12th International Conference on Fracture Mechanics of Concrete and Concrete Structures
FraMCoS-12
B.L.A. Pichler, Ch. Hellmich, P. Preinstorfer (Eds)

https://doi.org/10.21012/FC12.1380
MS07-3:3

AMINE-MODIFIED BIOCHAR SATURATED WITH CO_2 AS INTERNAL CARBONATION CURING ACTIVATOR FOR ENHANCING MECHANICAL PROPERTY OF CEMENT PASTE

RENMING WU[*], SHIPENG ZHANG[*] AND CHI SUN POON[*]

[*] The Hong Kong Polytechnic University, Department of Civil and Environmental Engineering
Hung Hom, Kowloon, Hong Kong
e-mail: ren-ming.wu@connect.polyu.hk; shipeng.zhang@polyu.edu.hk; cecspoon@polyu.edu.hk

Key words: Biochar, Modification, Internal carbonation curing, Cement paste

Abstract: Incorporation of carbon-negative biochar into cementitious materials has been recognized as one of the most promising ways to achieve global carbon neutrality. However, negative effect on mechanical strength occurs when adding high amount (>5% by weight) of biochar to replace cement due to the weak binding of interfacial transition zone between biochar and cementitious matrix. Therefore, it is imperative to develop an approach for enhancing the interfacial transition zone. In this study, we evaluated the carbon dioxide adsorption performance of amine-modified biochar and investigated the effect of biochar (5% replacement of cement by weight) saturated with CO_2 as internal carbonation curing supplier on the mechanical property of cement paste. Diethanolamine (DEA) was employed to modify biochar to enhance the CO_2 adsorption capacity and subsequent constraint on CO_2. Higher CO_2 adsorption (1.84 mmol/g) was achieved in modified biochar compared to pristine biochar (0.33 mmol/g) at 30 ℃, and more CO_2 (80.94% versus 4.33%) was retained in pores of modified biochar after being exposure to the air atmosphere. The group incorporating modified biochar saturated with CO_2 exhibited similar compressive strength even compared to blank group without adding biochar (43.92 MPa versus 41.76 MPa). Improved compressive strength (41.77%, 28 days) of specimens with adding CO_2-saturated modified biochar was observed compared to pristine biochar saturated with CO_2, which can be attributed to the hydration acceleration resulted by filler and nucleation effect. This approach can effectively reduce the negative effect of adding high amount of biochar on the mechanical property of cement paste, further helping achieve global carbon neutrality.

1 INTRODUCTION

Cement, as the most consumed commodity by mass besides water worldwide, contributes nearly 7% of anthropogenic carbon emissions annually [1]. Adopting supplementary cementitious materials (SCMs) to partially replace cement in building and construction activities can help reduce the intensive CO_2 emissions resulting from cement production processes. Among numerous SCMs, biochar stands out due to its unique carbon-negative property [2].

Detailed research studies have been conducted on the effect of incorporating biochar into cementitious materials, including compressive strength, tensile strength, permeability resistance, shrinkage performance, and so on [3–6]. It is shown that negative effect on mechanical strength occurs with replacement of higher than 5% of the mass of cement with biochar due to the weak binding of interfacial transition zones (ITZs) between biochar and cementitious matrix [7]. Therefore, it is imperative to develop an

approach for enhancing the weak binding area.

Accelerated carbonation curing process has been recognized as an effective way to enhance the mechanical strength of concrete, which involves a chemical reaction between CO_2 and hydration products (e.g., C-S-H and calcium hydroxide) with generating stable calcium carbonates [8]. However, traditional accelerated carbonation curing is hindered by the low penetration of gas CO_2 into inner part of concrete, limiting the carbonation layer to the surface of concrete. Therefore, a novel concept, namely internal carbonation curing, is proposed to trigger the carbonation process from the inner part of concrete [9]. Inspired by the porous structure of biochar, it is possible to utilize biochar saturated with CO_2 as internal carbonation curing supplier in cementitious materials. It is reported that pre-saturated biochar with CO_2 can enhance the compressive strength of mortar due to the generated stable carbonates filling the voids present in the ITZs [8]. However, no studies have investigated the amount of residual CO_2 after the biochar is transferred from the chamber where the pre-adsorption of CO_2 process is conducted. Based on our knowledge, pristine biochar absorbs CO_2 mainly through physical mechanism, which will be released quickly due to the weak constraints. To strengthen the constraints of CO_2 in biochar, it is necessary to modify biochar, transferring from physical adsorption to chemical adsorption.

