

Fabrication of Binder Pitches Allowing for Low-Temperature Formation and High Coking Values and Examination of Mechanical Properties of Artificial Graphite Blocks Made of Binder Pitches

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Cite This: *ACS Omega* 2022, 7, 7845–7852

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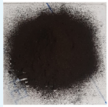






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Supporting Information

ABSTRACT: The present study focused on the development of a binder pitch to allow for low-temperature forming processes when fabricating coke-based artificial graphite blocks while increasing the density of the resultant blocks. To this end, high-softening-point (200 °C) pitches were fabricated. The pitch and byproducts obtained from the pitch synthesis were then used as binders to fabricate blocks with high mechanical strength and low porosity. Pitches were fabricated using pyrolyzed fuel oil (PFO), a petroleum residue. A high-softening-point (200 °C) pitch synthesized at 420 °C for 3 h was used as a binder pitch, and conventional pitch (124 °C) was synthesized at 400 °C for 1 h and then used. Pitch byproducts were extracted according to the boiling point of naphthalene (two rings) and anthracene (three rings) with varying numbers of aromatic rings by distillation. The largest amount of pitch byproduct was obtained in the temperature range from 220 to 340 °C, and the content of naphthalene in the byproduct was the highest over the entire temperature range. The fabricated pitches at 420 °C and byproducts were mixed to form modified pitches. It was found that their softening point and coking value (CV) decreased with the increasing content of the pitch byproduct. Low-boiling point components of the byproducts were removed from the modified pitches at the kneading process temperature (200 °C), and the mass-loss rate observed in the carbonization process temperature range (200–900 °C) was comparable to that of the high-softening-point pitch. The kneading rate of the pitch and byproduct was determined and selected based on the mass-loss rate described above, and blocks were then fabricated using a hot press. Subsequently, the fabricated blocks were subjected to heat treatment for carbonization (900 °C) and graphitization (2700 °C). After the heat treatment, the true density and apparent density of the blocks were measured, and the porosity of the blocks was calculated based on these values. The porosity of the graphite block fabricated using the pitch with a softening point of 120 °C was 21.84%, while the porosity of the graphite block fabricated using the modified pitch was 14.9%. For mechanical strength analysis, their compressive strength was measured. The compressive strength of the graphite block made of the conventional pitch (CP) was measured to be 47.59 MPa, while the compressive strength of the graphite block made of pitch mixed with a byproduct distilled at 220–340 °C was 58.79 MPa. This result suggested that a decrease in the porosity resulted in increased mechanical strength. The application of the modified pitches developed in the present study temporarily decreased the softening point of the high-softening-point pitch due to the effect of the added byproducts, allowing for a low-temperature forming process. It was also possible to fabricate artificial graphite blocks with low porosity due to the high CV of the high-softening-point pitch. As a result, blocks with high mechanical strength could be obtained.

	Method	Process	Phenomenon	Block image
	Adding Byproduct	Kneading : Low temperature Hot press : Low temperature	Softening Low viscosity Molding High C.V.	
	None	Kneading : Low temperature Hot press : Low temperature	Not softening Not molding	
	None	Kneading : Low temperature Hot press : High temperature	Not softening molding	
	None	Kneading : High temperature Hot press : High temperature	Over oxidation Not molding	

1. INTRODUCTION

Binder pitch is characterized by its flowability and coking property at a certain temperature.^{1–4} Due to these features, it is widely used as a binder that connects fillers. Commercial binder pitch is normally based on coal tar and has a softening point (SP) ranging from 100 to 120 °C. The caking property of pitch is attributed to the binder as a linker.^{5–7} In general, a pitch with a higher softening point provides a higher carbonization yield. This then reduces the porosity of the resultant carbon blocks. This means that high-density carbon blocks can be fabricated.⁸ However, this approach requires

higher temperatures for the kneading process and a hot press process in which fillers and pitch are mixed, thereby increasing the production cost of carbon blocks and graphite blocks. In short, an increase in the softening point of the binder pitch

