

ORIGINAL ARTICLE

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Effect of carbon dioxide–air concentration in the rapid curing process on the properties of cement-bonded particleboard

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Abstract This study deals with the effects of carbon dioxide (CO₂)–air concentration in the rapid curing method on the properties of cement-bonded particleboard manufactured using conventional cold pressing as the setting method. The hydration of cement was examined using X-ray diffraction, thermal gravimetry, and scanning electron microscopy. The results are as follows: (1) The properties of CO₂-cured boards improved with increasing CO₂ concentration. When 10% or 20% CO₂ was applied for 10 min of curing time, the properties of the CO₂-cured boards were comparable to those obtained by conventional 2-week curing. (2) The hydration process of cement could be accelerated within several minutes using CO₂ curing, even with a low concentration of 10%–20% CO₂; a reduction in calcium hydroxide was observed followed by rapid formation of calcium carbonate.

Key words Wood cement composites · Carbon dioxide · Curing cement

Introduction

During the manufacture of a cement-bonded wood composite, the curing of cement normally requires 2–3 weeks to achieve a high degree of hydration and to develop sufficient board strength. In our previous studies^{1,2} the utilization of carbon dioxide (CO₂) for curing cement-bonded particleboard (CBP) manufactured by a conventional cold-pressing method was reported to be successful, where the curing time was shortened to a few minutes, with significant improvement in the board properties. Accelerated formation of calcium silicate hydrate and calcium carbonate and the

interlocking of these hydration products are the main reasons for the superior strength of CO₂-cured boards. However, the concentration of the CO₂ used in the previous studies was almost 100%. This study investigates the possibility of recycling CO₂ from the exhaust gases of boilers and engines of wood industries, which contain about 20% CO₂, to accelerate the curing of CBP.

The objective of this study was to assess the fundamental properties of CBP manufactured by the conventional cold-pressing method for setting the cement and cured using various CO₂–air concentrations. The degree of cement hydration in relation to the mechanism of strength development using the CO₂ curing method was also investigated.

Materials and methods

Mixtures with equal proportions of Japanese cypress (*Chamaecyparis obtusa* Endl) and Japanese cedar (*Cryptomeria japonica* D. Don) particles were used to manufacture CBP.

Ordinary Portland cement (Osaka Sumitomo Co.) was used as a binder. The CBPs with a target density of 1.2 g/cm³ were manufactured at a cement/oven-dried particle/water weight ratio of 2.2:1.0:1.1. Hand-formed mats measuring 300 × 300 mm were cold-pressed to a target thickness of 12 mm and kept in an oven at 60°C for 24 h. The specimens measuring 50 × 210 mm cut from these boards were then used for each treatment condition.

For the treatments with CO₂, the specimens were placed in a reaction cell surrounded by a water jacket set at 60°C.¹ In this experiment, the specimens were subjected to carbon dioxide pressures of 1.0 and 7.5 MPa at about 50°C. The CO₂/air concentration ratios applied were 10%, 20%, 50%, and 100%. Following curing times of 10, 30, and 60 min, they were placed in an oven set at 80°C for 10 h. Later the specimens were conditioned at ambient temperature prior to property evaluation.

The CBPs for conventional curing were wrapped with polyvinylchloride (PVC) sheets immediately after clamping

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Fig. 1. Effect of CO₂ concentration on internal bond strength (IB) at various CO₂ pressures and curing times. **a** 1.0 MPa of CO₂ pressure. **b** 7.5 MPa of CO₂ pressure. Cvn, conventional 2-week curing.

