

ORIGINAL ARTICLE

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Rapid production of high-strength cement-bonded particleboard using gaseous or supercritical carbon dioxide

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Abstract This study deals with the effects of curing treatment with gaseous and supercritical carbon dioxide on the properties of cement-bonded particleboard (CBP) manufactured by the conventional cold-pressing method. The hydration of cement and the mechanism of improvement were examined using X-ray diffractometry (XRD), thermal gravimetry (TG-DTG), and scanning electron microscopy (SEM) observations. The results are as follows: (1) The curing of cement was accelerated concomitantly with the improvement in mechanical and dimensional properties of CBP significantly by curing with gaseous or supercritical carbon dioxide. (2) Supercritical carbon dioxide curing imparted boards optimal properties at a faster rate than did gaseous curing. (3) Accelerated formation of calcium silicate hydrate and calcium carbonate and the interlocking of those hydration products on the wood surface are potentially the main reasons for the superior strength of carbon dioxide-cured boards.

Key words Wood cement composites · Supercritical carbon dioxide · Carbon dioxide gas · Curing cement

Introduction

Curing ordinary portland cement is a slow, complex process, especially if the cement is used as a binder in composites containing lignocellulosics as aggregates or as reinforcement material. Water/alkaline-soluble extractives of the lignocellulosics or the chemical compounds that become soluble under the influence of cement–water interaction may inhibit the setting or curing of the cement.

It was indicated in a previous study¹ that the curing time of cement-bonded board manufactured by a conventional cold-pressing method was accelerated dramatically by supercritical CO₂ curing (which is at a critical pressure and temperature of 7.38MPa and 31°C, respectively²); in that study the specimens were subjected to a pressure of 7.4MPa at about 50°C for 90 min. This research demonstrated that supercritical CO₂-cured board can be twofold stronger than untreated board. The addition of CO₂ accompanied by a supercritical fluid might enhance the hydration process of cement and thereby the strength properties of the board. This improvement may be due to the production of high calcium carbonate content during hydration of the cement. To identify the optimum curing condition, further study with a wider range of pressures and curing times is necessary. Certain analyses are also required to clarify the mechanism by which we can improve CO₂ curing.

The primary objective of this study was to assess the fundamental properties of cement-bonded particleboard manufactured by a conventional cold-pressing method for setting the cement cured with gaseous or supercritical CO₂ at various curing times. Degrees of cement hydration in relation to the mechanism of strength development with the CO₂ addition were also investigated.

Materials and methods

Mixtures with proportionally equal amounts of the Japanese cypress (*Chamaecyparis obtusa* Endl) and Japanese cedar (*Cryptomeria japonica* D.Don) particles were used to manufacture cement-bonded particleboard (CBP).

Ordinary portland cement (Osaka Sumitomo Co.) was used as a binder. The CBPs with a target density of 1.2g/cm³ were manufactured at cement/oven-dried particles/water weight ratios of 2.2:1.0:1.1 with (1) supercritical CO₂ curing; (2) CO₂ gas curing; and (3) conventional curing (Fig. 1). The concentration of CO₂ used was about 95%. Hand-formed mats measuring 300 × 300mm were cold-

