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Curing and degradation processes of cement-bonded particleboard by supercritical CO_2 treatment

Abstract This study examined the effects of supercritical CO_2 treatment on the curing and degradation of cement-bonded particleboard (CBP). Significant correlations were found between the supercritical CO_2 treatment and mechanical properties during both curing and degradation processes. Internal bond (IB) strength, modulus of rupture (MOR), and modulus of elasticity (MOE) values of CBP achieved their maximums by supercritical CO_2 treatment in 30 min. These conditions indicated that supercritical CO_2 treatment accelerates the curing process rapidly and enhances the mechanical properties of the CBP. However, these values decreased in treatment from 60 min to 10 days and had a negative effect on board performance, indicating that supercritical CO_2 treatment over a longer time span leads to degradation of the CBP. Furthermore, X-ray diffractometry (XRD), thermal gravimetry (TG-DTG), and scanning electron microscopy (SEM) observation clarified that the mechanisms of degradation are directly affected by the mineralogical composition of the system, in particular, by the calcium carbonate content as caused by carbonation.

Key words Cement-bonded particleboard · Curing · Degradation · Supercritical CO_2 · Carbonation

Introduction

Cement-bonded particleboard (CBP) has been rapidly accepted in many countries for application in the building industry because of its excellent exterior properties. In the development of CBP, many studies have focused on under-standing the utilization of carbon dioxide (CO_2) in the manufacturing process. The addition of CO_2 during pressing reduces the setting time of CBP to a few minutes.[1–4] Geimer et al.[2] and Simatupang and Habighorst[3] used CO_2 injection to determine its effect on fabrication, pressing variables, and the optimal condition for carbonation. CO_2 injection provides a method for reducing the pressing time of cement-bonded wood composite boards and decreasing wood–cement incompatibility.[3] Qi et al.[5] showed that CO_2 injection in wood–cement composites containing 14% or 20% recycled waste medium density (MDF) fiber resulted in much higher strength and toughness, with lower water absorption properties. Hermawan et al.[6] demonstrated the rapid curing process of high-strength CBP using gaseous or supercritical CO_2. This research showed that supercritical CO_2-cured board can be two to three times stronger than untreated board. The addition of CO_2 accompanied by a supercritical fluid might enhance the hydration process of cement and the strength properties of the board.

On the other hand, it has often been reported that CO_2 degrades cement or concrete because of carbonation. Houst[7] reported that the most negative effects of carbonation of cement are lowering of pore solution pH and loss of protection against corrosion of the steel in reinforced concrete. Carbonation also causes a marked increase in porosity and reduction in strength of super-sulfated cement, probably as a result of carbonation of the ettringite.[8]

It has not yet been revealed whether the supercritical CO_2 treatment has a positive or negative effect on the performance of CBP over a longer time span. This research aims to clarify the curing and degradation processes of CBP under supercritical CO_2 treatment.

Materials and methods

Materials

Mixtures with proportionally equal amounts of particles of Japanese cypress (*Chamaecyparis obtusta* Endl) and Japanese cedar (*Cryptomeria japonica* D. Don) were used to

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manufacture CBP. Ordinary Portland cement of Osaka Sumitomo was used as a binder; CO_2 was used as a curing accelerator.

Manufacture of CBP

CBP with a target density of 1.2 g/cm^3 was manufactured at a cement/wood particle/water weight ratio of 2.5:1.0:1.25. As references, neat cement board (NC) was manufactured at a cement/water weight ratio of 2.5:1.25, and Ca(OH)$_2$ board was manufactured at a Ca(OH)$_2$/wood particle/water weight ratio of 3.0:1.0:1.5. Hand-formed mat of 230 × 230 mm was cold pressed to a targeted thickness of 12 mm and kept in an oven set at 60°C for 24 h. Four specimens of 50 × 210 mm prepared from these boards were then used for the curing treatment. The three curing treatments were (1) supercritical CO_2 treatment, 10 min to 10 days; (2) conventional curing treatment for 28 days (conventional); and (3) neither curing nor supercritical CO_2 treatment as the control. For treatment with supercritical CO_2, the specimens were placed in a reaction cell surrounded by a water jacket set at 40°C with pressure of 10 MPa and then placed in an oven at 80°C for 10 h, followed by conditioning at ambient temperature before further testing. The CBP for conventional curing was wrapped with a polyvinylchloride (PVC) sheet immediately after clamping and kept for 28 days at room temperature. This step was followed by drying and conditioning as already described. For the control, the CBP was produced with neither curing nor supercritical CO_2 treatment. It was immediately dried at 80°C for 10 h, followed by 1 week of conditioning at room temperature.

