is obtained by dividing the integrated intensity of the D band by the integrated intensity of the G band from Raman spectra. [d] Contact angle is obtained by drop shape method. [e] Tensile strength is averaged by testing 15 individual carbon fibers.

Fourier Transform Infra Red spectroscopy (FTIR; Nicolet200) in the range of 400−4000 cm^{-1}. The KBr sample pellets were prepared by mixing 0.5−2 mg of a sample with 100 mg of KBr. The structural changes of fibers were analyzed using Raman spectroscopy (785 laser line, the Renishaw in Via Raman microscope) and X-ray diffraction patterns (D-Max-2400 diffractometer), equipped with graphite monochromatized Cu Kα radiation (λ = 0.15418 nm). The mechanical properties of a single carbon fiber fixed on a paper frame were measured with a universal testing machine (Instron 5565, Instron Co.). Finally, to evaluate the change in the wettability of the carbon fibers irradiated at different doses, we measured contact angle (G-I, Kernco Instruments Co.) and dispersion ability in water/methanol (50/50 vol. %). For contact angle measurements, a 1 μL droplet of an aqueous solution was dropped onto the prepared carbon fiber, which was placed on an X−T stage. The contact angle of a liquid droplet on the carbon fiber surface was measured using contact angle analyzer equipped with a high speed camera. The 10 mg of the CF samples were dispersed by ultrasonication and subjected to agitation in a 20 mL water/methanol solution. The turbidities were then compared after 1 day at room temperature to confirm the dispersion ability in polar solvent.

RESULTS AND DISCUSSION

Since surface treatment of fibers is essential for improving the bonding between the fibers and a polymer matrix,[15] we have chosen electron beam irradiation as a tool for roughening the surface physically. The change in the surface morphology of carbon fibers subjected to electron beam irradiation at doses of 100, 200, and 300 kGy was observed using SEM and AFM (Figure 1). There is no distinctive morphological change for irradiated fibers at the SEM observation level (Figure 1a−d). However, when

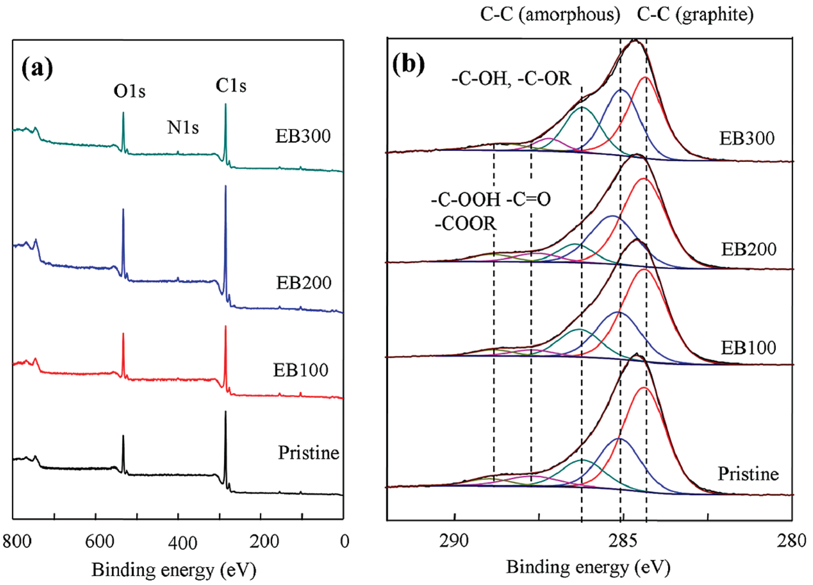

Figure 2. (a) Wide-scan XPS spectra and (b) C1s XPS spectra of pristine and electron-beam-irradiated carbon fibers.

looking at the topological change of carbon fibers before and after electron beam irradiation using AFM, we observed a distinctive increase in surface roughness (Figure 1e−h). We measured the surface roughness (RMS or Ra) after flattening the curved AFM images of carbon fibers (see Figure S1 in the Supporting Information and Table 1). Carbon fibers that were irradiated at a dose of 200 kGy exhibited the maximum value (approximately 2.792 nm) of surface roughness. However, with a higher dose of irradiation energy (300 kGy), the surface roughness of the carbon fibers decreased down to the value of the pristine carbon fiber. Assuming that the surface of carbon fibers consists of a hydrophobic microscopic domain with chemically active end planes,[15] it is thought that the electron beam firstly interacts with the end planes because the chemical activity of the end planes is 10 times that of basal planes.[16,17] Then, oxygen-containing functional groups are generated at chemically active dangling bonds because the electron beam irradiation of carbon fibers is carried out under atmospheric conditions. Eventually, the microscopic domain size on the surface of carbon fibers is reduced via oxidative evolution of carbon monoxide along the edge sites with a longer irradiation time. Our above assumption is quite consistent with the maximum value of the surface roughness for a specific irradiation time. As a result, the roughened fiber surface enhances mechanical interlocking between the fibers and the polymer matrix, thereby resulting in the improved interfacial shear strength of carbon fibers.

