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Manufacture of high density carbon blocks by self-sintering coke produced via a two-stage heat treatment of coal tar

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Abstract

High-strength and high-density carbonized carbon blocks from self-sintering coke were manufactured using coal tar and two-stage heat treatments (1st and 2nd stage treatments). First, the molecular weight distribution of the refined coal tar was controlled through a pressured heat treatment (1st stage treatment). Second, the 1st stage heat-treated coal tar (1S-CT) was treated using a delayed coking system (2nd stage treatment) to become the self-sintering coke. Finally, carbon blocks were molded from 2nd stage heat-treated coke (2S-C) and carbonized at 1200 °C for 1 h. Through rapid decomposition of the high molecular weight components in the coal tar at 360 °C in the 1st stage treatment, the molecular weight distribution of coal tar was confirmed to be controllable by the 1st stage treatment. Swelling during carbonization was observed in carbon blocks manufactured from 2S-C containing more than 15 wt% of volatile matter from 150–450 °C. The optimum conditions of the two-stage heat treatments were

confirmed to be 300 °C for 3 h and 500 °C for 1 h. The highest density and flexural strength of the carbonized carbon blocks manufactured from 2S-C were 1.46 g/cm³ and 69.2 MPa, respectively.

Keyword: Chemical engineering

1. Introduction

Various types of carbon materials such as powders, emulsions and blocks have been widely used as important components in the modern carbon industry. For example, carbon materials have been employed as biomedical substances, electrical matters, electronic stuff, and aerospace items. In the early stage of the carbon industry, pitch and coke were only developed as raw materials for the fabrication of graphite powder. However, after World War II, carbon materials have been extensively utilized for the aviation industry, which led to extraordinary advances in techniques for the manufacturing and processing of carbon materials. With the accelerated development of carbon industries, the manufacturing and processing techniques for artificial graphite blocks have been developed precisely and efficiently [1, 2, 3, 4, 5, 6, 7].

The manufacturing processes for the graphite blocks in the current industry include the following: (a) The coking process to remove the volatile matter, (b) The pulverization and sorting step for particle sizing, (c) The mixing of the coke and binder to prevent the swelling phenomenon, (d) Formation and calcination, (e) Repeating the impregnation and re-calcination to achieve a high-density and high-strength, and (f) Graphitization [8, 9, 10]. The most important factors in these processes are the types of coke and the optimal mixing ratio of binder and coke. At the same time, to manufacture high-density artificial graphite blocks, the impregnation and calcination steps need to be repeated, which is a critical problem because the repeated impregnation and calcination processes can dramatically increase manufacturing costs and time. To address those shortcomings, many researchers have investigated several advanced methods, such as using mesocarbon microbeads (MCMB) [11, 12, 13], utilizing self-sintering coke [14, 15], adding a sintering agent [16], and using mesophase powders [17, 18, 19].

The MCMB and mesophase powders exhibit self-sintering behavior through the heaviest fractions (β -resin) that fill the voids and create adhesion between the individual particles during pyrolysis. The heaviest fractions can be controlled by the choice of solvents. Thus, a manufacturing method of MCMB and mesophase powders requires a solvent-extraction process to remove the low-molecular-weight molecules, which causes swelling and increases the heaviest fractions. However, the

processing conditions of solvent extraction are very sensitive, and information on the solvent-extraction process is scarce [1, 2, 15, 20].

The sintering process of MCMB and mesophase powders was reported as consisting of two stages: a sintering step in the fluid phase in which the heaviest fractions fill the voids and cause adhesion, and a sintering step in the solid phase in which shrinkage and densification take place [11, 13, 19, 21]. Thus, petroleum residues have been mainly studied as raw materials for fluids since they allow easy control of the heaviest fractions.

In addition, MCMB and mesophase powder with the excellent self-sintering ability have a uniform mesophase structure. A molecule with a very high molecular weight is needed as an initiator of the mesophase structure, but a petroleum residue has few molecules with very high molecular weights. In this respect, it is difficult for the petroleum residues to form a uniform mesophase structure, and a solvent extraction process is necessary to remove the volatile matter, thus causing the expansion phenomenon. On the contrary, coal tar has a large amount of molecules with high molecular weights [22, 23, 24]. As such, it is expected that self-sintering carbon material can be produced without a solvent extraction process due to the characteristics of coal tar that can form a uniform mesophase structure.

In this study, self-sintering coke from coal tar has been developed to produce high strength, high density carbonized carbon blocks by using the two-stage heat treatments (1st and 2nd stage treatment) without the impregnation process. The fabrication process with the two-stage heat treatments to produce high-density carbon block using self-sintering coke from coal tar was first proposed in this study. Consequently, the purpose in this paper was to investigate the relationship between the two-step heat treatment conditions and mechanical properties according to the mesophase structure, insolubility analysis results, molecular weight distribution, amount of volatile matter and volume shrinkage analysis results and to optimize the manufacturing conditions for the two-stage heat treatments.

2. Experimental

2.1. Materials

The raw material for the fabrication of carbon block in this study was coal tar (POSCO Chem, Korea). The coal tar and tetrahydrofuran were mixed in a 1:1 ratio, which was then refined using a pressure filtering process. Then, the refined coal tar and tetrahydrofuran were separated by increasing the temperature to 80 °C via a rotary evaporator. Table 1 shows the elemental analysis (EA) and insolubility analysis of the refined coal tar. The ash in the refined coal tar was controlled to be less than 0.1 wt%.

Table 1. Insolubility and elemental analysis of the refined coal tar.

