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Modified oxidative thermal treatment for the preparation of isotropic pitch towards cost-competitive carbon fiber

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ABSTRACT

A modified oxidative thermal treatment was developed to increase the softening point of a pitch precursor while minimizing the pitch yield loss. An O_2/N_2 mixed gas was used as the reaction gas, and the softening point and pitch yield variations were measured at different O_2 concentrations. As a result, when softening point increased from 130 to 249 °C, the pitch yield remained almost constant (only 0.6% drop). Structural analysis performed via MALDI-TOF, FTIR, and ^{1}H and ^{13}NMR showed that condensation reaction between pitch molecules in the presence of O_2-containing gas followed a different mechanism depending on the O_2 concentration. In addition, the precursors were spun into pitch fibers and carbonized at 1100 °C. During the spinning, they exhibited excellent spinnability without breakage for more than 10 min of spinning. The obtained carbon fibers showed high tensile strengths comparable to that of a commercial isotropic-pitch-derived carbon fiber (0.83 GPa). The current study showed that the modified thermal treatment is useful for the preparation of cost-competitive pitch precursors suitable for carbon fiber production.

Introduction

The increasingly strict environmental policies throughout the world have forced the automotive industry to increase the fuel economy of internal combustion engine vehicles and to develop electric vehicles with longer driving range. The most feasible way to meet this demand is to reduce vehicle weight using lightweight materials. Carbon fibers as a form of carbon fiber reinforced plastic are considered one of the strongest candidates to replace conventional steel-based materials due to their outstanding mechanical properties (tensile strengths of up to 7 GPa and moduli up to 900 GPa) and low volumetric mass densities (1.75–2.00 g/cm) [1]. The automotive industry requires carbon fiber prices of less than $11/kg and tensile strengths of 1.7 GPa [2,3]. The requirement for the mechanical properties is not challenging, but the price requirement is difficult to satisfy. It must be lower than half the current prices of carbon fibers. In recent years, many research efforts have been devoted to developing low-cost carbon fibers.

Approaches towards low-cost carbon fibers must consider the price of the raw starting materials and process costs. Polyacrylonitrile (PAN)-based carbon fibers, which currently occupy greater than 90% market share, are not feasible because of the high price of the starting material (acrylonitrile) and the low production yield. Among the other types of precursors including pitch, cellulose and lignin, pitch is considered an attractive precursor due to the low-cost starting materials, such as coal-tar (by-product of the steel industry) and petroleum residues (by-product of the petrochemical industry). There are two types of pitch precursors: mesophase and isotropic pitches. Mesophase pitch-based carbon fibers exhibit high performances but suffer from the expensive processing cost. Whereas, isotropic pitch-based carbon fibers are poor in performances but cheap in manufacturing. In this regards, researches on pitch-based carbon fibers are focusing on either decreasing the cost of mesophase pitches preparation or increasing mechanical properties of isotropic pitch-based carbon fibers. Both carbon fibers can meet the demands of the automotive industry if the problems are resolved.

Recently, researches have been focused onto improving properties of isotropic pitches and the carbon fibers based on

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the pitches including bromination and fractionation of molecular weight distribution [4–9]. Also, there have been many efforts to find cheap and high performing raw materials: anthracene oil [4,5], hyper coal [6,7], vacuum residue (VR) [8,9] and pyrolysis fuel oil (PFO) [10,11]. Among the candidates, PFO has received particular research interest due to its low impurities and abundant aromatic content.

One of the most important characteristics of spinnable pitches is a softening point. Standard procedures to make carbon fibers are pitch synthesis, spinning, stabilization, and carbonization. Among the procedures, the pitch synthesis and stabilization are the most time and energy consuming and interdependent steps. As-spun fibers from the pitches with softening points lower than 250 °C are not suitable for stabilization, a process to convert as-spun pitch fibers into thermoset fibers. Therefore it is essential to keep softening points higher than 250 °C if the pitches used for fiber purpose. However, pitches generally have low softening points between 100 and 200 °C once synthesized. Therefore, an additional process to increase the softening point should be performed. In most cases, the softening point can be adjusted by removing low molecular weight components [6,12] or solvent extraction [13]. However, these methods result in substantial pitch yield loss, thereby increasing the production cost. Therefore, a new method for increasing the softening point without yield loss must be developed for the preparation of low-cost carbon fiber.

