바이오숯을 함유한 모르타르의 역학적 특성

Mechanical Properties of Mortar Containing Bio-Char From Pyrolysis

최 원 창[1] 윤 현 도[2)*] 이 재 연[3]
Choi, Won Chang Yun, Hyun Do Lee, Jae Yeon

Abstract

Bio-char, obtained from biomass as a by-product of the pyrolysis process, is used successfully as a soil amendment and carbon sequester in this limited study. Recent and active research from literatures has extended the application of bio-char in the industry to promote sustainability and help mitigate the negative environmental impacts caused by carbon emissions. This study aims to investigate the feasibility of high-carbon bio-char as a carbon sequester and/or admixture in mortar and concrete to improve the sustainability of concrete. This paper presents the experimental results of an initial attempt to develop a cement admixture using bio-char. In particular, the effects of the water retention capacity of bio-char in concrete are investigated. The chemical and mechanical properties (e.g., the chemical components, microstructure, concrete weight loss, compressive strength and mortar flow) are examined using sample mortar mixes with varying replacement rates of cement that contains hardwood bio-char. The experimental results also are compared with mortar mixes that contain fly ash as the cement substitute.

Keywords : Bio-char, Cement admixture, Compressive strength, Flow rate, Weight loss rate

1. Introduction

Cement is one of the most commonly used construction materials. Its highly energy-intensive production process consumes about 45% of its energy from burning fuel and 55% from calcinations. Globally, the cement industry produces about 5% of man-made carbon dioxide (CO2) annually. In the United States, cement is responsible for nearly 1% of all CO2 that is emitted. As is well known, the emission of CO2 contributes to the greenhouse gas (GHG) effect, and, therefore, many countries are trying to reduce CO2 emissions in order to mitigate the negative environmental consequences. Accordingly, any reduction in carbon emissions in the preparation of concrete will improve the material's sustainability and help the environment. One possible solution is the development of carbon sequestration in concrete and/or concrete admixtures. Such sequestering may reduce the carbon footprint of concrete and also improve its mechanical properties and durability. For one means of carbon sequestration, many studies show that bio-char has great potential to reduce GHG effects by sequestering carbonin soils. The estimated residence time of carbon in bio-char is in the range of hundreds to thousands of years, which is much longer than that of carbon in plant material, which takes place over decades. Therefore, this sequestration process using bio-char would reduce the release of CO2 back into the atmosphere when the carbon is stored in the soil.

Recently, efforts have been made to find

1) Dept. of CAAE Engineering, North Carolina A&T State University, Greensboro, NC, 27411, USA
2) Dept. of Architectural Engineering, Chungnam National University, Daejeon, 305-764, Republic of Korea
3) Dept. of Architectural Engineering, Mokwon University, Daejeon, 302-729, Republic of Korea

* Corresponding author : wiseroad@cnu.ac.kr 042-821-5622

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environmentally sound uses for high-carbon bio-char. To expand the practical applications of bio-char, the Canadian Bio-char Initiative encourages its use as an additive in several industrial areas, including the asphalt/concrete industry. However, it is a challenge to consume the high carbon content of bio-char in concrete. The carbon itself increases the water demand in the concrete and causes a reduction of compressive strength with an increase in replacement rate.

The overall research objective in this study is to provide quantitative information about bio-char so that it can be used as a carbon sequestration agent in concrete and/or as a self-curing agent. First, it is hypothesized that the high carbon content of bio-char can be captured in concrete without substantial negative side effects, such as reduction in compressive strength and durability. Second, it is hypothesized that the high water retention capacity of carbon in bio-char can help to reduce the evaporation of water in concrete and provide water for the hydration process.

In this study, the chemical and material properties (e.g., chemical components, microstructures, concrete weight loss, compressive strength and mortar flow) of bio-char are examined using sample mortar mixes that have varied replacement rates of bio-char. Two different curing methods, air-cured and moisture-cured, are used for the compressive strength testing. The experimental results are compared with those of other mortar mixes that include fly ash as a cement substitute.

2. Properties of Bio-char

Bio-char is a kind of charcoal that yields from the pyrolysis of biomass (the thermal treatment of natural organic materials in an oxygen-limited environment). During the pyrolysis reaction of the biomass that results in bio-char, the yield rates of bio-oil, bio-char, and syngas are affected by the type of feedstock and operating conditions, as seen in Fig. 1. The processing temperature also affects the carbon content of bio-char, in that the temperature is inversely related to the yield of bio-char, increasing from 56% to 93% between 300 and 800℃. Any further increase in temperature or reaction time decreases the bio-char yield without increasing its carbon content (this is due to an increase in ash). In the fast pyrolysis process, the yield of the bio-oil component can be maximized at about 500℃, with approximately 67% of the feedstock converted. The remaining 33% is converted to syngas (13%), water (6%) and high-carbon bio-char(14%).

