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A new pitch reforming from pyrolysis fuel oil by UV irradiation

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ABSTRACT

In this study, pyrolysis fuel oil (PFO) was reformed using heat-treatment and UV irradiation, along with a cross-linker at various concentrations. Oxygen elements of the reformed pitches were increased as the amount of the cross-linker was increased. UV-treated reformed pitches were also composed of more aromatic carbon compounds than pitches reformed by heat-treatment. The softening points of the reformed pitches were measured in the range of 113.6–181.1 °C according to the quantity of cross-linker used. The UV irradiation reforming is practical and helpful for the production of more aromatic pitch.

Introduction

Carbon materials are characterized by high specific stiffness, high specific strength, high conductivity, low density, etc., which result from the fundamental properties of the carbon atom; carbon materials therefore offer numerous advantages over other materials [1–3].

Carbon materials have been focused on the various industry applications such as electrode of steel engineering, cathode or anode blocks for the aluminum engineering, paste, refractory material for furnaces, carbon fibers, fuel cells, graphite brushes, nuclear graphite, and so on [4].

Worldwide, the number of carbon materials being used in different industries is high, especially those derived from fossil fuels. The use of coal tar and petroleum pitch for the preparation of carbon materials has increased significantly because of their low price and their wide range of specifications. Moreover, markets continuously require improvement of the quality of the products and reduction of costs [5,6]. Pyrolysis fuel oil (PFO) is a low-cost option under investigation as a carbon material feedstock. PFO is a high-boiling aromatic hydrocarbon product of petroleum residue oil from a naphtha cracking center (NCC). PFO has recently attracted considerable interest because of its high carbon contents [7]. It is considered a cheap and suitable raw material for the preparation of diverse carbon materials because of its unique structural properties and extremely rich aromatic contents [8,9].

In the preparation of pitch, the petroleum or coal tar must be reformed at temperatures greater than 300 °C under a nitrogen flow for several hours [10–12]. This reforming process is a time-consuming and expensive step, depending on the part size and the equipment required. Therefore, a new pitch-reforming method is needed that will reduce both time and costs. Ultraviolet (UV) irradiation can have a beneficial effect and can be used to initiate desired chemical reactions such as polymerization [13]. UV irradiation represents a simple, low-cost, and effective procedure [14].

In this study, PFO was reformed by heat-treatment and UV irradiation, and the properties of the reformed pitches were characterized under various reforming conditions. From these results, we evaluated the suitability of UV irradiation with heat-treatment as a reforming method.

Experimental

Reforming of PFO using UV irradiation

The PFO used in this study was the dark-brown oil in the waste liquid from the naphtha cracking process, supplied by GS Caltex Refinery Company in Korea. Preliminary tests were performed to determine the reforming conditions. The as-received PFO was reformed at various temperatures (150–250 °C) and times (1–3 h). The softening points determined from the preliminary tests are reported in Table 1. The softening point of prepared pitches was increased with increasing reforming temperature and time. But the softening point of pitch reformed for 3 h at 250 °C was no differences in comparison with that of pitch reformed 2 h at 250 °C. From these preliminary tests, the PFO conditions for reforming

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Table 1
Softening points of reformed pitches as a function of the reforming conditions.

Reforming conditions		Softening point (°C)
Temperature (°C)	Time (h)	
150	3	82.2
200	3	115.8
250	1	139.9
250	2	151.5
250	3	159.8

were chosen as 250 °C for 2 h, using a magnetic stirrer in a UV reactor (800 W). The 2,2-dimethoxy-2-phenylacetophenone (DMPA) as an UV initiator and dipentaerythritol hexaacrylate (DPHA) as a cross-linker were added during the UV irradiation. The chemical structures of DMPA and DPHA are presented in Fig. 1. The concentration of DMPA, which was used as a UV initiator, was fixed at 1 wt%. The DPHA as cross-linker was added in various concentrations, i.e., 3, 5, and 10 wt% with respect to PFO, as indicated in Table 2. A schematic of the preparation procedure of the heat- and UV-treated pitch is presented in Fig. 2.

