Improving the mechanical properties of a high density carbon block from mesocarbon microbeads according to oxidative stabilization

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In this study, a high density carbon block without binder was manufactured by mesocarbon microbeads (MCMB) from coal tar pitch. To develop the high density carbon block without a binder, MCMBs were oxidized at different levels of temperature. To verify the effect of oxygen content in the carbonized carbon block (CCB), an elementary analysis (EA) and X-ray photoelectron spectroscopy (XPS) were performed. The morphological and mechanical properties of the CCBs were investigated by using scanning electron microscopy (SEM), a shore hardness test, and a flexural strength evaluation. The results revealed that the oxygen content increased with stabilization temperature and the physical properties of the CCBs were considerably improved via oxidative stabilization. Small cracks between MCMB particles were observed in the CCBs that were stabilized over 250 °C. From the results of this study, the CCB from MCMBs stabilized at 200 °C for 1 h showed optimum mechanical properties and high density.

High-density and high-strength isotropic carbon blocks are materials that are utilized in modern high-tech industries due to their low electrical resistance and excellent mechanical properties at high temperatures1. In particular, high density and high strength isotropic carbon blocks are used as adequate materials in nuclear reactors, electrical contacts, electrodes, refractories, crucibles for chemicals, and semiconductors2–4.

High density isotropic carbon blocks have been produced by several methods. One method is to use fillers such as coke and binder pitch. This method entails repetition of calcination and impregnation, which leads to long manufacturing time. To reduce the manufacturing time, self-sinterable coke or mesophase pitch has been used. These raw materials are formed and carbonized via a cold isostatic pressing method without a binder in order to shorten the process time5–8. Also, MCMBs have been utilized as raw materials by isostatic pressing and carbonization. These alternative methods reduced the processing cost and made the workforce efficient. Among three alternatives, the method using MCMBs is especially easy to produce high density due to the spherical shape of the MCMBs. In particular, since 1973, the MCMBs has been frequently used by many researchers as precursors of high-density high-strength carbon blocks and rechargeable Li-ion batteries9–17.

The effect of oxidation stabilization on mesophase pitch has been reported in several studies18–21. The reported mechanism of the oxidative stabilization is explained in three steps. Initially, methylene hydrogens are reduced. Aldehyde ketone and carboxylic acid functionality are subsequently produced. Finally, ester and anhydride functionality are increased18. These oxidation mechanisms are used for different purposes in different application fields such as MCMBs, carbon fibers, isotropic pitch, and graphene.

Oxidative stabilization in the field of carbon fiber increases the carbonization yield and yields excellent mechanical properties19,20. When producing isotropic pitch having high aromatic carbon content, air blowing is applied by exploiting an oxidation mechanism18,20,23,24. The oxidation process is also used in the graphene process developed by Hummers25–27. The oxidative process was implemented for effective exfoliation of graphene oxide in Hummers method, and this approach has the disadvantage restacking occurs easily during reduction at about
700–1000 °C due to a π–π interaction. Also, the effect of oxidative stabilization on sintering of MCMBs during carbonization was studied in according with light and strong oxidative conditions. The oxidative stabilization in MCMB resulting in the transgranular and intergranular cracks was investigated.

In the present study, oxygen content produced via oxidative stabilization was used as an additive to facilitate carbon-carbon bonding so that high-density and high-strength isotropic carbon blocks without a binder were developed from MCMBs prepared from coal tar pitch. The correlation between the carbon block shrinkage, the time of crack formation, and the weight loss ratio according to the temperature range were investigated from the difference of added oxygen ratio. The swelling phenomenon was inhibited by increasing the aromatic carbon content and the amount of volatile matter was controlled. Optimum conditions to improve the mechanical properties were finally studied.