Received: November 30, 2021

Accepted: February 4, 2022

Published: February 23, 2022



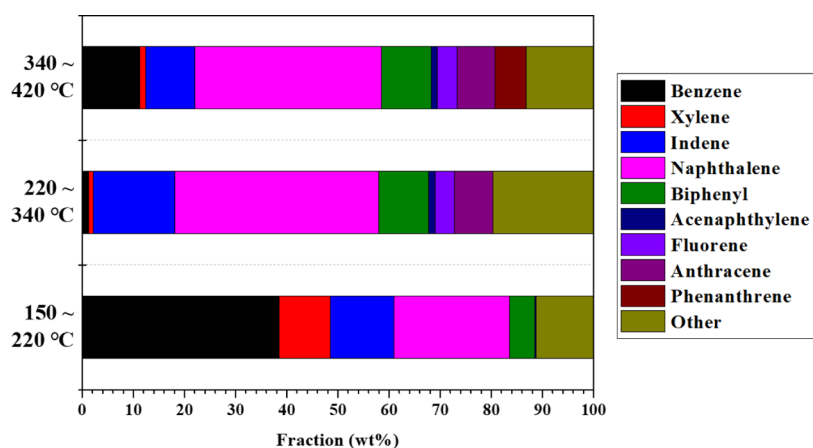


Figure 1. Component analysis of byproducts according to the temperature.

results in increased process costs in block production. A decrease in the softening point, however, leads to an increase in the porosity, thereby degrading the quality of the resultant carbon blocks.^{9–12}

A widely used method to increase the density of carbon blocks and decrease the operating temperatures of the kneading and hot press processes is to use mixed solvents. By adding solvents with high solubilities, such as toluene, tetrahydrofuran (THF), and *N*-methyl-2-pyrrolidone (NMP), a high-softening-point pitch can be subjected to the kneading process without adding high heat.¹³ However, high-purity solvents are mostly costly and also known to be harmful substances that may cause cancer when exposed to the human body. Thus, using these solvents requires a distillation process to allow their reuse and a process to remove harmful substances, thereby increasing the cost of initial process design and maintenance. Moreover, block manufacturers require additional design costs and sites for the necessary facilities if they adopt this method, thus making this approach less favorable.

To address these problems, it is necessary to develop a binder pitch with a low softening point and thereby decrease the operating temperatures of the kneading and hot press processes. Also, an ideal binder pitch with a higher carbonization yield must be used to decrease the porosity of the resultant products.^{8,14–16} However, a low softening point and a high carbonization yield tend to be in a trade-off relation. It is noted that the porosity of the block decreased as an effect of a higher cooking value, which, in turn, correlates to a higher softening point. However, there could also be the case of a pitch with a lower softening point, which flows more efficiently at lower temperatures and therefore fills the volume of the mold better than a pitch with a high softening point, thus creating a less porous block. For this reason, no binder pitch that simultaneously satisfies these two conditions at the same time has been reported. Fabricating a pitch that satisfies the two conditions above would decrease the porosity of the resultant products and thus reduce the costs required for additionally applying the impregnation process and introducing additional facilities.

Carbon blocks with lower porosity provide improved physical properties, e.g., higher strength, lower thermal expansion coefficient, and higher thermal stability and thermal conductivity, than those of their counterparts with higher porosity. Carbon blocks with improved properties can be used

at a lower cost in a wide range of applications, including nuclear power,¹⁷ semiconductors, lithium-ion battery,^{18–20} and steel and aluminum industries.²¹

In the present study, the pitches and byproducts produced during the pitch polymerization process were mixed to fabricate a pitch that can satisfy the two conditions described above (low softening point and high coking value). By doing so, the softening point of the pitch was lowered, and the carbonization yield during block fabrication was increased, thereby achieving higher mechanical properties. The obtained pitch byproducts were mixed well with the pitch as compared with other solvents because both were fabricated from the same raw materials. Also, the additional introduction of heteroatoms could be effectively prevented and thus these byproducts are highly suitable to be applied to materials that are sensitive to impurities. This approach lowers the softening point of the pitch and thus increases its flowability during the kneading process. This makes it easier to mix the pitch with fillers so that green blocks can be easily produced. The fabricated graphite blocks and carbon blocks exhibited lower porosity than their counterparts made of the conventional binder pitch, thereby providing higher strength.

2. RESULTS

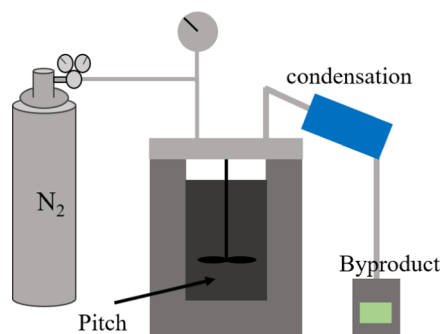
2.1. Physical Properties of Conventional Pitch (CP), High-Softening-Point Pitch (HP), and Modified Pitches.

