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Preparation of isotropic pitch precursor for pitch-based carbon fiber through the co-carbonization of ethylene bottom oil and polyvinyl chloride

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ABSTRACT

For the first time, polyvinyl chloride (PVC) was used as an easily-handled chlorine source for preparation of isotropic pitch-based carbon fiber (IPCF) incorporating ethylene bottom oil (EO) as a raw material. Pitch precursors were prepared by the chlorination–dehydrochlorination triggered by chlorine radicals originated from PVC; aromatization and poly-condensation reactions occurred by polyene-type radicals from PVC. Radical production and co-carbonization were facilitated by pretreatments of EO through vacuum distillation, bromination, and additional heat treatment. Pitches were prepared by the co-carbonization of pretreated EO and EO containing 20 wt% PVC, and had higher yields and better spinnability than those by simple distillation.

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Introduction

Carbon fiber (CF) has been used in a variety of advanced materials due to its superior mechanical, physical and thermal properties. However, its widespread use is limited, primarily by its high production costs. Carbon fiber has been used in the manufacturing of aerospace materials, sports equipment, military hardware and other high value-added applications [1]. Recently, the use of CF has expanded into other applications, including automotive body parts and wind turbine blades, to achieve weight reduction for the applications. In automobiles, CF offers an exciting opportunity to replace steel or aluminum with CF-reinforced composites [1–4]. The resulting weight reduction would facilitate the further development of electric vehicles (EVs) and plug-in type hybrid electric vehicles (PHEVs) [5,6]. For the effective use of CF composites as car-body frame materials, Jim deVries of Ford Motor Company recommended that the tensile strength, elongation ratio,

and Young's modulus be at least 1700 MPa, 1.5%, and 170 GPa, respectively, with a material price less than \$10/kg [1,7]. In terms of mechanical performance, polyacrylonitrile (PAN)- and mesophase pitch-based commercial CFs have already surpassed these thresholds. PAN and mesophase pitch-based CFs (PAN-CFs and MPCFs, respectively) fully satisfy the requirements as replacements for steel and/or aluminum in many applications [7,8]. The primary obstacle to the widespread commercialization of these CFs is the high cost of PAN and mesophase pitch-based CFs. Isotropic pitch-based CF (IPCF), which is cost-competitive with the aid of relatively high yield and low energy-consumption for processing compared to MPCFs, is considered to be a low-cost alternative to PAN- and mesophase pitch-based carbon fibers. However, IPCFs has not yet demonstrated the required mechanical properties, typically exhibiting a relatively low tensile strength of 0.5–1.0 GPa and Young's modulus of 30–50 GPa [1]. The low cost of IPCF continues to drive development in many application fields [9–11]. Considerable efforts have been made over the last two decades to prepare fiber-grade isotropic pitch precursors to improve mechanical properties of IPCFs, including polyolefin [12], biomass including lignin [7,10], ethylene bottom oil (EO) [9], and hyper coal (HPC) [11]. Among them, only a few studies have yielded pitch precursors that were mechanically suitable and could be fabricated from

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inexpensive raw materials For example, our group reported the development of a novel fiber-grade isotropic pitch precursors by bromination–dehydrobromination reactions based on EO-derived cycled fuel oil (CFO) and coal tar pitch (CTP) [13]. The properties of carbon fibers obtained from the isotropic pitch were suitable for CF-reinforced plastics (CFRPs) and ultimately used in car bodies. From these studies, our group demonstrated the potential of EO, CFO, and pyrolysis fuel oil (PFO) as potential raw materials for use in the production of IPCFs. Pitch precursors derived from EO are easily spun and represent a cost-effective means of producing IPCF [13,14]. A novel, low-temperature bromination–dehydrobromination method was shown to be necessary during the preparation of randomly connected raw EO molecules with CTPs without phase separation. Nevertheless, there remains much room for improvement in the preparation of EO-derived pitch precursors. Gas- or liquid-phase reactions of EO and CTP with bromine or chlorine require large amounts of potentially dangerous halogenated reagents, which require special handling and produce strong acidic byproducts. To prevent corrosion, these reactions also require expensive, high-purity bromine or chlorine. These requirements are the major reasons for the exorbitant cost of pitch precursors. Therefore, our group selected polyvinyl chloride (PVC) as an alternative chlorine source for the chlorination–dehydrochlorination reaction. PVC is a relatively inexpensive solid-state polymer that easily decomposes into chlorine and polyene-type radicals at temperatures greater than 250 °C [15]. Dried chlorine radicals, in particular, boast relatively low corrosivity and can be readily generated from the decomposition of PVC. Over the last three decades, PVC has been used to prepare mesophase pitch [16–18], and to modify the properties of coal-tar derived mesophase pitch [19–23]. To the best of our knowledge, almost no attention has been directed toward the use of chlorine radicals generated from the decomposition of PVC during the preparation of isotropic pitch precursors. Analogous to bromination–dehydrobromination, chlorine radicals induce methylene bridge formation between aromatic units during the chlorination–dehydrochlorination reaction. Note that the reactivity of chlorine radicals is greater than that of bromine radicals. This higher reactivity results in a lower cost and lower corrosivity at the reaction temperature. Therefore, the amount of chlorine radicals required for halogenation is less than that of bromine radicals. In addition, the remaining polyene-type radicals from PVC decomposition can react with EO molecules to improve the pitch yield. These radicals can also modify the molecular structure of the pitch, increasing the number of naphthenic groups through aromatization, cyclization and condensation. The primary concern when using PVC as the halogen source for co-carbonization with EO is the high temperature required for PVC decomposition, a process which produces chlorine radicals above 250 °C (Fig. 1) [15]. The weight loss of EO when heated to 250 °C can be more than 40 wt% before the