The typical microstructure of bio-char is a highly microporous cellular/irregular structure, which explains its high specific surface area. The macropore structure (mm scale) of bio-char produced from biomass inherits its architecture from the feedstock and is an important factor for its adsorption. In concrete mixtures, this porous structure and high carbon content in bio-char demands much water, which affects the workability of concrete. The Federal Highway Administration (FHWA) notes that the high carbon content in fly ash affects air entraining agents, which in turn, attains the desired air content and water to gain the desired workability. Accordingly, a reduction in the workability in concrete

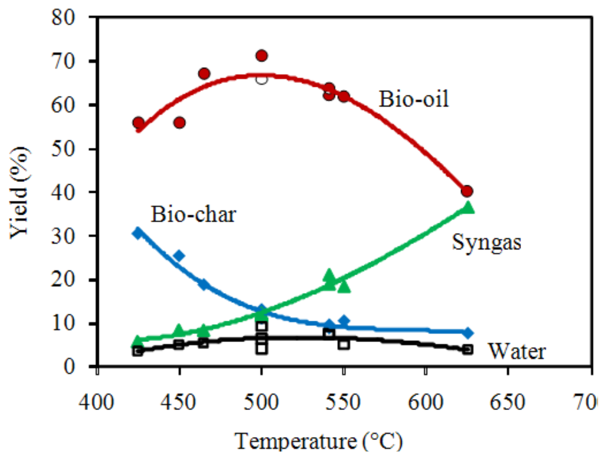


Fig. 1 Relative proportion of products from fast pyrolysis of biomass

mixes could be expected.

The absorbed water in bio-char, however, does not bond chemically with carbon so that the absorbed water would be released during the hydration procedure, which may aid the hydration process during the early age of the concrete. Furthermore, this water retention capacity of bio-char provides good curing conditions for concrete and helps to develop the concrete microstructure and pore structure such that it also improves the concrete's durability and material properties. The water retention capacity of bio-char also reduces water evaporation from the concrete, which reduces both the plastic shrinkage and drying shrinkage of the concrete. This concept is similar to that of a self-curing agent in concrete.

The typical chemical components of bio-char, as obtained from switchgrass, hardwood, rice husk ash (RHA) and coal fly ash with high lime content (Class F) and low lime content (Class C),are compared in Table 1. These chemical component percentages by mass are obtained from X-ray fluorescence spectroscopy.

The addition of fly ash in concrete improves the concrete's material properties, such as compressive strength, workability and durability. To obtain the values for these properties, the American Society for Testing and Materials (ASTM) C618 guide addresses the chemical and physical requirements of coal fly ash and raw or calcined natural pozzolan for use in concrete. Fly ash, even without fulfilling the chemical requirements on ASTM C618, provides excellent strength gain and a possible application for concrete. That is, not all fly ash meets ASTM C618 requirements however, depending on the application, meeting the requirements may not be necessary. Among the chemical requirements shown in Table 2, the carbon content, measured by the loss of ignition (LOI) of less than 6% for coal fly ash, is needed.

The chemical components of bio-char indicate a possible application as a supplementary cementitious material. In the case of switchgrass char, the amount of silica (SiO_2) is 43.63%, which is close to that of Class F fly ash. The major acidic oxides (SiO_2 + Al_2O_3 + Fe_2O_3) are close to 50%, which is the minimum requirement for pozzolanic activity in accordance with ASTM C618, as shown in Table 2. While the amount of silica in hardwood char is below for the pozzolanic activity. It may be inappropriate for the cement substitute.

The magnesium oxide content is 1.55% and 0.48% in the switchgrass and hardwood char, respectively. These percentages satisfy the required value of 5% maximum.