Ultimate analysis [wt %]				Proximate analysis [%]		
C	H	N	S	TI	QI	Ash
91.77	5.74	1.75	0.64	5.81	-	0.1

2.2. Manufacturing procedure

The manufacturing method of carbonized carbon blocks via the proposed two-stage heat treatments [25] is shown in Fig. 1. First, the coal tar was refined using the tetrahydrofuran as a solvent. The refined coal tar was heated at temperatures of 300, 330 and 360 °C for 1 and 3 h in the pressurized heat treatment (1st stage treatment). Here, the pressure of the 1st stage treatment was increased to about 9, 12, and 15 bar depending on the temperature, respectively. Second, the 1st stage heat-treated coal tar (1S-CT) was once again heated to 500 °C in the delayed coking system (2nd stage treatment) to produce coke. Third, 2nd stage heat-treated coke (2S-C) was pulverized, sieved to under 75 µm in size, and formed into small rectangular plates with the dimensions of 15×15×3 mm and 60×15×3 mm using cold compression with approximately 28 MPa, and this rectangular plates were prepared each of three times according to the manufacturing conditions. Finally, the green carbon blocks were carbonized at 1200 °C for 1 h at the heating rate of 1 °C/min. As-prepared carbonized carbon blocks were analyzed to determine the shore hardness, surface texture, and bending strength.

The 2S-C was named based on two factors: the temperature (300, 330 and 360 °C) and time (1 and 3 h) in the 1st stage treatment, and the time (1 and 3 h) in 2nd stage treatment. For example, 2S-C, which is prepared by the 1st stage treatment at 300 °C

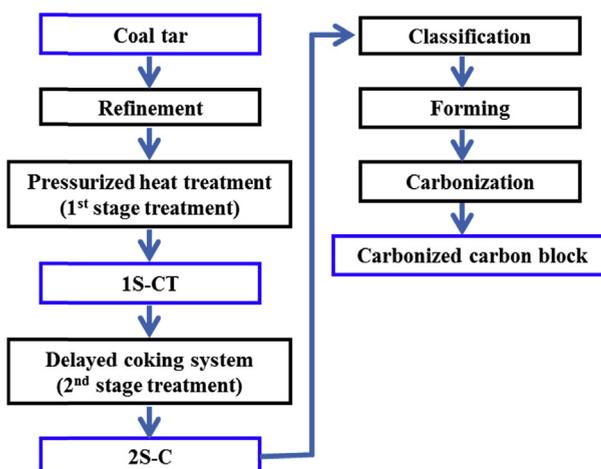


Fig. 1. Schematic diagram of two-stage heat treatments for manufacturing the carbon block from coal tar.

for 3 h and the 2nd stage treatment at 500 °C for 1 h, is denoted as C3003-1. The sample names of the carbon blocks are labeled as CB followed by the name indicating the used 2S-C.

2.3. Analytical tools

The composition of the refined coal tar and 2S-Cs were analyzed using an elemental analyzer (EA, TruSpec, LECO, USA). Insolubility was measured via quinoline insolubility (QI) and toluene insolubility (TI) based on ASTM D-2318 and ASTM D-4072, respectively. Polarization microscope analyses were carried out to characterize the optical microstructure of coke using polarized light microscopy (PLM, BX51M, Olympus, Japan). Thermogravimetric analysis (TGA, STA 409 PC, Netzsch, Germany) was performed to examine the weight loss at a rate of 5 °C/min at 900 °C under a nitrogen flow of 20 ml/min. The variation in the molecular weight was investigated using a matrix assisted laser desorption ionization-time of flight-mass spectrometer (MALDI-TOF-MS, Bruker Autoflex Speed TOF/TOF, Bruker, USA). The surface image of the carbon blocks was analyzed by scanning electron microscopy (SEM, JSM-6700F, JEOL Ltd., Japan). Hardness was examined using a constant loader (CL, CL-150, Kobunshi Keiki, Japan) and a shore hardness test (SH, Type-D, Kobunshi Keiki, Japan) according to the ASTM D-2240. The flexural strengths of the carbonized carbon blocks were measured using a universal testing machine (UTM, WL2100, WITHLAB, Korea) in accordance with the method for the three-point bending strength based on the ASTM C-1161.

3. Results and discussion

3.1. Heat-treatment conditions for self-sintering cokes

3.1.1. 1st stage treatment

The carbon, hydrogen, nitrogen and sulfur contents of the 1S-CTs prepared under different temperatures and times are shown in Table 2. The C/H ratio increased along

Table 2. Elemental analysis of the 1S-CTs at different heating temperatures and times.

1 st stage condition	C [wt%]	H [wt%]	N [wt%]	C/H ratio
300 °C 1h	91.20	5.74	0.72	1.32
330 °C 1h	92.43	5.72	0.79	1.35
360 °C 1h	92.70	5.65	0.97	1.37
300 °C 3h	92.75	5.46	0.76	1.42
330 °C 3h	93.13	5.31	0.82	1.46
360 °C 3h	92.96	5.62	0.97	1.38

with the increases of the reaction temperature and time. The C/H of the 1S-CT treated at 300 °C for 3 h is higher at around a 0.1 ratio than that of the 1S-CT treated at 300 °C for 1 h. Additionally, the C/H ratio of the 1S-CT treated at 330 °C for 3 h is higher than that of the 1S-CT treated at 300 °C for 1 h. This result implies that the components with low molecular weights are decomposed and polymerized into polycyclic aromatic hydrocarbons (PAHs), which have a higher molecular weight. However, the C/H ratio of the 1S-CT treated at 330 °C for 3 h was higher than that of the 1S-CT treated at 360 °C for 3 h. This result indicates that the aromaticity was broken rapidly at the reaction temperature of 360 °C under around 15 bar [26, 27]. Additionally, it demonstrates that the distribution of the molecular weights in the refined coal tar can be controlled by the 1st stage treatment. Fig. 2 shows the TI and QI of the 1S-CTs. When condensation polymerization was active due to increasing the reaction temperature, the QI and TI also increased. The change in the QI was approximately 10 wt% higher compared to the TI. Additionally, the 1S-CTs treated at 360 °C for 1 h and 360 °C for 3 h had the same QI.