Herein, we developed a biochar modification approach utilizing diethanolamine (DEA) to strongly retain CO_2 in biochar for subsequent internal carbonation curing in cement paste, further enhancing the ITZs between biochar and cementitious matrix.

2 MATERIALS AND METHODS

The wood waste was pyrolyzed at 500 ℃ for 1 hour with a heating rate of 10 ℃/min in a tubular furnace. The resultant biochar was designated as pristine biochar (PBC). 1 g PBC was transferred into 50 ml ethanol solution, followed by adding 2 g DEA into the mixture. After stirring and heating at 75 ℃ for 2 hours to reach a homogeneous impregnation, the slurry was transferred to a vacuum drying oven for 48 hours to remove the remaining ethanol. The resultant biochar after amine modification process was designated as amine-modified biochar (ABC).

In this research, the water to cement ratio was kept at 0.4 for all groups. In order to fabricate the specimens with adding biochar saturated with CO_2, biochars were transferred into a chamber with pure CO_2 gas at 30 ℃ for 2 hours. After pre-adsorption process, the biochars saturated with CO_2 were utilized to replace cement with the amount of 5% by weight in the paste, which was then cast into $20 \times 20 \times 20$ mm^3 cube specimens. Samples with adding PBC and ABC saturated with CO_2 were designated as PBS and ABS repectively. Specimens with adding PBC and ABC without CO_2 were named as PBN and ABN, respectively. In addition, blank group contains no biochar. All specimens were placed in a saturated calcium hydroxide solution for subsequent tests.

X-ray powder diffractometer (XRD) was employed to investigate the mineral compositions in cement paste. Thermogravimetric analysis (TGA) was utilized to evaluate the thermal stability of cement powder and biochar. ASAP 2020 was used to assess the CO_2 adsorption and desorption performance of biochar. The compressive strength of specimens was investigated after curing for 1, 3, 7, and 28 days at room temperature with a loading rate of 2.4 kN/s.

3 RESULTS AND DISCUSSION

3.1 CO_2 adsorption and desorption

The CO_2 adsorption and desorption performance of biochars were assessed based on ASAP 2020 as shown in Fig. 1. It can be observed that ABC demonstrated higher CO_2 adsorption capacity at 0 ℃ and 25 ℃ compared to PBC. Distinct hysteresis loops in ABC can be ascribed to the strong sequence between DEA and CO_2, resulting in high CO_2 remaining in biochar even under desorption conditions [10]. Further investigation of CO_2

adsorption and desorption performance was conducted through thermogravimetric analyzer as shown in Fig. 1c. Adsorption process was performed at 30 ℃ under 2 bars of pure CO_2 gas for 1 hour, followed by desorption process in which the purging gas was switched from CO_2 to air under atmosphere condition. The CO_2 adsorption capacity of ABC was 1.84 mmol/g, which was nearly six times that of PBC (0.33 mmol/g). After the desorption process, 80.94% pre-adsorbed CO_2 remained in ABC while only 4.33% pre-adsorbed CO_2 was kept in PBC, which was consistent with the results obtained from ASAP 2020. A high amount of residual CO_2 in biochar would provide the basis for subsequent internal carbonation curing of cement paste.

3.2 Compressive strength analysis

The compressive strength of specimens at 1, 3, 7, and 28 days was presented in Fig. 2. Amine-modified biochar barely exhibited compressive strength of 1 day, which can be ascribed to the significant delay effect of amine on hydration process [11]. In comparison, the addition of PBC and PBS showed a slight increase in 1-day compressive strength over control group, which was due to the internal water curing by PBC [8]. A significant increase (20.56%) of early strength of 3 days was observed in specimens with adding PBS compared to PBC, which can be attributed to the internal carbonation curing triggered by the residual CO_2 in biochar. However, no statistically significant difference in strength was observed between specimens with adding PBC and PBS. By contrast, the addition of ABS demonstrated pronounced enhancement on 7-days and 28-days compressive strength over group with adding ABC, achieving an 80.03% and 64.31% increase respectively. In particular, the compressive strength of specimens with ABS (43.92 MPa) was slightly higher than that of control group (41.76 MPa), suggesting the remarkable application prospects.

