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The effect of carbon black on reforming of pyrolysis fuel oil for a binder pitch

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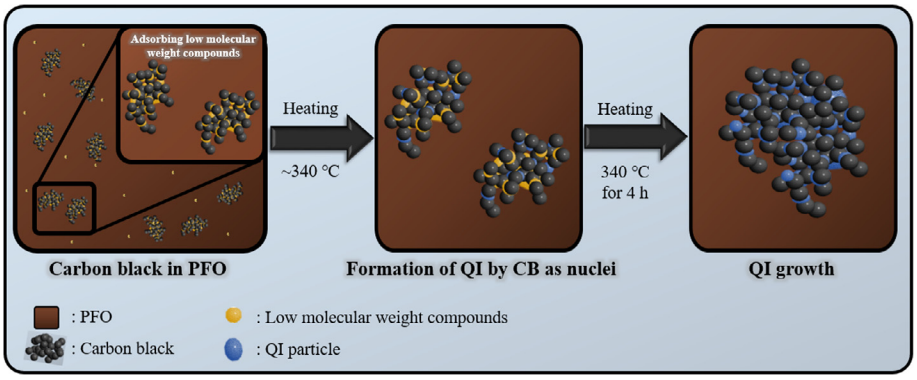
HIGHLIGHTS

- Pitch was reformed from PFO by adding carbon black to increase its QI content.
- Carbon black in the pitch served as nuclei for the growth of QI particles.
- QI content of pitch increased and its SP decreased on the addition of carbon black.

GRAPHICAL ABSTRACT

Carbon black was added to PFO to increase the QI content of the reformed pitch by serving as nuclei for the growth of QI particles.



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ABSTRACT

Pyrolysis fuel oil (PFO) has been reformed to increase the quinoline-insoluble (QI) content by adding carbon black for use as a binder pitch because petroleum-based pitch generally has a low QI content. The prepared pitch was analyzed for its aromaticity (f_a), QI content, molecular weight distribution, coking value (CV), softening point (SP), and carbonization yield. The QI content of the reformed pitches increased from 0.4% to 14.1%, whereas the average molecular weight of only quinoline-soluble content decreased by increasing the carbon black content. These results indicate that carbon black adsorbs low-molecular-weight compounds and serves as nuclei for the growth of QI particles. For these reasons, the SP and carbonization yield showed a decreasing tendency, but increased when QI sharply increased.
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1. Introduction

Binder pitches are used as a binder in the manufacture of artificial graphites because cokes, which are a main precursor of artificial graphite, have little coking power [1]. The binder pitches are divided into coal-tar pitch and petroleum pitch on the basis of their precursors [2–4]. The binder pitches from coal tar are commonly used because their quinoline-insoluble (QI) content is higher than that of petroleum pitches. However, the coal-tar pitches have a higher content of impurities such as sulfur, nitrogen and ash compared to the petroleum pitches. These impurities cause puffing during heat treatment, which reduces the mechanical strength of

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the artificial graphite. Therefore, a purification process is needed in the manufacture of the coal-tar-based pitches prior to their use as binders. However, petroleum pitches have few impurities compared to coal-tar pitch; they therefore exhibit reduced puffing during the heat treatment. However, the QI content of the petroleum pitches is very low, typically less than 1% [5–10]. The extent to which the QI content can be increased using heat treatment is limited; thus, an alternative method is required to increase the QI content [11–13].

In the preparation of artificial graphite and cokes, the influence of the QI content of the binder pitch on the structure and properties has been extensively studied. The QI content reduces the optical texture size of the cokes and improves the mechanical strength of the artificial graphite and cokes. The QI increases the viscosity of the binder pitch; thus, an appropriate QI content is required. The binder pitch for the synthesis of artificial graphite typically contains 10–15 wt% QI.

In this study, to prepare petroleum-based binder pitch with high QI content, we reformed PFO using heat treatment by adding amorphous carbon black as an additive as an alternative method to control the QI content in the reformed pitch. The effect of the presence of the carbon black during the reforming of the PFO on the growth of the QI particles was investigated. On the basis of the results of this study, we evaluated the suitability of the reformed pitches as a binder pitch.

2. Experimental

2.1. Materials

In this study, PFO (Yeochun NCC Co. Ltd., produced by NCC (Naphtha Cracking Center), Republic of Korea) was used as a precursor for the binder pitch without any further purification. Carbon black (Chezacarb AC-60; Unipetrol RPA, Litvinov, Czech Republic) was used as an additive for the binder pitch.