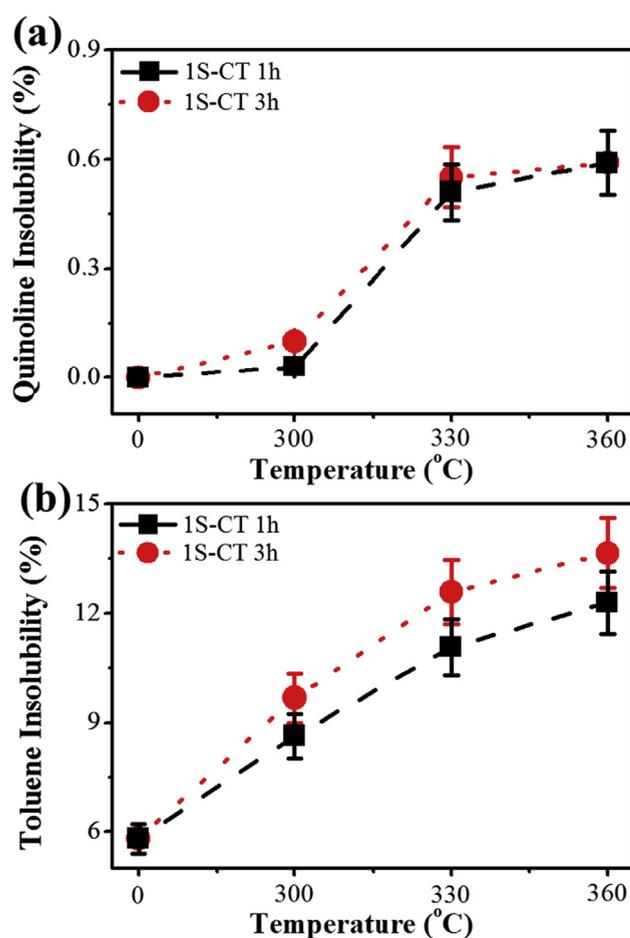


Fig. 2. Effect of the reaction temperature after the 1st stage treatment for 1 and 3 h on the QI and TI of 1S-CT: (a) QI and (b) TI.

From the Table 2 and Fig. 2, the C/H ratio of the 1S-CT treated at 360 °C for 3 h was 0.08 lower than that of the 1S-CT treated at 330 °C for 3 h; however, the TI was higher and the QI was similar in the above mentioned conditions. In other words, these results indicate that when the 1S-CT is treated at 360 °C for 3 h, the amount of high molecular weight components corresponding to TI and QI and the amount of low molecular weight components simultaneously increase [26, 28].

Fig. 3 shows the molecular weight distribution and the molecular weight ratio using the MALDI-TOF-MS spectra. In Fig. 3(b), the molecular weight range is divided into 15 ranges using the MALDI-TOF-MS spectra. The molecular weight ratio of the 1S-CTs treated at 300 °C and 360 °C in the 1st stage treatment was the highest ratio from 2-4 and 6–15, respectively [29, 30]. In particular, the molecular weight ratio in Range 1 increased proportionally to the reaction temperature from 330 °C to 360 °C. Thus, Fig. 3 suggests that reaction temperatures above 330 °C dramatically increase the low molecular weight components of the 1S-CT, as noted in Table 2 and Fig. 2.

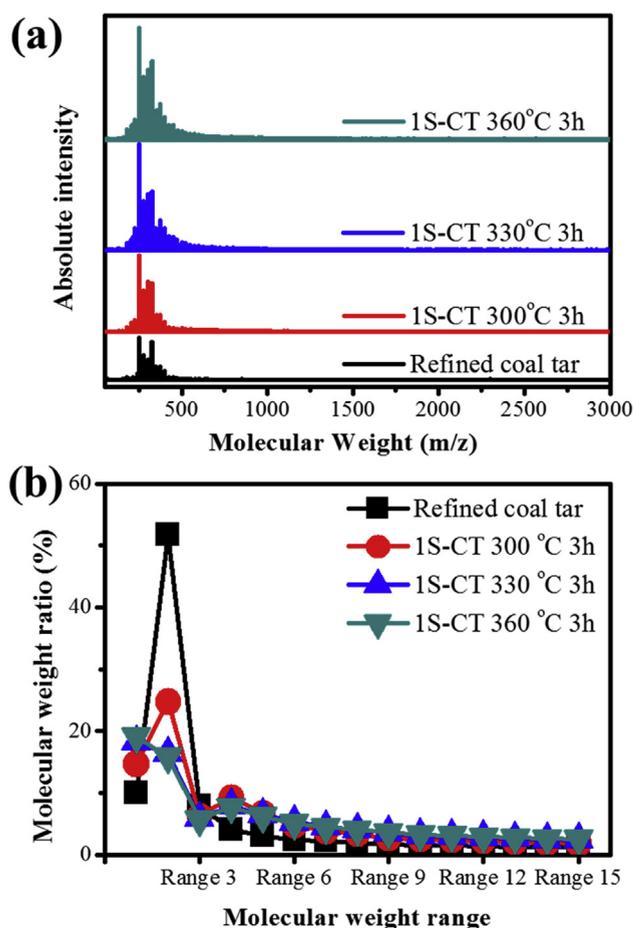


Fig. 3. MALDI-TOF-MS spectra (a) and molecular weight ratio in the molecular weight range of from 1 to 15 (b).