formation of chlorine radicals begins. Thus, it is necessary to improve the reaction efficiency of EO in the co-carbonization reaction with PVC.

In this work, we closely examined the use of PVC in the preparation of an isotropic pitch precursor for IPCF production. To improve the reaction efficiency of the co-carbonization of EO and PVC and the spinnability of the resulting pitch precursor, EO was pretreated either by vacuum distilled at 270 °C for 1 h (EOvd), with 5 wt% bromination at 110 °C for 2.5 h (EOBr), or by heat treated under pressure at 370 °C for 1 h (EOp).

Experimental

Raw materials and pitch preparation

EO was supplied by Hanwha Chemical Co. Ltd. (Republic of Korea) and used as a raw material without further treatment. The EO pretreatments were as follows: vacuum distillation at 270 °C for 1 h (EOvd), 5 wt% bromination at 110 °C for 2.5 h (EOBr), and heating under pressure at 370 °C for 1 h in an autoclave (EOp). Pure-grade bromine (Bromine, JIS special grade; Wako Pure Chemical Industries, Ltd., Japan) was used for bromination.

Pretreated EOs were further heat-treated with the addition of 5 wt% and 20 wt% PVC (the degree of polymerization was approximately 1100; Wako Pure Chemical Industries, Ltd.) at 370 °C for 3 h under a flow of Ar at a heating rate of 5 °C/min. The obtained pitches were successively deposited by thin-layer evaporation (TLE) to control the softening point (SP) up to 260 °C. The prepared precursor pitches are denoted as EOvdPVC5t, EOvdPVC20t, EOBrPVC20t and EOpPVC20t. To compare EO and PVC co-carbonized pitches, EO was heat-treated at 370 °C for 3 h under a flow of N₂ and successively deposited by TLE to obtain precursor pitches with the same SP. These are denoted as EOad and EOadt. Fig. 2 summarizes the preparation processes used for the precursor pitches. Samples were denoted as EO, EOad, EOadt, EOvd, EOvdPVC5t, EOvdPVC20t, EOBr, EOBrPVC20t, EOp, and EOpPVC20t.

The prepared precursor pitches were melt-spun using a laboratory type mono-filament melt spinning apparatus equipped with a mono-filament spinneret (diameter of nozzle: 0.2 mm, length/diameter of nozzle (L/D)=2; Kasen Co. Ltd., Japan) for estimating spinnability. Spinning was carried out at 310 °C (SP+50 °C) with the pitch being extruded at a rate of 50 mg/min after 1 h of annealing under N₂ pressure. The precursor pitches were spun at winding speeds of 400 rpm (376 m/min), 600 rpm (564 m/min), 800 rpm (752 m/min), 1000 rpm (940 m/min), and 1200 rpm (1,128 m/min). Fig. 3 shows a schematic detailing the melt spinning apparatus and the spinning nozzle configuration.

Sample characterization

The thermo-pyrolytic properties of PVC, EO and pretreated EOs were examined by thermogravimetric analysis (TGA) (TG/DTG6300; EXSTAR SII, SEIKO Co. Ltd., Japan) from room temperature (RT) to 600 °C at a heating rate of 5 °C/min under N₂ flow.

The molecular weights (MWs) and distributions of the prepared pitch precursors were estimated by time-of-flight mass spectrometry (TOF-MS) (JMS-S3000; JEOL Co. Ltd., Japan) after dissolving the pitch in tetrahydrofuran to a concentration of 0.8 wt%. For the pitch analysis, the laser intensity was optimized to 52% with a delay time of 500 ns. For the EO and the pretreated EOs, the laser intensity was adjusted to 40% with a delay time of 200 ns to minimize the molecular decomposition. More than 100 test points were collected for each sample.

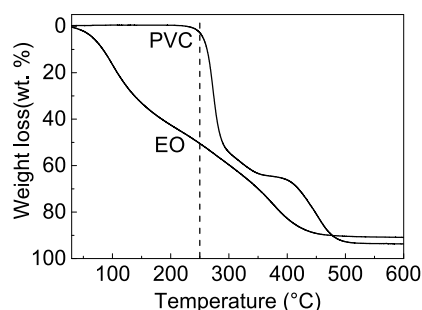


Fig. 1. Thermo-pyrolytic properties of PVC and ethylene bottom oil (EO) by TGA.

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