The byproducts generated during the pitch fabrication process were composed of polycyclic aromatic hydrocarbon (PAH) components, in which various isomeric compounds and hydrocarbons had been substituted with different materials. The byproduct compounds emitted at 150–220, 220–340, and 340–420 °C were therefore analyzed using gas chromatography–mass spectrometry (GC–MS) and then classified into similar chemical species, as shown in Figure 1. As can be seen in Figure 1, the obtained byproducts were mostly composed of PAH with one to three aromatic rings. Naphthalene-based compounds were found to account for the largest portion of the chemicals emitted. The yields of the fabricated pitch and pitch byproducts are presented in Table 1. The amounts of byproducts emitted were the largest in the temperature range between 220 and 340 °C, followed by the segment between 340 and 420 °C, and the segment between 150 and 220 °C. The pitch yield was measured to be about 24 wt %. This indicated that the amount of the obtained pitch was smaller than that of the byproduct emitted in the temperature

Table 1. Pitch and Byproduct Content Produced after PFO Polymerization

	pitch	150–220 °C byproduct	220–340 °C byproduct	340–420 °C byproduct	gas phase
yield (wt %)	24.3%	6.9%	48.8%	16.6%	3.4%

range from 220 to 340 °C. It was also confirmed that naphthalene-based compounds accounted for the largest portion of the components contained in pyrolyzed fuel oil (PFO). The obtained pitches were mixed with the byproducts, and these mixed pitches were named Modified Pitch 1 (150–220 °C), Modified Pitch 2 (220–340 °C), and Modified Pitch 3 (340–420 °C) according to the temperature range. Conventional pitch (CP) was synthesized at 400 °C for 1 h using the equipment shown in Figure 2. The softening point

**Figure 2.** Scheme of 5-L-scale autoclave system.

and coking value (CV) of CP were 124.4 °C and 49.8 wt %, respectively, which were comparable to those of commercial binder pitches. The high-softening-point pitch (HP) exhibited a softening point of 209.3 °C and a CV of 64.6 wt %. Since the prepared CP and HP have different polymerization temperatures, they exhibit different physical properties. Figure S2 shows a matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) graph to analyze the molecular weight distributions of CP and HP. The molecular weight of HP polymerized at a high temperature was formed to be larger. Because HP polymerized at high temperature has a larger molecular weight, HP exhibits higher SP and CV than CP.

The softening points and CVs of the mixed pitches by temperature segment and mass ratio are shown in Table 2. Among the nine pitches, those with the same mass ratio but containing different byproducts obtained from different temperatures exhibited similar properties. However, those with different mass ratios of byproducts showed a significant difference in their properties. The pitches with the byproduct content of 50 wt % were not used in block fabrication because they remained as liquid with high viscosity at room temperature. When the byproduct content was 10 wt %, however, even during the mixing phase, the pitch and byproduct were not homogeneously mixed. As a result, the amount of byproduct in the liquid phase was insufficient, thereby resulting in localized aggregation. This led to increased errors in softening point measurement and overestimated CVs. In addition, the average softening point of these mixed pitches was about 180 °C, only 33.3–25.3 °C lower than that of HP. This feature did not suit the intent of this study, and thus these samples were not used for further tests.

Table 2. Softening Point and CV of Modified Pitches According to the Content of the Byproduct Ratio

	commercial pitch		conventional pitch (CP)		high SP pitch (HP)		HP: byproduct (1:1)		HP: byproduct (7:3)		HP: byproduct (9:1)	
	SP (°C)	CV (wt %)	SP (°C)	CV (wt %)	SP (°C)	CV (wt %)	SP (°C)	CV (wt %)	SP (°C)	CV (wt %)	SP (°C)	CV (wt %)
modified pitch 1 [150–220 °C byproduct]	115 ± 0.4	51.4 ± 1.2	124.4 ± 1.1	49.8 ± 2.1	209.3 ± 3.1	64.6 ± 4.0	<25	49.7 ± 2.1	101.0 ± 4.5	49.7 ± 2.1	176 ± 15	57.6 ± 8.2
modified pitch 2 [220–340 °C byproduct]							<25	47.7 ± 3.1	94.8 ± 6.7	47.7 ± 3.1	184 ± 16	60.7 ± 7.3
modified pitch 3 [340–420 °C byproduct]							<25	46.5 ± 1.5	99.4 ± 5.1	46.5 ± 1.5	179.9 ± 16	58.4 ± 9.0
reference total [ref] byproduct]							<25	48.5 ± 2.5	97.4 ± 3.1	48.5 ± 2.5	182 ± 16	60.4 ± 8.1