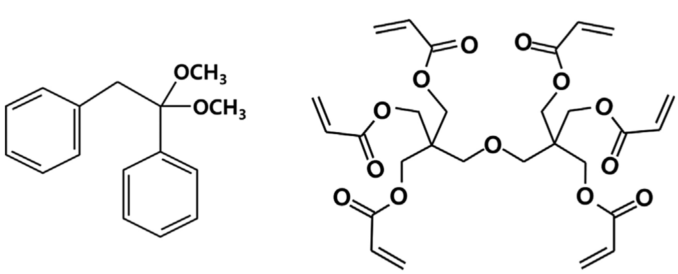
Analyses

Elemental analyses (Thermo, 1112 series) were performed to measure the C, H, N, O, and S contents of the prepared pitches. Fourier-transform infrared spectroscopy (FT-IR, Bio-Rad Laboratories, Inc., FTS-175C) was used to analyze the chemical structure of the components in the extracts. The molecular weight distributions of the as-received PFO and the reformed pitches were analyzed by matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry using toluene as the matrix. The softening point of each pitch was measured according to the ASTM D3104 standard procedure using a Mettler Toledo FP90. A small cup (with a pierced bottom) was filled with approximately 0.5 g of pitch. The cup was placed in the Mettler furnace and preheated to 20 °C below the expected softening point. The oven temperature was subsequently increased at a rate of 2 °C min^{-1} until a drop of pitch flowed through the hole. This temperature represents the softening point of the pitch.

Results and discussion

Elemental analysis of pitches

Table 3 shows the elemental analysis results for the PFO [15] and the reformed pitches prepared under different reforming conditions. The hydrogen contents of the reformed pitches decreased slightly after the UV irradiation and the addition of the cross-linker (from 7.10% for PFO to 6.84% for URP-C5). The number of carbon elements in the reformed pitches decreased as



(a) (b)

Fig. 1. Chemical structures of (a) 2,2-dimethoxy-2-phenylacetophenone (DMPA) and (b) dipentaerythritol hexaacrylate (DPHA).

Table 2
PFO-reforming conditions and sample identifiers.

Sample identifier	Reforming conditions			
	Temperature (°C)	Time (h)	UV irradiation[a]	Cross-linker (wt%)
RP-C0	250	2	X	0
URP-C0			O	0
RP-C5			X	5
URP-C3			O	3
URP-C5			O	5
URP-C10			O	10

[a] X: without UV irradiation, O: with UV irradiation

the amount of cross-linker used was increased, whereas the number of oxygen elements increased. The oxygen contents of reformed pitches were strongly affected by the quantity of cross-linker. These results are attributed to the high oxygen content of the DPHA ($C_{28}H_{34}O_{13}$) used as a cross-linker, as shown in Fig. 1. Increasing the oxygen contents of reformed pitches was considered to remaining of DPHA which had high oxygen content. Modified by the oxygen content of the pitch within the cross-linking agent because of the large pitch seems that the carbon content is low. It is considered that the carbon contents of pitches were decreased because the oxygen contents of pitches contained the cross-linker were increased.

Chemical analysis and aromaticity of pitches

Fig. 3 shows the FT-IR spectra of the reformed pitches prepared using different cross-linker concentrations. The FT-IR spectra of all of the reformed pitches are approximately the same. The FT-IR spectra of all of the reformed pitches showed large adsorption bands at approximately 3037 and 2920 cm^{-1}, corresponding to aromatic C—H and aliphatic C—H, respectively [16]. Bands associated with aromatic C—H—H and aromatic C═C bonds also appeared at 700–900 and 1600 cm^{-1}, respectively [17]. The appearance of a relatively broad absorption band at 3400–3500 cm^{-1} was attributed not only to the hydrogen-bonded —NH groups but also to the strong —OH stretching mode of water [18]. It was indicated that aromatic carbon compounds were produced by heat-treatment and UV irradiation reforming method. Sample RP-C0 contained a higher content of $—CH_3$ groups than sample UPR-C0 (see the band at 1371 cm^{-1}). The result shows that UPR-C0 is contained more aromatic carbon compounds than RP-C0. The spectra of reformed pitches with the cross-linker showed large adsorption bands at approximately 1728 and 1174 cm^{-1}, which correspond to the stretching vibrations of C═O and C—O, respectively [19]. These results further support the finding that the adsorption bands of oxygen bonds such as C═O and C—O are dramatically increased by increasing the quantity of cross-linker, which was already suggested by the results of the elemental analyses summarized in Table 3.

The aromaticity (F_α) and the H/C ratio of the reformed pitches are shown in Fig. 4. The aromaticity of each pitch was calculated from the FT-IR spectra and elemental analyses. The aromaticity indices were calculated from the spectra as follows [20,21]:

$$F_\alpha = 1 - \frac{\mathrm{H/C}}{X'(1 + (\mathrm{H}_a/\mathrm{H}_s))} \quad (1)$$

$$\frac{\mathrm{H}_a}{\mathrm{H}_s} = \frac{D_{3030}}{D_{2920}} \times \frac{1}{\varepsilon_A/\varepsilon_S} \quad (2)$$

where X' is the average number of hydrogens combined with non-aromatic carbons, generally assumed to be 2; H/C is a ratio derived from the elemental analysis results; $\mathrm{H}_a/\mathrm{H}_s$ is the