Evaluation of CBP properties

The mechanical and dimensional properties of the boards were tested in accordance with the Japan Industrial Standard (JIS) A 5908 (1994). The boards were cut into 50 × 210 mm samples for the static bending test and 50 × 50 mm samples for internal bond (IB) strength, thickness swelling (TS), and water absorption (WA) tests. Four test samples were prepared from each treatment group for the foregoing tests. The static bending test was conducted using a three-point bending test over an effective span of 180 mm (15 times the board thickness) at a loading speed of 10 mm/min. The chemical changes and the mineralogical composition of the curing and the degradation processes of the CBP were examined using X-ray diffractometry (XRD), thermal gravimetry (TGA-DTG), and scanning electron microscopy (SEM).

XRD analysis

Powdered samples of 100 mesh-pass taken from an IB test specimen were examined by XRD analysis using a method widely applied to analysis of cement hydration.[9,10] Step scan was measured using XRD (Cu-Kα) at 40 kV and 40 mA; 2θ ranged from 5.0° to 40.0° when scanning at 0.02°/min and 2.0°/min. The amount of unreacted clinkers taken at $2\theta = 32.2°$ and 32.6°, calcium hydroxide at $2\theta = 18.0°$, and calcium carbonate at $2\theta = 29.4°$ and 36.0° for the samples were determined and compared.

TGA analysis

Powdered samples of 100 mesh-pass were examined by a thermogravimetric analyzer (TGA 2050; TA Instrument). Thermal degradation of the specimens was observed from room temperature to 800°C at a heating rate of 10°C/min under nitrogen flow.

SEM observation

The specimens for SEM observation were prepared by cutting small sections from the fractured surfaces of the IB test samples. The small samples were observed using FE-SEM (JEOL JSM 6700F). The observation was performed by electron mode at a beam current of 10 μA and an accelerating voltage of 1.5 kV.

Results and discussion

Properties of CBP after treatment with supercritical CO_2

The average values for the IB strength of CBP treated with supercritical CO_2 for various time durations and conventional curing treatment for 28 days are presented in Fig. 1, which indicates the linear relationships between the mechanical properties and $\sqrt{t}$ (min). Square root of time or $\sqrt{t}$ (min) used in this experiment can be widely applied to analyzing the relationship between some properties of cement or concrete with the duration of time.[11–13] Figure 1 shows the IB strength of boards was strongly influenced by supercritical CO_2 treatment. With the increase in curing time by supercritical CO_2, the IB values of CBP were significantly increased compared with control values and values for conventional board. The IB value of CBP increased drastically from 0.6 to 1.19 MPa after 10 min of curing by supercritical CO_2 treatment. The IB value of board achieved the maximum value of about 1.22 MPa in 30 min of curing by supercritical CO_2 treatment. This condition indicated that supercritical CO_2 treatment accelerates the curing process rapidly and enhances the IB of the CBP. However, the IB values decreased after treatment from 60 min to 10 days; the IB value after treatment for 10 days was about 0.68 MPa. The IB value of conventionally cured boards was 0.56 MPa, which is remarkably lower than the values of the boards treated with the supercritical CO_2. The control board (no supercritical CO_2 treatment) had the lowest IB values.