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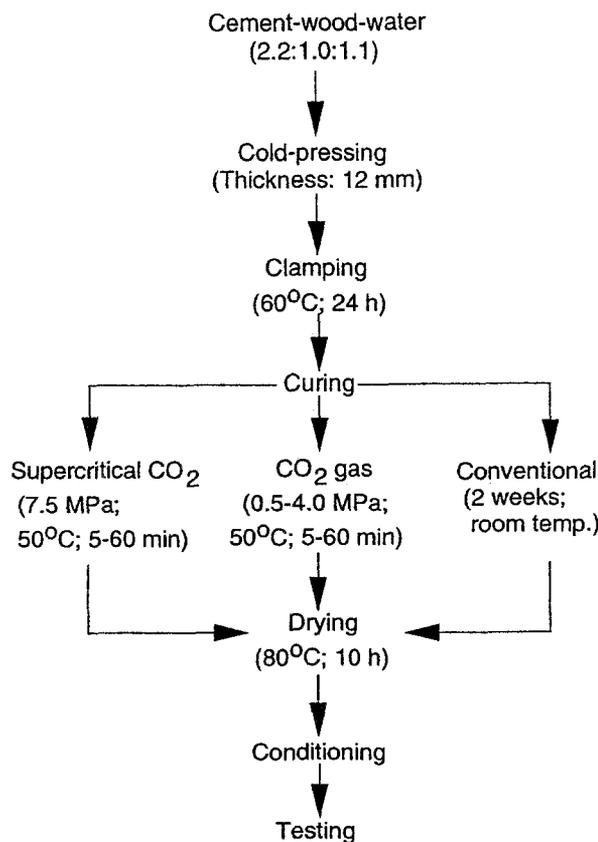


Fig. 1. Manufacturing cement-bonded particleboard

pressed to a target thickness of 12mm and kept in an oven at 60°C for 24h. The 50 × 210mm specimens prepared from these boards were then used for each treatment condition.

For treatment with gaseous and supercritical CO₂, the specimens were placed in a reaction cell surrounded by a water jacket set at 60°C.¹ In this experiment specimens were subjected to CO₂ pressures of 0.5, 1.0, 2.0, and 4.0MPa in the gas phase, and 7.5MPa in the supercritical phase, with a temperature around 50°C. After curing for 5, 10, 15, 30, and 60min, the specimens were placed in an oven at 80°C for 10h. Later, specimens were conditioned at ambient temperature prior to testing.

The CBPs for conventional curing were wrapped with polyvinylchloride (PVC) sheets immediately after clamping and were kept at room temperature for 2 weeks. This step 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). All of the specimens were cut into various test samples as follows: 50 × 210mm for the static bending test and 50 × 50mm for internal bond (IB) strength, thickness swelling (TS), and water absorption (WA) tests. Three test samples were prepared from each treatment for the static bending, IB, TS, and WA tests. In addition, the static bending tests were conducted using a three-point bending test over an effective span of 180mm (15× thickness) at a loading speed of 10mm/min. The hy-

dration degrees of composites were examined using X-ray diffractometry (XRD), thermal gravimetry (TG-DTG), and scanning electron microscopy (SEM).

XRD analysis

Powdered samples of 120 mesh-pass taken from an IB test specimen were examined by XRD analysis. The method used in this experiment is widely applied to the analysis of cement hydration.^{3,4} Step scan measurements were done using XRD (Cu-K α) at 40kV and 40mA; 2 θ ranged from 3.0° to 80.0° when scanning at 0.02°/min and 2.0°/min. The amount of unreacted clinkers taken at 2 θ = 32.2° and 32.6°, calcium hydroxide at 2 θ = 18.8°, and calcium carbonate at 2 θ = 35.9°, 39.4°, 43.1°, and 48.5° were determined and compared with those of the samples.

Thermal analysis

Powdered samples of 200 mesh-pass were examined by a thermogravimetric analyzer (TGA 2050; TA Instruments). The thermal degradation of the specimens were observed ranging from room temperature to 1000°C at a 10°C/min heating rate and nitrogen flow at 100ml/min. The amount of calcium hydroxide and calcium carbonate generated were determined.^{4,6}

SEM observation

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 JSM-5310 (Jeol).