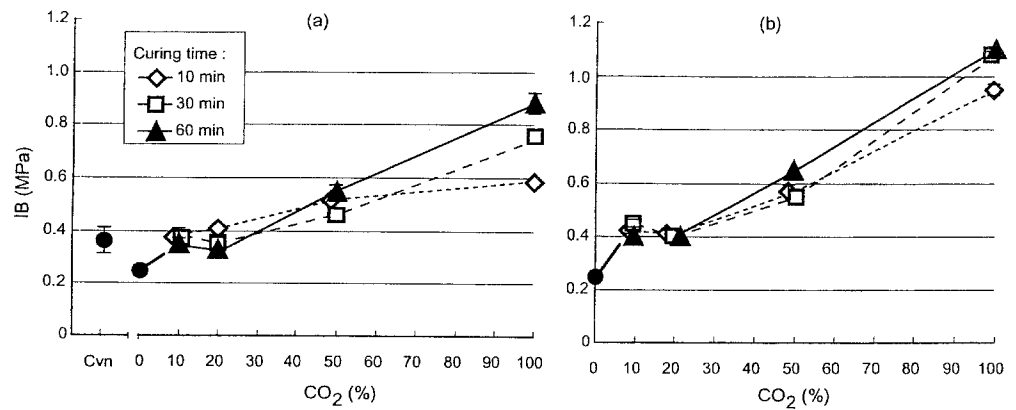
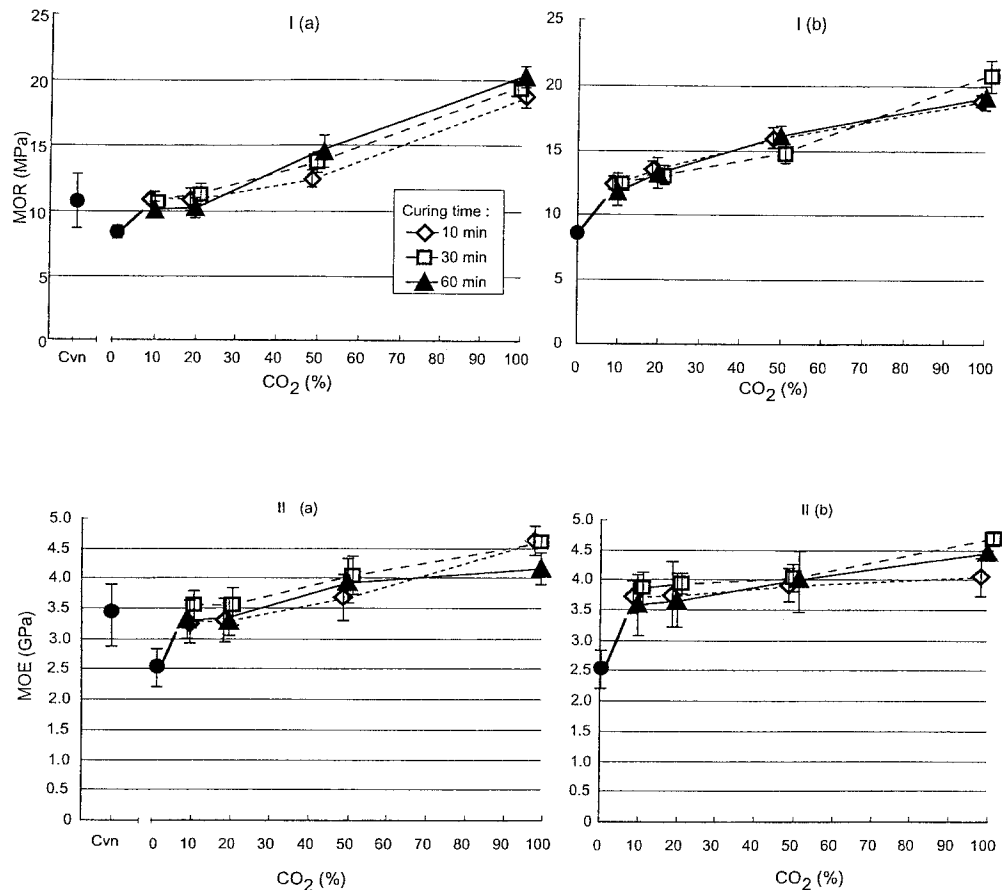


Fig. 2. Effect of CO₂ concentration on bending properties at various CO₂ pressures and curing times. **I** Modulus of rupture (MOR). **II** Modulus of elasticity (MOE). **a** 1.0 MPa of CO₂ pressure. **b** 7.5 MPa of CO₂ pressure. See Fig. 1



and were kept at room temperature for 2 weeks. This period was followed by drying and conditioning.

