Preparation of carbon discs using petroleum-based binder pitch reformed with carbon black

Sangmin Lee, Kyung Hoon Kim and Young-Seak Lee♣

Department of Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon 34134, Korea
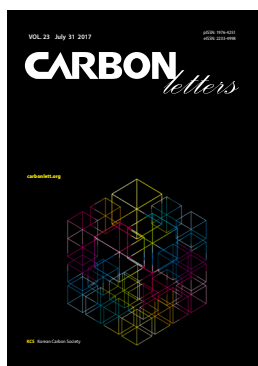
Carbon materials are widely used in various industry applications, such as a carbon fibers, graphite brushes, aluminum engineering and binders, because carbon materials have high specific strength, high conductivity, excellent thermal shock resistance, and other favorable properties [1-4]. These carbon materials are prepared from various precursors, such as polyacrylonitrile (PAN), phenolic resins and pitches. Among these precursors, pitches are more economical than PAN and phenol resin, and it is possible to control the pitch properties according to the manufacturing conditions so pitches are widely used [5-8]. Pitches are generally divided into coal tar-based pitches and petroleum-based pitches. The raw materials of the petroleum-based pitch are obtained through petroleum refining processes, such as fluidized catalytic cracking decant oil, vacuum residue and pyrolyzed fuel oil (PFO). These residue oils are reformed to petroleum-based pitches that are solid at room temperature and for which the molecular weight is controlled through cyclization, aromatization and polymerization conducted using high-temperature heat treatment [9-13].

Carbon composite materials demand high performance at a reasonable cost. For this purpose, the binder pitch used in carbon composite materials must have excellent properties like coke yield and impregnation into a substance [14,15]. However, petroleum-based pitches have lower coke yields than coal-tar pitch. To overcome this problem, researchers are studying ways to make a more careful selection of raw feedstock and modifications of the binder pitch with additives [14,16].

We prepared a petroleum-based binder pitch from PFO using heat treatment with carbon black as an additive to improve the coking yield and compressive strength of carbon discs. We investigated the effects of the embedding of carbon black in PFO on the softening point (SP), solvent solubility of pitches, and compressive strength of the carbon block.

The feed stock of the petroleum pitch used in this study was PFO (Yeochun NCC Co. Ltd., Korea). Carbon black (Chezacarb AV-60, Unipetrol RPA, Litvinov, Czech Republic) was used as an additive for preparing the binder pitch. The coke (PMCTECH Co., LTD., Korea) used as the filler of the carbon disc was sieved to obtain a particle size of less than 75 μm. A 1.2 L reactor was used for PFO reforming. PFO and the carbon black mixture were placed in the reactor and heat treated at 380°C for 4 h. At that time, the heating rate was 2°C/min with a stirring rate of 200 RPM, and the flow rate of inert gas into the reactor was 0.5 L/min. PFO and the carbon black mixture were prepared by mixing different amounts of carbon black with PFO. The added amounts of carbon black were 0%, 0.5%, 1.0% and 1.5% (w/w) of the total mixture weight of 500 g. The reforming conditions and sample names according to the content of carbon black in the PFO are summarized in Table 1.

The SP of the prepared pitch was measured using a ring and ball method according to the ASTM D 36 standard. The quinoline insoluble (QI) content in the pitches was determined using the modified ASTM D 4746-14 standard procedure. Here, 1 g of pitch was placed into 25 mL of solvent and then mixed for 1 h at 75°C for quinoline. The mixed solution was filtered under reduced pressure through a 15 μm filter crucible. Finally, the crucible was washed with acetone several times and dried at 100°C in an oven [17]. The coking value of the reformed pitches was measured according to the standard method ASTM D 2416.