Results and discussion

Properties of CO₂-cured boards

The average values for IB strength of the CBPs are presented in Fig. 2. The IB strength increased drastically from 0.3MPa to 1.3MPa when CO₂ was added as a supercritical CO₂ phase at 5min curing time. The optimum IB value of the board at 1.5MPa was obtained after 10min of curing, and it showed an insignificant fluctuation until 60min of curing time. It was observed that the optimum value was similar to the IB value obtained previously.¹

The IB values of the gaseous CO₂-cured boards with curing times of less than 30min were lower than that of supercritical CO₂ curing. However, when applying pressures of 2.0 and 4.0MPa after 30min of curing, the IB values were similar to those of supercritical CO₂-cured boards. The

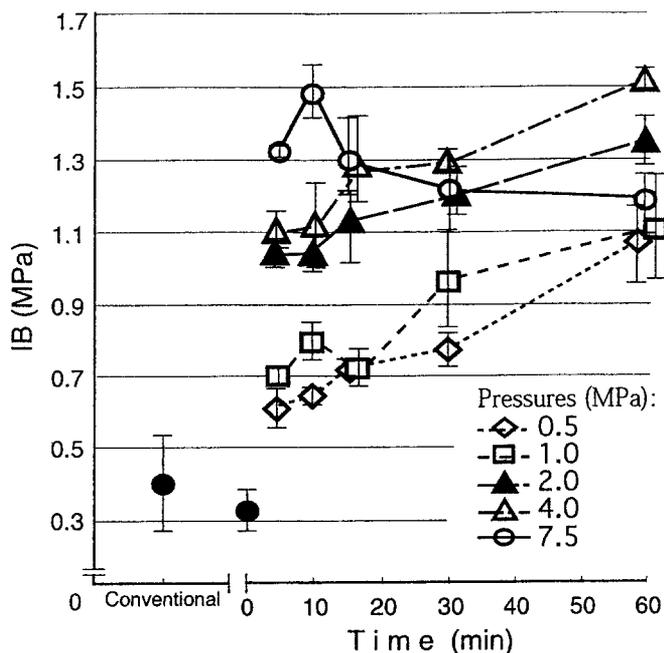


Fig. 2. Internal bond strength (*IB*) of various boards

addition of CO_2 at pressures of 0.5 and 1.0 MPa yielded the lowest bonding property and showed proportional improvement at a longer curing time.

The *IB* values of either gaseous or supercritical CO_2 -cured boards seemed to reach a saturated level of 1.3–1.5 MPa. One of our preliminary studies indicated that the properties were similar when the pressure increased up to 10 MPa for 90 min. It was also observed from the previous report¹ that the *IB* of supercritical CO_2 -cured boards was about 1.4 MPa when the curing time was 90 min.

The *IB* of the conventionally cured boards was 0.4 MPa, which is markedly lower than the values for the boards cured with gaseous or supercritical CO_2 .

Figure 3 shows the modulus of rupture (*MOR*) and modulus of elasticity (*MOE*) of boards cured under various CO_2 pressures and curing times. It was observed that the *MOR* values of the boards cured with gaseous CO_2 were saturated more rapidly as the CO_2 pressure increased. It increased significantly from 10 MPa to about 21 MPa when CO_2 curing at a pressure of more than 2.0 MPa for more than 10 min was achieved.

The *MOE* values of CBPs seemed to reach a saturated level of about 5 GPa with any curing conditions of CO_2 , resulting in a significant increase from 2.9 GPa. The bending properties obtained in this study were similar to those of the previous study,¹ especially for the *MOR* at 10 and 20 min of curing.

The *MOR* and *MOE* values of the conventionally cured boards were 11.1 MPa and 3.5 GPa, respectively. These values are significantly lower than those of the CO_2 -cured boards.

The *TS* and *WA* values of the boards after 24 h of water soaking are shown in Fig. 4. After 5 min of curing, the *TS* values decreased from 4.7% to around 1.5% when CO_2 at