3.1.2. 2nd stage treatment

Table 3 summarizes the names of the samples and their respective solubility analyses according to the 2S-C manufacturing conditions. When the reaction conditions of the 2nd stage treatment were 500 °C for 1 h, C3301-1 exhibited increased QI and TI of approximately 10 wt% more than that of C3001-1. However, the QI and TI of C3601-1 drastically decreased. In addition, ‘C3301-1 and C3303-1’ and ‘C3301-3 and C3303-3’ showed that the QI and TI produced in the 2nd stage treatment decreased as the reaction time in the 1st stage treatment increased from 1 to 3 h at 330 °C. This result indicates that the 1S-CTs, which were processed at a temperature in excess of 330 °C in the 1st stage treatment, suppressed the generation of the high molecular weight components corresponding to QI and TI in the 2nd stage treatment [14]. All of the 2S-C exhibited a uniform mesophase structure, as shown in Fig. 4.

The weight loss as measured by the thermogravimetric analyses of the 2S-Cs are presented in Fig. 5. A swelling phenomenon was observed in the carbonized carbon blocks manufactured from C3303-1 and C3603-1 that contained more than 15 wt% volatile matter. The carbon blocks that were made of 2S-Cs with less than 15 wt% volatile matter retained a rectangular shape after carbonization. C3301-3, C3601-3, C3003-3 and C3603-3, which were processed for 3 hours in the 2nd stage treatment, exhibited a total weight loss of less than 10 wt%, and the volume shrinkage was less than 20 wt%. Additionally, the carbon blocks

Table 3. Insolubility analysis and naming of 2S-C according to each manufacturing condition.

Sample Name.	Condition				Content [wt%]		
	1 st stage treatment		2 nd stage treatment		Coking yield	QI	TI
	Temp. [°C]	Time [h]	Temp. [°C]	Time [h]			
C3001-1	300	1	500	1	-	85.5	87.5
C3301-1	330	1	500	1	-	95.6	95.7
C3601-1	360	1	500	1	46.1	89.4	90.4
C3003-1	300	3	500	1	45.6	80.2	82.2
C3303-1	330	3	500	1	47.1	81.9	84.0
C3603-1	360	3	500	1	50.5	77.6	80.4
C3001-3	300	1	500	3	44.8	89.3	89.6
C3301-3	330	1	500	3	43.1	97.0	97.6
C3601-3	360	1	500	3	43.2	99.5	99.6
C3003-3	300	3	500	3	40.2	99.6	99.7
C3303-3	330	3	500	3	47.3	92.9	93.5
C3603-3	360	3	500	3	44.5	99.2	99.3

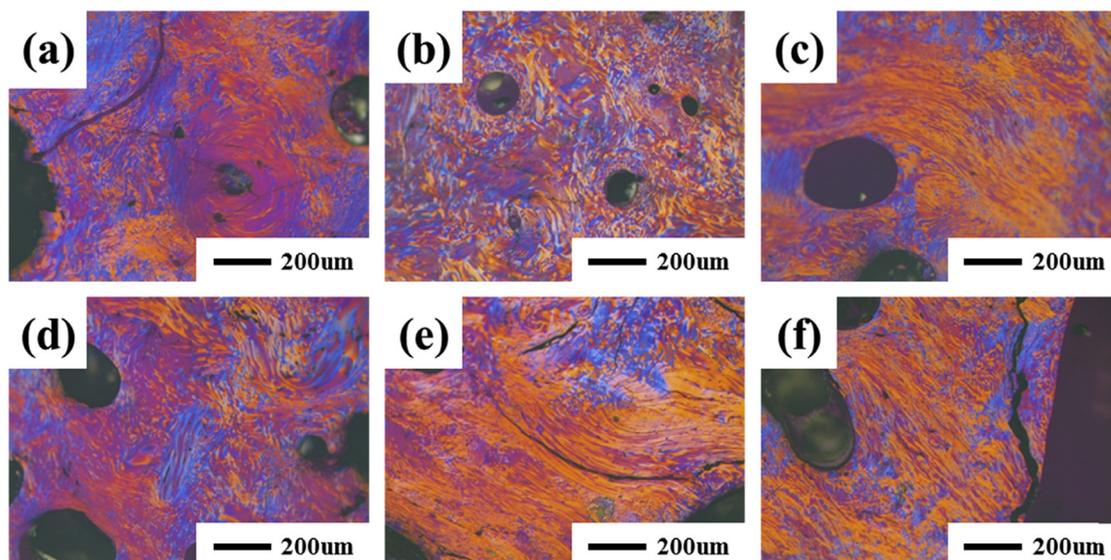


Fig. 4. Polarized-light micrograph of 2S-C: (a) C3001-1, (b) C3301-1, (c) C3601-1, (d) C3003-1, (e) C3303-1, and (f) C3603-1.

that were prepared from 2S-Cs with less than 10 wt% volatile matter were easily squashed before carbonization.

3.2. Mechanical properties of carbonized carbon blocks

The slopes in the Fig. 5 are clearly divided into 3 sections: over 620 °C, 450–620 °C and 150–450 °C [1, 11, 21]. The weight loss ratio from 150 °C to 620 °C of the 2S-Cs that manufactured at 500 °C for 1 h in the 2nd stage treatment was significantly greater than that of the 2S-Cs that was manufactured at 500 °C for 3 h in the 2nd stage treatment. The total weight loss of the 2S-Cs that were manufactured at 500 °C for 3 h was drastically decreased to less than 10 wt% except for C3001-3 and C3303-3.

Table 4 shows that optimal conditions of the 2nd stage treatment to produce the high density carbon block are 500 °C for 1 h. Thus, CB3003-1 exhibited an apparent density of 1.46 g/cm³, which was higher than the reported density of approximately 1.40 g/cm³ [31]. Cracks with the size of approximately 100–500 μm were found in CB3601-1, as shown in the Fig. 6(a). CB3001-1 containing less than about 15% volatile matter showed cracking and swelling phenomena as presented in Fig. 6(b). The CB3603-1 was so inflated that the original shape of the rectangular plate had completely disappeared after carbonization (Fig. 6(c)). CB3001-1 exhibited the best mechanical properties among the CB3001-1, CB3301-1 and CB3601-1 samples. CB3003-1 shows the highest flexural strength of 69.2 MPa among the CB3003-1, CB3303-1 and CB3603-1 samples. In addition, the flexural strength of CB3003-1 in this study was higher than the previously reported value of approximately 60 MPa [32].

