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Manufacture of Cement-Bonded Particleboards from Korean Pine and Larch by Curing of Supercritical CO_2 Fluid*1

Jin-Suk Suh*2, Dede Hermawan*3, and Shuichi Kawai*3

ABSTRACT

Cement-bonded particleboard is being used as outdoor siding material all over the world, because this composite particularly bears a light weight, high resistance against fire, decay, and crack by cyclic freezing and thawing, anti-shock property, and strength enhancement. Construction systems are currently changing into a frame-building style and wooden houses are being constructed with prefabrication type. Therefore, they require a more durability at outdoor-exposed sides.

In this study, the cement hydration property for Korean pine particle, Japanese larch particle and face- and middle layer particles (designated as PB particle below) used in Korean particleboard-manufacturing company was investigated, and the rapid manufacturing characteristics of cement-bonded particleboard by supercritical CO_2 curing was evaluated.

Korean pine flour showed a good hydration property, however, larch flour showed a bad one. PB particle had a better hydration property than larch flour. The addition of Na_2SiO_3 indicated a negative effect on hydration, however, $MgCl_2$ had a positive one.

Curing by supercritical CO_2 fluid gave a conspicuous enhancement in the performances of cement-bonded particleboards compared to conventional curing. $MgCl_2$ 3%-added PB particle had the highest properties, and $MgCl_2$1%-added Korean pine particle had the second class with the conditions of cement/wood ratio of 2.7, a small fraction-screened particle and supercritical curing. On the contrary, the composition of non-hammermilled or large fraction-screened particle at cement/wood ratio of 2.2 was poorer. Also, the feasibility for actual use of 3%-added, small PB particle-screened fraction was greatest of all the conventional curing treatments.

Relative superiority of supercritical curing vs. conventional curing at dimensional stability was not so apparent as in strength properties.

Through the thermogravimetric analysis, it was ascertained that the peak of a component $CaCO_3$ was highest, and the two weak peaks of calcium silicate hydrate and ettringite and $Ca(OH)_2$ were present in supercritical treatment. Accordingly, it was inferred that the increased formation of carbonates in board contributes to strength enhancement.

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*2 Korea Forest Research Institute, Seoul 130-012, Korea

*3 Wood Research Institute, Kyoto University, Uji, Kyoto 611-0011, Japan

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1. INTRODUCTION

There are many manufacturing companies in wood-based panels industry in Korea. In 1999, 8 plywood companies produced 734,000 m^3 plywoods, 4 PB companies did 672,000 m^3 particleboards, and 6 MDF companies did 843,000 m^3 MDFs. However, inorganic-bonded particleboards are not being now manufactured and aren't used in Korea. This seems to be due to our construction systems and inflexible market circumstance relying on a concrete pouring-into-form method. This inorganic-bonded wood composite characterizes a light weight, high resistance against fire, decay, and crack by cyclic freezing and thawing, anti-shock property, and strength enhancement. Accordingly, the merits of this composite board are attributed to compromise of characteristics of wood and inorganic materials.

In relation to this study, the CO_2 which is released from a carbonate of either ammonium, potassium or sodium during pressing into cement paste was known to be effective of the setting of cement (Simatupang, 1990). The pressurized CO_2 gas was also introduced into cement-bonded wood particle/fiber board for rapid setting (Simatupang and Habighorst, 1993; Suh and Simatupang, 1995). In recent years, a few rapid curing systems were developed in Japan. Of these approaches, one is to use such additives as $MgCl_2$, $CaCl_2$, $NaHCO_3$ and Na_2SiO_3 with steam-injection pressing or hot platen pressing as a setting treatment which is subsequently followed by a curing treatment using autoclaving or heating (Nagadomi *et al.*, 1996). As a newly contrived technique, combining conventional cold pressing(or clamping) as a setting and supercritical CO_2 curing treatment was also applied to rapid production of cement composites (Dede Hermawan *et al.*, 1999).

