Study of the Molecular-Weight Distribution of Binder Pitches for Carbon Blocks

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ABSTRACT: The present study aimed to identify the required characteristics of binder pitches in the filler-binder mixing process to effectively manufacture graphite blocks. To this end, a binder pitch was separated into pitch fractions of varying molecular-weight segments. The role and effectiveness of each pitch fraction were then analyzed with respect to their molecular-weight distribution. As a result, the optimal molecular-weight distribution was determined. More specifically, a coal-tar pitch was separated into solvent-soluble and solvent-insoluble fractions. The molecular-weight distribution was determined according to this classification, and the characteristics of each pitch fraction were examined. The pitch separation process was conducted using three solvents: hexane, toluene, and quinoline. The resulting pitch was separated into the following pitch fractions: hexane-soluble (HS), hexane-insoluble-toluene-soluble (HI-TS), toluene-insoluble-quinoline-soluble (TI-QS), and quinoline-insoluble (QI). Fourier transform infrared (FT-IR) spectrum, matrix-assisted laser desorption ionization-time of flight (MALDI-TOF), and softening point of each pitch fraction were measured. Also, pitch samples were refabricated while varying the mixing ratio of these pitch fractions, and carbon blocks were then prepared using them. The compressive strength and porosity of these blocks were measured and compared. The P154_B pitch with a high content of TI-QS was used to fabricate a green block. Due to the high viscosity of the binder used, the fluidity was not sufficiently high, and thus, the green block made of this pitch had relatively low strength. The other blocks had similar levels of strength. After the carbonization process, the carbon block with a high content of HS (P352_B-C) and the carbon block with the HS content removed (P073_B-C) showed lower compressive strength than their respective green-block counterparts (P352_B and P073_B). However, their strength was higher compared to those of the other carbon blocks. In the case of carbon block P073_B-C, the HS content was completely removed, and thus, the content of TI-QS (β-resin) was relatively high. Accordingly, this carbon block ended up with large amounts of components that had high coking values (CVs), and this contributed to limiting the formation of pores. Therefore, the compressive strength of this carbon block was high. In the case of the carbon block with a high content of HS (P352_B-C), a suitable level of viscosity was achieved because the HS components ensured high fluidity. As a result, blocks with higher density and compressive strength could be fabricated. The major findings of the present study confirm that producing carbon blocks with high mechanical properties requires binder pitches with a balanced combination of suitable viscosity to ensure sufficiently high fluidity and a proper level of CV to effectively suppress the formation of pores in the mixing and molding process.

1. INTRODUCTION

Graphite blocks have been widely used in various industrial fields, including in nuclear reactors, aerospace applications, as electrode materials in metallurgical industries, and as blast furnace hearths. These materials can be successfully applied in such a wide range of industries because they exhibit excellent thermal stability, electrical conductivity, and thermal conductivity and have a lower density than metallic materials. These characteristics are optimized when these graphite blocks have low porosity and high strength.

When fabricating graphite blocks, fillers, and binders are used in a mixed form. Carbon materials, such as coke and graphite, are mainly used as fillers, while pitch is widely used as a binder. The pitch maintains its fluidity and adhesion within a specific temperature range, so the fillers and binders are combined at a specific temperature during the mixing process. The mixed raw materials are formed into green blocks through a series of forming processes, such as cold isotropic pressing (CIP), hot pressing, or extrusion. These green blocks are then subjected to graphitizing heat treatment at 2500 °C or higher to form graphite blocks.

