BIOLOGICAL, MECHANICAL, AND THERMAL PROPERTIES OF COMPRESSED-WOOD POLYMER COMPOSITE (CWPC) PRETREATED WITH BORIC ACID

Mustafa Kemal Yalinkilic
Associate Professor

Yuji Imamura
Professor

Munezoh Takahashi
Professor

Wood Research Institute
Kyoto University
Uji, Kyoto 611, Japan

and

Zafer Demirci
Research Assistant

Ahmet Cihangir Yalinkilic
Forest Product Engineer

Faculty of Forestry
AIB University
Duzce Bolu, Turkey

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ABSTRACT

Compressed-wood polymer composite (CWPC) was prepared by in situ polymerization of vinyl monomers, styrene (ST), methylmethacrylate (MMA), and their combination (50:50, v/v) under hot-compression of treated sapwood of Japanese cedar (*Cryptomeria japonica* D. Don.) to a dry set of 50 and 70% of original radial dimension. Boric acid (BA) was impregnated into wood at 1.00% aqueous solution concentration prior to monomer treatment. CWPC with and without BA-pretreatment was tested in terms of biological resistance and mechanical and thermal properties.

Boric acid pretreatment imparted CWPC total resistance against decay test fungi *Tyromyces palustris* and *Coriolus versicolor*, representing brown- and white-rot fungi, respectively. CWPC showed remarkable resistance against Formosan subterranean termite *Coptotermes formosanus*, and BA-pretreatment contributed to a total inactivation of termite activity. Surface hardness of CWPC was superior to wood polymer composite (WPC) obtained at the same polymerization temperature and time by a conventional heat process in an oven without compression. Modulus of elasticity and rupture were also considerably improved with this newly introduced in situ polymerization process, suggesting the great potential of CWPC for exterior use. Thermal analysis revealed a reducing effect of boron on heat release of CWPC during combustion.

Keywords: Wood-polymer composite, boric acid, biological resistance, mechanical properties, surface hardness, compressed wood, thermal resistance, vinyl monomers.

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INTRODUCTION

It is usually important for wood to be dimensionally stable and resistant to biological deteriorating organisms under hazardous conditions. These properties are more essential for exterior applications than for indoor ones. Therefore, appropriate preservatives are impregnated into the wood, and treatments for reducing dimensional changes are applied. One important method for improving dimensional stability under humid conditions is the forming of wood polymer composite (WPC) within the wood by bulking the cell wall with vinyl monomers (Fruno 1976), which also impart desirable mechanical properties (Meyer 1984). This method is considered one of the "nonbonded-nonleachable" bulking treatments aimed at excluding water from wood (Rowell and Banks 1985).

In the homo-polymerization process, the polymer is located almost completely in the lumen; only minor amounts are polymerized in the cell wall. Loading the capillaries with polymer reduces the rate of water diffusion into the cell walls. But given enough time at high humidity, water will eventually reach the cell walls and cause substantially the same volume of swelling as in untreated wood (Langwig et al. 1969). Consequently, WPC obtained by vinyl polymerization is very water-repellent; however, its dimensional stability is not constant but liable to change over time with continuous wetting (Meyer 1981, 1984). Fruno (1991) reported that polymer in the cell lumen contributes little to the antiswelling efficiency (ASE) of wood in comparison with polymer in the cell wall.

In order to increase the ASE of WPC, a number of things have been tried, such as addition of polar solvents to nonpolar monomer in an attempt to swell the cell-wall structure and fix it in a swollen state (Langwig et al. 1969). Also tried has been monomer or polymer grafting with the reactive groups on wood components within the cell wall, separately or in combination with the nongrafted bulk polymers formed in the wood voids (Rowell et al. 1982). However, after the solvent has evaporated, in the first case, the wood is only partially loaded. This, in turn, decreases the strength properties, and these properties of WPC obtained with the grafted-nongrafted polymer combination are roughly equivalent to those of untreated wood. Therefore, no process previously proposed has found broad application in the industry, most likely because of the high cost of monomer loading and also because of inefficient dimensional stabilization and inadequate biological and fire resistance.

Since filling of the large lumen spaces in wood requires high loading of monomer, which is technically and economically impractical, any treatment system by which wood acquires a similar level of water repellency and ASE but with a lesser amount of monomer loading will be more desirable.

