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Effects of stabilization variables on mechanical properties of isotropic pitch based carbon fibers

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ABSTRACT

Optimization of the stabilization process for manufacturing low-cost carbon fibers was performed. By simply varying both heating rate (0.5–10 °C/min) and starting temperature (25–230 °C), the resulting fibers possessed different properties such as densities, oxygen contents, and weight gains due to the oxygen up-takes. Subsequent oxidative reactions led to changes in chemical compositions of the fibers. Therefore, this study suggests that more concerned design with complementary parameters such as starting temperature and heating rate, significantly reducing stabilization time down to 56.5 min with the comparable mechanical properties of the conventional isotropic pitch based CFs.

Introduction

Carbon fibers (CFs) are used in various applications such as automobile, aerospace, sports, and many other components because of their excellent mechanical, thermal, and electrical properties [1–4]. However, the aforementioned applications using CFs have been limited so far since a large scale CFs production cost is prohibitively expensive for the commercialization. Therefore, significant research effort in the last several decades has been devoted to reducing CFs production cost by developing cheaper precursor materials, minimizing stabilization time, simplifying carbonization, or etc. A typical CFs manufacturing process flow consists of fiber spinning, oxidative stabilization, carbonization, graphitization, and surface treatment process [5].

Among these processes, the stabilization is the most important step because the oxidative behavior of precursor fiber greatly affects the final mechanical properties of the CFs. Also, stabilization process is considered as the most time consuming and expensive step. Long time stabilization at relatively low temperature used in the conventional process flow was considered to allowing oxidant to uniformly diffuse through precursor fiber [6]. Without this uniform oxidant diffusion through the fiber precursor, uneven stabilization or rapid oxidation can yield the final carbon fiber possessing poor properties [7,8]. In this regard, it is challenging to achieving the reduced stabilization time while maintaining a suitable degree of stabilization. Various process modifications such as stabilization temperature, time, heating rate, atmosphere, pressure, and multi-step stabilization [9–13] have been proposed. Many companies and researchers have been striving for reducing stabilization process, but it still remained difficult to optimize and deploy reliably.

In this study, we report a systematic study on optimizing the stabilization process by varying heating conditions such as a heating speed and the starting temperature. Based on our previous study [14], the stabilized fibers with a density range of 1.35–1.36 g/cm^3 yielded CF with the highest tensile strength regardless of the stabilization conditions. Here, petroleum-based isotropic pitch fibers were first stabilized at various temperatures in ambient air atmosphere at heating rate of 0.5–10 °C/min and then densities of the corresponding fibers were characterized. After the oxidative

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stabilization at various conditions, the stabilized fibers were carbonized at 1200 °C under nitrogen atmosphere. Then, chemical and physical properties of stabilized fibers and tensile properties of the CFs were measured and then correlated. The study revealed a possibility to shorten the stabilization process time by eliminating unnecessary temperature ranges. In addition, a combination of variables such as starting temperature and heating rate was investigated for a further reducing stabilization time. We, therefore, demonstrated a procedure to optimize stabilization for developing a cost effective process.

Experimental

Preparation of pitch-based carbon fibers

A commercial isotropic pitch (SN-280, Anshan, China) was melt-spun into pitch fibers using a 12-hole spinneret at 335 °C with a diameter of 150 μm and an aspect ratio of 3 under nitrogen atmosphere. The prepared pitch fibers possessed the diameter of 12.2 ± 0.8 μm. The as-spun pitch fibers were stabilized at 290 °C for 30 min using a convection oven in ambient air atmosphere with various starting temperatures of 25, 150, 170, 190 and 230 °C and various heating rates of 0.5, 1, 5 and 10 °C/min. The stabilized fibers were then carbonized at 1200 °C under nitrogen flow in a tube furnace at a heating rate of 5 °C/min.