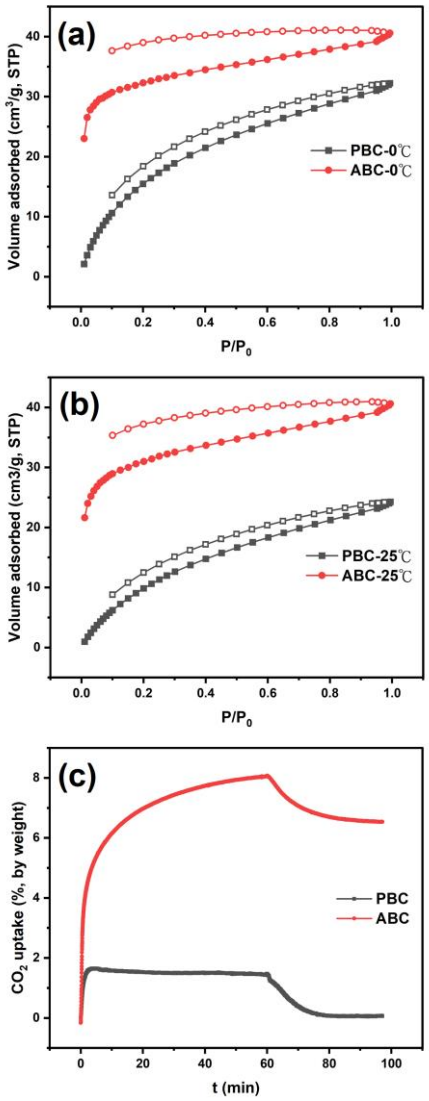

Figure 1: CO_2 adsorption and desorption.

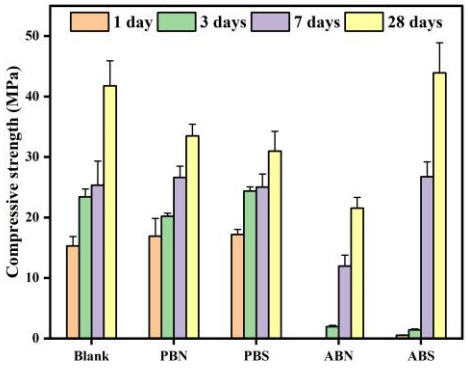

Figure 2: Compressive strength of all samples.

3.3 TGA analysis

Fig. 3 shows the TGA curves of all five types of cement paste in 7 days. It can be observed that specimens with adding biochars showed higher amount of calcium carbonate than that of control group, which can be attributed to the enhanced effect of biochar on carbon dioxide adsorption. In particular, more AFt, C-S-H, and AFm were present in the ABS group, which was due to the promoting effect of hydration process. In addition, less CH in ABS group can be explained by the increased amount of calcium carbonate, which involved the internal carbonation curing triggered by CO_2 released from amine-modified biochar, resulting transition from CH to CC. Therefore, the compressive strength of ABS group was enhanced as shown in Fig. 2.

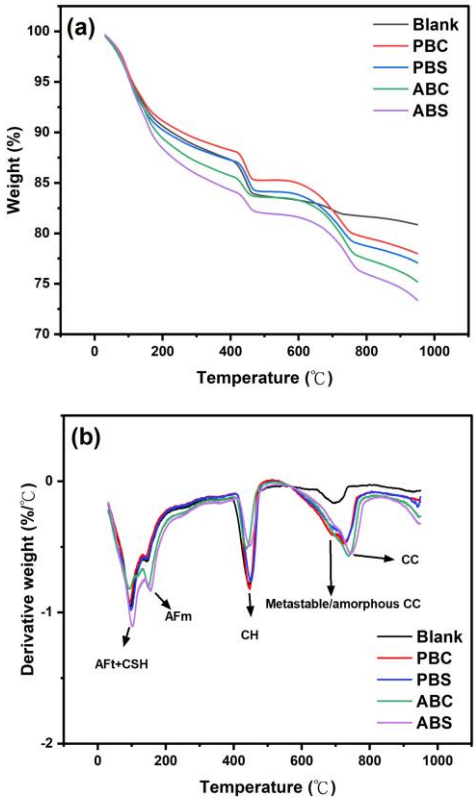

Figure 3: TG and DTG of all samples.

3.4 QXRD analysis

The mineral composition of cement paste in 7 days was quantified through XRD. As depicted in Fig. 4, the addition of ABC decreased the amount of calcium hydroxide (CH) and ettringite, which can be ascribed to the retarding effect of cement hydration process. In comparison, pronounced ettringite was observed in ABS group. In particular, the ABS group exhibited a higher content of monocarboaluminate (Mc), which can be attributed to the reaction between hydration product and released CO_2 from amine-modified biochar. This reaction served as internal carbonation curing for specimens, which can be utilized to explain the increased compressive strength [12]. Therefore, it can be a promising approach to employ amine-modified biochar saturated with CO_2 as internal carbonation curing activator to enhance the mechanical strength of cement paste.