As an alternative to reducing monomer loading without affecting the ASE of WPC, sytrene (ST) and methylmethacrylate (MMA) were polymerized in situ during hot-compression of wood in the radial direction to a target dimension (Yalinkilic et al. 1998a). The "compressed-wood polymer composite (CWPC)" is, in a way, similar to the "Compreg" process developed earlier in the 1940s (Stamm and Seborg 1951), by which veneers are impregnated with a water-soluble phenol-formaldehyde resin and compressed under heating at 140 to 150°C. CWPC was developed to achieve better access of the impregnated vinyl monomers into void spaces of the wood cell wall at a much lower polymer load and process temperature. This is aimed to impart to WPC higher ASE and mechanical properties. As expected, CWPC exhibited total dimensional stability after submersion in tap water or boiling water or after ten cycles of accelerated artificial weathering. This was attributed to the polymerization of monomers in the cell wall rather than in the lumen, as shown by scanning electron microscopy (SEM) (Yalinkilic et al. 1998a).

On the other hand, it is known that WPC obtained by vinyl polymerization is susceptible to fungal attack, since vinyl monomers become nontoxic chemicals after polymerization (Imamura et al. 1998; Yalinkilic et al. 1997a, 1998b; Lutomsky 1975; Ibach and Rowell 1995). Some of the resistance of WPC to fungi is attributed to the moisture exclusion effect of bulking, which reduces the water absorption of wood at high loading levels of monomer. Filling the voids in wood with bulk polymers containing bioactive materials grafted onto or copolymerized with carrier polymers, therefore, has been suggested to inhibit biological attack (Rowell 1983). In this case, controlled release of bioactive materials from the polymer matrix is of vital importance to the biological resistance of WPC. In situ co-polymerization of the organotin vinyl monomers was found to be an effective method of chemically fixing trialkyltin toxicant to wood components via polymers for long-term protection of wood against biodeterioration (Subramanian et al. 1981a, b). Similarly, boric acid (BA) pretreatment of WPC obtained by ST and MMA improved the biological performance and boron immobility. However, applied monomer load was extremely high (Yalinkilic et al. 1998b). Cyclic weathering proved that BA-pretreated CWPC attained better immobility of boron than BA-pretreated WPC. Efficient polymerization of the monomers on the cell wall prevented water access into wood (Yalinkilic et al. 1998a). The present study, therefore, deals with the biological and thermal resistance and mechanical properties of CWPC with or without boron pretreatment with the aim of developing a technically feasible composite of superior quality.

MATERIALS AND METHODS

Chemicals, impregnation processes, and polymerization conditions

Wood specimens measuring 20 (tangential) × 20 (radial) × 10 (longitudinal) mm and 25 (tangential) × 20 (radial) × 150 (longitudinal) mm were prepared for biological and mechanical tests, respectively, from air-dried sapwood of *Cryptomeria japonica* D. Don. Boric acid was used as a test boron compound and impregnated into wood at 1.00% aqueous solution concentration (2.00% solution concentration was used for thermal analysis specimens), and the wood was dried under ambient conditions for 3 weeks before monomer treatment. ST, MMA, and a mixture of the two (50:50, v/v) were used as vinyl monomers and were purified of accompanying inhibitors through a cleaning procedure with 15% sodium hydroxide (NaOH) and dry calcium chloride ($CaCl_2$) granules. Benzoyl peroxide or VAZO [α,α′-Azobis-isobutyronitrile{$NC(CH_3)_2CN{:}NC(CH_3)_2CN$}] (No. 136-02, an efficient radical initiator at 60°C, Nacalai Tesque, Inc., Kyoto, Japan) was used as a catalyst. Prior to introducing a monomer solution containing both the catalyst and divinyl benzene as a crosslinker, wood specimens were vacuumed for 30 min to accelerate absorption. The soaking period was 30 min. Impregnated wood specimens were then wrapped in aluminum foil before in situ polymerization under hot-compression at 60°C and 90°C catalyzed by VAZO or benzoyl peroxide, respectively, for 4 h. WPC specimens were prepared as control at the same levels of the parameters by heating in a conventional oven. All the necessary measurements of weight and size of the wood specimens were made before and after treatment. Twenty replicates were used for each treatment.

Weight percent gain (WPG) (%,w/w) due to chemical load was calculated from the following equation

$$\mathrm{WPG}(\%\mathrm{w/w}) = [(W_{of} - W_{OI})/W_{OI}] \times 100 \quad (1)$$

where W_{OI} = oven-dried weight (g) of a wood specimen before impregnation, and W_{of} is the final oven-dried weight of the treated block.

In order to understand the effect of precompression or postcompression on the mechanical properties of CWPC, one series of specimens was precompressed at 90°C to 50% of initial radial dimension prior to in situ polymerization.

Weathering

CWPC blocks for biological tests were exposed to 10 cycles of weathering. Weathering was conducted according to JIS A 9201 (1991) by immersing wood specimens in deionized water stirred with a magnetic stirrer (400–500 rpm) at 25°C for 8 h, followed by drying at 60°C for 16 h. After each leaching period, water was added to a ratio of 10 volumes of water to 1 volume of wood. Ten replicates were used for each treatment type.