Characterization

The thermal properties of as-spun pitch fibers were analyzed using a thermogravimetric apparatus (SETSYS Evolution TGA, SETARAM Instrumentation, Caluire, France). Specimens were heated from 40 °C to 400 °C at a heating rate of 0.5, 1, 5 and 10 °C with an air flow rate of 50 mL/min. The stabilization starting temperatures and the amounts of oxygen uptake were monitored using a thermogravimetric analyzer. The weight of pitch fibers used for the each analysis was approximately 10 mg. The densities of as-spun pitch fibers and stabilized fibers were determined by a Sartorius YDK03 Density Determination Kit (Sartorius AG, Goettingen, Germany). The Archimedean principle is applied for measuring the density of pitch fibers. Another method of density measurement, a density gradient column of liquid (POLYTEST, Ray-Ran, UK) was prepared to determine the densities carbonized fibers. Two liquids, 1,1,2,2-tetrabromoethane (98%, Daejung Chemical Co., Korea) and benzene (99.5%, Daejung Chemical Co., Korea), were used to build the density gradient, and glass beads with accurately known densities floated in the column. The each fiber samples were inserted and left for 8 h in the column. At least three specimens were tested to calculate the densities of the fibers in each condition.

FT-IR spectroscopy (Nicolet IS10, USA) was performed to investigate the change in the oxygen functional groups during the stabilization using the KBr pellet technique. The mixed pellet was prepared with 400 mg of spectrometric grade KBr and 2 mg of sample. The mixture of the sample and the salt was crushed using a pestle and a mortar. The powder mixture was placed in a KBr die kit and pressed with a hydraulic laboratory press. Each sample was scanned 16 times at a resolution of 16 cm^{-1} with a range of 4000–400 cm^{-1}. All spectra were collected in the absorbance mode with an automatic baseline correction and then transformed to transmittance.

Elemental analysis (Flash 2000, Thermo Scientific, USA) was carried out to measure the amounts of oxygen in the bulk of the CF samples. Oxygen was analyzed using helium gas at 1060 °C for 500 s.

The mechanical properties of the CFs were examined by a mechanical tester for a single fiber (FAVIMAT+, Textechno, Germany) with a test speed of 5 mm/min. The gauge length was 25 mm, and 20 specimens were measured for each experimental point.

X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Scientific, USA) analysis was performed using monochromated Al Kα (1486.6 eV) X-rays to examine the type of chemical bond of nitrogen and the elemental composition on the surface of as-spun and stabilized pitch fiber samples. The survey spectrum was collected from 0 eV to 1350 eV, and the binding energies were referenced to the C1s line at 284.8 eV.

Results and discussion

Thermal analysis of the stabilized pitch fibers

The thermal characteristics of as-spun pitch fibers were analyzed using TGA. Fig. 1a shows a TGA thermogram obtained from as-spun pitch fiber to mimic oxidative stabilization at a heating rate of 1 °C/min under ambient air atmosphere. There were three regions showing different weight changes as a function of temperature. A slight increase in weight was observed from 40 to 175 °C (region I) with increasing the temperature. Then, the weight significantly increased up to 310 °C (region II) with a weight gain of ~10 wt.%. Finally, at temperature above 310 °C, there was a significant weight loss (region III).

In the region I, a small amount of weight gain was observed even though pitch fibers were exposed under oxygen, indicating that temperature was not high enough to overcome energy barrier for inducing oxygen diffusion into the fibers. It is interesting to observe that the weight gain dramatically increased from 175 °C due to oxygen diffusion in the region II. From our previous result by in-situ mass spectroscopy, oxygen uptake and gas evolution

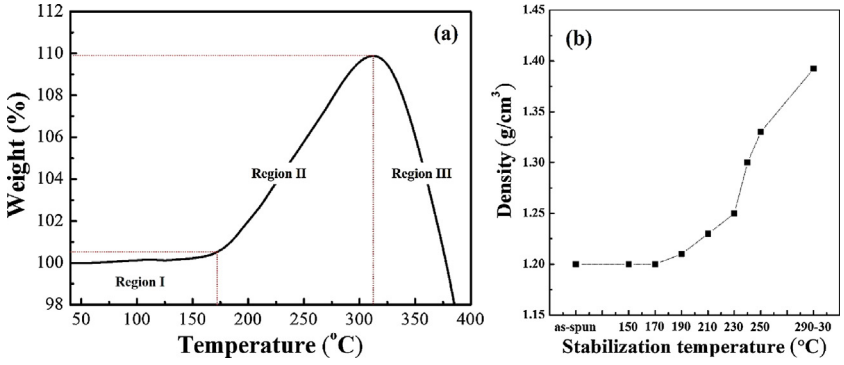

Fig. 1. (a) TGA thermogram of as-spun pitch fiber from 40 to 400 °C at a heating rate of 1 °C/min under an air atmosphere and (b) density changes of stabilized pitch fibers as a function of stabilization temperature.

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