Results and Discussion

Preparation of MCMBs with a uniform size. The CTPs produced at five heat treatment temperatures formed different mesophases, as shown in Fig. 1. The mesophase structure became clear in accordance with the increase of heat treatment temperature. The heat-treated CTP containing mesophase spherules started to appear at 400 °C and the mesophase pitch of complete anisotropic development was exhibited at temperatures above 480 °C. Uniform mesophase spherules less than 75 μm for the production of high density, high strength carbon blocks were observed under heat treatment of 430 °C. Figure 2(a) shows the average particle diameter of the mesophase spherules prepared at 430 °C. All of the mesophase spherules were smaller than 40 μm and the average particle diameter was 13.53 μm. Figure 2(b) shows a SEM image of extracted MCMBs from the CTP shown in Fig. 1(b). Uniformity of around 14 um size was verified via the SEM image, and a rough surface of the MCMBs was confirmed. The yield of MCMBs treated at a growth temperature of 430 °C is over 65% after extraction by tetrahydrofurane (THF).

MCMB properties with oxidative stabilization. The results of the elementary analysis of the stabilized and raw MCMBs are summarized in Table 1. As the stabilization temperature was increased, the carbon ratio decreased and the ratio of other components increased. Since a representative element of the other components is the oxygen content, it is considered that the oxygen content also increased as the stabilization temperature was increased. The hydrogen ratio decreased sharply at stabilization temperature above 200 °C. The C/H ratios were 3.69, 2.35, and 2.95 for Raw MCMBs, S-MCMBs-200, and S-MCMBs-300, respectively. From these results, it appears that the aromaticity decreased and increased at the point based on the stabilization temperature of 200 °C. Oxygen content depending on oxidation stabilization temperature determined via X-ray photoelectron spectroscopy (XPS) is shown in Fig. 3(a). The five functional groups analyzed were C=O, C-O, C=O, O-C=O, C-OH, and H2O (chemisorbed O2 or adsorbed H2O) at 530.6, 532.4, 533.8, 534.3, and 563.3, respectively. With increasing temperature of oxidation stabilization, the functional groups of C=O and O=C=O were increased and H2O was removed. S-MCMBs-200 showed more C-OH content than the other samples. Thus, it can be concluded that the hydrogen ratio shown in Table 1 increases or decreases at the stabilization temperature of 200 °C due to the formation of -OH functional groups.

Mechanical properties of carbonized carbon blocks. Table 2 shows the mechanical properties of carbonized carbon blocks. The mechanical properties of the carbonized carbon block from Raw MCMBs were not analyzed due to the swelling phenomenon. CCB-200 exhibited the highest mechanical properties with a bending strength of 116 Mpa, a volume shrinkage of 31.51%, and a bulk density of 1.57 g/cm3. In the previously reported paper, the density of carbonized carbon block from MCMBs without binder was reported to be over 1.7 g/
cm³, and the flexural strength was noted to be about 90 MPa. Thus, the density of CCB-200 was lower than that of the previous report, but it showed higher flexural strength. In addition, as the content of oxygen increased, the flexural strength was expected to increase continuously, but it tends to decrease when it exceeds a certain amount. From these results, although addition of oxygen has the advantage of restacking the carbon during the carbonization process, it shows that the oxygen content, which involved above a certain amount, has the disadvantage of reducing the flexural strength and decreasing in density.

Correlation between thermal and morphological properties. Figure 3(b) shows the results of the thermogravimetric analysis of the stabilized MCMBs. There are three ranges based on the slope where the weight loss rate varies. The weight loss rate divided into three ranges from 30 °C to 1200 °C is indicated in Table 3. The fixed carbon of S-MCMBs-150 and S-MCMBs-200 and that of S-MCMBs-250 and S-MCMBs-300 is approximately 0.3% and 1.6% higher than that of Raw MCMBs, respectively. However, the amount of remaining total weight treated in S-MCMBs-250 and S-MCMBs-300 is around 1% less than that of Raw MCMBs, as shown in Table 3. The amount of volatile matter from 30 °C to 600 °C is highest for Raw MCMBs and S-MCMBs-150 whereas S-MCMBs-300 has the largest amount of volatile matter from 850 °C to 1200 °C. From these results, it can be seen that a large amount of oxygen content was released from 850 °C to 1200 °C.