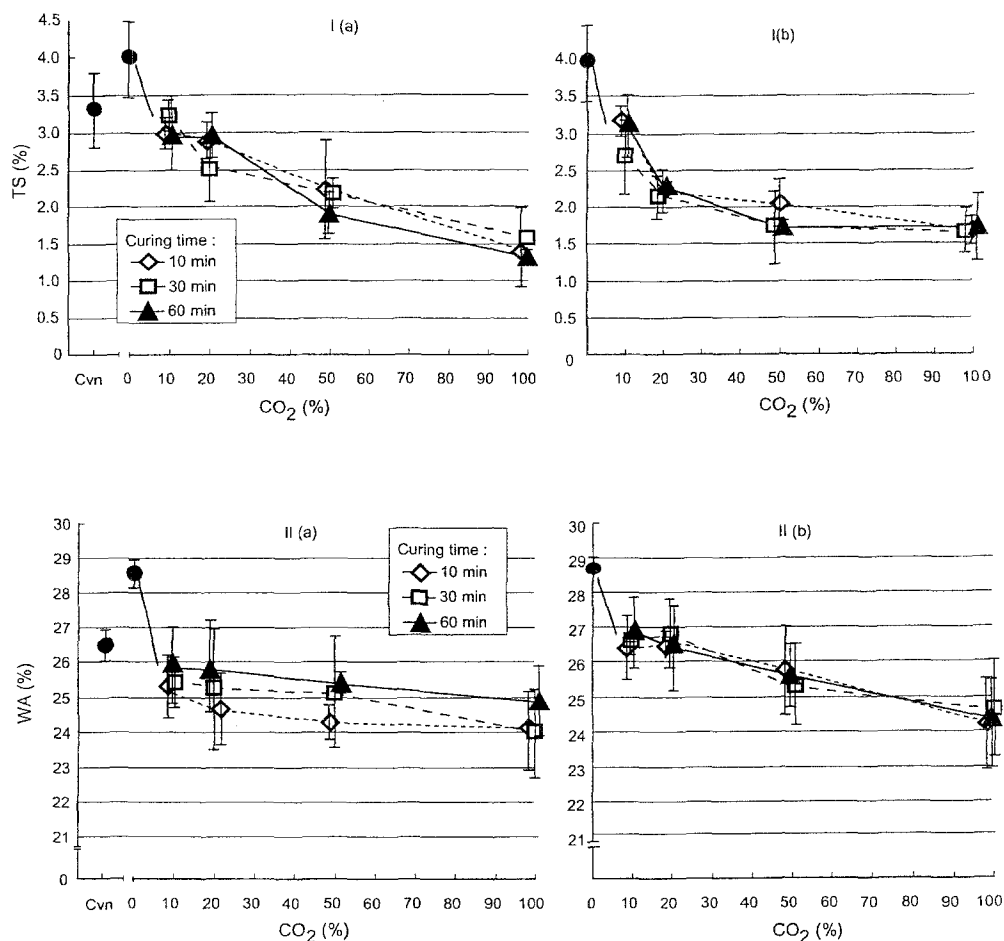
The mechanical and dimensional properties of the boards were tested in accordance with the Japan Industrial Standard JIS A 5908 (1994). The boards were cut into 50 × 210 mm pieces for the static bending test and 50 × 50 mm pieces for internal bond (IB) strength, thickness swelling (TS), and water absorption (WA) tests. Three test samples were prepared from each treatment for the above tests. The static bending tests were conducted using a three-point loading system over an effective span of 180 mm (15 times the board thickness) at a loading speed of 10 mm/min. The hydration degrees of composites were examined using X-

ray diffractometry (XRD), thermal gravimetry (TG-DTG), and scanning electron microscopy (SEM).