During this high-temperature heat treatment process, however, coking of the pitch occurs, and as a result, the pitch loses weight. The lost mass is discharged in a gaseous form.
Table 1. Physical Property of Coal-Tar Pitch and Each Fraction

| softening point (°C) | raw | HS | HI-TS | TI-QS | QI |
|----------------------|-----|-----|-------|-------|----|
| coal-tar pitch       | 103 | ND < 35 | 56.0 | ND > 35 | 92.35 |

| EA (%) | C | H | N | S | O | H/C | CH3/CH2 | density (g/cm3) |
|--------|---|---|---|---|---|------|---------|-----------------|
|         | 4.35 | 0.84 | 0.68 | 1.78 | 0.57 | 0.071 | 0.661 | 1.327 |

2. RESULTS

2.1. Pitch Properties Based on Pitch Fraction by Solvent Extraction. The softening point of the coal-tar pitch was 103 °C. As shown in Table 1, this coal-tar pitch contained a small amount of S (0.68%) and N (0.84%). The H/C ratio was 0.57. The real density was 1.327 g/cm³, which was lower than that of graphite or coke. The coal-tar pitch was classified according to molecular weight into four types: hexane-soluble (HS), hexane-insoluble-toluene-soluble (HI-TS), toluene-insoluble-quinoline-soluble (TI-QS), and quinoline-insoluble (QI). The respective contents of HS, HI-TS, and TI-QS were 23, 49, and 28 wt %. The weight content of QI was very low, below 0.1 wt %, and was not considered in the present study. Since the softening point of HS was below 30 °C, at room temperature HS existed in the form of a highly viscous liquid. The softening point of HI-TS was 56.0 °C, while the softening point of TI-QS could not be measured because it was 350 °C or higher. The CV of HS, which had the highest molecular weight, was measured to be 18.60 wt %, while HI-TS and TI-QS exhibited CVs of 42.16 and 76.00 wt %, respectively. This indicated that the CV of the pitch fractions increased with increasing molecular weight.

Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) was conducted on each pitch fraction to accurately determine their molecular-weight distribution. The MALDI-TOF graph is shown in Figure S1. According to the results, each pitch fraction was expressed as a combination of segments corresponding to their respective molecular weight ranges. Given that pitches are composed of varied but similar chemical species, the pseudo-component standard was employed to determine each segment, as follows: segment 1 (100–178 m/z), segment 2 (178–356 m/z), segment 3 (356–534 m/z), segment 4 (534–712 m/z), segment 5 (712–890 m/z), segment 6 (890–1068 m/z), segment 7 (1068–1246 m/z), and segment 8 (1246–1424 m/z). The MALDI-TOF values of each of the three pitch fractions were converted into ratios as the weight percent of the respective segments, as shown in Figure 1.21

Figure 1. MALDI-TOF of coal-tar pitch according to segment.

Segment 1 had the lowest molecular weight, while segment 8 had the highest molecular weight. In HS, the ratio of segment 2 was the highest, but segment 3—segment 8 showed the lowest values. As shown in Table 2, the content of HI-TS was the highest at 48.77 wt %. In HI-TS, the ratios of segment 2 and segment 3 were the highest. In TI-QS, segment 3 and segment 4 were the highest. The ratios of segment 5, segment 6, segment 7, and segment 8 were relatively high compared to the other pitch fractions, but the difference was not significant. To sum up, segment 2 was the highest in HS, segment 2 and segment 3 were the highest in HI-TS, and segment 3, segment
4, and segment $\text{S}$ were the highest in TI-QS. Given that soluble and insoluble fractions were separated depending on the affinity between the solvent and each pitch fraction, the molecular-weight boundaries were not clearly defined. Nonetheless, it was confirmed that the overall molecular weight increased in the order HS < HI-TS < TI-QS, meaning the softening temperature varied according to the molecular weight. The HS with a high content of low-molecular-weight segments showed the lowest softening point. The softening point increased with the increasing content of high-molecular-weight segments. The TI-QS fraction, in particular, had a very high content of high-molecular-weight segments, and thus, it was impossible to measure its softening point using this MALDI-TOF analysis method.

Figure 2 shows the IR analysis results of each pitch fraction. The raw sample is a coal-tar-based pitch, which is known to contain less aliphatic chins in its aromatic rings than a petroleum-based pitch. As shown in the IR results, large peaks were not observed in the range from 3050 to 2850 cm$^{-1}$, in which aliphatic C–H stretching peaks are known to frequently appear. The largest aliphatic C–H stretching group peak was observed in HS, which was the lightest component. These peaks were also observed in HI-TS and TI-QS, although the intensity was low. Aromatic C–H bending peaks observed in the range from 900 to 600 cm$^{-1}$ indicate the presence of nonsubstituted small- and medium-sized polycyclic aromatic hydrocarbons. Peaks in the 1300–1100 cm$^{-1}$ range are related to the geometric distortion of C–C bonds and the vibration of the defect mode. Thus, these peaks indicate the presence of odd-carbon number rings.