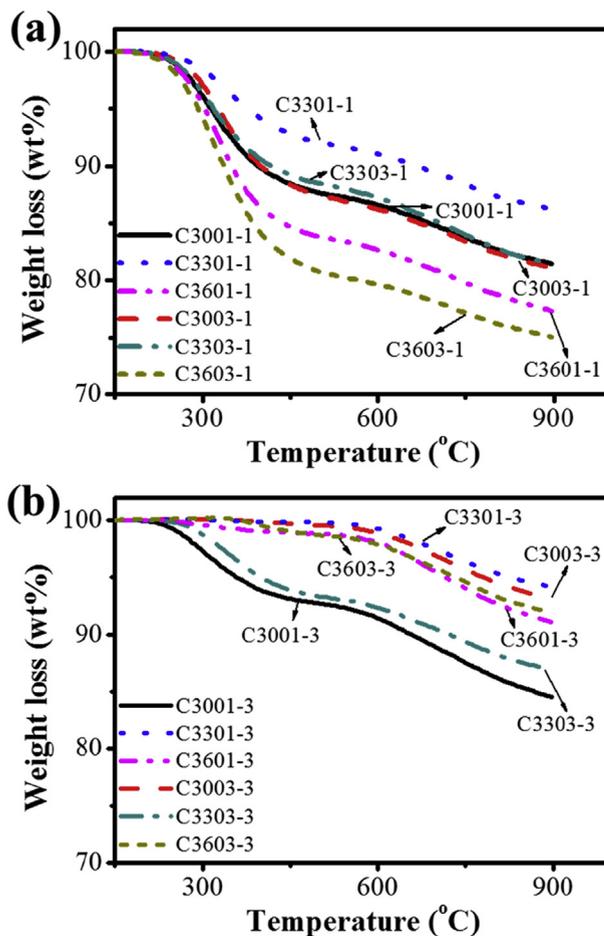


Fig. 5. TGA curve of 2S-Cs: (a) after being manufactured at 500 °C for 1 h in the 2nd stage treatment and (b) after being manufactured at 500 °C for 3 h in the 2nd stage treatment.

From these results, it was determined that the swelling phenomenon occurs in carbon blocks that are manufactured from 2S-Cs that contains over 15 wt% volatile matter. Heat-treatment at 300 °C for 3 h is the optimal conditions for the self-sintering process to achieve the best properties. Furthermore, it can be inferred that the molecular weight ratio of range 1 and ranges 2–4, as mentioned in Fig. 3, are important factors for improving the mechanical properties of carbon blocks.

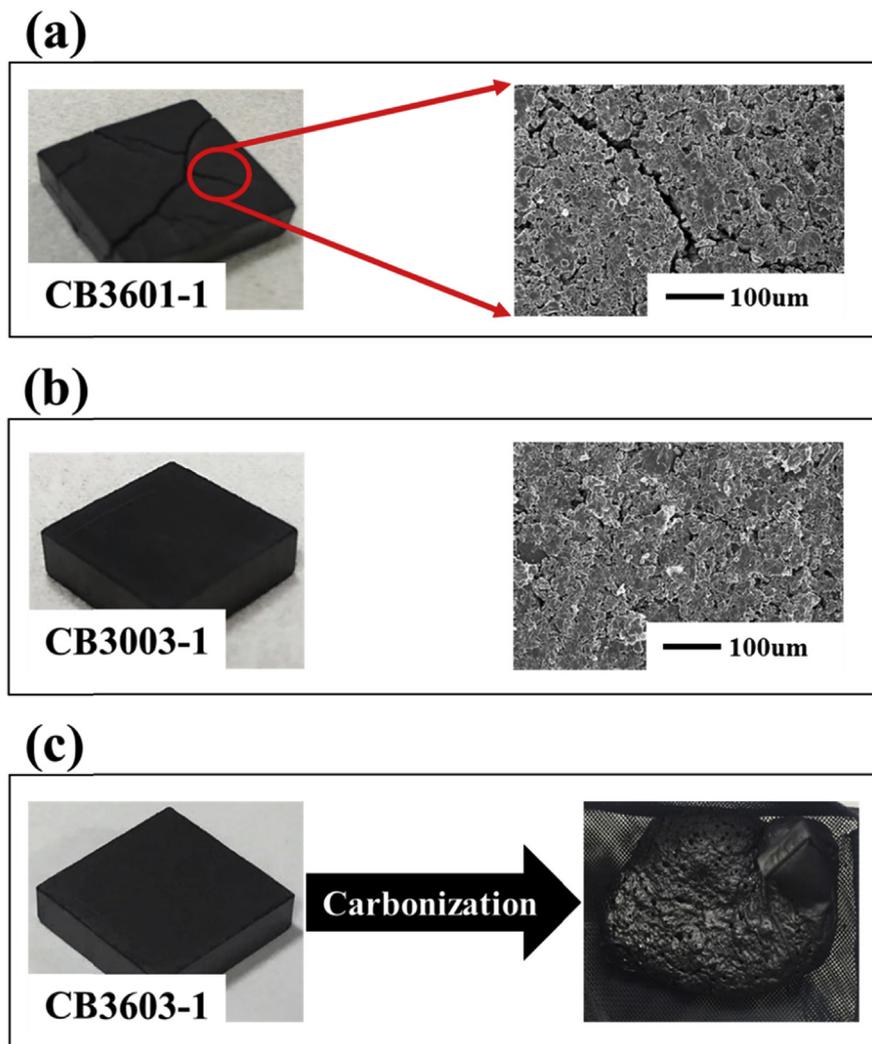
3.3. Morphological properties based on volatile matter content

The SEM images of the surfaces of the carbon blocks carbonized at 1200 °C are shown in Fig. 7. In Fig. 7(a, c and d), the particle shapes are relatively difficult to find. In Fig. 7(b, e and f), there are clear small cracks between the particles. A substantial amount of cracks between 100 and 500 μm is observed in Figs. 6(a) and 7(c).