Looking into Korean wood resources, the forest plantations are growing steadily, and the softwood resource occupies a great part of these stocks. The aim of this study is to investigate a compatibility of Korean pine and larch particles with cement and to manufacture the cement-bonded composite by using rapid curing system of supercritical fluid of CO_2.

2. MATERIALS and METHODS

2.1 Experimental materials

Wood species of Korean pine (*Pinus koraiensis* Sieb. et Zucc.) and Japanese larch (*Larix leptolepis* (Sieb. et Zucc.) Gordon) were used to prepare wood flour and particle. Wood flour and particle from face- and middle layer particle used in the Korean PB manufacturing factory also were used. And, the ordinary Portland cement (type Ⅰ) was used. The curing reagents of $MgCl_2$ and Na_2SiO_3 were used as the additives.

2.2 Measurement of hydration temperature

For hydration test, milled flour was prepared with Wileymill. The flour was screened with passing into 0.38 mm opening (40 mesh), using

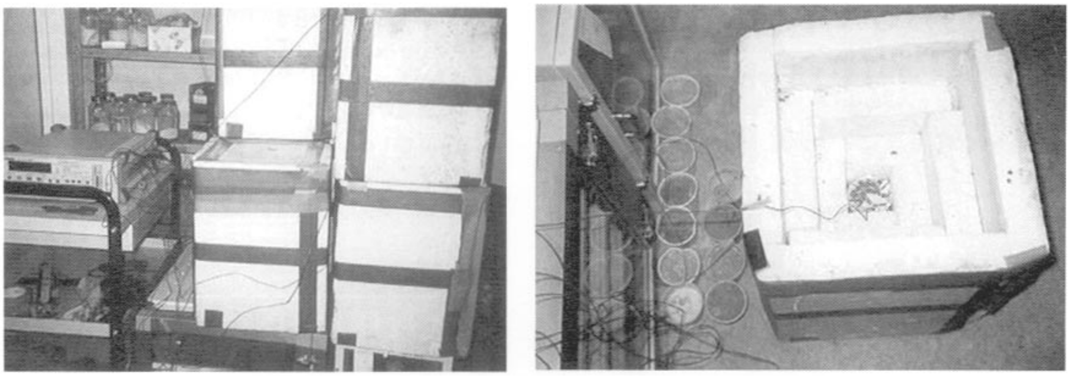


Fig. 1. Set-up for measuring the hydration temperature. (Left: Data logger was equipped for measuring hydration values, Right: Thermocouple was connected with wood flour-cement mixure.)

IIDA sieve shaker.

For cement paste preparation, 200 g of cement, 100 g of distilled water and 15 g of wood flour were uniformly mixed. Following this formulation, neat cement slurry or wood flour-mixed cement were prepared, and then water was poured with/without the additive.

The evenly stirred cement paste was poured into vinyl cup which was put in styrofoam box. Data logger (Advantest R7326B) recorded hydration temperature at a certain interval with the thermocouples into cement paste for 24 hrs (Figure 1).

From these data, inhibitory index and compatibility factor (C_A-factor) were measured (M. Hachmi *et al.*, 1990).

Fig. 2. Supercritical CO_2 curing apparatus.

2.3 Manufacture of boards by supercritical CO_2 fluids treatment and conventional treatment

For manufacture of cement-bonded particleboards, Coarse Korean pine and larch particles were crushed into smaller particles with a hammer-mill, and then the particles were screened to two types dimension of particles i.e. large fraction of 6 mm retention(+) and small fraction of 6 mm passing(-) and 1.35 mm retention(+). Also, face- and middle layer particles were mixed and separated to small and large fraction-screened particles.

The apparatus for supercritical CO_2 fluid treatment consisted of an autoclave-shaped vessel as main part and pump, cooler, water heating bath, support jack, hoist and liquified CO_2 bombe as subsidiary part (Figure 2).