XRD analysis

Powdered samples (passing through 120 mesh size) taken from the IB test specimen were examined by XRD analysis. Step scan measurements were done using X-rays (Cu-K α) at 40 kV and 40 mA, with the 2θ ranging from 3.0° to 80.0°, corresponding to a scanning speed of 0.02° and 2°/min. The amount of unreacted clinkers taken at $2\theta = 32.2^\circ$ and 32.6° , calcium hydroxide at $2\theta = 18.8^\circ$, and calcium carbonate at

Fig. 3. Effect of CO₂ concentration on dimensional stability at various CO₂ pressures and curing times. **I** Thickness swelling (TS). **II** Water absorption (WA). **a** 1.0 MPa of CO₂ pressure. **b** 7.5 MPa of CO₂ pressure. See Fig. 1



$2\theta = 35.9^\circ, 39.4^\circ, 43.1^\circ,$ and 48.5° were determined and compared with those of the samples.^{1,3,4}

Thermal analysis

Powdered samples passing through 200 mesh size were examined using the thermogravimetric analyzer TGA 2050 (TA Instruments). The thermal degradation of the specimens ranging from room temperature to 1000°C at 10°C/min heating rate and nitrogen flow of 100ml/min were observed. The amounts of calcium hydroxide and calcium carbonate generated were determined.⁴⁻¹²

SEM observations

The test specimens for SEM observation were prepared by cutting small sections from the fractured surfaces of the IB test samples. The small samples were mounted on specimen stubs and then coated with gold for examination in the JSM-5310 (Jeol).

Results and discussion

Properties of CO₂-cured boards

The average values for the IB strength of the CBPs cured at different pressures and concentration ratios of CO₂ are presented in Fig. 1. The IB strength of CO₂-cured boards improved proportionally when the concentration ratio of CO₂ applied was increased. When 10% or 20% CO₂ and 1.0 MPa of pressure was applied for curing, the IB strength increased to about 0.4 MPa. These IB values were similar to those obtained by conventional 2-week curing, and they were insignificantly different for curing times of 10, 30, and 60 min. A similar trend was observed for boards cured at pressure of 7.5 MPa; addition of 10% or 20% CO₂ resulted in improved IB strength, from about 0.2 MPa to 0.4 MPa and remained almost constant at all curing times.

The IB strength of the CBPs increased to about 0.5 and 0.6 MPa, respectively, when 50% CO₂ was added. Extension of the curing time up to 60 min did not result in any differences in the IB values. When 100% CO₂ was applied, the longer curing time gave rise to higher IB values, especially at 1.0 MPa of CO₂ pressure, where the IB increased drastically to about 1.0 MPa.

Figure 2 shows the effect of the CO₂ concentration ratio on the moduli of rupture (MOR) and elasticity (MOE) at

different CO₂ pressures. It was evident that the bending properties improved when the concentration ratio of CO₂ was increased, and they showed insignificant fluctuation over curing times of 10, 30, and 60 min. The MOR and MOE values of the CO₂-cured boards were similar to those of the conventionally cured boards when up to 20% CO₂ was added, irrespective of the curing time.

Figure 3 shows the TS and WA values of the boards after 24 h of water soaking. Increasing the CO₂ concentration ratio enhanced the dimensional stability, and no significant differences were indicated up to 60 min of curing time. Similar to other properties, the dimensional stability of CO₂-cured boards was comparable to that of conventionally cured board when up to 20% CO₂ was applied.

It was evident that the curing process using CO₂-air mixtures had a favorable effect on the mechanical and dimensional properties of CBP, especially at pressure of 7.5 MPa, where the properties of CBP increased at a faster rate. Because the mixture of CO₂-air is used for the curing process, the phase behavior of the mixture is difficult to determine. The pressure of the mixture at 7.5 MPa and about 50°C is higher than that of the supercritical point of each component (e.g., nitrogen, oxygen, carbon dioxide). In addition, no interaction or reaction is expected between the CO₂ and air under these conditions due to the rather stable condition of those components. According to the finding by Reid, et al.¹³ that the properties of the mixture are determined by averaging the pure component constants, which hopefully characterize the constant of the critical point, the pressure of 7.5 MPa in this study could be estimated as a supercritical phase. However, no drastic differences in the properties were observed between the CBPs of 1.0 and 7.5 MPa. Because the ideal critical point of pure CO₂ pressure is 7.3 MPa, a uniform supercritical condition may not be obtained in the pressure range of this experiment. This trend was also observed in our previous study,¹ where pure CO₂ was introduced in the pressure range of 0.5–10.0 MPa. Therefore, further study with a wider range of pressure and temperature applied is necessary to identify the effect of both pure CO₂ and CO₂-air mixture phases on the properties of cement-bonded board.

