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Preparation of isotropic pitch-based carbon fiber using hyper coal through co-carbonation with ethylene bottom oil

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ABSTRACT

A spinnable pitch was developed from the tetrahydrofuran-soluble fractions (THFS) of hyper coal (HPC) and used to prepare carbon fibers. THFS-derived pitch from bituminous coal-derived HPC showed excellent spinnability and the obtained carbon fibers had a tensile strength of over 800 MPa with a diameter of 13 μm following heat treatment at 800 °C for 5 min. Thus, HPC was shown to be a useful alternative precursor for the preparation of low-cost and general-performance carbon fibers.

Introduction

Carbon fibers are now used in many fields due to their various mechanical, thermal, and electrical properties. However, the high cost of carbon fibers has always limited their more widespread application. In order to establish a large market for carbon fibers as a useful material in low-energy and environmental applications, the production cost of carbon fiber should be reduced to less than $10/kg [1]. The cost of precursor materials, such as polyacrylonitrile copolymer and spinnable pitch, currently accounts for almost 50% of the total manufacturing cost of carbon fibers [2], indicating that the development of a low-priced spinnable pitch may be the most effective way of reducing these high production costs.

During the last two decades, dozens of efforts have been made to develop precursors using inexpensive renewable resources and other alternative materials, such as biomass and inexpensive aromatic hydrocarbon residues, such as lignin and ethylene bottom oil (EBO). For example, lignin-based carbon fibers [3–5], liquefied wood-based carbon fibers [6,7], biotar-based carbon fibers [8,9], and anthracene oil-based carbon fiber [10] have been developed to modify spinnable precursors obtained from coal tar or FCC-DO-derived spinnable pitch precursors for pitch-based carbon fibers. Some of these strategies succeeded in obtaining low-cost spinnable pitch precursors but suffered from low pitch yields, low carbonization yields, and pitches with relatively poor spinnability.

Our group has tried to use hyper coal (HPC) as an effective and inexpensive raw material for the development of functional carbon materials because it has a relatively high aromatic hydrocarbon fraction and a low ash content. HPC is an ash-free coal, generally produced by thermal coal extraction using 1-methylnaphthalene under high pressure (2 MPa) at temperatures below 400 °C [11]. HPC thus consists of extractable components, free of minerals (less than 100 ppm), and exhibits high extraction yields exceeding 60%, high fluidity, and a higher calorific value than raw coal. These properties result in significant advantages in terms of energy savings, environmental protection, and prospects for development. However, HPC also contains many light components that are easily volatilized and decomposed. Its high oxygen content also leads to a high thermal reactivity, which prevents it from being used as a raw material for functional carbon material production [11,12]. So far, the use of HPC has been limited to an additive for coke production and as a fuel for combustion and gasification [13]. HPC is inexpensive relative to coal tar and FCC-DO because it is a direct extract of coal. HPC usually contains a very low ash content and shows excellent thermoplasticity [12], which makes it useful as a raw material in binders, impregnation pitch, and spinnable pitch for carbon fiber production. Thus, the production costs of carbon fiber could be reduced by use of an HPC-derived pitch.

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However, HPC exhibits several undesirable properties that must be dealt with prior to its use as a precursor for functional carbon materials. (1) HPC contains molecules with very high molecular weights and a broad molecular distribution. (2) HPC contains high levels of oxygenated molecules, and (3) HPC contains very reactive molecules, such as vinyl toluene and its derivatives, dicyclopetadiene, and indene derivatives.

To date, attempts to develop a spinnable pitch directly from HPC have failed for the reasons above. Several attempts have been made to address these problems. (1) To select a particular molecular weight range to prepare a spinnable pitch precursor, different molecular weight HPC fractions were used as raw materials after fractionation of solubles and non-solubles using various solvents. (2) To decrease the amount of oxygenated functional groups, we tried to prepare a spinnable pitch through the co-carbonization of HPC with ethylene bottom oil (EBO). EBO is a relatively inexpensive and abundant carbon resource, composed of over 90% of one or two six-membered-ring compounds with almost no oxygenated functional groups.

This paper examines the effects of co-carbonization of EBO and selected HPC fractions and the preparation of a spinnable isotropic pitch precursor. In particular, we focused on the pyridine- and tetrahydrofuran-soluble fractions of HPC as raw materials for a spinnable isotropic pitch precursor.

Experimental

Materials

Two varieties of HPC obtained from different ranks of coal were supplied by Kobe Steel Co. Ltd. as parent materials. HPCs from bituminous coal (Australian) and sub-bituminous coal (Indonesian) are designated as A-HPC and B-HPC, respectively. The pyridine-soluble (PS) and THF-soluble (THFS) fractions of HPC were prepared by simple solvent extraction. The HPC and solvent were mixed at a weight ratio of 1/10 and stirred at room temperature for 12 h. Then, the mixture was separated by paper filtration and the solvent in the soluble fraction was removed in a rotary evaporator. EBO was obtained from the Korean SK Company.