The coke was molded with the petroleum binder pitch under a pressure of 100 MPa at 150°C into a mold (20 mm in diameter and 5 mm in height). The carbon disc was carbonized at 1000°C for 1 h at a heating rate of 5°C/min under inert conditions. The density of

Table 1. Reforming conditions and sample names

Sample name	Holding		N₂ gas flow (L/min)	PFO content (g)	Carbon black content (g)
	Temp (°C)	Time (h)			
PP-1	380	4	0.5	500	0
PP-2	380	4	0.5	497.5	2.5
PP-3	380	4	0.5	495	5
PP-4	380	4	0.5	492.5	7.5

Temp, temperature; PFO, pyrolyzed fuel oil.

Table 2. Characterization of reformed pitch

Sample	Yield (%)	SP (°C)	QI (%)	CV(%)
PP-1	27	104	0.2	37.4
PP-2	26.5	105	3.7	41.7
PP-3	28.1	113	5.2	48.6
PP-4	28.7	115	11.4	52.8

SP, softening point; QI, quinoline insoluble; CV, coking value.

Fig. 1. Variation of quinoline insoluble (QI) content and coking value with the amount of added carbon black.

Fig. 2. Weight loss and density reduction rate of the carbon disc using (a) PP-1, (b) PP-2, (c) PP-3, and (d) PP-4 binder pitch after carbonization.

the carbon disc was measured according to the standard method ASTM C 838.The compressive strength of the prepared carbon disc was measured using a micromaterial tester (Instron 5848; Instron, USA).

The reforming yield, SP, QI and coking value results of the binder pitch reformed with the carbon black added to PFO are presented in Table 2. The all-PFO reforming conditions were converted into the pitch after the heat treatment. The PFO reforming yields were similar in the all-binder pitch samples. The SP values of PP-1, PP-2, PP-3, and PP-4 were 104°C, 105°C, 113°C, and 115°C, respectively. The SP values were similar in the all-binder pitch samples. However, in the PP-3 and PP-4 modified with 5 g and 7.5 g of carbon black, the SP values were higher because the QI content of high molecular weight compounds was increased by the carbon black addition. The variation of the QI content and coking value with the amount of added carbon black is shown Fig. 1. The QI values of the reformed pitch were 0.5%, 3.7%, 5.2%, and 11.4%, respectively. The QI content increased with an increasing amount of carbon black. It is well-known that carbon black acts as a nucleus for growth of mesophase pitch [18,19]. Therefore, in this study, the addition of carbon black to PFO during the heat-treatment resulted in the growth of the QI particles. The coking value of the binder pitch increased according to the increase in the QI content. The presence of QI content affects the coking value and the density of the pitch [20].

Fig. 2 shows the weight loss and density reduction rate of the carbon disc using the petroleum-based binder pitch reformed with the addition of different carbon black amounts after the carbonization. The carbon disc prepared from coke and PP-1 binder pitch had a weight loss of approximately 14%. For the carbon discs prepared from coke and PP-2, PP-3
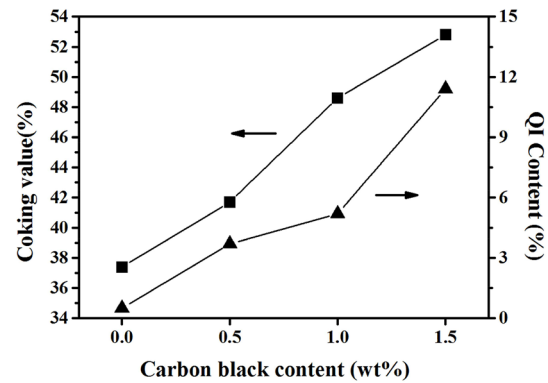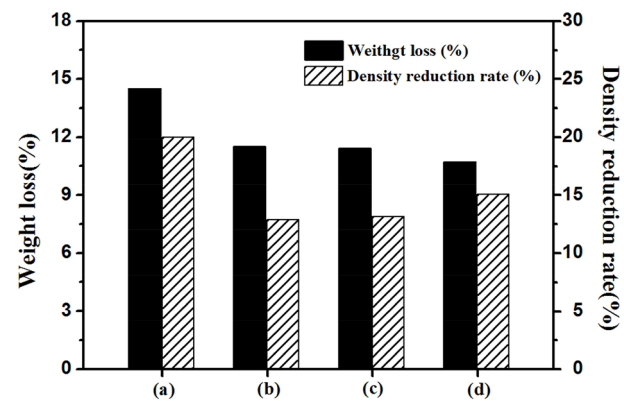
and PP-4 pitch samples, the weight loss was approximately 11%, 11%, and 10%. These weight losses occurred because the coking value increased according to carbon black addition during the PFO preforming process. The density variation of the carbon disc using the PP-1 binder pitch after carbonization decreased to approximately 20% compared with before carbonization. For the carbon disc obtained using the PP-2, PP-3, and PP4 samples, the density variation decreased to approximately 12.9%, 13.2%, and 15.1% compared to before carbonization. This density reduction tendency was similar to the weight loss trend. Increased QI content provided a pathway for the release of volatiles compounds from the binder during the carbonization [21]. Therefore, the carbon disc using the PP-1 binder underwent more volume expansion than carbon discs obtained using PP-2, PP-3 and PP-4. In preparing the carbon disc in this work, the ratio of the coke as a filler to the petroleum-based binder pitch was 8:2. Therefore, although the coking value of the binder pitch increased, it had little effect on the weight loss and density reduction of the carbon disc due to low weight ratio of the binder pitch.