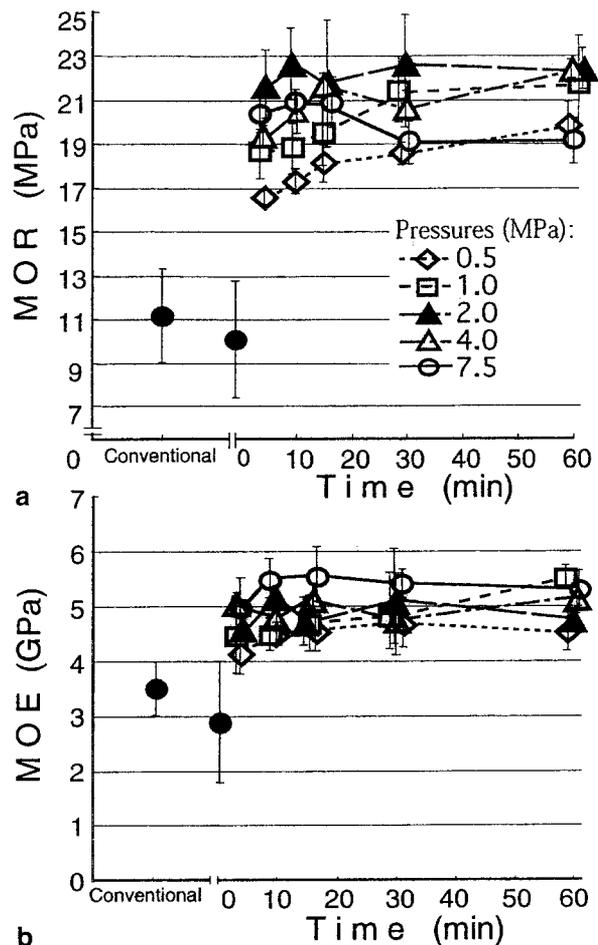


Fig. 3. Bending properties of various boards. **a** Modulus of rupture (*MOR*). **b** Modulus of elasticity (*MOE*)

pressures of 7.5 and 4.0 MPa was used for curing. In the meantime, when curing with CO_2 at pressures below 2.0 MPa, the *TS* decreased to about 2.0%. Furthermore, the stability of CBPs fluctuated insignificantly until 60 min of curing time. A similar trend was observed for the *WA* of supercritical cured board and at a gas phase of 2.0 MPa, which decreased during the early curing. The *WA* decreased proportionally with increasing curing time when the CO_2 was applied at a pressure of 4.0 MPa. The *WA* values of the CBPs cured by CO_2 at pressures of 0.5 and 1.0 MPa were almost similar to untreated and conventionally cured boards over several curing times. The dimensional stability of supercritical CO_2 -cured boards obtained in this study was somewhat higher than for those reported previously.¹

Improved mechanism of CO_2 curing treatment

The CO_2 curing treatment imparted boards significantly higher mechanical and dimensional properties. The retardation effect of wood extractives on cement hardening was successfully eliminated and the cement hardening was accelerated by treatment with CO_2 . CO_2 might improve the