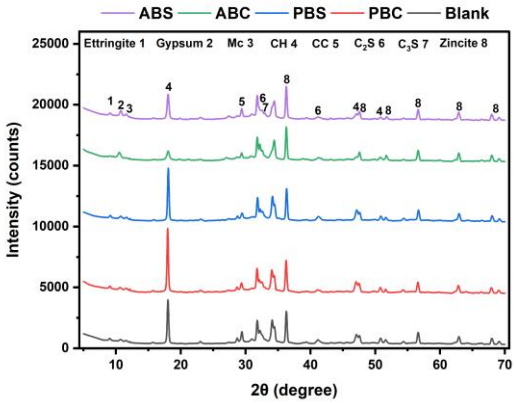

Figure 4: XRD of all samples.

4 CONCLUSIONS

In this study, the feasibility of amine-modified biochar saturated with CO_2 to enhance the mechanical property of cement paste was investigated. The amine-modified biochar achieved 1.84 mmol/g CO_2 adsorption capacity at 30 ℃, remaining 80.94% of pre-adsorbed CO_2 in biochar under atmospheric conditions. Residual CO_2 in biochar was released in subsequent curing process for cement paste, resulting in an increase of monocarboaluminate. Increased compressive strength (31.15%) was observed in cement paste with adding CO_2-saturated amine-modified biochar compared to that with

pristine biochar, demonstrating that it can be a promising approach to employ amine-modified biochar saturated with CO_2 as internal carbonation curing activator to enhance the mechanical strength of cement paste.

REFERENCES

[1] Mishra, G., Danoglidis, P. A., Shah, S. P., Konsta-Gdoutos, M. S., 2023. Carbon Capture and Storage Potential of Biochar-Enriched Cementitious Systems. *Cement and Concrete Composites*, 2023, 140, 105078.

[2] Barbhuiya, S., Bhusan Das, B., and Kanavaris, F., 2024. Biochar-Concrete: A Comprehensive Review of Properties, Production and Sustainability. *Case Studies in Construction Materials*, 2024, 20, e02859.

[3] Gupta, S., and Kua, H. W., 2018. Effect of Water Entrainment by Pre-Soaked Biochar Particles on Strength and Permeability of Cement Mortar. *Construction and Building Materials* 2018, 159, 107–125.

[4] Gupta, S., Kua, H. W., and Pang, S. D., 2018. Biochar-Mortar Composite: Manufacturing, Evaluation of Physical Properties and Economic Viability. *Construction and Building Materials* 2018, 167, 874–889.

[5] Gupta, S., Kua, H. W., and Pang, S. D., 2020. Effect of Biochar on Mechanical and Permeability Properties of Concrete Exposed to Elevated Temperature. *Construction and Building Materials* 2020, 234, 117338.

[6] Praneeth, S., Guo, R., Wang, T., Dubey, B. K., and Sarmah, A. K., 2020. Accelerated Carbonation of Biochar Reinforced Cement-Fly Ash Composites: Enhancing and Sequestering CO_2 in Building Materials. *Construction and Building Materials* 2020, 244, 118363.

[7] Senadheera, S. S., Gupta, S., Kua, H. W., Hou, D., Kim, S., Tsang, D. C. W., and Ok, Y. S., 2023. Application of Biochar in Concrete – A Review. *Cement and Concrete Composites* 2023, 143, 105204.

[8] Kua, H. W., and Tan, S. M. H., 2023. Novel Typology of Accelerated Carbonation Curing: Using Dry and Pre-Soaked Biochar to Tune Carbon Capture and Mechanical Properties of Cementitious Mortar. *Biochar* 2023, 5 (1), 36.

[9] Gupta, S., Kua, H. W., and Low, C. Y., 2018. Use of Biochar as Carbon Sequestering Additive in Cement Mortar. *Cement and Concrete Composites* 2018, 87, 110–129.

[10] Zhang, J., Li, Q., Zhang, J., Liu, H., Wang, H., and Zhang, J., 2025. Enhanced CO_2 Absorption in Amine-Based Carbon Capture Aided by Coconut Shell-Derived Nitrogen-Doped Biochar. *Separation and Purification Technology* 2025, 353, 128451.

[11] Lu, Z., Kong, X., Jansen, D., Zhang, C., Wang, J., Pang, X., and Yin, J., 2020. Towards a Further Understanding of Cement Hydration in the Presence of Triethanolamine. *Cement and Concrete Research* 2020, 132, 106041.

[12] Liu, S., Xiong, G., Zhao, K., Hao, L., Su, Y., Zhang, S., and Poon, C. S., 2024. Mechanism of Organic Additives-Induced Carbonation Activators on Affecting Cement Mortars. *Cement and Concrete Composites* 2024, 154, 105744.