The effectiveness of the CO₂ addition also depends on the degree of the initial setting of cement from which the calcium hydroxide [Ca(OH)₂] is provided as a medium to produce the crystalline formation of calcium carbonate (CaCO₃). The initial setting of cement is also important to produce the calcium silicate hydrate (CSH). This CSH and CaCO₃ are mainly responsible for the strength development of CBP.¹ In this experiment, the board was manufactured using the conventional cold-pressing method for setting the cement.

Improvement mechanism of the CO₂ curing

XRD analysis

The CO₂ curing treatment produced significantly faster curing of CBP than the conventional curing method. Rapid

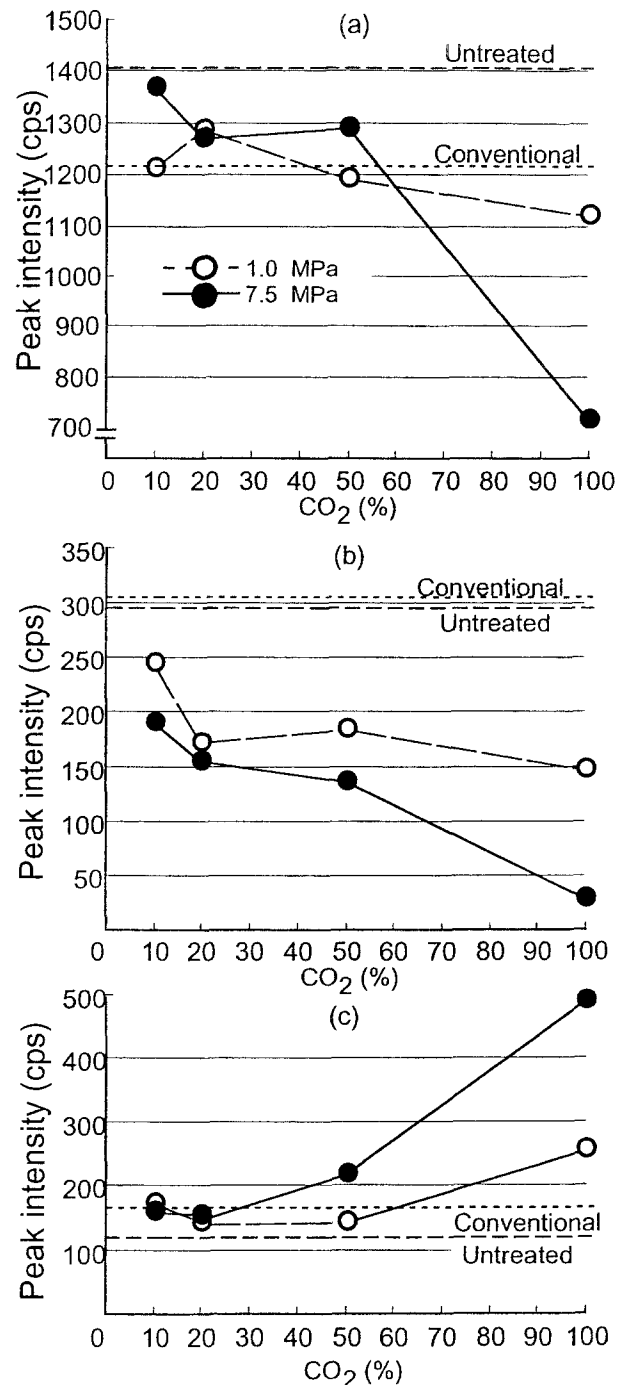
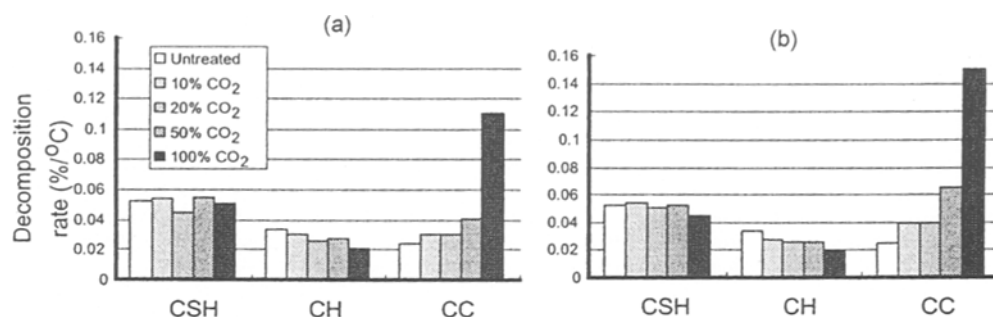