When the byproduct content was 30 wt %, the softening point of the pitches was measured to be about 100 °C. The three pitches in this set showed a similar CV at about 47 wt %. When HP was mixed with the byproduct at a mass ratio of 7:3, the softening point and CV of the resultant modified pitches were similar to those of their CP, except that their softening point and CV were slightly higher. This was because HP was able to mix well with the byproduct at 150 °C, providing sufficient flowability. For the same reason, the softening point of the mixed pitches using HP was lower. When HP was mixed with the byproduct at a mass ratio of 7:3, the CV of the resultant modified pitches was similar to that of their CP because the byproduct emitted during the pitch polymerization process was emitted again during the heat treatment. The reference total pitch was the pitch manufactured using the distilled byproduct without being divided by the temperature range. When compared to the modified pitches, the reference total pitch showed a similar CV and softening point.

A thermogravimetric analysis (TGA) was conducted to examine the thermal properties of the modified pitches, and the results are presented as TGA graphs, as shown in Figure 3.

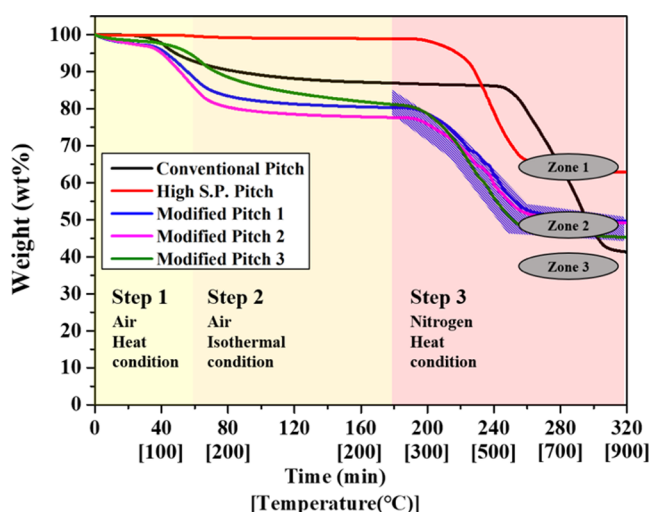


Figure 3. Amount of the mass decrease of the pitch with temperature and time.

In Step 1, both CP and HP showed a mass loss of up to 5 wt % when the temperature reached 200 °C, but the modified pitches showed a mass loss of 7–16 wt % in the same temperature range.

In Step 2, both CP and the modified pitches underwent a rapid mass loss. For CP, this rapid mass loss was interpreted as the evaporation and the release of the existing low-molecular-weight components. Given that the mass loss observed in HP during Step 2 was less than 1 wt %, the mass loss observed in the modified pitches was attributable to the removal of the byproducts. The byproduct content of the modified pitches was initially 30 wt %; however, during the test, the content was decreased by about 20 wt %. In other words, the byproduct content of the modified pitches after the test was 10 wt % or

lower. Although Modified Pitch 2 and Modified Pitch 3 were fabricated using the byproducts with a boiling point of 220 °C or higher, a significant mass loss occurred in both Step 1 and Step 2. This was attributed to the fact that the vapor pressure of the polyaromatic hydrocarbon components that comprised these byproducts increased with the increasing temperature due to their thermodynamic properties, causing a large portion of the byproducts to be lost during Step 1 and Step 2.

In Step 3, the mass loss pattern observed at 900 °C was largely divided into three zones. The mass loss in HP with a high softening point was found in Zone 1 with a high carbonization yield, while the mass loss in CP was found in Zone 3 with a low carbonization yield even though the softening point of CP was higher than those of the modified pitches. The modified pitches were initially expected to have a lower CV than CP due to their low softening point; however, in reality, the mass loss in the modified pitches was concentrated in Zone 2 with a higher carbonization yield than that in Zone 3.

When green blocks are heat treated, a mass loss occurs, and thus pores are generated. This mass loss is mainly attributed to the evaporation of volatile substances generated during the coking of binder pitches. Given that green blocks were fabricated after all components with low boiling points were removed as they went through the kneading process, Step 3 of the TGA graphs is associated with pore formation.