These results showed that the coal-tar pitch and all of the fraction samples were mainly composed of aromatic rings, as well as hydrogens that had not been substituted with aliphatic chains. In all of the pitch fractions, most peaks were observed in the range from 1700 to 700 cm$^{-1}$. In HS, in particular, the 1600 cm$^{-1}$ peak was much larger than that in the other pitch fractions. This peak was attributed to the carbon–carbon double bond (C=C) stretching. This peak gradually disappeared as the content of high-molecular-weight segments increased. However, it was confirmed that most of the other peaks remained in all of the pitch fractions. This was attributed to the fact that some light components had remained in the insoluble fractions because the separation process was conducted using solvents.

MALDI-TOF and IR data of refabricated pitches (while varying the mixing ratio of pitch fractions) are shown in Figure S2. Figure S2a shows the MALDI-TOF data of refabricated pitches including raw pitch. The molecular-weight distribution of P352 was slightly shifted toward light molecular weight than that of Praw. Also, the molecular-weight distribution of P154 and P073 was slightly shifted toward heavy molecular weight than that of Praw. Figure S2b shows the IR data of the refabricated pitches. Refabricated pitches remarkably exhibit an aromatic C–H bending peak (900–600 cm$^{-1}$). It seems that the HS fraction ratio increased.

2.2. Binding Characteristics of Each Pitch Fraction.

Pitches were fabricated using the separated pitch fractions while appropriately varying their mixing ratio, and the optimal pitch fraction that exhibited the best characteristics as a binder was determined. The ratio of HI-TS, which had the highest content, was set to a certain level, and the ratios of HS and TI-QS were adjusted to fabricate different pitches. P073 was additionally fabricated by completely removing the HS content, which was the lightest component. P352 with the highest content of HS showed the lowest softening point. Both P154 with the highest content of TI-QS and P073 with the HS content removed showed a high softening point of about 111 °C. The P253 pitch was fabricated to have ratios similar to the raw pitch.

CV values were estimated and adjusted, considering the ratio of each pitch fraction. Figure 3 shows images of the green blocks made of the pitch fractions. Figure 3a shows an image of the green block made of HS. Even after the molding process, this green block exhibited characteristics similar to clay. However, large cracks appeared on the surface of the green block. Figure 3b shows an image of the green block made of HI-TS. This block had a rigid body with a smooth surface. As shown in Figure 3c, on the surface of the green block made of TI-QS cracks occurred in the direction perpendicular to the
binder pitches are determined not only by the specific pitch fractions. These results confirmed that the characteristics of binder pitches are determined not only by the specific molecular-weight segments of each pitch fraction but also by the interactions between the respective pitch fractions. After the carbonization process, carbon block TI-QS-B_C, which was composed of β-resin, exhibited the highest compressive strength. In the case of TI-QS-B_C, there was no significant difference in compressive strength before and after the carbonization process. Its compressive strength was similar to that of Raw-B_C. Among the pitch fractions examined in the present study, HS and TI-QS were not used to produce green blocks. For a more objective comparison, the pitches were refabricated, and the characteristics of each pitch fraction were more accurately assessed. The specific ratios of each pitch fraction are summarized in Table 3.