Compared with the neat cement boards and Ca(OH)$_2$ boards as references, the IB values of neat cement boards were much higher, in contrast with the much lower values of Ca(OH)$_2$ boards. As with the results for the IB of CBP,
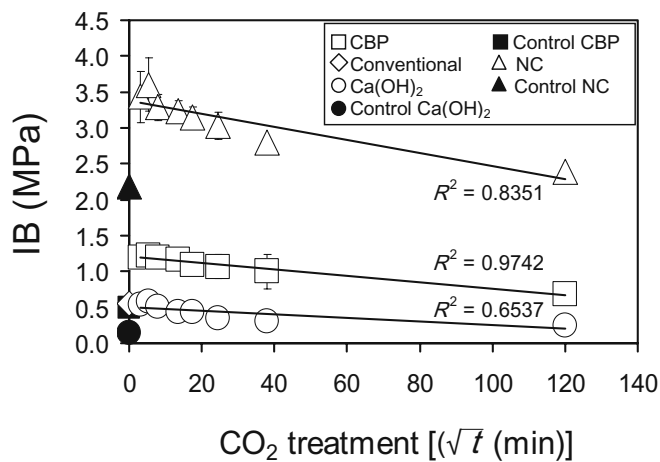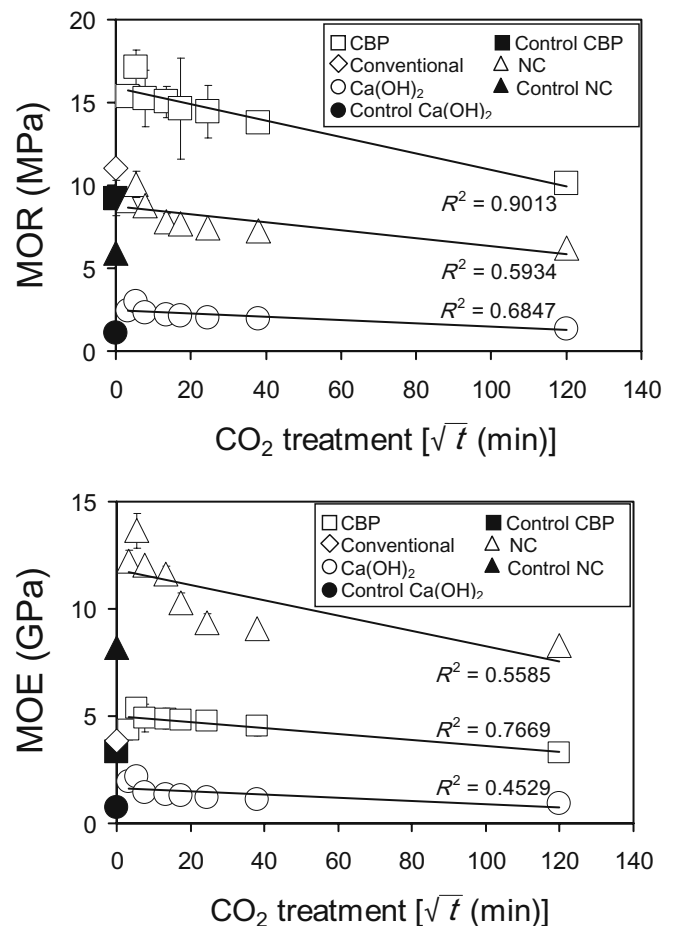
Fig. 1. Effect of supercritical CO_2 treatment on internal bond strength (*IB*) of the cement-bonded particleboard (*CBP*), neat cement boards (*NC*), and *Ca(OH)$_2$* boards at various curing times

the graph of the neat cement boards and $Ca(OH)_2$ boards shows decreased IB values with increased curing time of supercritical CO_2 treatment.