Figure 4 shows the morphological analysis of CCB according to the stabilization process conditions. The swelling phenomenon can be observed in Fig. 4(a,b). Hence, the amount of weight loss from 30 °C to 600 °C is considered to be the main factor responsible for the swelling phenomenon. The borderslines among MCMBs particles in Fig. 4(d,e) showing significant weight loss from 850 °C to 1200 °C were distinctly observed. Also, weight loss from 850 °C to 1200 °C was reported as the temperature range as having the smallest volume shrinkage. It is thus concluded that small cracks among MCMBs particles are mainly caused by the amount of weight loss from 850 °C to 1200 °C. Consequently, we verified that oxidative stabilization treated above 250 °C weakens the mechanical

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**Table 1.** Elementary analysis of MCMBs according to stabilized condition.

| Samples         | Elemental analysis [wt%] | Ratio of atoms C/H |
|-----------------|--------------------------|---------------------|
| Raw MCMBs       | 96.15 2.17 1.32 0.36 3.69 | C/H                |
| S-MCMBs-150     | 95.17 3.13 1.05 0.65 2.53  |
| S-MCMBs-200     | 94.10 3.34 0.78 1.78 2.35  |
| S-MCMBs-250     | 92.80 2.79 0.84 3.57 2.77  |
| S-MCMBs-300     | 91.83 2.59 1.14 4.44 2.95  |
properties resulting from the amount of the volatile matter at a certain temperature range from 850 °C to 1200 °C increased by the amount of oxygen contents.

Based on the above results, it is reasonable to conclude that sintering, as illustrated in Fig. 5, occurs during the carbonization process. The first step shows oxygen content in CCB according to the XPS results. The second step from 30 °C to 600 °C in the carbonization process is explained by abundant volatile matter, considerable volume shrinkage, and the swelling phenomenon of the carbon block manufactured from Raw MCMBs. The final step presents that the weight loss at a temperature range from 850 °C to 1200 °C produced small cracks with a small volume shrinkage.

![Figure 3. Characteristic analysis of Stabilized MCMBs. (a) XPS spectra of Raw MCMBs, S-MCMBS-200, S-MCMBS-250, and S-MCMBS-300. (b) Thermogravimetric analysis of Raw and Stabilized MCMBs in nitrogen atmosphere at a heating rate of 5 °C/min.](image)

| Sample Name | Shore hardness [HS] | Bending strength [Mpa] | Volume shrinkage [%] | Bulk density [g/cm³] |
|-------------|---------------------|------------------------|----------------------|---------------------|
| CCB-150     | 90                  | —                      | 20.22                | 1.35                |
| CCB-200     | 94                  | 116                    | 31.51                | 1.57                |
| CCB-250     | 85                  | 43                     | 29.78                | 1.48                |
| CCB-300     | 85                  | 14                     | 29.54                | 1.42                |

Table 2. Mechanical properties of carbonized carbon blocks from MCMBs.

| Samples      | Weight loss rate [%] |
|--------------|----------------------|
|              | Total weight loss    | 30–600 °C | 600–850 °C | 850–1200 °C |
| Raw MCMBs    | 10.35                | 7.23       | 2.47       | 0.65        |
| S-MCMBS-150  | 10.31                | 7.43       | 2.39       | 0.49        |
| S-MCMBS-200  | 10.33                | 5.93       | 3.68       | 0.72        |
| S-MCMBS-250  | 11.17                | 5.07       | 3.65       | 2.45        |
| S-MCMBS-300  | 11.76                | 4.05       | 4.52       | 3.20        |

Table 3. The amount of change in the weight loss rate of MCMBs classified by three carbonization temperature ranges.
Conclusion
From the aforementioned results the following conclusions were drawn. First, the carbon block from Raw MCMBs showed more than 100 um cracks due to the weight loss from 30 °C to 600 °C. Second, as more volatile matter was incorporated corresponding to the weight loss from 850 °C to 1200 °C, more borderlines among MCMBs particles distinctly appeared. In addition, the bending strength was decreased. Third, carbon blocks from stabilized MCMBs have higher volume shrinkage and weight loss rate than carbon blocks from Raw MCMBs. Fourth, bending strength decreased as the oxygen content increased at stabilization temperature over 250 °C. Finally, in order to manufacture high density carbon blocks that are carbonized at 1200 °C, the MCMBs should be stabilized at temperature in a temperature range of 150–250 °C under an air atmosphere.