The mass losses observed in Step 3 were calculated, as shown in Table 3. The results showed that Modified Pitches 1 and 2 showed a mass loss similar to HP, and Modified Pitch 3 showed a larger mass loss. This was because, in Modified Pitch 3, the byproducts that had not been removed in Step 1 and Step 2 were removed in a temperature range between 350 and 400 °C, resulting in an even lower carbonization yield. This significantly low carbonization yield of Modified Pitch 3 was attributable to the use of the byproducts with a boiling point of 340 °C or higher.

Overall, the modified pitches and CP show a similar total mass loss at 40–50%. Given that the binder pitch content of green blocks is about 20–30 wt %, this mass loss pattern is less likely to make a significant difference. Therefore, the kneading process, in which HP and fillers are mixed, is performed by adding byproducts in proportion to the binder content.

2.2. Physical Properties of Blocks. Green blocks, carbon blocks, and graphite blocks were fabricated using CP, HP, and the modified pitches as binder pitches. The fabricated blocks were named by adding to the end of each pitch sample name the following suffixes: “-B” for green blocks, “-CB” for carbon blocks, and “-GB” for graphite blocks. All green blocks were fabricated in the same experimental conditions without changing the process temperature and time according to their softening points. However, in the kneading process of HP, the binder pitch did not soften at 200 °C, and thus they were mixed in a solid–solid mixing process. During the hot press process as well, it was difficult to shape and form blocks at 200 °C. Thus, these blocks were separately fabricated at 300 °C. Figure S1 shows the manufactured green block image. Figure S1a,b shows a green block manufactured with HP, the

Table 3. Mass Reduction Ratio of Pitch in Step 3 (200–900 °C)

	conventional pitch (CP)	high SP pitch (HP)	modified pitch 1	modified pitch 2	modified pitch 3
coking yield at N ₂ atmosphere (200–900 °C)	46.07 wt %	63.80 wt %	62.18 wt %	63.54 wt %	56.00 wt %

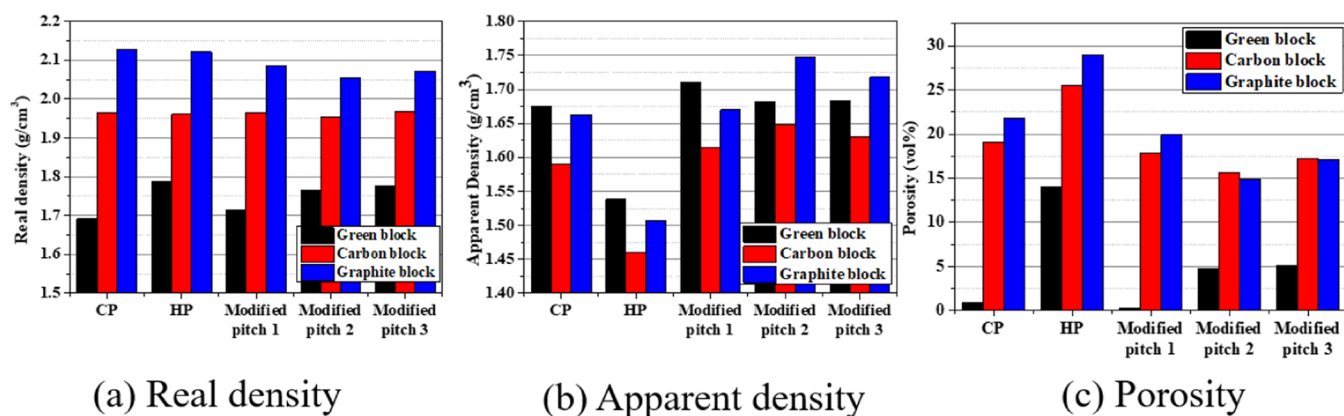


Figure 4. Real density, apparent density, and porosity of block according to modified pitches.

green block manufactured at 200 °C could not maintain the block shape, and the block manufactured at 300 °C maintained a similar shape to green blocks manufactured from other pitches.