Fig. 8 shows the results for the weight loss by dividing the treatment temperatures in the carbonization process into three ranges. CB3001-1 and CB3003-1 had a

Table 4. Characteristics of the carbonized carbon blocks manufactured from 2S-C.

Sample Name.	Weight loss ratio [wt%]				Shore hardness [Hs]	Flexural strength [MPa]	Volume shrinkage [%]	Bulk density [g/cm ³]
	Total ratio	From 150-450 [°C]	From 450-620 [°C]	From 620-1200 [°C]				
CB3001-1	23.7	11.6	2.2	9.9	63	28.0	35.9	1.362
CB3301-1	18.0	7.2	2.0	8.7	71	3.3	25.3	1.217
CB3601-1	20.5	15.3	2.3	2.9	65	1.6	21.3	1.120
CB3003-1	24.3	11.6	2.9	9.8	72	69.2	40.4	1.466
CB3303-1	23.4	10.8	3.0	9.6	72	17.7	33.7	1.324
CB3603-1	-	18.1	2.5	-	-	-	-	-
CB3303-3	14.4	6.1	1.8	6.5	76	22.9	29.8	1.315

**Fig. 6.** Change of carbon block after carbonization: (a) SEM image of CB3601-1 after carbonization, (b) SEM image of CB3003-1 after carbonization, (c) photo of CB3603-1, before and after carbonization.

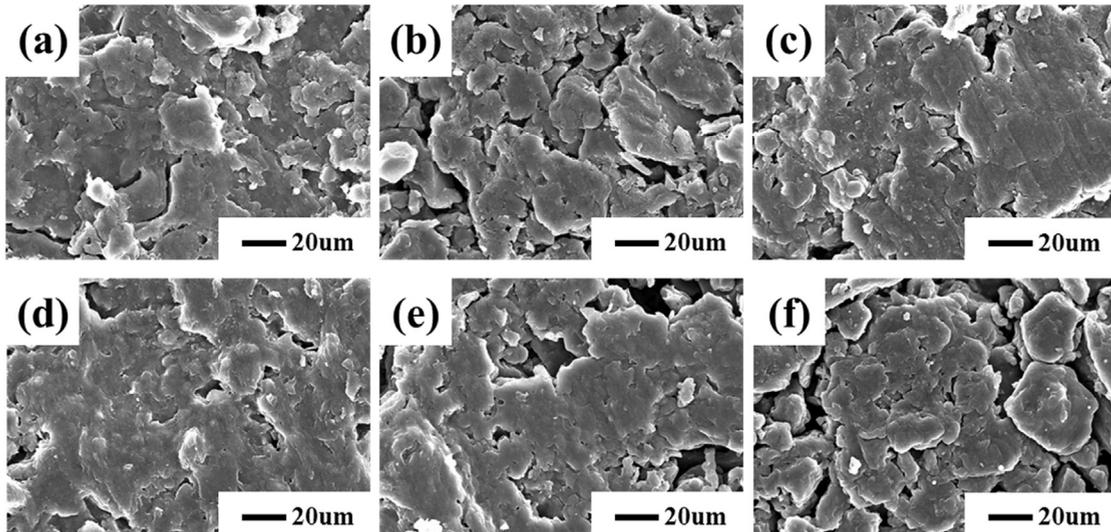


Fig. 7. SEM images of carbonized carbon blocks: (a) CB3001-1, (b) CB3301-1, (c) CB3601-1, (d) CB3003-1, (e) CB3303-1, and (f) CB3303-3.

significant difference in the amount of weight loss in the 450 °C–620 °C temperature range, and CB3003-1 and CB3303-1 differed in their weight losses in the 150 °C–450 °C range. The quantity of the weight loss from 150 °C to 620 °C is thought to be an important factor that affects the mechanical property of the bending strength. The small cracks among coke particles, which reduce mechanical properties, were more pronounced when the volatile matter at 450–620 °C were smaller, as shown in Fig. 7. However, comparing the results for CB3301-1 and CB3303-3 in Table 4, the flexural strength of CB3303-3 was better. This result is due to the occurrence of small cracks that reduce the flexural strength of the carbon blocks when the

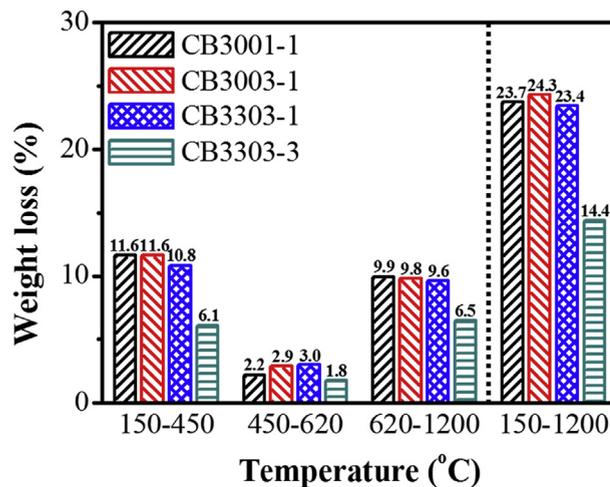


Fig. 8. Weight loss of the carbon blocks at reaction temperatures in the range of 150–450 °C, 450–620 °C, 620–1200 °C and 150–1200 °C during carbonization.