Figure 2 shows the modulus of rupture (MOR) and modulus of elasticity (MOE) values of CBP after supercritical CO_2 treatment and conventional curing treatment for 28 days. The maximum average MOR and MOE values were 17.1 MPa and 5.38 GPa, respectively, in 30 min. This finding shows that supercritical CO_2 treatment allowed more rapid curing of cement and contributed to increasing calcium carbonate content, which could strengthen the mechanical properties of the boards. Hermawan et al.[6] found similar trends: the mechanical properties of CBP manufactured by a conventional cold-pressing method were improved significantly by curing with CO_2 at either the gaseous or supercritical phase. However, the MOR and MOE values decreased with increased treatment time and had a negative effect on board performance. MOR and MOE values were 10.1 MPa and 3.3 GPa, respectively, after 10 days of treatment. Compared with the neat cement boards and $Ca(OH)_2$ boards as references, similar results were also found in the MOE and MOR values. The graph of the neat cement boards and $Ca(OH)_2$ boards show decreased MOR and MOE values with increased supercritical CO_2 treatment time. It seemed reasonable to conclude that some degradation occurred during supercritical CO_2 treatment over a longer time span, as mentioned earlier, degrading the bending strength of CBP, neat cement boards, and $Ca(OH)_2$ boards.

The TS and WA values of the CBP after 24 h of water soaking are shown in Fig. 3. Significant correlations were observed between the TS and WA and the supercritical CO_2 treatment. The highest TS and WA values of the control boards were 1.2% and 25.4%, respectively. When the board was treated with supercritical CO_2 for 10–30 min, TS and WA were slightly reduced. The minimum average TS and WA values were 0.8% and 21.2%, respectively, in 30 min. Hermawan et al.[6] found similar results, in which the dimen-

Fig. 2. Effect of supercritical CO_2 treatment on bending properties at various curing times of cement-bonded particleboard (CBP), neat cement boards (NC), and $Ca(OH)_2$ boards. *MOR*, modulus of rupture; *MOE*, modulus of elasticity
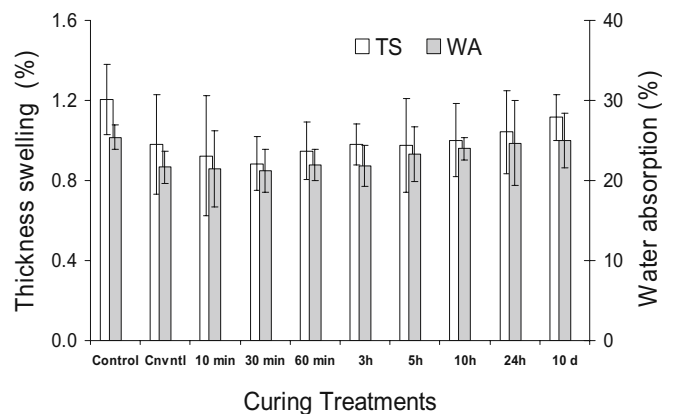
Fig. 3. Effect of supercritical CO_2 treatment on dimensional stability of CBP at various curing times. *TS*, thickness swelling; *WA*, water absorption

sional stability improved significantly when boards were treated with supercritical CO_2 for a shorter time. However, the TS and WA values increased with the longer curing time by supercritical CO_2. The TS and WA of boards treated for 10 days were 1.1% and 27.1%, respectively, which is higher

than TS and WA values of boards treated with supercritical CO_2 and almost equal to values of control boards. This result suggests that the supercritical CO_2 treatment over a longer time span may result in decrease of dimensional stability, apparently through increased hygroscopic ability, which could result from the carbonation process. Boards treated with supercritical CO_2 over a longer time span were found to be porous, and the pores might have absorbed more water, resulting in higher WA and TS values. John et al.[14] and Meyer[15] also found that carbonation may have a deleterious effect on the hardened cement paste, as it appears to decrease strength and increase porosity.