The principle of supercritical CO_2 fluid treat-

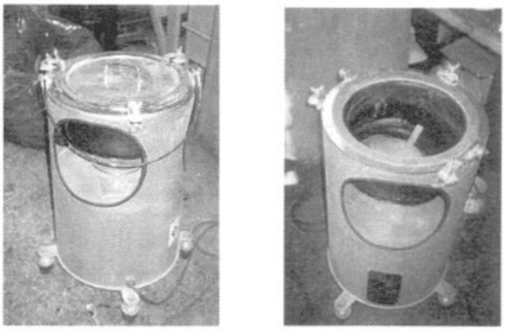


Fig. 3. OMNI Mixer. (Right: Cover opened)

ment is that CO_2 bears critical phase between gas and liquid under such a high pressure over 7.38 MPa and a temperature over 31 °C.

It is also known that the mixing ratio among cement, wood particle and water is an important factor for curing and setting of board (Simatupang and Geimer, 1990). In this study, cement-to-wood ratios (abbreviated as C/W ratio below) were 2.2 and 2.7, and at the same time water/cement ratio was 0.5. Target density of board was 1.2 g/cm^3, and dimension of board was 1.2 cm (thickness) × 23 cm (width) × 23 cm (length).

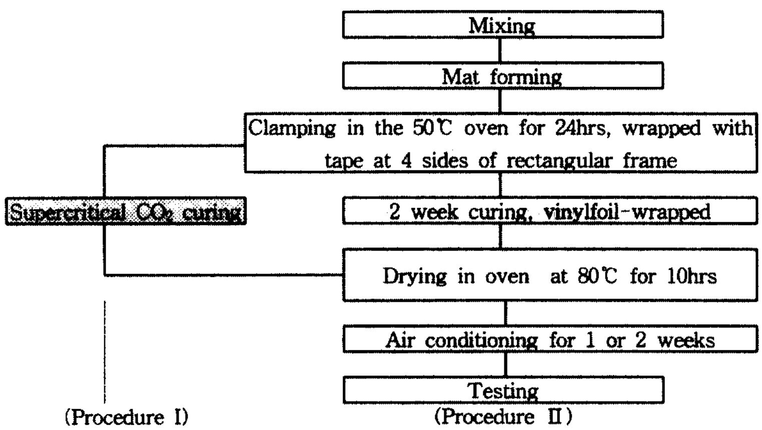
Manufacturing process of cement-bonded particleboard is similar to that of dry-type particle or fiber board. The contents are as follows:

The side of clamped set was surrounded with a broad tape. This was first set at 50°C for 24 hrs in the convection dryer. This hardened set was taken out of dryer, tape was distripped, and loosened.

From this set, one part was given for a conventional 2 weeks curing, and the other part was for a supercritical CO_2 curing (Figure 4). The specimens were subjected to pressure of 7.5 MPa at about 50°C for 15 min as the supercritical treatment. These treated specimens were stacked in air-conditioned room for two weeks, and thereafter given for testing mechanical and physical properties.

The manufacturing procedures of cement-bonded particleboards were described as in the below diagram.

The experimental variables were species/types of particle, particle geometry, cement/wood ratio, addition of $MgCl_2$, and curing treatment methods as in Table 1. As an explanation for



Procedure II : Conventional curing

Fig. 4. Manufacturing diagram of cement-bonded particleboards.

Table 1. Experimental design for manufacture of cement-bonded particleboards.