The LOI of bio-char obtained from switchgrass ranges from 5% to 35%. These values are more than the 10% maximum as required for pozzolans, which means that the bio-char contains carbon that reduces the pozzolanic activity of the char. The carbon itself is not pozzolanic, and its presence

Table 1 Chemical compositions (% by mass)

Element	Switchgrass F.P. char	Hardwood char	Rice Husk Ash	Fly Ash Class F	Fly Ash Class C
Al_2O_3	0.49	0.6	0.4	25.8	16.7
CaO	3.65	22.37	0.9	8.7	24.3
Cl	0.47	0.03	-	-	-
Fe_2O_3	0.76	2.36	0.5	6.9	5.8
Na_2O & K_2O	6.07	1.41	1.8	0.6	1.3
MgO	1.55	0.48	-	1.8	4.6
MnO	0.15	0.83	-	-	-
P_2O_5	3.86	0.2	-	-	-
SiO_2	43.62	5.67	82.6	54.9	39.9
SO_3	0.99	0.27	0.1	0.6	1.3
Other	0.25	0.51	-	-	-
Total	61.86	34.73	86.3	99.3	93.9

Table 2 Chemical requirements coal fly Ash and raw or calcined natural pozzolan for Use in Concrete (ASTM C618-08a)

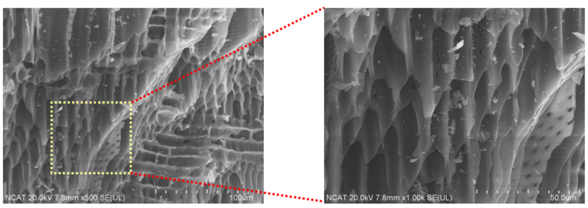
	Class N	Class F	Class C
SiO_2 +Al_2O_3 + Fe_2O_3, min, %	70.0	70.0	50.0
SO_3, max, %	4.0	5.0	5.0
Moisture content, max, %	3.0	3.0	3.0
Loss of ignition (LOI), max, %	10.0	6.0	6.0

serves as filler to the mixture. Cordeiro and et al. have confirmed that RHA with high LOI could be used successfully as a supplementary cementitious material in concrete due to its high content (over 80%) of silica. Concrete with RHA exhibits superior performance in mechanical and durability tests as compared with the reference mixture.

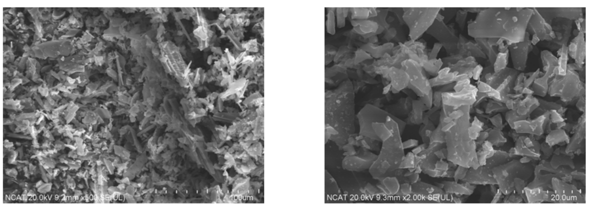
3. Experimental work

3.1 Materials preparation and mortar mixes

Hardwood char obtained from slow pyrolysis, which is commercially available, was prepared in this study to examine the water retention effects of mortar mix samples. As mentioned earlier, the chemical components of hardwood char show a high content of carbon along with a few acidic oxides. It is necessary to isolate the factor of the water retention capacity of the bio-char in order to determine the overall effect of water in the mortar mixes. Fig. 2 shows the microporous cellular shape of bio-char as found from scanning electron microscopy (SEM). After grinding the bio-char with a mechanical grinder, the cellular structure is destroyed totally, as shown in Fig. 2 (b). It is important that the bio-char is ground into a very



(a) Bio-char before grinding



(b) Bio-char after grinding with mechanical grinder

Fig. 2 SEM image of hardwood bio-char

fine form so that the cellular shape of the bio-char does not affect the absorption process in the mortar mixes.

The main variables in this study are mortar mixes that contain different amounts of bio-char replacement. For this research, a mixture of cement (typical Portland cement) and fine aggregate (i.e., sand) was cast in 2 in. (50 mm) by 2 in (50 mm). cubes. A suite of test mortar samples with a water to cement ratio of 0.5 was used with 1 kg of cementitious material and 3 kg of sand. The mixtures are identified according to their bio-char content and/or fly ash content of the total cementitious material, and also according to curing condition, i.e., moisture-cured or air-cured. A total of 11 mortar mixes were considered for the compressive strength testing, and selected mortar mixes from these 11 mixes were used for the flow test and weight loss test. Detailed mortar mix information for each test is shown in Table 3.

3.2 Specimens and test set-up

To examine the water retention rates, the weight loss was measured by filling containers made from PVC pipe with a 4 in (100 mm). inside diameter. The pipe was cut into uniform 5 in (125 mm). lengths. Careful consideration was given to use a slip-in connector with a smooth surface for the bottom of the cylinder. The slip-in connector then was glued to the bottom of the cylinder. After sufficient drying, each cylinder was weighed, and the weight recorded.

When mixing the different concrete mixes for this study, all the dry ingredients were mixed in a commercial-grade mixing machine. Any mixer will suffice, but it is important that all the ingredients are mixed thoroughly.

