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Significant reduction in stabilization temperature and improved mechanical/electrical properties of pitch-based carbon fibers by electron beam irradiation

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ABSTRACT

Carbon fibers are produced using an electron beam, which can reduce the temperature and time in their stabilization processes compared with the existing processes that use heat treatment. Pitch fibers with a stabilization index (SI) of more than 90% are obtained under a lower heat treatment temperature after an electron beam irradiation of 3000 kGy. It is contributed that electron beam irradiation facilitates dehydrogenation and the introduction of oxygen. Carbon fibers stabilized under the conditions of 3000 kGy and 250 °C show 563 MPa and 69 GPa for tensile strength and Young's modulus, respectively. In addition, the electrical conductivity of carbon fibers is approximately 600 S/cm with SI of more than 84%. Therefore, the electron beam reduces the time and energy required to stabilize the pitch fibers, and electron beam-treated carbon fibers show excellent tensile strength and electrical conductivity.

Introduction

Carbon fibers consist of six-membered crystallite carbon in a stacked structure. Carbon fibers have excellent properties, such as tensile strength, modulus, chemical stability, electrical conductivity [1], and a low coefficient of thermal expansion, due to the sp^2 hybridization of the carbon bond and the orientation of the crystallite due to the heat treatment [2,3]. High-performance carbon fibers are used as a reinforcement for composites due to their mechanical characteristics, such as tensile strength and modulus. Carbon fibers have been widely used in civil and architectural engineering, energy, automobile, and aerospace industries, as well as in sports and leisure industries. For this reason, the production yield of carbon fibers has increased from 15,000 tons to 40,000 tons over the past ten years [4,5]. Carbon fibers can be prepared from polyacrylonitrile (PAN), petroleum- or coal-based pitch, and rayon, among these, PAN-based carbon fibers have been the most highly produced until now [6]. However, the use of PAN-based carbon fibers in bulk goods, such as in the sports and leisure industries, has been limited because their unit price is high [7]. Therefore, pitch-based carbon fibers with inexpensive raw materials and high productivity have recently been shown as a promising alternative [8,9].

An important part of the production process of pitch-based carbon fibers is the stabilization of the pitch fibers before a high heat treatment. Stabilization prohibits the melting of pitch fibers during carbonization and maintains the fiber morphology, providing oxygen on the inside and on the surface of the pitch fibers. In addition, this process is key factor for determining the mechanical properties of the final carbon fibers [10,11]. The present stabilization process is performed using heat, which is cost prohibitive considering the slow heating rate and the high stabilization temperature [12,13]. Thus, the stabilization process using heat treatment must be improved.

Electron beam (E-beam) irradiation is an effective method because of various advantages, such as low operating costs, clean operation, and the possibility of using at room temperature. E-beam irradiation has already been used in polymer technology, such as polymerization, crosslinking, and setting without an initiator [14,15]. Studies on the stabilization of pitch fibers using E-beam irradiation are lacking although the stabilization of PAN fibers (the formation of a ladder structure by cyclization) using E-beam irradiation has been studied [16–19]. In addition, it is possible to reduce the heat-treatment temperature and the stabilization time of pitch fibers if E-beam irradiation is used, which also reduces the operation cost and provides a simple process.

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In this study, we aimed to determine the effect of E-beam irradiation on the stabilization of pitch fibers during carbon fiber production. Pitch fibers were treated with heat and E-beam irradiation, and then the stabilized pitch fibers were carbonized. The characteristics of the stabilized carbon fibers were investigated to evaluate the stabilization level. The physical properties of the carbon fibers prepared under the stabilization conditions were also investigated.

Experimental

Materials

Pitch fibers used in this stabilization experiment were prepared from a pitch reforming pyrolysis fuel oil (PFO), which was a petroleum-based residue and was obtained from GS Caltex. Co., Korea. The PFO contained more than 90 wt% carbon and more than 6 wt% hydrogen, as shown in Table 1. Additionally, nitrogen and sulfur impurities were present at 2.19 and 0.1 wt%, respectively, in the PFO. 500 g of the PFO was heated from room temperature to 360 °C at a heating rate of 2 °C/min under a 2 L/min nitrogen flow with a 200 rpm impelling rate. The sample was then maintained at 360 °C for 4 h and subsequently naturally cooled. The obtained isotropic pitch had a softening point of 250 °C [20,21]. Air gas (20.8% O_2 + N_2 balance) and nitrogen gas (ultra-pure, 99.95%) were used in the stabilization process by heat and carbonization, respectively. All of the gases were purchased from Special Gas Co., Korea.

Preparation of pitch fibers

The pitch fibers were prepared from reformed pitch using a novel melt-spinning method. In this method, a metal-syringe apparatus with a 10 g sample capacity was used to extrude the melted pitch through a mono-hole spinneret with a diameter of 0.3 mm. The following melt-spinning conditions were maintained throughout the process: a tip-to-collector distance of 20 cm and a collector speed of 1200 rpm. The spinning temperature and extrusion pressure of the pitch for the melt-spinning process were 300 °C and 10 bar, respectively. The diameter of the obtained pitch fibers was approximately 15–20 μm.