Species/Types of partcle	Particle size	Cement/ Wood ratio	Addition of $MgCl_2$ (%)	Curing method	Notifications on board type
Korean pine	Large	2.2	1	Supercritical	K-L-I-1-Scf
				Conventional	K-L-I-1-Conv
		2.7	1	Supercritical	K-L-II-1-Scf
				Conventional	K-L-II-1-Conv
	Small	2.2	1	Supercritical	K-S-I-1-Scf
				Conventional	K-S-I-1-Conv
		2.7	1	Supercritical	K-S-II-1-Scf
				Conventional	K-S-II-1-Conv
Larch	Non-hammer milled and smal	2.7	3	Supercritical	L-NH-II-3-Scf
				Conventional	L-NH-II-3-Conv
			5	Supercritical	L-NH-II-5-Scf
				Conventional	L-NH-II-5-Conv
	Small	2.7	3	Supercritical	L-S-II-3-Scf
				Conventional	L-S-II-3-Conv
PB particle	Small	2.7.	3	Supercritical	PB-S-II-3-Scf
				Conventional	PB-S-II-3-Conv

notifications on board type, K-S-II-1-Scf, for example, designates the board composition manufactured with Korean pine small fraction-screened particle, C/W ratio of 2.7, and 1% addition of $MgCl_2$ by supercritical CO_2 curing.

2.4 Testing methods and analysis

Actual density, bending strength, bending MOE, internal bond strength, thickness swelling and water absorption were tested to evaluate board properties by two curing systems. The test was conformed to the particleboard standards JIS A 5908-1994 and KS F 3104-1997.

For detection of thermal decomposition of board constituents, thermogravimetric analysis was carried out with thermogravimetric analyzer TGA 2050. For this analysis, it was ground into fine grit (200 mesh passing) flour with both supercritical treated- and conventional treated board specimen. Then amount of about 30 mg was loaded and temperature was raised till 1,000°C with conditions of heating rate of 10°C/min, nitrogen flow of 100 ml/min.

3. RESULTS and DISCUSSION

3.1 Hydration properties

In hydration test, neat cement slurry reached peak temperature 51.5℃ at 10 hrs without addition of additives as shown in Figure 5. Korean pine showed an average peak temp. 40.9℃ at 15.3 hrs, whose measurements of temperature ranged from 40.1 to 41.6°C at times 14.75 to 16.5 hrs. Larch had continuous temperature decrease phenomenon from initial time showing no peak. Korean pine showed a good hydration compatibility with cement, figuring inhibitory index value of 6.0% and CA-factor of 84.3%.

The effects of addition 1%, 3% and 5% of additives, $MgCl_2$ and Na_2SiO_3 (anhydrous), on Korean pine flour-mixed cement paste were investigated. An addition of Na_2SiO_3 indicated a

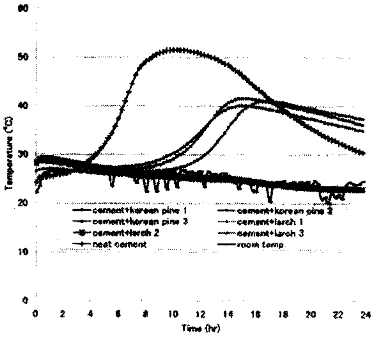


Fig. 5. Hydration curve of Korean pine and larch flour-mixed cement paste and neat cement slurry.

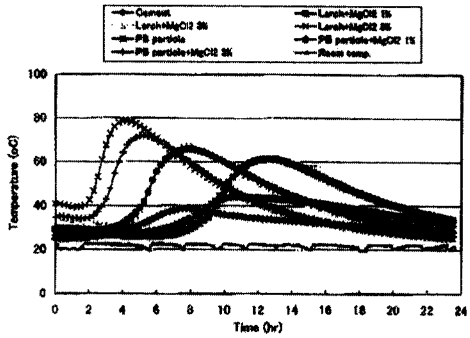


Fig. 7. Hydration curve of larch and PB particle flour-mixed cement paste by addition of $MgCl_2$

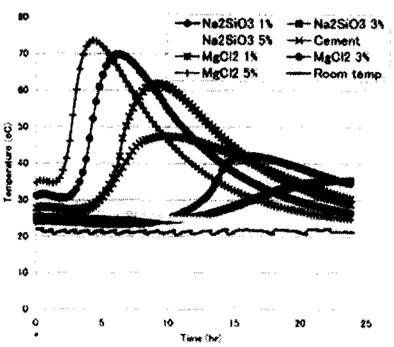


Fig. 6. Hydration curve of Korean pine flour-mixed cement paste according to addition of additives.