Once a visual inspection ensured that all the dry ingredients were mixed together thoroughly, the water was added to the mixture. Once the concrete

Table 3 Mortar mix designs for weight loss, flow, and compressive strength testing

<table>
<tr><th>Mix No.</th><th>I.D.</th><th>Cement (g)</th><th>Bio-Char (g)</th><th>Fly Ash (g)</th><th>Sand (g)</th><th>Water/Cement Ratio</th><th>Curing</th></tr>
<tr><td>1</td><td>C0M*,**</td><td>1000</td><td></td><td></td><td rowspan="11">3000</td><td rowspan="11">0.5</td><td rowspan="8">Moisture-cured</td></tr>
<tr><td>2</td><td>C5M*,**</td><td>950</td><td>50</td><td></td></tr>
<tr><td>3</td><td>C10M*,**</td><td>900</td><td>100</td><td></td></tr>
<tr><td>4</td><td>C15M**</td><td>850</td><td>150</td><td></td></tr>
<tr><td>5</td><td>C20M**</td><td>800</td><td>200</td><td></td></tr>
<tr><td>6</td><td>F10M**</td><td>900</td><td></td><td>100</td></tr>
<tr><td>7</td><td>F20M**</td><td>800</td><td></td><td>200</td></tr>
<tr><td>8</td><td>C5F5M*,**</td><td>950</td><td>50</td><td>50</td></tr>
<tr><td>9</td><td>C0D</td><td>1000</td><td></td><td></td><td rowspan="3">Air-cured</td></tr>
<tr><td>10</td><td>C5D</td><td>950</td><td>50</td><td></td></tr>
<tr><td>11</td><td>C10D</td><td>900</td><td>100</td><td></td></tr>
</table>

Note: * indicates weight loss testing ** indicates flow testing.

was mixed thoroughly, which depended on the type of mixing used, the concrete was placed into the cylinder in a uniform fashion. Due to the 5 in (125 mm). height of the cylinders, the concrete was put into the cylinders in three steps. First, the cylinders were filled roughly halfway, and then the concrete mix was tamped with a metal pipe with an approximate ¾ in. diameter. The cylinder then was filled to the top, tamped down, filled again to the top, and then smoothed with a trowel.

Although the different mixes had different water to cement ratios, they were made in the same manner. Once all the mixes were made, the initial weights were recorded immediately after mixing, after which the weights were recorded in the following intervals: 1 hour, 3 hours, 6 hours, 1 day, 2 days, 3 days, 7 days, 10 days, 15 days, 20 days, and 28 days. Thus, the weights were recorded and the charts were created using the amount of water that had evaporated from the concrete.

In addition, in order to determine the workability of the mortar mix samples, a flow test was conducted by measuring the percentage of mortar flow in accordance with ASTM C1437. This test was designed to determine the water content needed for a cement paste sample. The test utilizes a specially designed table that repeatedly raises and drops a known quantity of mortar 25 times. During the test, the mortar will spread (or flow) to form a circular mass, and the diameter of the mass is measured and compared to the initial size. In this study, the flow test was conducted twice for each mortar mix, and the average values were computed.

Finally, to measure the compressive strength in the specimens during the hydration process, the cube samples were tested at 14 days, 28 days, and 56 days after casting. After 24 hours, the specimens were demolded and then moisture-cured for 28 days followed by air curing at room temperature. All specimens were air-dried for 24 hours prior to the compressive strength testing at 14 days and 28 days. For the air-cured specimens, all of the specimens were demolded after 24 hours and air-cured at room temperature.

4. Test results and discussion

4.1 Water retention

Fig. 3 shows the weight loss over time for all the mixes. The weight loss for the control concrete mix (without bio-char) is greater than that for the concrete mixes with bio-char replacement, regardless of the replacement rate, and even if more free water is present in the specimen, which has less cement after hydration. In short, the weight loss

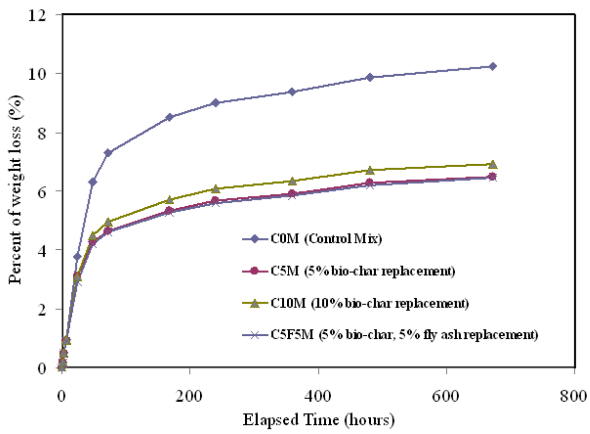


Fig. 3 Percentage of weight loss

over time due to moisture evaporation is found to be less for the mortar mixes that include bio-char than that for the conventional mix. These results indicate that mortar mixes that include bio-char exhibit better water retention than mixes that do not contain bio-char.