Methods
Materials. The raw material used in this study was coal tar pitch (CTP) obtained from OCI Company Ltd in Korea. The characteristics of the coal tar pitch are listed in Table 4. An elemental analysis (EA) of the coal tar pitch revealed the following: carbon (93.50%), hydrogen (4.49%), nitrogen (1.34%), and sulfur (0.46%). A solubility analysis based on Quinoline Insolubility (QI) and Toluene Insolubility (TI) was also carried out. The carbon yield of CTP was 44.9% at 900 °C, as indicated in Fig. 6(a).
Preparation of MCMBs. Figure 6(b) shows the experimental procedure to manufacture carbonized carbon blocks from MCMBs. CTP, employed as raw material, was heated at 400–500 °C under a nitrogen atmosphere by using the reactor presented in Fig. 6(c). Heated coal tar pitch in a quantity of 10 g was mixed with tetrahydrofuran (THF) of 100 ml at 50 °C for 12 h, and then extracted by vacuum filtration. Additionally, the extracted MCMBs were washed twice with toluene at 80 °C. The as-prepared MCMBs were heated under an air atmosphere at 150–300 °C for 1 h to increase oxygen content, and this heat treatment was carried out in the device shown in Fig. 6(c). Four kinds of MCMBs according to the stabilization process were manufactured at 150, 200, 250, 300 °C, and respectively designated as S-MCMBs-150, S-MCMBs-200, S-MCMBs-250, and S-MCMBs-300.

Manufacturing carbon blocks. First, raw MCMBs and stabilized MCMBs were classified in a sieve under 75 μm (200 mesh). The raw MCMBs and stabilized MCMBs were then molded without a binder under 28 Mpa by cold compression into two discs of 15 × 15 × 3 mm and 60 × 10 × 3 mm5. The green carbon blocks were carbonized at 1200 °C for 1 h with a heating rate of 1 °C/min in a nitrogen atmosphere. Two types of carbonized carbon blocks (CCB) from MCMBs were then prepared. Also, four kinds of CCB which treated by different stabilization temperatures respectively at 150, 200, 250, 300 °C, were classified as CCB-150, CCB-200, CCB-250, and CCB-300.

Characterization. The composition of CTP and MCMBs was analyzed using an elemental analysis (EA, TruSpec, LECO Corp., USA). Toluene insolubility (TI) and Quinoline insolubility (QI) were respectively determined according to ASTM D 4072 and ASTM D 2318 standards. The thermal behavior of the CTP and MCMBs was analyzed by a thermogravimetric analysis (TGA, STA 409 PC, Netzsch Corp., Germany) at a heating rate of 5 °C/min to 900 °C in a nitrogen flow. A polarization microscopy analysis and a particle diameter analysis were carried out using polarized light microscopy (PLM, BX51M, Olympus Corp., Japan). The surface images of the MCMBs and CCBs was obtained using scanning electron microscopy (SEM, JSM-6700F, JEOL Ltd., Japan). The oxygen content of MCMBs was determined via X-ray photoelectron spectroscopy (XPS, AXIS-NOVA, Kratos Inc., Japan). The density of the CCBs was investigated by the Archimedes drainage method. The shore hardness test (SH, Type-D, Kobunshi Keiki, Japan) was performed in accordance with the ASTM D 2240 standard.

| Elemental analysis [wt %] | Insolubility analysis [%] |
|--------------------------|---------------------------|
| C | H | N | S | C/H | TI | QI |
| 93.5 | 4.49 | 1.34 | 0.46 | 1.74 | 32.1 | 9.7 |

Table 4. Characteristics of the coal tar pitch.
The flexural strengths were examined by a Universal Testing Machine (UTM, WL2100, WITHLAB Ltd., Korea) according to equation (1)\[^{11,13,34}\]:

\[
\sigma_f = \frac{3 \cdot P \cdot L}{2 \cdot w \cdot t^2}
\]

where \(P\) is the breaking force of the specimen, and \(L\) is the span of bending test (30 mm), \(w\) is the width of specimen (10 mm), \(t\) is the thickness of the specimen (3 mm).

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**Author Contributions**

U.S.I. and D.H.J. conceived, designed the idea and performed the experiments and wrote the paper. J.Y.K. and B.R.L. helped in the design of the research, assisted with a preparation of some reactor for the research. D.H.P. discussed experimental design, discussed data interpretations and edited the manuscript. All authors discussed the results and commented on the manuscript.

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