Chemical changes and mineralogical characteristics

The results of XRD analysis of the CBP after treatment with supercritical CO_2 compared to controls and conventional boards are shown in Fig. 4. We observed that calcium carbonate ($CaCO_3$) intensity rose with increased curing time of supercritical CO_2 treatment, indicating that the carbonation process was accelerated with any curing treatment by supercritical CO_2. Figure 4a,b shows that the peak intensities of $Ca(OH)_2$, C_2S, and C_3S of the control board (Fig. 4a) were almost equal to those of the conventional board (Fig. 4b). During hydration, the hydrates dicalcium silicate (C_2S) and tricalcium silicate (C_3S) form calcium silicate hydrate (CSH) and calcium hydroxide [$Ca(OH)_2$].[6] The peak intensities of $Ca(OH)_2$, C_3S, and C_2S of control and conventional boards ranged from 800 to 2,000 cps. $Ca(OH)_2$ intensity decreased with increasing treatment time. Hermawan et al.[6] found similar trends, in which the carbonation process was accelerated with any curing conditions of CO_2, resulting in a significant decrease of the peak intensities of $Ca(OH)_2$ of the treated boards. The carbon content of the control board observed at $2\theta = 29.4°$ was around 4.1%, whereas the value for the conventional board was around 3.8%. Figure 4c,d shows the peak intensities of $CaCO_3$ of CBP treated by supercritical CO_2 for 30 min and 10 days, respectively. Peak intensities of $CaCO_3$ of the boards treated by supercritical CO_2 increased drastically from 30 min to 10 days. This phenomenon indicated that carbonation occurred when the crystalline phase of $CaCO_3$ increased proportionally with the longer curing time by supercritical CO_2. The peak intensities of $CaCO_3$ of the boards treated by supercritical CO_2 ranged from 3,400 to 4,400 cps. This relevance with the high carbon content value of board was about 26.2% with 30 min of treatment by supercritical CO_2 and 32.2% with 10 days of treatment.

Relationships between temperature and weight loss, and the derivative weight for various CBP in TG and DTG curves, are shown in Fig. 5. Successive decomposition reactions or mass losses occurred with an increase of temperature. There was little weight loss of neat cement and conventional board during the heating process (Fig. 5a,b). Compared with neat cement and conventional board, weight loss of board treated by supercritical CO_2 was higher and occurred with an increase in time of supercritical CO_2 treatment. The total weight loss values of board from
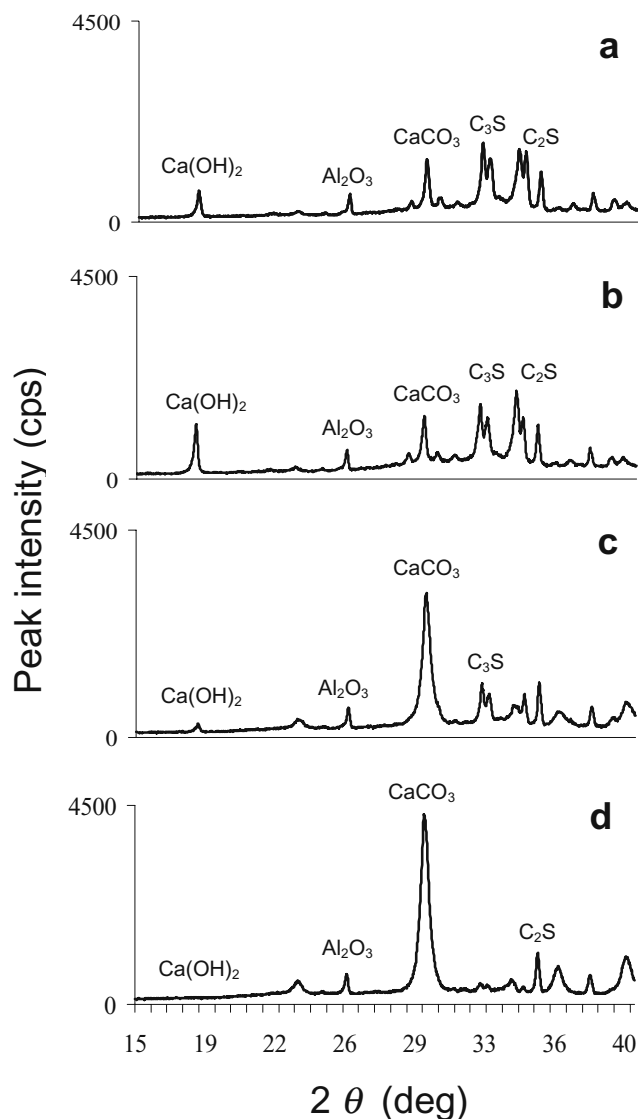
Fig. 4. X-ray diffractometry (XRD) patterns of various curing treatments of CBP: control (**a**); conventional (**b**); 30 min (**c**); 10 d (**d**)

heating from 25°C to 800°C were 28% after 30 min of treatment by supercritical CO_2 and achieved 38% after 10 days of treatment. Therefore, the thermal stability of board treated by supercritical CO_2 was believed to decrease with increasing curing time of those treatments.