4.2 Flow test

Fig. 4 shows the considerable reduction in the percentage of flow as the replacement rate with bio-char increases. As expected, this reduction could be caused by the porous microstructure and water retention capacity of the carbon in the bio-char. When the replacement rate with bio-char increases, the mortar mixes dramatically lose their workability above a 5% replacement with bio-char. The mortar mix with a 20% replacement rate with bio-char crumbled during testing, so it was impossible to measure the percentage of flow properly due to this sample's extremely low workability. An increase in the amount of fly ash as a cement substitute up to 20% reduces the flow to 10.2% percent. The results found in the literature indicate that the fly ash has a LOI above 3%. It is likely the water requirements are higher.

Limited results from these experiments indicate that 5% to 10% replacement with bio-char is comparable to 20% replacement with fly ash. However, the appropriate amount of bio-char that is needed to obtain the desired workability might vary depending on the LOI level in the bio-char.

4.3 Compressive strength

The test results presented in Fig. 5 indicate that the concrete's compressive strength at 28 days decreases with an increase in bio-char content, except for the specimens with the replacement rate of 5% of bio-char C5M. The compressive strength values at 28 days and 56 days are slightly higher than that for the control specimen, C0M. In comparison to conventional mixes that do not contain bio-char replacements for the cement, the bio-char additive reduces the amount of water evaporation from the

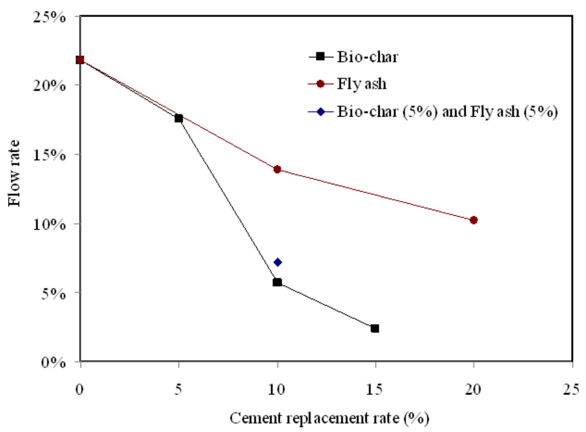


Fig. 4 Flow rate for the selected mortar mixes

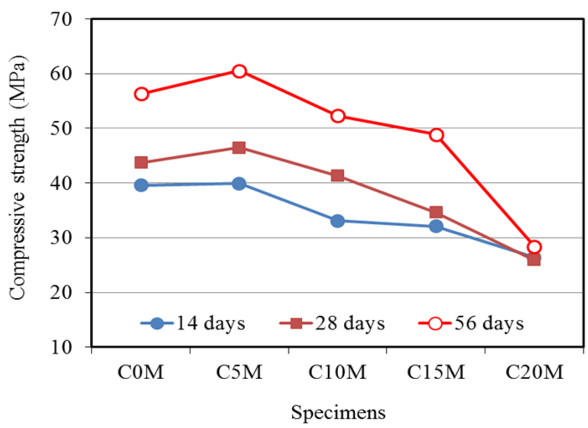


Fig. 5 Development of compressive strength

mortar mixes so that it helps maintain the moisture content in concrete during its early stages, which in turn leads to the desired strength. In this way, bio-char seems to play a role as a self-curing agent. Similar results were obtained from mortar mixes with bio-char under air-cured conditions. Although the amount of cement was reduced by 5%, the compressive strength was maintained as compared to that for the control specimen. A noticeable reduction in compressive strength is seen in specimen C10D due to its low cement content and the difficulty of compaction due to its low workability.

In short, the replacement rate of 5% with bio-char might be adequate without any significant reduction in compressive strength.

The variation in compressive strength values with mix proportions at various ages is shown in Table 4. All of the test results are the average values of at least three specimens.

As increasing the replacement rate of bio char in the mortar mixes, no well-defined cones failure and columnar vertical cracking at inside was observed as shown in Fig. 6 (b).