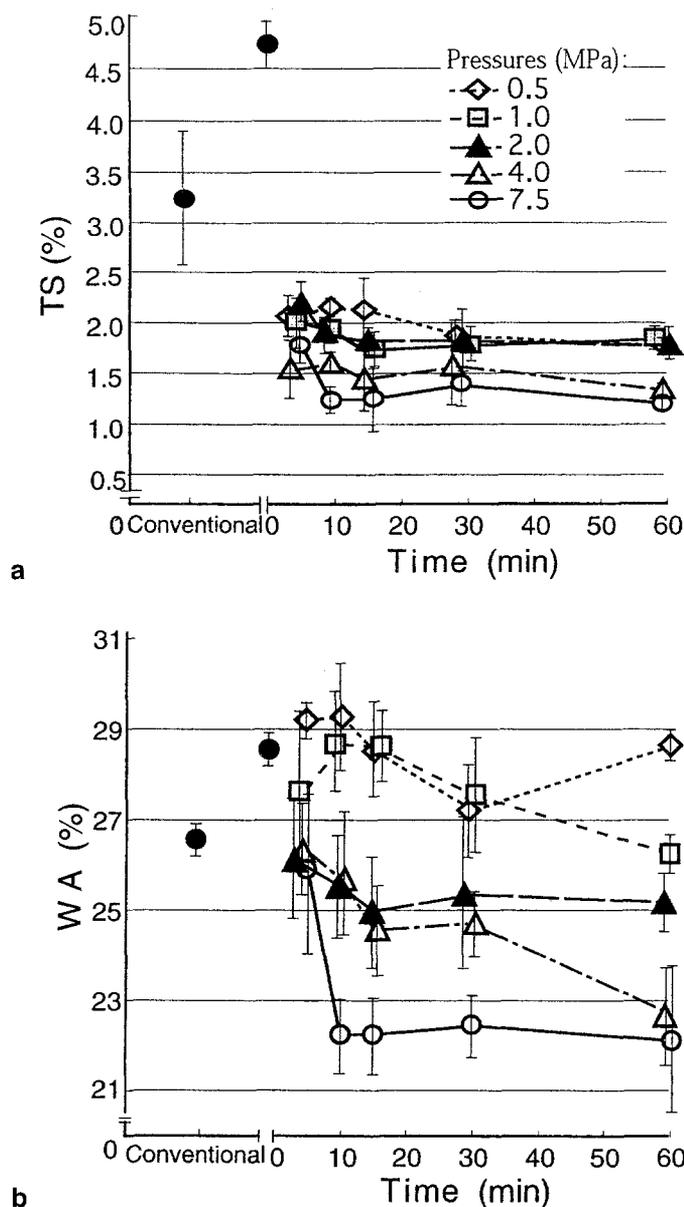
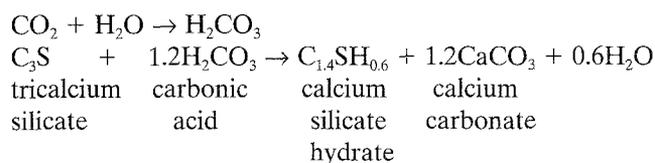


Fig. 4. Dimensional stability of various boards. a Thickness swelling (TS). b Water absorption (WA)

precipitation of calcium hydroxide, and hydrolyzation of the clinker phases are promoted, thereby enhancing cement hydration. Formation of hydration products (e.g., calcium silicate hydrate and calcium carbonate), which are mainly responsible for the strength properties of cement, is accelerated by the addition of CO_2 .⁷ It is known that during the cement hydration process dicalcium silicate [Ca_2SiO_4 (C_2S)] and tricalcium silicate [Ca_3SiO_5 (C_3S)] are hydrated to form calcium silicate hydrate [$\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ (CSH)] and calcium hydroxide [$\text{Ca}(\text{OH})_2$]. When CO_2 is added to cement, calcium carbonate (CaCO_3) is formed.^{1,8-10}

In addition, the emergence of calcium silicate hydrate and calcium carbonate was accelerated by the strong reaction of the carbonic acid with the clinker phases of cement owing to CO_2 dissolving in water.¹¹ The reaction of the clinker is shown in the following scheme.⁷



Relevant results of the XRD analysis are shown in Fig. 5. The cement hydration of the supercritical CO_2 -cured boards at pressures of 2.0 and 4.0 MPa was accelerated; the peak intensities of cement clinkers (Fig. 5a) were relatively lower than those of the untreated and conventionally cured boards. After 15 min of curing, the intensities of cement clinkers decreased with the increase in curing time. The addition of CO_2 at a pressure of 1.0 MPa could not accelerate the early stage of cement hydration; the peak intensities of cement clinkers were almost the same as conventionally cured boards at all curing times. The hydrolysis process of the cement clinkers cured at a pressure of 0.5 MPa was the slowest. However, the reaction process accelerated and the intensities of cement clinkers decreased with the longer curing time.

In the latter case of cement hydration, however, formed calcium hydroxide is carbonized to calcium carbonate. It was noted that the carbonization process was accelerated with any curing conditions of CO_2 , resulting in a significant decrease in peak intensity of calcium hydroxide in the treated boards (Fig. 5b). The peak intensity of the supercritical CO_2 -cured board and of pressures of more than 1.0 MPa were significantly lower than those of the untreated and conventionally cured boards. Among those treated boards, the degree of cement hydration of CBPs cured at a pressure of 0.5 MPa was lowest at the shorter curing time. However, the intensity of calcium hydroxide decreased with the longer curing time and seemed to reach a high level of hydration after 60 min of curing.