2.3. Mechanical Strength of the Refabricated Pitches with Respect to Their Binding Characteristics. Table 4 shows the measured apparent density and real density of the green blocks and carbon blocks made of the refabricated pitches (fabricated while varying the mixing ratio of the pitch fractions). Among them, P352-B with a high content of HS showed the lowest real density, while P154-B with a high content of TI-QS had the highest real density. The real density of these pitches slightly varied according to the mixing ratio, but the difference was not significant. The real density of P073-B with the HS content completely removed was lower than that of P253-B. The apparent density was the highest in P352-B and the lowest in P154-B. The porosity estimated based on these results also showed similar trends. P154-B showed the highest porosity among them. This was attributed to the fact that in the mixing process of P154-B (THF insoluble 28.4 wt %), the binder pitch was not sufficiently dissolved in THF, and thus, the components were not fully mixed. In the mixing process of P352-B, in contrast, the binder pitch was fully dissolved. Thus, its apparent density was measured to be the highest.

For this approach to be applied in the actual process, the viscosity of the binder pitch needs to be lowered to the point where an appropriate level of fluidity can be achieved. These binder pitches can be successfully used in the mixing process only when this condition is met. After the carbonization process, P073-B_C had the lowest porosity, while P154-B_C showed the highest porosity.

The real density and porosity of P352-B_C, however, were different from our expectations. This pitch was expected to have the highest porosity and lowest real density because its HS content was the highest. Instead, however, both its real density and porosity were the second highest. These properties were similar to those of Raw-B_C. Figure 4 shows the compressive strength and flexural strength of the refabricated pitches before and after carbonization. Before the carbonization process, all of the green blocks except for P154-B exhibited a compressive strength of about 40 MPa. The compressive strength of P154-B was 33.4 MPa. Given that P154-B (2.1 cP) contained pitch fractions that were insoluble in THF in large quantities, it was deemed that the mixing had not been sufficiently effective. After carbonization, the blocks showed lower compressive strength. This was because the porosity was increased due to the loss of binder pitch during the carbonization process. All of the blocks except for P352-B_C showed a compressive strength of about 20 MPa. P352-B_C exhibited the highest compressive strength at 26.6 MPa. The flexural strength also shows a similar tendency to the compressive strength. It exhibited the high strength in the order P352-B_C > P073-B_C > Raw-B_C > P154-B_C > P253-B_C. P352 was the pitch with the lowest softening point and contained the largest amount of HS. Accordingly, the compressive strength was the highest when TI-QS (β-resin) was used as a binder. However, when the refabricated pitches, which were used to determine the role of each pitch fraction with varying molecular-weight segments, were considered, it was found that ensuring an appropriate level of fluidity by adjusting the HS content was also an important factor in the process.

3. DISCUSSION

The pitch fractions of the binder pitch were prepared, and pitches were refabricated using the pitch fractions. Then, the compressive strength and porosity of the resulting green blocks were measured and analyzed to examine their characteristics as binders. As shown in Figure 4, there was no significant difference in compressive strength between the green blocks made of TI-QS and the carbon blocks made of the same pitch fraction. This confirmed the significance of the β-resin. With its
very high CV, β-resin does not allow gases to be generated inside the block. Also, no cracks occurred during the molding phase and thus closed pores formed in smaller numbers inside the block. For that reason, there was no significant difference found in the level of compressive strength before and after carbonization.

Compared with Raw-B_C, the compressive strength of Raw-B, a green block before carbonization, was about twice higher. This was because the raw pitch was sufficiently dissolved in THF, i.e., up to 19.88 wt % of the pitch was fully dissolved, thereby causing the binder pitch to be uniformly distributed around the filler. This contributed to its high compressive strength.

These characteristics were also observed in the refabricated pitches. P154-B, with the highest content of TI-QS, showed similar trends. P073-B with a similar softening point had a relatively low content of TI-QS, and thus, it exhibited low viscosity and high compressive strength. P073-B and P253-B, green blocks before carbonization, had a similar compressive strength. After carbonization, however, the compressive strength was higher in P073-B_C with a higher content of HI-TS, which provided higher CVs than HS.

These results confirm that when the binder has a low viscosity in the mixing process, it tends to be uniformly distributed around the filler. Based on this characteristic, it is possible to fabricate blocks that have high strength in the green block form. Similar results were also found in the green block made of P352-B with a high content of HS. The reason that the compressive strength of the carbon block made of P352-B_C was higher than that of the refabricated pitches was that HS components, which belonged to low-molecular-weight segments, existed in large quantities in the block molding process. These HS components were deemed to have densely filled the space between the fillers, thereby contributing to the increased strength of the block.