Because oxygen-containing functional groups were expected to appear on the surface of electron-beam-irradiated fibers, FT-IR and XPS measurements were carried out as a function of the irradiation dose. From FT-IR spectra (see Figure S2 in the Supporting Information), the irradiated fibers exhibited higher peak intensities at 3400 (νOH), 3100 (νNH), 1640 (νC=O), and 1400 cm^{-1} (νC=C, aromatic) than the pristine fiber, indicating that both aromatization and oxidation occur via electron beam irradiation.[18] The band near 2400 cm^{-1} is due to unbalance between the sample and the blank spectrum. On the other hand, XPS analysis gives a semi-quantitative insight into the functional groups on the surface of the fibers before and after electron beam irradiation. The wide-scan XPS spectra in Figure 2 a imply that the surface of the carbon fibers contains only the expected three elements (e.g., C, O, and a negligible amount of N), because the electron beam irradiation of carbon fibers was carried out under atmospheric conditions. Quantitative peak analyses were also carried out to determine the concentrations of the surface elements (Table 1). It was found that the O1s/C1s ratio and N1s of irradiated carbon fibers increased with an increase in the overall dose of irradiation energy. Consequently, electron beam irradiation of the carbon fibers introduced oxygen and nitrogen atoms from the air, resulting in the modification of the fiber surface. Furthermore, we have analyzed strong C1s spectra (Figure 2 b) in order to analyze the types and amount of functional groups in detail. The strong peak at 284.3 eV can be assigned to the sp^2-bonded carbon atoms, whereas the broad peak at 285.2 eV originates from the sp^3-bonded carbon atoms (i.e., dangling bonds)[19,20] In addition, the intensified peaks of −COOH, −COO and −C−O− at 290.5, 288.6, and 286.7 eV, respectively,[21] also indicate a substantial introduction of oxygen-containing functional groups on the outer surface of the fibers. Thus, the hydroxyl or ether groups existing in the pristine carbon fiber were transformed into quinine and carboxylic acid groups by using electron beam irradiation. This transformation suggests that the oxygen functional groups become further oxidized to form carbonyl and carboxylic acid groups (C=O and COOH) at a higher dose of irradiation energy.[22] It is generally accepted that the functional groups on the surface of the carbon fibers contribute to fiber/matrix adhesion due to chemical bonds or polar interactions between the fibers and matrix.[23]

To evaluate the degree of structural perturbation of the fibers caused by electron beam irradiation, the Raman characterization tool was chosen because of its high sensitivity to the crystallinity of the near surface (up to 10 nm).[24,25] Moreover, we obtained Raman spectra at a low laser power density (below 0.5 mW/cm^2) using a 785 nm laser wavelength for the pristine and electron-beam-irradiated fibers in order to avoid any heating effect. As shown in Figure 3, there is a relatively strong, but broad D-band (defect-induced mode) at 1400 cm^{-1} and a small G band (E_{2g2} graphite mode) around 1600 cm^{-1}.[26] The D band becomes intensified and the R value (defined as I_D/I_G, the integrated

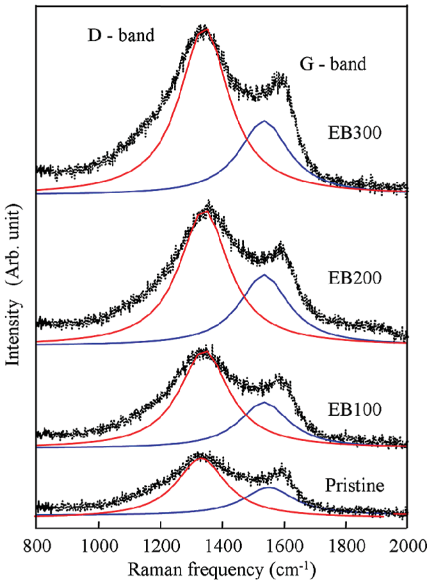

Figure 3. Raman spectra of pristine and electron-beam-irradiated carbon fibers using 785 nm excitation wavelength laser.