The peak intensity of calcium carbonate in the treated boards increased drastically, as shown in Fig. 5c. This phenomenon indicated that the latter stage of cement hydration was accelerated using either gaseous or supercritical CO_2 . In general, the calcium carbonate increased proportionally with the longer curing time and higher CO_2 pressure. After 60 min of curing, the peak intensities of calcium carbonate of supercritical CO_2 - and gaseous CO_2 -cured boards were in the range of 420–550 cps. The peak intensities of untreated and conventionally cured boards were not more than 165 cps.

Figure 6 shows the results of TG-DTG analysis of CBPs after 10 min of curing time. For all samples, successive decomposition reactions or mass losses occurred with an increase in temperature. The mass losses did not occur at a regular level but over several ranges. A constant mass plateau was not seen for the applied treatments, resulting in poorly distinguished decomposition stages, particularly at temperatures below 500°C.

The DTG curves consist of a series of peaks corresponding to the rate of decomposition or mass losses. A peak maximum indicates a value equivalent to the points of each inflection shown in the TG curve. From the DTG curve, it is evident that the mass losses occurred at temperatures below

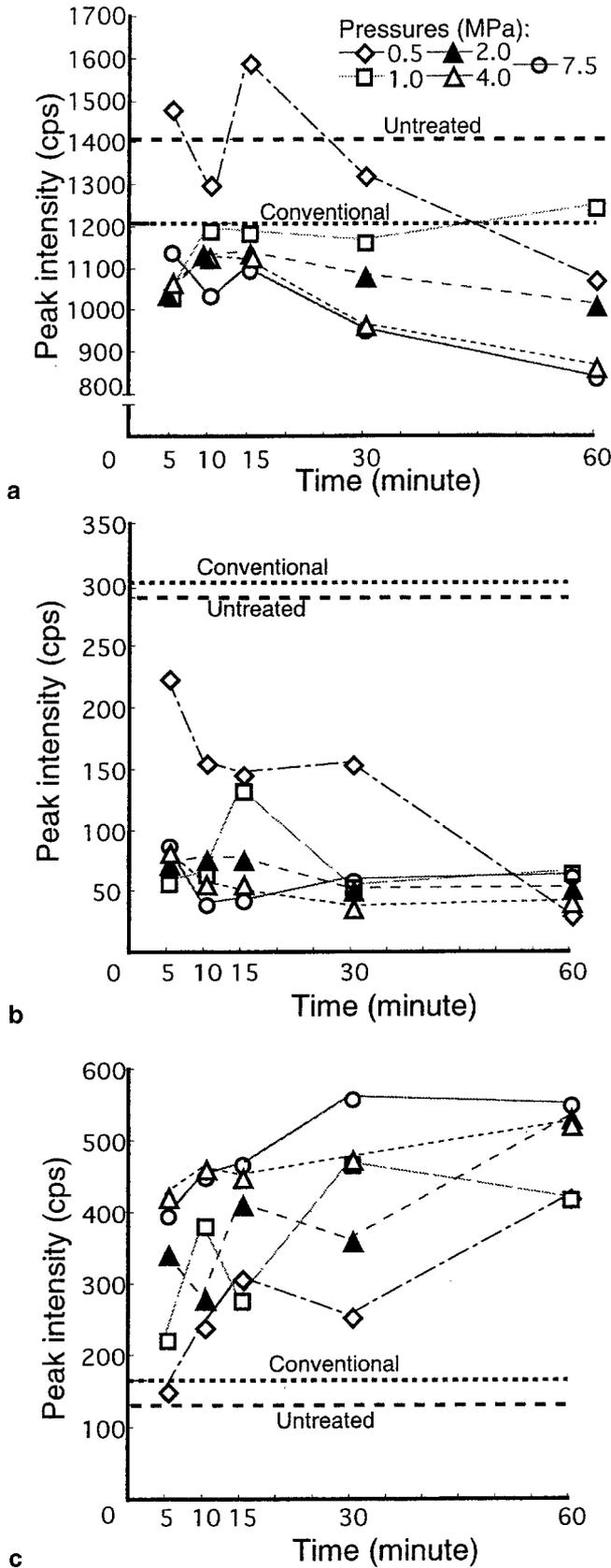


Fig. 5. X-ray diffractometry (XRD) patterns of cement-bonded particleboards (CBPs). a Cement clinkers. b Calcium hydroxide. c Calcium carbonate