The true density, apparent density, and porosity of the obtained green blocks, carbon blocks, and graphite blocks were measured and calculated, as shown in Figure 4. Figure 4a presents the true density of each block. The true density of the green blocks was higher when the pitches with higher softening points were used because their molecular weight was higher. For the same reason, CP-B showed the lowest true density, followed by Modified Pitch 1-B, Modified Pitch 2-B, Modified Pitch 3-B, and HP-B. However, the true density of the carbon blocks was significantly higher in all five samples because low-molecular-weight components were removed and polymerized while the binder pitches were heat treated. CP-GB and HP-GB showed the highest true density, and the true density of Modified Pitch 1-GB, Modified Pitch 2-GB, and Modified Pitch 3-GB was lower than $2.1 \text{ g}/\text{cm}^3$ in all three cases. This relatively low density was attributed to the byproducts added in the mixing process participating in the carbon polymerization.

Figure 4b presents the apparent density of each block. The HP-based blocks showed a lower apparent density than those fabricated using other pitches. This was because the added components were not sufficiently mixed in the mixing process, a solid–solid powder mixing process. The apparent density of the modified pitch-based blocks was higher than that of the CP-based blocks. Among the graphite blocks, Modified Pitch 2-GB showed the highest apparent density.

Based on these results, $[(\text{real density} - \text{apparent density}) / \text{real density}]$ was calculated, as shown in Figure 4c. The HP-based blocks, which were fabricated while the components were not sufficiently mixed, showed the highest porosity. The second highest porosity was found in the blocks fabricated using CP, which exhibited the lowest carbonization yield in the TGA results. The blocks fabricated using Modified Pitch 1 showed a high carbonization yield during the carbonization process, but their porosity was found to be higher than that of the blocks fabricated using Modified Pitch 3. The blocks fabricated using Modified Pitch 2, which showed high carbonization yield in the TGA results and high true and apparent densities, showed the lowest porosity.

3. DISCUSSION

The blocks fabricated using the modified pitches were found to have lower porosity than those fabricated using CP with a boiling point of 120 °C. This was because the softening point of the pitch was lowered with the addition of the byproduct, thereby decreasing the temperature of the mixing process and leading to increased carbonization yield. It was also found that the properties of the modified pitches slightly varied depending on the temperature segment. As can be seen in Figure 4c, the porosities of the carbon blocks and graphite blocks fabricated using the modified pitches were lower than those of the blocks fabricated using CP or HP. To examine the effect of this feature on the mechanical strength of the blocks, the compressive strengths of the green blocks, carbon blocks, and graphite blocks were measured, as shown in Figure 5. The

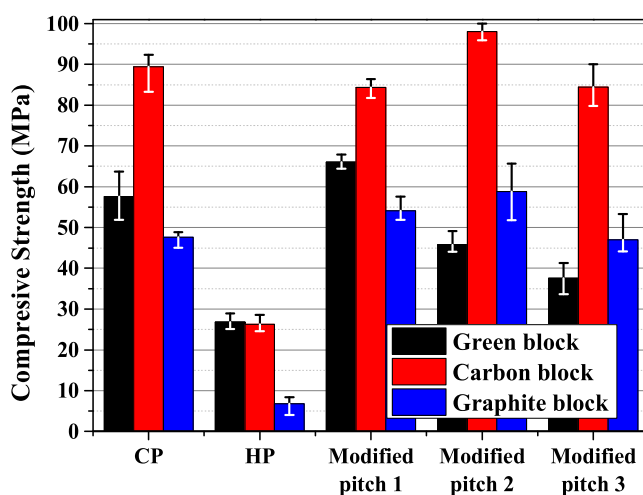


Figure 5. Compressive strength of block according to modified pitches.

HP-based blocks showed very low compressive strength, and this was expected from the porosity results. However, the modified pitches fabricated using this HP showed completely different characteristics. The carbon blocks fabricated using the modified pitches showed a compressive strength similar to that of the carbon blocks fabricated using CP. However, the blocks fabricated using Modified Pitch 2 with the lowest porosity showed a compressive strength of about 100 MPa. The graphite blocks exhibited lower compressive strength than the carbon blocks. The compressive strengths and porosities of

these heat-treated blocks showed a similar trend, and this suggests that the porosity of the blocks is related to their mechanical strength.