It was also confirmed that the HS, HI-TS, TI-QS, and QI that constituted the binder pitch had different effects on the graphite block manufacturing process. HS has a low CV but serves to uniformly distribute insoluble substances, such as fillers, TI-QS, and QI, during the mixing and molding process. By doing so, it densely fills the empty spaces between the fillers, which result from the intrinsic shape of the filler. HI-TS has effects similar to HS, but due to its higher CV, it can more effectively suppress the formation of pores. However, HI-TS requires a sufficiently high temperature during the mixing process to achieve the same level of fluidity as HS. Due to its high CV, TI-QS serves to suppress the formation of pores, preventing the occurrence of swelling or cracking during the carbonization process. However, it does not have a softening point, which makes it difficult to maintain an appropriate level of fluidity during the mixing and molding process, which makes it less applicable in practice. However, it was difficult to manufacture the blocks by a single fraction, as explained in Figure 3. Also, it showed a low value in compressive strength, as shown in Figure 4. Therefore, it is noted that the combination of each pitch fraction is necessary for manufacturing a carbon block.

### 4. CONCLUSIONS

In the present study, a binder pitch was separated into soluble and insoluble fractions using solvents. Each pitch fraction of varying molecular-weight segments was analyzed to assess their characteristics as binders. MALDI-TOF was conducted on each pitch fraction to determine their molecular-weight distribution. Based on the results, each pitch fraction was expressed as a combination of segment 1 to segment 8. HS was mainly composed of segment 2 components, while HI-TS was composed of segment 2–4 components. Also, TI-QS was mainly composed of segment 3 and segment 4. Since it was difficult to fabricate blocks using only the TI-QS components (β-resin), the pitches were refabricated using the pitch fractions.

Given the intrinsic nature of the block manufacturing process, the pitches that contained more components that were more soluble in THF exhibited higher strength when fabricated in the green block form. After the carbonization process, P073, with the highest CV, showed the highest strength, except for P154, which had low strength in the green
block form. This was because smaller amounts of gases were generated during the coking of the binder, thereby preventing the formation of pores. In the case of P352, high compressive strength was maintained even after carbonization because the empty spaces between the fillers were densely filled during the mixing and molding process. Likewise, the interactions between the pitch fractions contributed to improving the strength of the blocks.

Therefore, when selecting a suitable binder pitch, it is necessary to check to see whether it provides an appropriate level of viscosity to ensure sufficient fluidity in the mixing and molding process and whether its CV is capable of effectively suppressing the formation of pores during the carbonization and graphitization process.

5. EXPERIMENTAL SECTION

5.1. Raw Materials. A commercial coal-tar pitch (Handan, China, with a softening point of 103 °C) was used as a binder. Its physical properties are shown in Table 1. The pitch was separated into solvent-soluble and solvent-insoluble fractions using the following solvents: hexane, toluene, quinoline, and tetrahydrofuran (THF). All of these solvents were purchased from Samchun Reagents. Needle coke (PMC Tech) was used as the filler for carbon block fabrication. It was crushed and sorted using a jet mill (at a crushing speed of 6000 rpm and a classification speed of 6000 rpm).

5.2. Processes. 5.2.1. Solvent Separation Process. The solvent separation process was conducted by stirring 20 g of the pitch and 2000 mL of hexane at 55 °C for 1 h. The mixed solution was filtered with a filter size of 0.20 μm. The hexane-soluble part of the pitch was obtained by removing the solvent through an evaporation process at 65 °C. The soluble-part and insoluble-part samples were further dried at 70 °C. Following the drying process, 20 g of the toluene-insoluble part was mixed with 500 mL of toluene and then stirred at 55 °C for 1 h. This solution was then filtered with a filter size of 0.20 μm. The toluene-soluble part of the pitch was obtained by removing the solvent through an evaporation process at 80 °C. The soluble-part and insoluble-part samples were further dried at 70 °C. Finally, 5 g of the toluene-insoluble part was mixed with 500 mL of quinoline, and then, this solution was stirred at 150 °C for 1 h. This solution was then filtered with a filter size of 0.20 μm. Its soluble-part sample was obtained by removing the solvent in vacuum at 200 °C. Through these procedures, four pitch fractions were obtained and named HS (hexane-soluble), HI-TS (hexane-insoluble-toluene-soluble), TI-QS (toluene-insoluble-quinoline-soluble), and QI (quinoline-insoluble), respectively. The ratio of each fraction is shown in Table 2.