Stabilization of pitch fibers by E-beam irradiation and carbonization

The following stabilization conditions were used. **(1) E-beam irradiation only**: the pitch fibers were placed on a trailer belonging to the E-beam accelerator and then were covered with a thin layer of aluminum foil to prevent blowing of the fibers. The trailer was adjusted with a moving speed of 10 m/min. The E-beam accelerator was controlled to radiate 20 kGy of absorbed dose per turn under 1.14 MeV of voltage and 15.2 mA of current. Finally, each pitch fiber sample was radiated with an E-beam absorbed dose of 1000, 2000, and 3000 kGy, respectively, at room temperature. To prevent melting of the pitch fibers due to excess energy, the pitch fibers were naturally cooled when irradiated with 500 kGy of absorbed dose. At 4000 kGy of absorbed dose, the pitch fibers were melted; therefore, the maximum absorbed dose was fixed at 3000 kGy in this study. The samples prepared in stabilization condition of E-beam irradiation only were named as 1000E, 2000E, and 3000E depending on E-beam absorbed dose. **(2) Heat-treatment after E-beam irradiation**: the stabilization level of pitch fibers subjected to E-beam irradiation only did not significantly increase. Therefore, a heat treatment was added after E-beam irradiation. The samples prepared from stabilization condition (1) were placed in a box-type oxidation furnace and then heat treated at 250, 260, 270, and 280 °C, respectively, for 2 h at a heating rate of 1 °C/min under air atmosphere. The air gas flowed at a rate of 500 mL/min during the heat treatment. The samples prepared in stabilization condition of heat-treatment after E-beam irradiation were named as 1000E250H, 2000E250H, and 3000E250H depending on E-beam absorbed dose and heat-treatment temperature. **(3) E-beam irradiation after heat-treatment**: for an in-depth investigation of the effect of E-beam irradiation on the stabilization of pitch fibers, the two processes mentioned in the stabilization condition (2) were switched. The heat treatment and E-beam irradiation conditions were the same as those listed above. The samples prepared in stabilization condition of E-beam irradiation after heat-treatment were named as 250H1000E, 250H2000E, and 250H3000E depending on heat-treatment temperature and E-beam absorbed dose. **(4) Heat-treatment only**: to compare the characteristics of E-beam-treated pitch fibers, the fibers were only subjected to heat treatment for comparison group. The heat-treatment conditions were the same as those listed above. The samples prepared in stabilization condition of heat-treatment only were named as 250H, 260H, 270H, and 280H depending on heat-treatment temperature. Pitch fibers treated with heat and E-beam irradiation were carbonized at 1000 °C for 1 h at a heating rate of 5 °C/min under nitrogen atmosphere to evaluate the physical properties of the carbon fibers.

Table 1
The characteristics of PFO.

Properties		PFO
Elemental analysis (wt%)	C	90.59
	H	6.18
	O	0.94
	N	2.19
	S	0.1
Average molecular weight		261.5
Atomic mole ratio (C/H)		1.09

Evaluation of stabilized pitch fibers

Elemental analysis (EA) was conducted to determine the atomic changes in the pitch fiber according to the stabilization conditions. An elemental analyzer (EA 1112, Thermo Fisher Scientific, USA) was used, and each sample was burned at 1800 °C. Then, the quantity of atoms was detected from the residue using a heat conduction indicator. To examine the chemical structures of the pitch fibers obtained before and after stabilization, Fourier-transform infrared spectroscopy (FT-IR) was performed. An IR spectrometer (FTS-175C, Bio-Rad Laboratories, Cambridge Inc., USA) was used, and the scanned wavelength area was between 3800 and 450 cm^{-1}. The thermal behavior of the samples according to the stabilization conditions was observed from 25 to 1000 °C under nitrogen and air atmosphere, respectively, at a heating rate of 10 °C/min using a thermoanalyzer (TGA/DSC 1; Mettler-Toledo Inc., Korea). X-ray diffraction (XRD) was also conducted to analyze the stabilization level of the pitch fibers according to the stabilization conditions. An X-ray diffractometer (8 DISCOVER, Bruker AXS, Germany) was employed with Kα X-ray lines generated from a Cu target to analyze the samples from 10 to 80° of 2θ.

Measurement of mechanical and electrical properties of carbon fibers

The tensile strengths of single fibers after carbonization were measured using a single fiber tester (FAVIMAT+, Textechno, Germany) equipped with a load cell of 210 cN. The carbon fiber for tensile testing was fastened to a 25-mm long clamp, and a tensile load was then applied at a speed of 5 mm/min. The tensile