negative effect on hydration. The more Na_2SiO_3 added, the less peak temperature and the more peak temperature-reaching time realized. Accordingly, the peak temperature and its time occurred 42.2°C and 15.75 hrs at 1% addition of Na_2SiO_3. Relating to effectiveness of Na_2SiO_3, it was reported that this additive reacted selectively to species, that is, this additive was slightly effective to mechanical properties of boards made from *Betula Ermanii* Cham., however, ineffective to those from *Picea jezoensis* Carr. and *Abies sachalinensis* Mast. (Namioka *et al.*, 1976).

On the contrary, $MgCl_2$ had a positive effect. The peak temperature increased and its reaching time was shortened, as the addition amount of $MgCl_2$ increased.

The highest hydration temperature values at 1, 3 and 5% addition of $MgCl_2$ showed 61.9℃ at 9.25 hrs, 69.9℃ at 6 hrs, and 73.7℃ at 4.25 hrs, respectively.

It was interested in the effect by addition level of $MgCl_2$ on larch known as a very poor cement-hardening species and wood flour from PB particle. The PB particle is not distinct in species, however, it allows a significant meaning in terms of efficient utilization of waste wood.

For larch, the peak temperature and its reaching time were shown 61.5℃ at 12.8 hrs, 67.6℃ at 7.75 hrs, and 78.9℃ at 4.25 hrs with addition level of 1%, 3% and 5% of $MgCl_2$, respectively. PB flour showed the highest hydration values of 65.9°C at 7.75 hrs and 71.9°C at 5.25 hrs with 1% and 3% addition of $MgCl_2$, respectively.

From a fact that the peak temperature-reaching time is coincident on 7.75 hrs with similar temperature between 3% $MgCl_2$-added larch and 1%

$MgCl_2$-added PB particle, it was inferred that PB particles is likely to hydrate better than larch.

3.2 Mechanical and physical properties of cement-bonded particleboards

The properties of cement-bonded particleboards were shown in Table 2. Treatment of supercritical fluid of CO_2 gave a remarkable property enhancement compared to conventional treatment. For example, treatment of supercritical CO_2 fluid with a small fraction-screened PB particle at C/W ratio of 2.7, 3%-addition of $MgCl_2$ (composition PB-S-Ⅱ-3-Scf) showed the highest density of 1.30 g/cm³ and the highest strength properties of bending MOR of 11.72 MPa, bending MOE of 4.70 GPa, and internal bond strength of 1.50 MPa. Treatment of supercritical CO_2 fluid with a small fraction-screened Korean pine particle at C/W ratio of 2.7, 1%-addition of $MgCl_2$ (composition K-S-Ⅱ-1-Scf) showed density and bending strength properties next to the composition of PB-S-Ⅱ-3-Scf. However, internal bond strength 0.44 MPa was not in same way as bending properties, and shown rather less effective than composition PB-S-Ⅱ-3-Conv.

For larch, supercritical treatment gave a feasibility reaching performance requirements for actual use environment. The supercritical treated cement-bonded larch particleboards showed bending MORs, 7.17 and 7.44 MPa. It was proved that the hammermilled small fraction-screened larch particle was slightly higher than the non-hammermilled at density, strength and dimensional stability, assuming the effect of particle geometry (shape and dimension). In spite of this feasibility, the conventional treatment exhib-

Table 2. Mechanical and physical properties of cement-boned particleboards.