To adjust softening points of pitches, air-blowing has been widely investigated by researchers. Previous studies demonstrated that air-blowing is a simple and effective way to increase the softening point [14–20]. Air produces oxidative thermal condensation between the molecular components at elevated temperatures, increasing the average molecular weight and softening point [21,22]. However, air consists of not only 21% O_2 but also inert gases, including 78% N_2. These inert gases facilitate volatilization of light components via the blowing effect and reduce the pitch yield. We hypothesize that using gas with a higher O_2 concentration than air would be a more effective way to increase the softening point because a higher O_2 concentration would enable the condensation reaction to progress at a lower gas flow rate, suppressing the volatilization of light components that can minimize the pitch yield loss. Many studies were performed on pitch air-blowing, but few studies proposed its feasibility for carbon fiber applications, especially with respect to the mechanical properties of carbon fibers derived from air-blown pitches and their spinnability.

Herein, we investigated oxidative thermal treatment using O_2/N_2 mixed gas with varying O_2 concentrations as an effective way to increase the softening point of pitch without loss of pitch yield. PFO was used as the starting material. The effects on the softening point and yield were examined at varying O_2 concentrations. For comparison, the effects of vacuum distillation and the gas flow rate were also examined. The reaction between O_2 and hydrocarbons is exothermic and highly dependent on the concentration [23]; thus, the O_2 concentration was limited to 50% for safety. To ensure the possibility of the pitches via the treatment for carbon fiber production, the pitches were melt-spun to analyze their spinnability, and the mechanical properties of the resulting carbon fibers were measured and compared with the control.

Experimental

Preparation of pitch precursor

For the petroleum raw material, PFO (*Hanwha-Total Co., South Korea*) were used to synthesize pitch precursor. The pitch precursor was prepared via oxidative thermal treatment. In a typical process, 700 g of PFO was added to a 1 L reactor (*Autoclave Korea, South Korea*) and heat treated at 360 °C for 5 h under vigorous agitation. To create an oxidative atmosphere, O_2-containing reaction gas was blown into the reactor at a flow rate of 0.5 L/min throughout the entire reaction. The O_2-containing reaction gas was prepared by mixing O_2 and N_2 gases. Using this method, two series of pitch were prepared. First, the O_2 concentration in the reaction gas was set to 0%, 20%, 35% or 50% by volume to produce a series of pitches labeled POx-00, POx-20, POx-35 and POx-50, respectively. Another series of pitch was prepared by setting the flow rate of the reaction gas to 0.7, 1.0 and 2.0 L/min at a fixed O_2 concentration of 20%. These pitch samples were designated POx-20-F07, POx-20-F10 and POx-20-F20. For the comparison with non-oxidative thermal treatment, an additional experiment with the exactly same setting except N_2 flow was performed. Vacuum distillation at the same temperature at 8 h Pa for 1 or 2 h produced POx-00-V1 and POx-00-V2, respectively. The obtained pitch precursors are listed in Table 1.

Preparation of carbon fiber

For the carbon fiber preparation, pitch samples were melt-spun at approximately 50 °C above their softening points. A mechanical batch-type melt-spinning unit equipped with a 12-hole spinneret with a diameter of 150 μm and an aspect ratio of 3 was used. The as-spun fibers were stabilized at 210 °C for 15 h in an air atmosphere to provide proper stabilization. Then, the fibers were carbonized at 1100 °C for 1 h in an inert atmosphere. The heating rates of stabilization and carbonization processes were 0.5 °C/min and 7.5 °C/min, respectively. For a control, a commercial isotropic pitch, SN-270 (SIOCARB, China), with a softening point of 278 °C was spun and heat treated following the same method.

Material characterization

The carbon, hydrogen, nitrogen and sulfur contents of the PFO and pitches were analyzed using a FLASH EA-2000 Organic Elemental Analyzer (*Thermo Scientific*), and the oxygen content was

Table 1
Pitch preparation conditions.

Sample name	Temperature (°C)	Holding time (h)	O_2 concentration in the reaction gas (vol%)	Flow rate of the reaction gas (L/min)
POx-00	360	5	0	0.5
POx-00-V1	Step 1: 360	Step 1: 5	Step 1: 0	Step 1: 0.5
	Step 2: 360	Step 2: 1	Step 2: –	Step 2: vacuum
POx-00-V2	Step 1: 360	Step 1: 5	Step 1: 0	Step 1: 0.5
	Step 2: 360	Step 2: 2	Step 2: –	Step 2: vacuum
POx-20	360	5	20	0.5
POx-20-F07	360	5	20	0.7
POx-20-F10	360	5	20	1.0
POx-20-F20	360	5	20	2.0
POx-35	360	5	35	0.5
POx-50	360	5	50	0.5

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