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Evaluating the stabilization of isotropic pitch fibers for optimal tensile properties of carbon fibers

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ABSTRACT

The stabilization effects of isotropic pitch fibers on the tensile properties of the resulting carbon fibers were systematically studied to develop a simple method for finding a suitable degree of stabilization. As the stabilization temperature (250–290 °C) and duration (30–180 min) increased, the densities of the stabilized fibers increased from 1.31 to 1.47 g/cm^3, indicating that oxygen up-take and chemical reactions led to changes in their chemical compositions. Stabilized fibers with higher densities resulted in lower density carbon fibers due to the removal of oxygen-related gases during carbonization. Each stabilization temperature had an optimal duration for obtaining high tensile strengths, which was correlated with the oxygen content after stabilization. Interestingly, when the stabilized fibers had densities of 1.35–1.36 g/cm^3, the resulting carbon fibers showed the highest tensile strength regardless of the stabilization conditions. Therefore, it is suggested that the density of the stabilized isotropic pitch fibers is a reasonable index for the evaluation of the degree of stabilization for producing high-performance carbon fibers.

Introduction

Carbon fibers (CFs) are manufactured via heat treatments such as stabilization and carbonization of precursor fibers using polyacrylonitrile (PAN), pitch, and rayon [1–3]. Stabilization is one of the key steps because precursor fibers should be infusible before carbonization, which plays an important role in increasing yield of high-performance CFs [4–7]. Even though the process conditions and duration vary depending on the type of precursor fiber, stabilization is the longest step in CF industries because oxygen diffusion takes time to induce reaction. Therefore, there areextensive studies on the development of cost-effective stabilization with reduced stabilization times at lower temperatures [8–12]. In addition, determining the degree of stabilization is another issue in deciding the optimal stabilization conditions. During stabilization, significant physical and chemical changes occur in the precursor fibers, which are detected and measured to quantify the degree of stabilization.

In the case of PAN fibers, chemical reactions such as cyclization, dehydrogenation, and oxidation are major factors leading to changes in the fibers. C≡N bonding in the main chain of PAN is converted into C=N bonding by cyclization, which can be detected by Fourier transform infrared spectroscopy (FT-IR). The degree of stabilization or the reaction extent has been defined using the ratio of peak intensities at 1595 and 2243 cm^{-1} in the FT-IR spectra, which are assigned to C=N and C≡N, respectively [13]. Takaku et al. suggested an experimental approach of measuring the density of stabilized fibers to determine the optimal degree of stabilization, and it was found that stabilized fibers with a density of 1.34–1.39 g/cm^3 resulted in high tensile strength carbon fibers [14]. They claimed that densities higher than 1.39 g/cm^3 indicated excessive stabilization, which introduced more microvoids in the

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carbon fibers and decreased the tensile strength. The density of PAN fiber was found to be 1.18 g/cm^3, which shows that the density increases significantly during stabilization.

Pitch intrinsically contains aliphatic and aromatic carbons, and it is well known that oxygen uptake under air atmosphere introduces oxygen bridge structures via oxidation, dehydrogenation, and cross-linking, which prevent fibers from fusing togetherduring carbonization [15]. In detail, weight gain occurs due to an increase in oxygen as ketone functional groups and the loss of aliphatic carbons in pitch. Then, continuous oxidation causes weight loss due to the degradation and removal of carbon contents as carbon monoxide and carbon dioxide. This reaction leads to the breakage of carbon bonds and cross-linking of pitch molecules via the insertion of oxygen. Weight gain of 5–10% was measured by TGA as a good evaluation of stabilization for producing high strength CFs [16]. Similar to the stabilization of PAN, spectroscopy techniques such as FT-IR have been used to observe the chemical structural evolution of pitch fibers [17]. However, these methodologies require complicated apparatuses or analysis systems even though they cannot give quantified criteria for stabilization.

In this study, petroleum-based isotropic pitch fibers were stabilized at various holding temperatures after heating at rates of 1 and 10 °C/min and then carbonized at 1200 °C to quantify the degree of stabilization. The chemical and physical properties of stabilized fibers and the tensile properties of CFs were measured. We made a correlation between the density of stabilized fibers and the tensile strength of the CFs. To the best of our knowledge, an intensive study of density to estimate the degree of stabilization of pitch fibers has not been reported in the open literature.

Experimental

Fiber spinning

Commercial isotropic pitch SN-280 (Anshan, China) was used to produce pitch fiber. The softening point of the pitch was first measured at a scanning rate of 3 °C/min using a Mettler SP unit (DP70, Mettler Toledo, USA) followed by measurement of the viscosity. The shear viscosity measurement of the pitch was conducted using a plate–plate rheometer (ARES G2 rheometer, TA Instrument Inc., USA); the plate–plate fixture diameter is 25 mm. Approximately 1 g of pitch powder was pelletized at 10,000 psi for 5 min into a 12 mm diameter and 3 mm tall cylindrical sample and then loaded on the bottom plate. The viscosity measurement was conducted under nitrogen atmosphere at the target temperature.

Once the range of spinning conditions was obtained from the steady shear viscosity measurements, the isotropic pitch was melt-spun in a 12-hole spinneret with a diameter of 150 μm and an aspect ratio of 3. The spinning temperature was 335 °C. As a result of the melt-spinning, pitch fibers with diameters of 12.2 ± 0.8 μm were prepared and used for the study. Details of elemental information and molecular weight of pitch fibers were in Table S1 and Fig. S1 in the Supplementary material, respectively.

Stabilization and carbonization

For stabilization, the as-spun fibers were placed in a convection oven under air atmosphere. The temperature was increased at rates of 1 and 10 °C/min to 250–290 °C and held for 30–180 min. The stabilized fibers were taken out of the oven as soon as it reached a certain stabilization time and naturally cooled down to room temperature. After stabilization, the fibers were carbonized at 1200 °C with a heating rate of 5 °C/min under nitrogen atmosphere in a furnace.

Characterization

The weight change was measured using a thermogravimetric analyzer (TGA Q50, TA Instruments, USA). To mimic the stabilization conditions, the samples were heated at rates of 1 and 10 °C/min to 250–290 °C under air atmosphere. After reaching the target temperatures, the samples were held for up to 180 min. The weight of samples used for each test was ~10 mg.

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.

X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Scientific, USA) 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 CFs samples. The survey spectrum was collected from 0 eV to 1350 eV, and the binding energies were referenced to the C 1s line at 284.8 eV.

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.

A Sartorius YDK03 Density Determination Kit (Sartorius AG, Goettingen, Germany) was used for measuring densities of precursor pitch and stabilized fibers, which the Archimedean principle was applied. Fiber samples immersed in ethanol were subjected to the force of buoyancy. The specific gravity of the sample can be determined if the density of the ethanol is known using the following relationship:

$$\rho(f) = \frac{W(a)\cdot\rho(e)}{W(a) - W(e)}$$

where $\rho(f)$, $\rho(e)$, $W(a)$, $W(e)$ are the specific gravity of the fiber, the density of the ethanol, the weight of the fiber in air, and the weight of the fiber in ethanol, respectively. Four measurements were carried out and average values were reported.

As another 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 fibers 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.

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.

Results and discussion

Chemical structural evolution during stabilization

The chemical structural evolution of the as-spun pitch fibers during stabilization was investigated. FT-IR spectra of the as-spun fiber and its stabilized fibers heat treated at 250 °C for 30–150 min

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