Fig. 3 shows the compressive strength of the prepared carbon disc using coke and petroleum-based binder pitch reformed with different amounts of added carbon. The compressive strengths of the carbon discs obtained using PP-1,
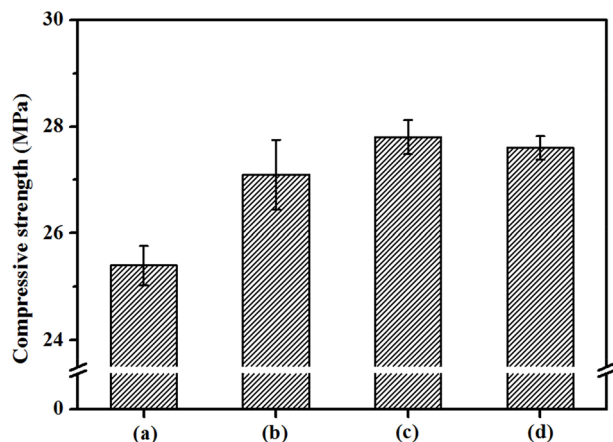
Fig. 3. Compressive strength of the carbon disc using petroleum-based binder pitch using (a) PP-1, (b) PP-2, (c) PP-3, and (d) PP-4 binder pitch.

PP-2, PP-3 and PP-4, which was reformed with added carbon black of 0, 0.5, 1.0, and 1.5 wt%, were 25.4, 27.1, 27.8, and 27.6 MPa, respectively. These compressive strength results were due to the reduction of the weight loss during the carbonization process of the carbon disc, which was due to the increase of the QI content and the coking value by the carbon black addition during the PFO reforming. However, the compressive strength of the carbon disc prepared by the PP-4 binder pitch was slightly less than the compressive strength of the carbon disc prepared by the PP-3 binder pitch because of the high QI content. The high QI content in binder pitch reduces the wetting capacity of binder pitches [22].

In conclusion, the QI content and coking value of the petroleum-based binder pitch reformed with addition of carbon black during PFO reforming increased for all samples because carbon black acted as the nucleus for the generation and growth of the QI component. The weight loss of the carbon disc prepared using the reformed pitch as the binder decreased according to the increase in the QI content of the binder pitch. The compressive strength of the carbon disc tended to increase with the QI content of the binder pitch due to the addition of carbon black. However, in the case of PP-4 reformed with 1.5 wt% of carbon black, the compressive strength decreased slightly because of the high QI content which reduced the wetting capacity of the binder pitch with coke.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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