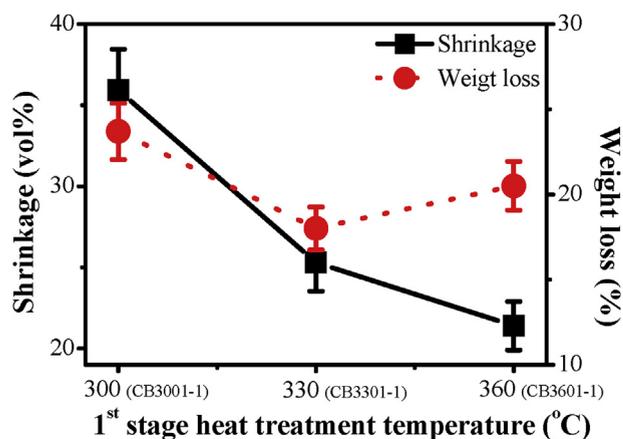


Fig. 9. Effect of the 1st stage treatment temperature on shrinkage and weight loss.

volatile matter evaporates in the temperature range of 620–1200 °C where the degree of volume shrinkage decreases [11, 22, 33].

Fig. 9 illustrates the optimum conditions of the 1st stage treatment for manufacturing high density carbonized carbon blocks based on the shrinkages and weight losses of CB3001-1, CB3301-1 and CB3601-1. Additionally, Fig. 9 showed a decrease in the volume shrinkage as the reaction temperature of the 1st stage treatment increased. In addition, the weight loss ratio of CB3601-1 was greater than that of CB3301-1 because the QI and TI of 2S-Cs were reduced by the decomposition of high molecular weight components at a reaction temperature of the 1st stage treatment above 330 °C. Also, it has been reported that the coke with mesophase structure is easily formed when the amount of H is small [14]. According to analysis above, it was determined that the amount of high molecular weight produced in the 1st stage treatment decreased the volume shrinkage and weakened the density and mechanical properties.

4. Conclusion

Self-sintering coke was developed from coal tar and used as raw material to produce high-density carbonized carbon blocks. The C/H ratio of the 1S-CTs treated at 330 °C for 3 h was the highest. As the reaction temperature increased during the 1st stage treatment, the QI and TI of the 1S-CTs increased. The MALDI-TOF-MS spectra showed that the low molecular weight components of the 1S-CTs significantly increased at reaction temperatures above 330 °C. All of the self-sintering coke prepared via the two-stage heat treatment from coal tar showed a uniform mesophase structure.

The carbon blocks manufactured from 2S-Cs containing over 15 wt% volatile matter at 150–450 °C were swollen. Furthermore, the small cracks in the carbonized

carbon blocks made of 2S-Cs containing less than 2 wt% volatile matter at 450–620 °C were distinctly increased. The weight loss from 150–620 °C in the carbonization process was found to be due to active volume shrinkage, resulting in a high density. The amount of weight loss from 620–1200 °C in the carbonization process was identified to be a factor that reduced the mechanical properties. Thus, the optimum conditions of the 1st stage treatment and 2nd stage treatment were confirmed to be 300 °C for 3 h and 500 °C for 1 h, respectively.

Declarations

Author contribution statement

Ui-Su Im: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Jiyoung Kim: Analyzed and interpreted the data.

Byung-Rok Lee: Analyzed and interpreted the data.

Dong-Hyun Peck: Contributed reagents, materials, analysis tools or data.

Doo-Hwan Jung: Conceived and designed the experiments.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

- [1] M.-D. Fang, W.-L. Tseng, J.-J. Jow, C.-M. Lee, H.-R. Chen, M.-S. Wu, et al., Improving the self-sintering of mesocarbon-microbeads for the manufacture of high performance graphite-parts, *Carbon* (50) (2012) 906–913.

- [2] M.R. Delpont, H. Badenhorst, Production of a self-adhering mesophase powder from anthracene oil for low pressure forming of graphite artefacts, *J. Mater. Sci.* 51 (2016) 6309–6318.
- [3] H.-L. Guo, P. Su, X. Kang, S.-K. Ning, Synthesis and characterization of nitrogen-doped graphene hydrogels by hydrothermal route with urea as reducing-doping agents, *J. Mater. Chem.* (1) (2013) 2248–2255.
- [4] J. Xiao, F. Li, Q. Zhong, J. Huang, B. Wang, Y. Zhang, Effect of high-temperature pyrolysis on the structure and properties of coal and petroleum coke, *J. Anal. Appl. Pyrolysis* 117 (2016) 64–71.
- [5] B. März, K. Jolley, T.J. Marrow, Z. Zhou, M. Heggie, R. Smith, et al., Mesoscopic structure features in synthetic graphite, *Mater. Des.* 142 (2018) 268–278.
- [6] P.R. Choi, S.-G. Kim, J.C. Jung, M.-S. Kim, High-energy-density activated carbon electrode for organic electric-double-layer-capacitor using carbonized petroleum pitch, *CARBON LETT* (22) (2017) 70–80.
- [7] J.H. Kim, I. Rhee, Y.C. Jung, S. Ha, Y.A. Kim, Optical sensitivity of DNA-dispersed single-walled carbon nanotubes within cement composites under mechanical load, *CARBON LETT* (24) (2017) 90–96.
- [8] C. Du, P. Ming, M. Hou, J. Fu, Y. Fu, X. Luo, et al., The preparation technique optimization of epoxy/compressed expanded graphite composite bipolar plates for proton exchange membrane fuel cells, *J. Power Sources* (195) (2010) 5312–5319.
- [9] K. Shen, Z.-H. Huang, K. Hu, W. Shen, S. Yu, J. Yang, et al., Advantages of natural microcrystalline graphite filler over petroleum coke in isotropic graphite preparation, *Carbon* (90) (2015) 197–206.
- [10] X. Chen, Y. Lu, X. Zhang, F. Zhao, The thermal and mechanical properties of graphite foam/epoxy resin composites, *Mater. Des.* 40 (2012) 497–501.
- [11] K. Shen, Z.-H. Huang, J. Yang, W. Shen, F. Kang, Effect of oxidative stabilization on the sintering of mesocarbon microbeads and a study of their carbonization, *Carbon* (49) (2011) 3200–3211.
- [12] M.-D. Fang, J.J. Jow, Y.H. Yeh, H.R. Chen, M.S. Wu, C.W. Kuo, et al., Improving the sintering behavior of mesocarbon-microbeads for the manufacture of high quality carbon products using a joint promoter comprising carbon black and glycidyl methacrylate, *Mater. Chem. Phys.* 149 (2015) 400–404.