The DTG curves (Fig. 5b) show three significant weight loss steps. The first step, at about 100°C, is related to drying (capillary pore residual water) or to decomposition of ettringite. The second step, at about 420°C, is caused by the decomposition of $Ca(OH)_2$ or portlandite. The third weight loss step, at about 740°C, can be attributed to the decomposition of $CaCO_3$. Similar results were reported by Hermawan et al.[6] and Klimesch and Ray[16] that decomposition of calcium silicate hydrate and calcium hydroxide occurred at about 100°C and 400°C, respectively. On the other hand, decomposition of $CaCO_3$ occurred at about 700°C. Compared with neat cement, the control board, and conventional board, the decomposition rate of $CaCO_3$ of the board
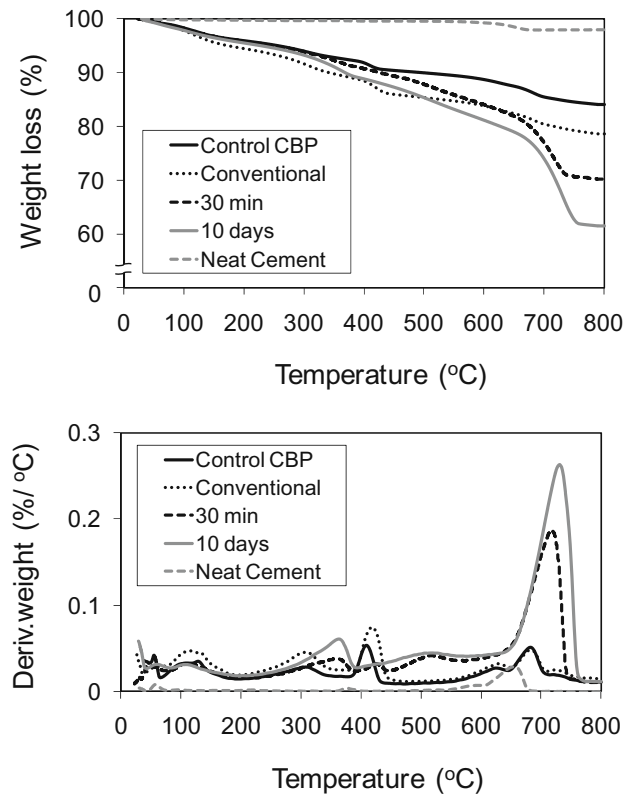
Fig. 5. Thermal properties of various boards: thermal gravimetry (TG) (**a**); DTG (**b**)

treated by supercritical CO_2 was higher and occurred with an increase in time of supercritical CO_2 treatment. From DTG curves, we concluded that the decomposition rate of $CaCO_3$ rose with increased supercritical CO_2 treatment. The rate of the weight loss of $CaCO_3$ increased from about 10% to 20% when treatment by supercritical CO_2 was applied from 30 min to 10 days.

Figure 6 shows the fracture surface of CBP observed by SEM. The control board (Fig. 6a) illustrates ettringite (Et) and cement clinker (CE) formation with no curing or treatment by supercritical CO_2. Under SEM observation, fibrous crystals of ettringite are found, with a needle-like form, permitting slight changes of chemical composition. The conventional board (Fig. 6b) shows cement clinker and calcium silicate hydrate (CSH) formation as a result of hydration. Treatment by supercritical CO_2 (Fig. 6c,d) shows substantial change in the structure of hydrate cement. The calcium carbonate (CC) formations are fully developed and better defined. CBP treated for 30 min (Fig. 6c) shows formation of calcium carbonate in small crystals as a result of carbonation. However, Fig. 6d shows that the appearance and amount of calcium carbonate crystals after 10 days of treatment were larger than that after 30 min. This finding suggests that higher CO_2 consumption, equaling longer time treatment by supercritical CO_2, could account for higher porosity[17] and lead to degradation of the CBP, which had a negative effect on the performance of boards (decreased mechanical properties and increased water absorption).