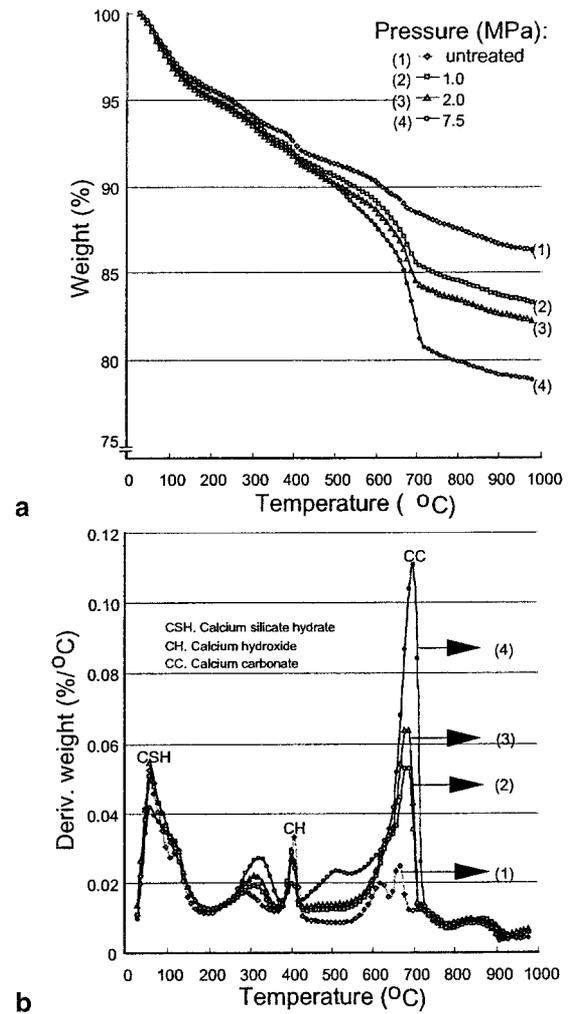


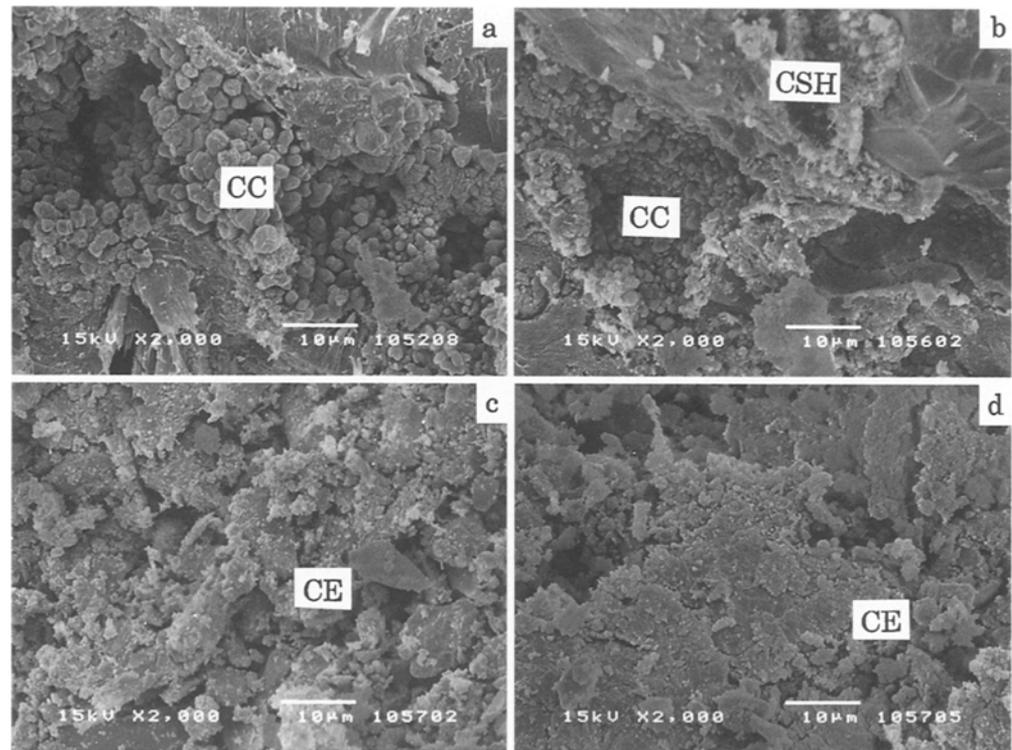
Fig. 6. Thermal properties of CBPs after 10 min of curing. a Thermogravimetry (TG). b Derivative thermal gravimetry (DTG)