- [13] B. Wu, Z. Wang, Q.M. Gong, H.H. Song, J. Liang, Fabrication and mechanical properties of in situ prepared mesocarbon microbead/carbon nanotube composites, *Mater. Sci. Eng.* 487 (2008) 271–277.
- [14] A. Guo, X. Lin, D. Liu, X. Zhang, Z. Wang, Investigation on shot-coke-forming propensity and controlling of coke morphology during heavy oil coking, *Fuel Process. Technol.* 104 (2012) 332–342.
- [15] D. Kocaefe, A. Sarkar, S. Das, S. Amrani, D. Bhattacharyay, D. Sarkar, et al., Review of different techniques to study the interactions between coke and pitch in anode manufacturing, in: B.A. Sadler (Ed.), *Light Metals 2013*, Springer International Publishing, Cham, 2016, pp. 1045–1050.
- [16] K. Shen, Z.-H. Huang, J. Yang, G. Yang, W. Shen, F. Kang, The use of asphalt emulsions as a binder for the preparation of polycrystalline graphite, *Carbon* (58) (2013) 238–241.
- [17] Y. Cheng, L. Yang, T. Luo, C. Fang, J. Su, J. Hui, Preparation and characterization of mesophase pitch via Co-carbonization of waste polyethylene/petroleum pitch, *J. Mater. Sci. Technol.* 31 (2015) 857–863.
- [18] Y. Zhao, Z. Liu, H. Wang, J. Shi, J. Zhang, Z. Tao, et al., Microstructure and thermal/mechanical properties of short carbon fiber-reinforced natural graphite flake composites with mesophase pitch as the binder, *Carbon* (53) (2013) 313–320.
- [19] H. Li, H. Li, J. Lu, X. Zhang, K. Li, Effects of air oxidation on mesophase pitch-based carbon/carbon composites, *Carbon* (49) (2011) 1416–1422.
- [20] S.-M. Lee, D.-S. Kang, J.-S. Roh, Bulk graphite: materials and manufacturing process, *CARBON LETT* (16) (2015) 135–146.
- [21] U.-S. Im, J. Kim, B.-R. Lee, D.-H. Peck, D.-H. Jung, Improving the mechanical properties of a high density carbon block from mesocarbon microbeads according to oxidative stabilization, *Sci. Rep.* (8) (2018) 11064.
- [22] H. Hsien-Lin, K. Tse-Hao, K. Wen-Shyong, C. Sung-Te, Influence of adding Mesocarbon Microbeads into C/C composites on microstructure and properties during carbonization, *J. Appl. Polym. Sci.* 102 (2006) 3102–3110.
- [23] Q. Shi, N. Pan, H. Long, D. Cui, X. Guo, Y. Long, et al., Characterization of middle-temperature gasification coal tar. Part 3: molecular composition of acidic compounds, *Energy Fuels* (27) (2013) 108–117.
- [24] M. Sun, X.-X. Ma, Q.-X. Yao, R.-C. Wang, Y.-X. Ma, G. Feng, et al., GC-MS and TG-FTIR study of petroleum ether extract and residue from low temperature coal tar, *Energy Fuels* (25) (2011) 1140–1145.

- [25] U.-S. Im, J. Kim, S.H. Lee, B.-R. Lee, D.-H. Peck, D.-H. Jung, Effects of two-stage heat treatment on delayed coke and study of their surface texture characteristics, *JOM* (69) (2017) 2460–2466.
- [26] J. Han, H. Kim, The reduction and control technology of tar during biomass gasification/pyrolysis: an overview, *Renew. Sustain. Energy Rev.* (12) (2008) 397–416.
- [27] J.S. Cha, S.H. Park, S.-C. Jung, C. Ryu, J.-K. Jeon, M.-C. Shin, et al., Production and utilization of biochar: a review, *J. Ind. Eng. Chem.* 40 (2016) 1–15.
- [28] A.P. Petrovykh, A.L. Abaturov, I.V. Moskalev, D.M. Kisel'kov, R.M. Yakushev, Heat treatment of anthracene oil under pressure, *Coke Chem.* (59) (2016) 296–308.
- [29] B.-J. Kim, Y. Eom, O. Kato, J. Miyawaki, B.C. Kim, I. Mochida, et al., Preparation of carbon fibers with excellent mechanical properties from isotropic pitches, *Carbon* (77) (2014) 747–755.
- [30] Q.A. Tran, R. Stanger, W. Xie, N. Smith, J. Lucas, T. Wall, Linking thermo-plastic development and swelling with molecular weight changes of a coking coal and its pyrolysis products, *Energy Fuels* (30) (2016) 3906–3916.
- [31] C. Zhou, P.J. McGinn, The effect of oxygen on the processing of mesocarbon microbeads to high-density carbon, *Carbon* (44) (2006) 1673–1681.
- [32] K. Shen, Z.-H. Huang, W. Shen, J. Yang, G. Yang, S. Yu, et al., Homogenous and highly isotropic graphite produced from mesocarbon microbeads, *Carbon* (94) (2015) 18–26.
- [33] Y. Cheng, T. Li, C. Fang, P. Liu, R. Yu, J. Hu, In situ preparation and mechanical properties of CNTs/MCMBs composites, *Comp. Part B* (47) (2013) 290–297.