The viscosity of the pitches was measured at 200 °C for 2 h to examine how their viscosity changed during the kneading process, as shown in Figure 6. The viscosity of HP with a

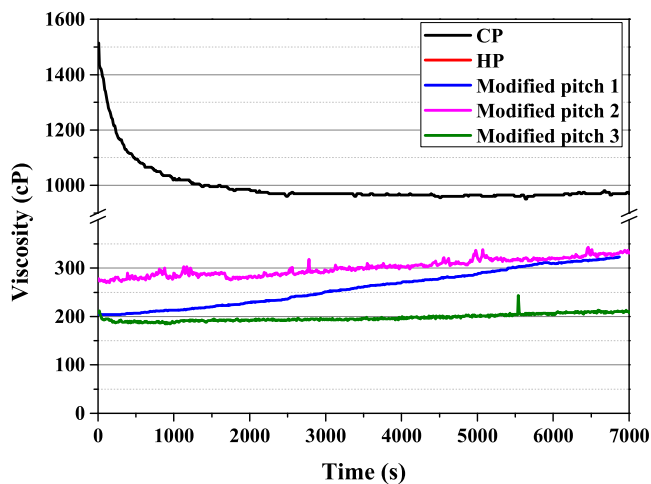


Figure 6. Viscosity of modified pitch with time (200 °C).

softening point of 200 °C was too high to be measured, and this confirmed that the actual mixing process was a solid–solid mixing process rather than a solid–liquid mixing process. The viscosity of CP remained at around 1000 cP for 2 h, and this means that the mixing strength of the kneader should be higher to sufficiently mix CP with fillers. In contrast, the viscosity of the modified pitches ranged from 200 to 350 cP, and it was also found that their viscosity gradually increased over time. The increasing rate was the highest in Modified Pitch 1, which contained the byproducts with the lowest boiling points. It was followed by Modified Pitch 2 and Modified Pitch 3 with higher boiling points. This viscosity increase in the modified pitches was attributed to the byproducts evaporating over time, as observed in Step 2 of the TGA graphs.

These byproducts were not sufficiently removed in the kneading process, and thus some of them remained in the hot press process, causing the modified pitch-based blocks to have lower true density than their CP and HP-based counterparts. This feature, however, adds to flowability in the hot press process and thus connects fillers more densely, thereby resulting in increased apparent density. These byproducts are considered to contribute to increasing the compressive strength and reducing the porosity of the resultant blocks because their light components participate in the formation of blocks with the help of the internal pressure of the blocks generated during the hot press process and the heat energy resulting from the carbonization process. This is considered to be similar to the coal tar process in which QI (quinoline insoluble) is first removed and then the remaining light components are used to fabricate needle coke.

4. CONCLUSIONS

Binder pitches were fabricated using PFO and the byproducts were generated when fabricating pitches using PFO. Artificial graphite blocks were then fabricated using coke fillers and the fabricated binder pitches, and their density and mechanical strength were examined. The softening point of the binder

pitches was found to be affected by the use of byproducts, and the effect of this feature on the overall process efficiency was further studied. The softening point of the modified pitches fabricated using pitch byproducts was lower because the molecular weight of the added byproducts was relatively low. Thus, it was possible to perform the forming process at a lower temperature. The thermal characteristics of the modified pitches were analyzed, and the results showed that their mass loss observed in the temperature range from 200 to 900 °C, in which pores were formed in the blocks, was similar to that of the HP. This means that these modified pitches can be treated in the same kneading and hot press processes as commercial binder pitches with a softening point of 120 °C. Therefore, it was possible to fabricate blocks with low porosity. Indeed, the porosity of the carbon blocks fabricated using Modified Pitch 2 was 18% lower than that of their CP. In the graphite blocks, the figure was 32% lower than that of the CP-based graphite blocks. Meanwhile, the viscosity of the modified pitches was lower than that of CP and HP, and this was considered to help the kneading process to proceed in a more uniform manner while adding to flowability between fillers, thereby increasing the density of the resultant products during the hot press process. The lower porosity of the blocks led to an increase in their mechanical strength. The use of the modified pitches temporarily lowered the softening point of HP, and thus it was possible to perform the kneading and hot press processes at a lower temperature. The high coking value of HP also contributed to reducing the porosity of the resultant blocks while thus significantly improving their mechanical properties.