Table 4 Compressive strength of mortar mixes

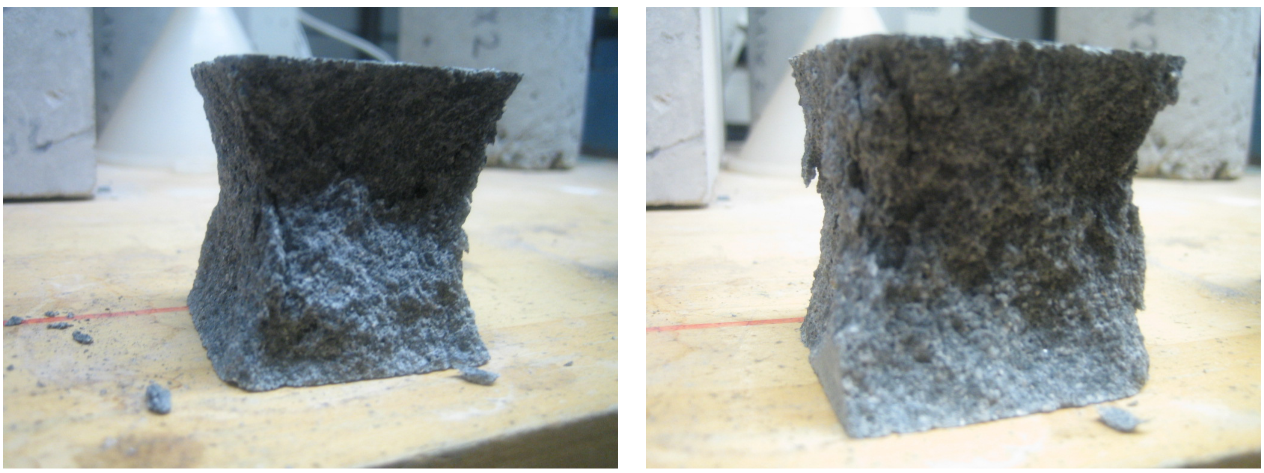
Mix No.	I.D.	Compressive Strength (MPa)		
		14 days	28 days	56 days
1	C0M	39.6	43.7	56.3
2	C5M	39.9	46.5	60.5
3	C10M	33.1	41.3	52.3
4	C15M	32.1	34.6	48.9
5	C20M	26.4	25.9	28.4
6	F10M	33.6	48.1	44.6
7	F20M	26.1	31.6	39.4
8	C5F5M	31.8	32.7	33.7
9	C0D	35.5	37.5	37.1
10	C5D	33.5	36.8	37.1
11	C10D	25.4	23.2	24.6

5. Conclusions

The following conclusions are drawn from the limited experimental testing undertaken in this study.

(1) Hardwood bio-char in mortar mixes demands more water to obtain desired workability due to its carbon content and microstructure.

(2) Weight loss rate over time due to moisture evaporation is found to be less for mortar mixes that contain bio-char than for the conventional mix. This finding indicates that mortar mixes that contain bio-char exhibit



(a) C0M (b) C10M

Fig. 6 Failure mode for mortar cube

better water retention than those that do not contain bio-char.

(3) The results for both the percentage of flow and compressive strength tests indicate that a certain amount of bio-char could be added to concrete mixtures as a carbon sequester and/or cement substitute up to a 5% replacement rate without a significant reduction in compressive concrete strength and a comparable percentage of flow. Bio-char replacement has the potential to help internal curing in concrete mixtures due to improved hydration over time under drying conditions compared to conventional concrete. Similar results for compressive strength testing are observed also with specimens under dry curing conditions.

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요 지

바이오매스에서 얻어지는 바이오차는 토질 개량제와 탄소 격리제로 제한적인 분야에서 성공적으로 사용되고 있다. 현재 산업전반에서 CO2 에 의한 환경에 부정적인 영향을 완화시키고 지속가능성을 증진시키기 위한 연구가 활발히 진행되고 있다. 이에 본 연구에서는 고탄소 바이오차를 탄소 격리제 또는 시멘트의 혼화재로써 활용 가능성을 평가하고자 하였다. 견목재에서 얻어진 바이오차를 혼화재로 사용하여 시멘트 배합조건을 달리하면서 모타르의 압축강도, 마이크로구조, 압축강도, 유동성, 중량감소와 같은 화학적, 물리적 재료성질을 평가하였다. 또한 플리이애쉬를 사용한 모르타르의 역학적 특성과 비교 평가하였다.

핵심 용어 : 바이오숯, 시멘트 혼화재, 압축강도, 유동성, 중량감소율