Types of board	Density (g/cm³)	MOR (MPa)	MOE (GPa)	Internal bond strength (MPa)	Thickness swelling (%)	Water absorption (%)
K-L-I-1-Scf	1.12	7.64	2.82	0.30	2.45	29.5
K-L-I-1-Conv	1.04	1.70	0.37	0.02	12.0	42.2
K-L-II-1-Scf	1.23	8.78	2.11	0.42	1.51	24.4
K-L-II-1-Conv	1.08	1.40	0.34	0.02	8.79	40.5
K-S-I-1-Scf	1.21	9.01	2.32	0.39	1.64	27.1
K-S-I-1-Conv	1.11	2.70	0.89	0.08	5.17	32.3
K-S-II-1-Scf	1.27	10.59	2.93	0.44	0.97	24.8
K-S-II-1-Conv	1.21	4.75	1.74	0.17	1.91	24.8
L-NH-II-3-Scf	-	-	-	-	-	-
L-NH-II-3-Conv	0.84	0.32	0.08	-	24.15	59.0
L-NH-II-5-Scf	1.18	7.17	1.79	0.31	1.03	21.4
L-NH-II-5-Conv	0.95	0.89	0.17	-	17.3	45.4
L-S-II-3-Scf	1.24	7.44	2.39	0.43	0.88	23.3
L-S-II-3-Conv	1.02	1.64	0.52	0.02	8.46	44.8
PB-S-II-3-Scf	1.30	11.72	4.70	1.50	0.97	17.2
PB-S-II-3-Conv	1.23	7.62	2.18	0.74	0.84	19.8

Note. 1. In this table, the strength of 1 MPa is equal to 10.1972 kgf/cm².
2. The contents on types of board follows Table 1.
3. It means that '-' marks were not furthermore tested owing to poor strength properties.

ited the poorest strength and dimensional stability.

The composition PB-S- Ⅱ -3-Conv was favorest at the conventional treatment as well as supercritical treatment. To say it again, it was suggested that the high performance board could be obtained by both curing treatments, utilizing waste wood-based particle.

Relative superiority of supercritical curing vs. conventional curing for the first grade performance group, PB-S- Ⅱ -3-Scf and K-S- Ⅱ -1-Scf, was presented as ratio values of 1.5 and 2.2 in bending MOR, ratio values of 2.2 and 1.7 in bending MOE, ratio values of 2.0 and 2.6 in internal bond strength, respectively. However, the trend of relative superiority of supercritical curing vs. conventional curing in dimensional stability varied between 1.2 and 2.0.

As the effect of C/W ratio, ratio of 2.7 (condition Ⅱ) was more dimensionally stable and somewhat higher in strength than the C/W ratio of 2.2 (condition Ⅰ), which was evident at both curing treatments in cement-bonded Korean pine particleboards. This phenomenon was attributed by a better coverage of cement on particle surface. In species/types of particle, hammer-milled Korean pine particle formed a good board profile by a supercritical treatment. As a result, bending strengths of these boards ranged from 7.64 MPa to 10.59 MPa.

Specifically, boards using the small fraction-screened PB particle resulted in a mirror-shaped board surface and a rigid board profile. It seems to be due to decomposition of suger components inhibiting a cement hardening at beforehand drying in PB manufacturing companies. Relevant to this, Simatupang (1990) referred to the natural seasoning effects of wood for improving cement hydration properties.

Except for the conditions of PB-S- Ⅱ -3-Scf and K-S- Ⅱ -1-Scf, dimensional properties by supercritical treatment showed a great improvement effect. Through this treatment, thickness swelling ranged from 0.9% to 2.5%, and water absorption from 17.2% to 29.5%.

Also, it was shown that cement-bonded larch particleboard had rather a better dimensional stability, compared to cement-bonded Korean pine particleboard manufactured with small fracton-screened particle, C/W ratio of 2.7 and supercritical treatment.