5. EXPERIMENTAL METHODS

5.1. Manufactured Process of Conventional Pitch, High-Softening-Point Pitch, and Modified Pitches.

Binder pitches were polymerized from PFO (LG Chem) using the equipment shown in Figure 2. The HP (SP: 209 °C) was polymerized at a temperature of 420 °C (3.5 °C/min) for 3 h. Also, CP (SP: 124 °C) was synthesized at 400 °C (3.5 °C/min) for 1 h. Two pitches were synthesized at 1 bar and nitrogen atmosphere. In an attempt to determine the effect of the pitch byproduct type on the block fabrication process, byproducts were classified according to the boiling point of naphthalene (two rings) and anthracene (three rings) among the most widely known byproducts. Pitch byproduct was produced by distillation over temperature segments of 150 °C, the temperature where the pitch and byproducts were mixed; 220 °C, the boiling point of naphthalene; 340 °C, the boiling point of anthracene; and 420 °C, the final polymerization temperature. The yields of the fabricated pitch and pitch byproducts are presented in Table 1. First, the byproduct was heat treated at 150 °C in a silicone oil bath and then the prepared pitch was added little by little and mixed for 1 h. The prepared pitch and the pitch byproduct were mixed at mass ratios of 1:1, 7:3, and 9:1, respectively. Table 2 presents the softening point and CV of CP, HP, and modified pitches. Also, to compare the properties of these modified pitches with those of commercial binder pitches, a PFO-based pitch, i.e., CP, was fabricated using the same raw materials as used in HP. The reference total pitch was manufactured using HP and the distilled byproduct without dividing by the temperature range.

5.2. Fabrication of Graphite Blocks. **5.2.1. Procedure of Fabricating Green Blocks Using the Fabricated Binder and Commercial Coke.** Petroleum coke (D50 = 44 μm, Asbury coke) was used as a filler. The filler and binder were mixed at a

mass ratio of 8:2 and then kneaded using a kneader at 200 °C for 2 h. After the kneading process, some aggregated parts were pulverized using a pulverizer (700 rpm) for 10 min until a uniform powder was obtained. The powder was put in a mold, pressed at a pressure of 100 MPa at 200 °C for 1 h using an axis hot press (1.55 cm diameter × 1.55 cm height), and then cooled to room temperature to fabricate green blocks.

5.2.2. Thermal Treatment for Green Blocks. Two types of thermal processes were employed to fabricate carbon blocks and graphite blocks. Carbon blocks were fabricated by heating the obtained green blocks from room temperature to 900 °C at a heating rate of 1 °C/min and then keeping them at 900 °C for 1 h. Graphite blocks were then fabricated by heating the carbon blocks to 2700 °C at a heating rate of 5 °C/min and then keeping them at 2700 °C for 1 h. Carbonization and graphitization were conducted at nitrogen and argon gas atmospheres, respectively.

5.3. Analysis. **5.3.1. Analysis of Properties of the Pitches.** The softening points of the modified pitches and the conventional pitch were measured using a softening point analyzer (DP-70, Mettler Toledo) according to ASTM D3416. CV of the pitch samples was measured according to ASTM D2416. Viscosity was measured using Rotational Viscometer (TH-L3 PLUS, CAS, Republic of Korea) at 200 °C and 0.1–200 rpm. The thermal characteristics of the modified pitches and the conventional pitch were analyzed via a TGA (TGA-50H thermoanalyzer, Shimadzu, Japan). The applied temperature pattern consists of the following three steps. The TGA analysis was performed in three steps. In Step 1, the pitches were heated in an air atmosphere to the temperature of the kneading process (25–200 °C, 5 °C/min). Step 2 corresponded to the kneading process, in which the pitches were kept at 200 °C for 2 h in an air atmosphere. In Step 3, the pitches in the form of green blocks were heat treated in a nitrogen atmosphere (200–900 °C, 5 °C/min).

5.3.2. Physical Properties of Blocks. The helium density and the apparent density of the block samples were measured. The helium density was measured using AccuPyc 1340 (Micromeritics, Atlanta) and the apparent density was measured by the Archimedes method. Compression tests were conducted using cylindrical specimens (1.55 cm diameter × 1.55 cm height). The compression load was applied along the axis at a crosshead speed of 1 mm/min. The mechanical strength tests were considered mean and standard deviation for 10 measured values.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c06750>.

Figure S1: Image of the green block (Photograph courtesy of Jong Hoon Cho; Copyright 2021). Figure S2: MALDI-TOF analysis of CP and HP. Figure S3: Correlation coefficient of compressive strength and porosity. Table S1: Elemental analysis data of resultant products after kneading (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Korea Evaluation Institute of Industrial Technology (KEIT) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (10083621, Development of Preparation Technology in Petroleum-Based Artificial Graphite Anode) and also the Technology Innovation Program (20006696, Development of Isotropic Graphite Block for Semiconductor Process) funded by the Ministry of Trade, Industry & Energy (MOTIE).

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