Fig. 4. X-ray diffractometry (XRD) patterns of cement-bonded particleboards (CBPs). **a** Cement clinkers. **b** Calcium hydroxide. **c** Calcium carbonate

carbonization has been reported to enhance cement hydration and cause inhibitors (e.g., free carbohydrates) that retard the hydration of cement to lose their inhibitory effects.^{1–12,14}

The results of the XRD analysis after 10 min of curing are shown in Fig. 4. The rate of cement hydration of the CO₂-cured boards was accelerated; the peak intensities of cement clinkers (Fig. 4a) were relatively lower than those of untreated boards, and they decreased when the concentra-

Fig. 5. Effect of CO₂ concentration on the thermal property of CBPs at various CO₂ pressures after 60 min of curing. **a** 1.0 MPa of CO₂ pressure. **b** 7.5 MPa of CO₂ pressure



tion ratio of CO₂ was increased. Even though the CO₂ concentration ratio used was low (i.e., 10% or 20%), cement hardening was accelerated and seemed to reach a high level of hydration, similar to the conventional 2-week curing.

The carbonization of calcium hydroxide into calcium carbonate occurred during the later phase of cement hydration. This carbonization process was accelerated with both 1.0 and 7.5 MPa CO₂ pressures, irrespective of the CO₂ concentration levels. The peak intensities of calcium hydroxide of the treated boards decreased with the increasing CO₂ concentration ratio, as shown in Fig. 4b.

The peak intensities of calcium carbonate are presented in Fig. 4c. It was observed that the intensities of calcium carbonate increased with increasing concentration ratio and pressure of CO₂. The addition of 10% or 20% CO₂, at either 1.0 or 7.5 MPa of CO₂ pressure, accelerated the later phase of cement hydration. After 10 min of curing the intensity of calcium carbonate of the CO₂-cured boards were similar to that of conventionally cured board. In addition, the degree of cement hydration of CBPs cured at 7.5 MPa of CO₂ pressure was higher than that of 1.0 MPa of CO₂ pressure.

TG-DTG analysis

Figure 5 shows the typical results of DTG analysis of CBPs after 60 min of curing. Successive decomposition reactions occurred with an increase in temperature, as reflected in the decreased weight of all samples. It is evident that decomposition of CSH and Ca(OH)₂ occurred at temperatures around 100°C and 400°C, respectively. Decomposition of CaCO₃, on the other hand, occurred at around 700°C.⁸ According to the DTG curves, the decomposition rate of Ca(OH) decreased with increasing CO₂ concentration ratio.

The degree of cement hydration at the later stage was accelerated when CO₂ was added, irrespective of its concentration. The rate of the weight loss of CaCO₃ increased from about 0.02%/°C to 0.03%/°C when up to 20% CO₂ and 1.0 MPa of CO₂ pressure were applied; and it was accelerated to 0.04%/°C at 7.5 MPa of CO₂ pressure. The addition of 50% and 100% CO₂ accelerated the hydration process of cement, as indicated by the faster rate of decomposition of CaCO₃.

SEM observations

To confirm the findings in the above analyses, the fractured surface of the CBP was examined using SEM. Figure 6

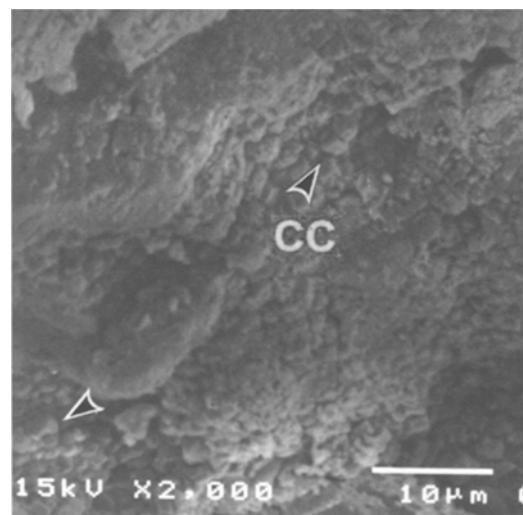


Fig. 6. Scanning electron microscopy of the fractured surface of CBP under 20% CO₂ addition and 7.5 MPa of CO₂ pressure. CC, calcium carbonate (arrowheads)