200°C owing to the decomposition of calcium silicate hydrate. However, the mass losses for this period could also be caused by decomposition of a small amount of wood powder and water. Furthermore, the decomposition of calcium hydroxide occurred at a temperature around 400°C. The maximum peak of calcium hydroxide of supercritical CO₂-cured board was the lowest owing to the high degree of carbonization. The next maximum peak occurred at a temperature around 700°C owing to the decomposition of calcium carbonate. The maximum peak of the supercritical CO₂-cured board was highest, followed by the gaseous CO₂-cured board and untreated board, respectively.

Figure 7 shows the fractured surface of a CBP seen by scanning electron microscopy (SEM). The supercritical CO₂-cured board (Fig. 7a) and gaseous CO₂-cured board (Fig. 7b) illustrate calcium carbonate and calcium silicate hydrate formation when CO₂ was added.

The addition of CO₂ appears to result in a substantial change in the structure of hydrated cement. The calcium carbonate formations are fully developed and better de-

Fig. 7. Scanning electron microscopy photographs of fractured surfaces of CBPs. **a** Supercritical CO₂-cured board. **b** CO₂ gas-cured board. **c** Untreated board. **d** Conventionally cured board. *CC*, calcium carbonate; *CSH*, calcium silicate hydrate; *CE*, cement clinker



fined. These formations result from the hydration of all basic cement compounds. They are believed to be interlocked with the calcium silicate hydrate and wood surface. The fluid cement paste flows into cracks and cell lumens on the rough wood surface and then crystallizes to form cement plugs that interlock the cement and wood.^{12,13} Those interactions appear to result in the excellent strength of the composite. Therefore, this mechanical interlocking process is probably an important mechanism contributing to the strength.

Figure 7c,d show the fracture surfaces of untreated board and conventionally cured board, respectively. There was interference with cement hydration, and the formation of calcium silicate hydrate and calcium carbonate did not occur. A mass of amorphous bodies was found that apparently did not develop the interlocking strength potential brought about by calcium silicate hydrate and calcium carbonate.

Conclusions

The mechanical and dimensional properties of cement-bonded particleboard, manufactured by a conventional cold-pressing method followed by a curing treatment using either gaseous or supercritical CO₂, were improved significantly. Moreover, curing was accelerated dramatically to a few minutes rather than a week.

The optimum properties of the boards manufactured by supercritical CO₂ curing were mostly similar to those of

gaseous CO₂ curing. However, the optimum properties of the supercritical CO₂-cured boards could be achieved earlier than those with gaseous CO₂ curing.

The high production levels of calcium silicate hydrate and calcium carbonate during the hydration of cement, and the interaction between those hydration products with wood surfaces are considered the main reasons for the superior strength properties obtained in CO₂-cured boards.

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