Preparation of spinnable isotropic pitches and carbon fibers

HPC, PS, and THFS fractions of HPC were selected as precursors and mixed with EBO at a weight ratio of 5/5. Atmospheric distillation (AD) or pressurized distillation (PD) was performed at 320 °C for 1 h to prepare basic pitches. The basic pitches were then continuously heat-treated under vacuum of 5 hPa at different temperature range of 200–300 °C for varying durations to remove their volatile components and adjust their softening points (SPs) to around 200 °C. The prepared spinnable pitches were spun into pitch fibers at a temperature of SP + 50 °C using a melt spinning method through a stainless steel die (diameter = 0.2 mm, length/diameter = 2) using a laboratory-scale spinning apparatus under a nitrogen pressure of 0.1 MPa and various rotation velocities (400, 600, 800 rpm; the diameter of the roller was 30 cm, so 100 rpm = 94 m/min). The spun pitch fibers were then stabilized by heating from room temperature to 270 °C at a heating rate of 0.5 °C/min in an air flow (200 mL/min) and holding for 1 h. The fibers were then carbonized by heating them at 5 °C/min to 800 °C in a nitrogen flow (100 mL/min) and holding for 5 min.

Characterization of pitches and carbon fibers

Elemental analysis

The carbon, hydrogen, and nitrogen contents of samples were determined with an elemental analyzer (MT-5 CHN Corder, Yanako), and the oxygen content was determined by the difference (O = 100 − C–H–N).

^{13}C NMR

^{13}C NMR analyses were carried out using a JEOL ECA400 apparatus to calculate the aromaticity of raw materials and pitches and to estimate changes in the functional groups of samples. Samples of about 100 mg were packed in a zirconia standard sample rotor (diameter 5 mm, length 50 mm). Spectra were acquired by high-power proton decoupling with a spectral width of 15 kHz, an acquisition time of 0.05 s, a pulse of 90° (6 μs), a delay time of 100 s, and 400–2300 scans per spectrum. Chemical shifts were calibrated against the methyl carbon resonance of solid hexamethyl benzene (17.4 ppm) as an external standard. The carbon aromaticity degree (f_a) of the sample was measured by comparing the integral for the aromatic carbon band in the^{13}C spectrum (100 to 170 ppm chemical shift region) with the sum of the integrals for both the aliphatic carbon band (0–70 ppm region) and the aromatic carbon band (100–170 ppm region).

Thermogravimetry (TG)

The thermal properties of raw materials were analyzed using a thermogravimetric apparatus (EXSTAR SII, TG/DTA6300) with a heating rate of 5 °C/min from 25 °C to 800 °C under 100 mL/min nitrogen flow. To evaluate oxidative reactivity, the pitch fibers were characterized by TG at a heating rate of 0.5 °C/min from 25 °C to 500 °C under 100 mL/min air flow.

Time of flight-mass spectrometry (TOF-MS)

The molecular weight distributions of raw materials and pitches were evaluated with TOF-MS. The raw materials and pitches were dissolved in THF at a concentration of 0.5 wt%, and 0.5 μL of each solution was deposited onto the target cell. The target was allowed to dry completely before analysis. The samples were detected using the spiral mode of a TOF-MS (JMS-S3000) apparatus. The laser power was varied from 40 to 60% of the available power with changes in the high mass detector gain. The obtained spectra are the sum of 100 laser shots and acquisitions.

X-ray diffraction (XRD)

XRD analyses were performed on a RINT 2200 (Rigaku, Japan) operating with Cu Kα radiation (λ = 0.15406 nm) generated at 40 kV and 30 mA. Scans were done at 1.0°/min for 2θ values between 5° and 90°.

Scanning electron microscopy (SEM)

The morphology of the carbon fibers was observed by SEM (JEOL-6700F, 3 kV) after coating with 10 nm of osmium tetroxide.

Tensile strength

The diameter and tensile strength of the carbon fibers were measured using a laser analyzer (M550A, Anritsu) and a tensile strength tester (Tensilon UTM-II-20, Oirentec Corp.) in accordance with JIS7601.

Results and discussion

Analysis of raw materials

HPC samples, soluble fractions of HPC, and EBO were characterized by a series of analytical methods. The main characteristics of the raw materials are summarized in Table 1. The elemental analyses and ^{13}C NMR data show that the HPC and its soluble fractions contained high levels of oxygen and relatively low f_a. These properties will result in cross-linking reactions at low temperatures, forming non-meltable solids. EBO contains a