Fig. 6. Scanning electron micrographs of fracture surface of CBP: control (**a**); conventional (**b**); 30 min (**c**); 10 d (**d**). *CC*, calcium carbonate; *CSH*, calcium silicate hydrate; *CE*, cement clinker; *Et*, ettringite
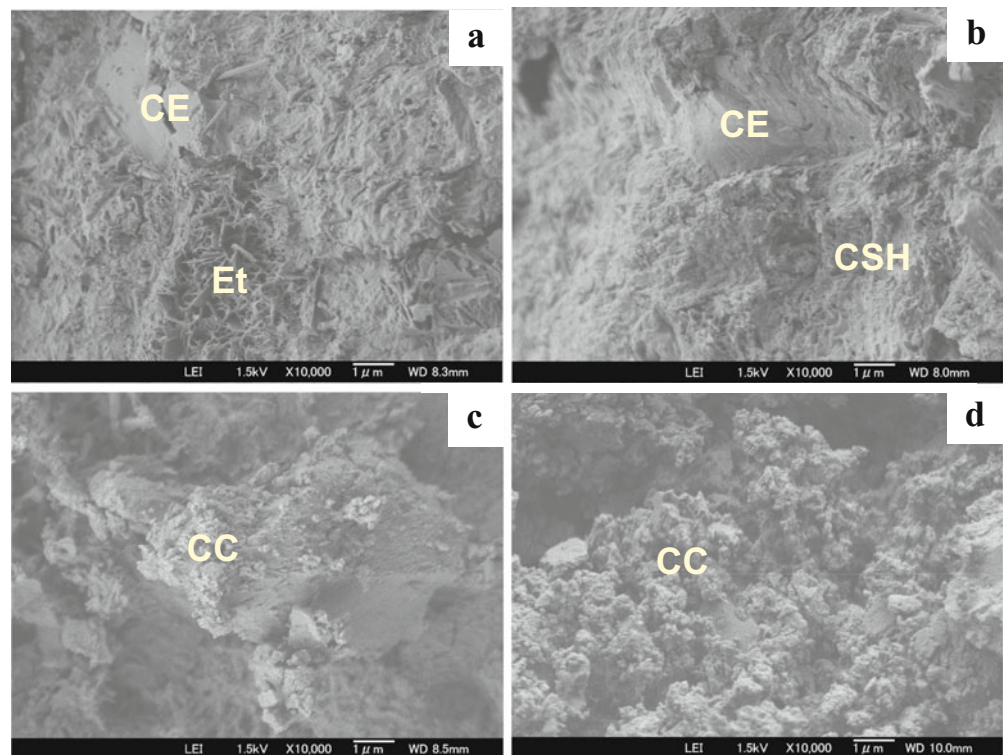
Conclusions

Supercritical CO_2 treatment affects the curing and degradation of CBP. The performance of board can be changed after it is treated with supercritical CO_2. During a shorter treatment time, the mechanical properties (IB, MOR, and MOE) of CBP achieved maximum values, which indicated that supercritical CO_2 accelerates the curing process and enhances the mechanical properties of board. Dimensional stability also improved significantly when the board was treated with supercritical CO_2 for a shorter time. However, with a longer time span of treatment, IB, MOR, and MOE values decreased and had a negative effect on board performance. It was considered that supercritical CO_2 treatment over a longer time span leads to degradation of CBP. Results shown by XRD, TG/TGA, and SEM analysis clearly indicate that the mechanisms of degradation are directly affected by the mineralogical composition of the system, in particular, by the calcium carbonate content as caused by carbonation.

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