intensity of the D band divided by the integrated intensity of the G band) increases at a dose of 300 kGy. This result suggests that a certain number of defects were formed by the electron beam irradiation of the chemically active edge sites of a microscopic domain. At the same time, oxygen-related functional groups were introduced on the outer surface of the fibers by such electron beam irradiation. However, no distinctive change in the X-ray patterns of carbon fibers after electron-beam irradiation (see Figure S3 in the Supporting Information) indicates that electron beam irradiation is very effective for modifying the near-surface properties of carbon fibers. To confirm the effectiveness of the electron beam on the near-surface, we measured the tensile strength of individual carbon fibers before and after electron beam irradiation. We found that there is no degradation in the tensile strength of carbon fibers even at a higher dose of electron beam irradiation (see Table 1).

Finally, we evaluated the wettability of electron-beam-irradiated carbon fibers by measuring both contact angle and dispersibility in water/ethanol solution. With increasing electron beam irradiation energy, water contact angle decreases from 92 to 78° because of the introduction of hydrophilic functional groups (Table 1). Regarding the determination of the dispersibility of carbon fibers, we have used the following procedure. First, 10 mg of the pristine and electron-beam-irradiated fibers was dispersed in water/ethanol solution (20 mL) using a magnetic stirrer at 300 rpm for 1 day. We observed a relatively transparent suspension for the pristine sample that is largely precipitated in a polar solvent (Figure 4). In contrast, the suspensions containing electron-beam-irradiated fibers were dispersed well and thus opaque.

To further explore the distinctive differences in the dispersibility of the pristine and electron-beam-irradiated fibers in a polar solvent, we measured the absorption spectra of all samples. All suspensions showed absorption profiles similar to those of conventional carbon materials (e.g., carbon black) (Figure 4). According to Lambert—Beer's law ($A = \log I_0/I = \varepsilon Cl$), where the absorbance A can be expressed in terms of extinction coefficient (ε), the concentration of carbon fibers (C) and the light path (l)), the measured intensity of the absorbance at a wavelength of 500—700 nm is directly proportional to the amount of dispersed fibers within the solution. As a result, the electron-beam-irradiated fibers at a dose of 200 kGy showed the best dispersibility in a polar solvent because they exhibited the maximum roughness and had a large amount of hydrophilic functional groups on the surface of the carbon fibers. However, we observed a low dispersibility of fibers for fibers that were irradiated at a higher dose of irradiation, which was consistent with AFM observation (Figure 1) as well as Raman results (Figure 3).

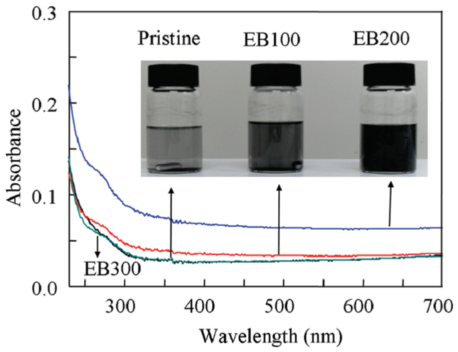

Figure 4. Optical absorption spectra of pristine and electron-beam-irradiated carbon fiber suspensions.

CONCLUSIONS

We have shown electron beam irradiation to be effective as a surface modification tool for introducing wettability on the surface of carbon fibers, without any deterioration in the mechanical strength of the fibers. The effectiveness of electron beam irradiation was demonstrated by a twofold increase in surface roughness as well as a large amount of oxygen functional groups on the surface of carbon fibers, thereby resulting in a low contact angle and high dispersibility in a polar solvent. Eventually, such fibers having a rough surface and chemically active functional groups are expected to be useful as reinforcing filler in the fabrication of high-performance carbon-fiber-reinforced plastics, because such a rough surface is effective for achieving mechanical interlocking between the fibers and the polymer matrix, and functional groups are effective for obtaining good adhesion because of chemical bonds between the fibers and the polymer matrix.

ASSOCIATED CONTENT

Ⓢ Supporting Information. AFM images, FT-IR spectra, and X-ray diffraction patterns (PDF). The material is available free of charge via the Internet at http://pubs.acs.org.

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