shows an example of the fractured surface of the CBP under 20% CO₂ addition. CaCO₃ was formed as a result of the hydration of all basic cement compounds. It was noted in our previous study and other research work^{1,15,16} that these formations are believed to interlock with CSH and wood surfaces.

Conclusions

The mechanical and dimensional properties of CO₂-cured boards improved as the CO₂ concentration ratio during the curing process increased. When 10% or 20% of CO₂ was applied for 10 min of curing time, the properties of CO₂-cured boards were similar to those of the 2-week curing.

The hydration process of cement accelerated with increasing CO₂ pressure, irrespective of the CO₂ concentration. The intensities of Ca(OH)₂ decreased with an increasing CO₂ concentration ratio, followed by accelerated formation of CaCO₃.

The exhaust gas from boilers and engines of cement-board industries or cement factories is suggested to be applicable for the rapid manufacturing process for cement-bonded particleboard.

References

1. Hermawan D, Hata T, Umemura K, Kawai S, Nagadomi W, Kuroki Y (2001) Rapid production of high-strength cement-bonded particleboard by using gaseous or supercritical carbon dioxide. *J Wood Sci* 47:294–300
2. Hermawan D, Hata T, Umemura K, Kawai S, Kaneko S, Kuroki Y (1999) New technology for manufacturing high-strength cement-bonded particleboard using supercritical carbon dioxide. *J Wood Sci* 46:85–88
3. Nagadomi W, Kuroki Y, Eusebio DA, Ma L, Kawai S, Sasaki H (1996) Rapid curing of cement-bonded particleboard. V. Mechanism of strength development with fortifier and accelerator during steam injection pressing. *Mokuzai Gakkaishi* 42:977–984
4. Ma L, Kuroki Y, Nagadomi W, Kawai S, Sasaki H (1998) Manufacture of bamboo-cement composite. III. Effects of sodium carbonate on cement curing by steam injection pressing. *Mokuzai Gakkaishi* 44:262–272
5. Klimesch DS, Ray A (1997) The use of DTA/TGA to study the effect of ground quartz with different surface areas in autoclaved cement: quartz pastes use of the semi-isothermal thermogravimetric technique. *Thermochim Acta* 306:159–165
6. Abdelrazig BEI, Main SD, Noweel DV (1992) Hydration studies of modified OPC pastes by differential scanning calorimetry and thermogravimetry. *J Thermal Anal* 38:495–504
7. Zhou X, Lin X, Huo M, Zhang Y (1996) The hydration of saline oil-well cement. *Cement Concrete Res* 26:1753–1759
8. Bhatti JI (1991) A review of the application of thermal analysis to cement-admixture systems. *Thermochim Acta* 189:313–350
9. Ramachandran VS (1969) Application of DTA in cement chemistry. Chemical Publishing, New York
10. Barta R (1972) In: Mackenzie RC (ed) *Differential thermal analysis*. Academic, London, p 207
11. Mackenzie RC (1964) In: Taylor (ed) *The chemistry of cement*. Academic, London, p 271
12. Ben-Dor L (1983) In: Ghosh A (ed) *Advances in cement technology*. Pergamon, Exeter, UK, p 673
13. Reid RC, Prausnitz JM, Poling BE (1987) *The properties of gases and liquids*. McGraw-Hill, New York
14. Simatupang MH, Habighorst C (1993) The carbon dioxide process to enhance cement hydration in manufacturing of cement-bonded composites: comparison with common production method. *For Prod Soc* 3:114–120
15. Ahn WY, Moslemi AA (1980) SEM examination of wood-portland cement board. *Wood Sci* 13:77–82
16. Kayahara M, Tajika K, Nakagawa H (1979) Strength increase of wood-cement composites. *Mokuzai Gakkaishi* 25:552–557