2.2. Reforming of PFO

The reforming process is based on a reported procedure involving heat treatment and distillation in a 1.2 L reactor [14]. The reforming was conducted by heat treatment in the presence of different concentrations of carbon black in PFO (0, 0.5, 1.0 and 1.5 wt %; the total weight of the mixture was 500 g). The mixture was reformed from room temperature to 340 °C at a heating rate of 2 °C/min under a 4 L/min N_2 gas flow and a 200 rpm agitation rate. The samples were maintained at 340 °C for 4 h and naturally cooled to room temperature. The reformed pitches were labeled as PCB-X, where X is the concentration of the carbon black in the PFO as shown in Table 1.

2.3. Characterization

Elemental analysis of the reformed pitches was conducted using an elemental analyzer (EA; EA1112, CE Instrument, Italy). Fourier transform infrared spectroscopy (FT-IR; Nicolet 6700, Thermo Fisher Scientific Inc., USA) was used to analyze the chemical structure of the components in the reformed pitches. The aromaticity values were calculated from the elemental analysis results and FT-IR spectra according to the following equations [15,16]

$$F_a = 1 - \frac{H/C}{X'(1 + (H_a/H_s))} \quad (1)$$

$$H_a/H_s = \frac{D_{3030}}{D_{2920}} \times \frac{1}{\varepsilon_A/\varepsilon_S} \quad (2)$$

where X' is the average number of hydrogen atoms combined with non-aromatic carbon atoms, generally assumed to be 2; H/C is the atomic ratio between hydrogen and carbon; H_a/H_s is the hydrogen combining ratio of aromatic and aliphatic compounds; $\varepsilon_A/\varepsilon_S$ is 0.5 times the absorptivity coefficient; and D_{3030}/D_{2920} is the ratio between the peak intensities of the aromatic C—H bond (D_{3030}) and the aliphatic C—H bond (D_{2920}).

The molecular weight distribution was investigated using a matrix-assisted laser-desorption ionization time-of-flight mass spectrometer (Voyager-DE STR Biospectrometry workstation, Life Technologies Co., CA) with DHB (2,5-dihydroxybenzoic acid) as the matrix. The coking value (CV) and QI of the reformed pitches were measured according to standard methods ASTM D 2416 and ASTM D 4746, respectively. To investigate thermal properties of the reformed pitches, thermogravimetric analysis (TGA; SDT Q600, TA Instruments Ltd., USA) was conducted at heating rate of 10 °C/min and at temperature of up to 1000 °C under N_2 atmosphere, and carbonization yield of the pitch was based on the TGA result at 1000 °C [17]. The softening point (SP) was investigated using a softening-point apparatus (FP90, Mettler Toledo International Inc., Switzerland) following ASTM 3104 standard. A ring-shaped mold was filled with the prepared pitch, then placed in the SP apparatus and was heated at a rate of 2 °C/min until the pitch is flowing down to the bottom.

3. Results and discussion

3.1. Chemical properties

Table 2 shows the elemental analysis results of the carbon, hydrogen and other element content in the reformed pitches [18]. The hydrogen content of the reformed pitches increases with the amount of carbon black, whereas the carbon content shows no clear tendency. However, the H/C mole ratio of the reformed pitches is little changed among PCB-0, PCB-0.5 and PCB-1.0, then slightly increase at PCB-1.5 during the reforming process because of the increase in aliphatic compounds or the reduction of aromatic compound size.

Fig. 1 presents the FT-IR spectra of the reformed pitches with different carbon black content. The FT-IR spectra show adsorption bands for aliphatic C—H bonds at approximately 2920 cm^{-1} and aromatic C—H bonds at approximately 3030 cm^{-1}. Adsorption bands associated with aromatic C—H—H bonds and C=C bonds appear at 700–900 cm^{-1} and 1600 cm^{-1}, respectively [19–21].

Table 1
Reforming conditions of the pitches.

Sample name	Reforming conditions			
	Temp. (°C)	Time (h)	PFO (g)	Carbon black (g)
PCB-0	340	4	500.0	0
PCB-0.5	340	4	497.5	2.5
PCB-1.0	340	4	495.0	5.0
PCB-1.5	340	4	492.5	7.5

Table 2
Elemental content of the reformed pitches.

Sample name	Elemental content (wt%)			H/C (mol ratio)
	C	H	Other elements	
PCB-0	92.10	6.65	1.25	0.867
PCB-0.5	92.73	6.68	0.59	0.864
PCB-1.0	92.54	6.68	0.78	0.866
PCB-1.5	92.25	6.73	1.02	0.875

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