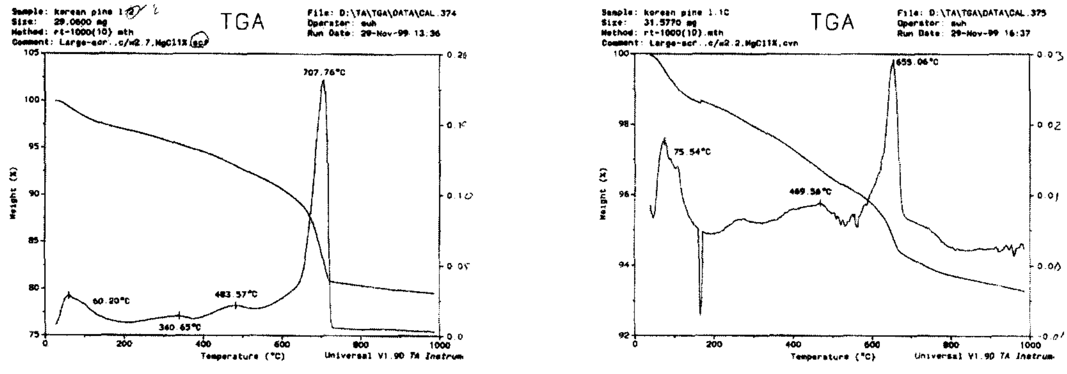
3.3 Thermogravimetric analysis

TGA was used to analyze a thermal decomposition of chemical formations in hardened board, and the thermal reactions were compared among the treatments applied. The highest peak existed at zone of $CaCO_3$ at the temperature of 707.8℃, the next peak was zone of CSH (calcium silicate hydrate) and ettringite at the temperature of 60.2°C, and the lowest peak, zone of $Ca(OH)_2$ at the temperature of 483.6℃ by supercritical treatment as shown in Figure 8. Of these peaks, the former peak of zone of $CaCO_3$ was very high than the latter weak two peaks. Accordingly, it was observed that the supercritical treatment expedited formation of carbonates. On the contrary, the peak heights were very low at conventional treatment. In result, it was inferred that a formation of $CaCO_3$ in cured board contributed to the strength enhancement.

4. CONCLUSION

Korean pine showed a good compatibility at cement hydration reaction and larch had a hardest-to-curing properties. And, an addition of Na_2SiO_3 indicated a negative effect, however, $MgCl_2$ had a positive effect on hydration.

The treatment of supercritical CO_2 fluid endowed a conspicuous enhancement of prop-



(I) (II)

Fig. 8. TGA curve of cement-bonded particleboard specimen.
I : Supercritical CO_2 fluid curing treatment
II : Conventional curing treatment

erty, compared to conventional treatment.

From these results, it was ascertained that the high performance's board could be fabricated with waste wood-based particle by supercritical treatment, and also the feasibility for actual use by conventional treatment was great with PB particles.

As an effect of particle geometry, the hammer-milled and small fraction-screened particle gave the higher performance than the non-hammer-milled. In cement-to-wood ratio of 2.7, boards were more dimensionally stable and resulted in a somewhat superior strength compared to the ratio of 2.2.

Relative superiority of mechanical properties in supercritical treatment vs. conventional treatment for PB-S-II-3 and K-S-II-1 exhibited the high ratio values of 1.5 and 2.2 in bending MOR, ratio values of 2.2 and 1.7 in bending MOE, ratio values of 2.0 and 2.6 in internal bond strength, respectively. And, cement-bonded larch particleboard had rather a better dimensional stability compared to cement-bonded Korean pine particleboard with small fracton-screened particle.

On the other hand, thermal decomposition of the chemical formations in hardened board structure was ascertained through TGA. In results, the highest peak of $CaCO_3$ was present at the temperature of 707.8°C, the next peak of CSH (calcium silicate hydrate) and ettringite was present at the temperature of 60.2°C, and the lowest peak, $Ca(OH)_2$ at the temperature of 483.6°C. Of these peaks, the latter weaks were weak. Accordingly, it was inferred that the strength enhancement of the supercritical treated boards was due to a increased formation of carbonates.

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