5.2.2. Pitch Mixing Process. Afterward, pitches were fabricated using the obtained pitch fractions while appropriately varying their mixing ratio. The ratio of HI-TS, whose content was the highest, was set to 50 wt %, and the ratios of HS and TI-QS were adjusted as desired. Each pitch fraction mixture (10 g) was mixed with 1000 mL of THF, and this solution was stirred at 55 °C for 1 h. The mixed solution was then dried at 150 °C for 4 h in an air atmosphere to fabricate the pitches. Table 3 shows the mixing ratios of each pitch fraction. P073 was additionally fabricated by completely removing the HS content, which was the lightest component.

5.2.3. Carbon Block Manufacturing Process. Mixtures of the filler and binder were prepared to fabricate carbon blocks. The pitch (15 g) was mixed with 50 mL of THF, and the solution was stirred at 55 °C for 1 h. After that, 35 g of needle coke was added and sufficiently mixed. The mixed samples were dried at 150 °C for 2 h in an air atmosphere. These samples contained aggregated pitch and needle coke and thus were crushed before use. Green blocks were prepared by placing each powder in a cylindrical mold with a capacity of 15.5 mL and then pressed at the softening point and 100 MPa for 1 h using an axis hot press. Following that, these blocks were cooled down to room temperature. In the case of TI-QS, it was impossible to measure the softening point, and thus, the process proceeded at 300 °C. The prepared green blocks were heat-treated at 900 °C (1 °C/min) for 1 h in an electric furnace to fabricate the carbon blocks.

5.3. Characterization. The softening point of mixed pitch and pitch fraction was measured using a softening point analyzer (DP-70, Mettler Toledo, in KRICT) according to ASTM D3416. The coking value (CV) of the pitch sample was measured according to ASTM D2416. The viscosity was measured using Viscotest 700 (Hydramotion) by pitch dissolved in THF (pitch/THF = 1 g:4 mL). The carbon, hydrogen, sulfur, and nitrogen contents were analyzed using a Thermo Fisher Scientific Flash 2000 organic elemental analyzer (in Korea Research Institute of Chemical Technology [KRICT]). The blended feedstocks were characterized using a Bruker ALPHA-T infrared spectral analyzer. The samples were measured from 4000 to 500 cm⁻¹ at a resolution of 2 cm⁻¹ using dried KBr pellets. To analyze the molecular weight of the prepared pitch, the pitch was sorted into powder with a particle size of 25 μm or smaller. Then, the sorted powder was mixed with 7,7,8,8-tetracyanoquinodimethane (TCNQ), and the resulting mixture was loaded into a MALDI target-plate cell by the water-spotting method for MALDI-TOF (Autoflex Speed TOF/TOF, Bruker) analysis.

Helium density and apparent density were measured to analyze the block sample. The helium was measured using an AccuPyc 1340 (Micromeritics, Atlanta), and the apparent density was measured by the Archimedes method. The compression tests were carried out on cylindrical specimens (15.5 mm diameter × 15.5 mm height). The compression load was applied along the axis using a crosshead speed of 1 mm/min. In the mechanical tests, the data were expressed as mean and standard deviation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00323.

MALDI-TOF data of pitch fraction and raw pitch (Figure S1); FT-IR and MALDI-TOF analysis of refabricated pitches (Figure S2); and real density, apparent density, and porosity of block according to pitch fraction (Table S1) (PDF)

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Notes
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