Biological assay

Decay test.—A decay test was conducted to determine the performance under hazardous conditions of CWPC 50% compressed, and the contribution of BA to decay resistance of CWPC before and after weathering. A monoculture decay test was conducted according to JIS A 9201 (1991) using a brown-rot fungus *Tyromyces palustris* (Berk. Et Curt) Murr. [FFPRI 0507: Fungal accession number of Forestry and Forest Products Research Institute, Tsukuba, Japan] and a white-rot fungus *Coriolus versicolor* (L. ex Fr.) Quel. [FFPRI 1030]. Test blocks were sterilized with gaseous ethylene oxide after oven-dried weights were measured. Three specimens with the same treatment were placed in a glass jar that contained a medium of 250 g quartz sand + 80 ml nutrient solution with fully grown fungal mycelia; they were then incubated at 26°C for 12 weeks. Nine replicates were tested for each decay fungus. The extent of the fungal attack was expressed as the percentage of mass loss.

Termite test.—Leached specimens of 50 and 70% compressed CWPC and of WPC were exposed to subterranean termites in accordance with Japanese Wood Preservation Association (JWPA) Standard No. 11-1 (1992). A test wood block was placed at the center of the plaster bottom of a cylindrical test container (80 mm in diameter). One hundred and fifty undifferentiated workers of Formosan subterranean termite *Coptotermes formosanus* Shiraki and 15 soldiers were introduced into each test container. Two series of the four separate containers that contained only the polymer specimen made from an ST+MMA mixture (50:50 v/v) in a mold, or without any specimens for starvation were also prepared for comparison. The assembled containers were set on dampened cotton pads to supply water to the blocks and were kept at 28°C and >80% RH in the dark for 3 weeks. Termite mortality was determined regularly, and mass loss of a test wood block due to termite attack was determined based on the differences in the initial and final dry weights of the block after the debris of the termite attack was cleaned off. Four replications were made for each treatment.

Mechanical properties

Hardness test.—Specimens 10 (tangential) × 10 (radial) × 5 (longitudinal) cm in size were impregnated with the monomers as above. BA was applied only to the CWPC obtained with the ST+MMA combination. Nine specimens were used for each treatment group. Sets of three were subjected to ordinary polymerization at 90°C in an oven, and polymerization at 60 and 90°C under compression to 50% of original radial dimension. Brinell hardness was determined according to Japanese Industrial Standard JIS Z 2117 (1977). In this test, a 10-mm diameter steel ball was embedded into the tangential surface of the wood at a head speed of 0.5 mm/min to a depth of 0.32 mm. The test was replicated at 5 locations (4 inner corner points and the center) on each specimen after the wood had been conditioned at 20°C and 60% RH for 6 weeks prior to testing.

Static bending.—Specimens [5 (tangential) × 10 (radial) × 140 (longitudinal) mm] were cut from wood blocks [25 (tangential) × 20 (radial) × 150 (longitudinal) mm] for pre- and postcompressed CWPC processes. The modulus of elasticity (MOE) and modulus of rupture (MOR) were measured after the specimens had been conditioned at 20°C and 60% RH for 6 weeks. The span was 100 mm, and the loading speed was 10 mm/min. Eight specimens were tested for each treatment. The MOE and MOR were calculated from the load-deflection curves by the following equations:

$$\mathrm{MOE} = (\mathrm{dPl}^3)/(4\mathrm{bh}^3\mathrm{dY}) \quad (2)$$

$$\mathrm{MOR} = (3\mathrm{Pl})/(2\mathrm{bh}^2) \quad (3)$$

where P is maximum load, dP is load to proportional limit, l is span, b is width of specimen, h is thickness of specimen, and dY is deflection. The specific gravity of all specimens was calculated based on the the ovendry weight and volume.

Evaluations of test results

Decay, termite, and mechanical test results were evaluated by a computerized statistical program (STATGRAPHICS 1985–1991) composed of analysis of variance and following Duncan tests at the 95% confidence level. Statistical evaluations were made on homogeneity groups (HG), of which different letters reflected statistical significance.

Thermal properties

Thermogravimetry (TG) and differential thermal analysis (DTA) tests were conducted in order to elucidate the effect of boron pretreatment on combustion behavior of CWPC. Wood specimens sized as for the decay test were impregnated with the 2.00% solution of BA before in situ polymerization of vinyl monomers. Dry CWPC was then ground into a fine powder for thermal analysis. Thermogravimetry is a technique whereby a sample is continuously weighed as it is heated at a constant, preferably linear rate. In the present study, sample temperature at 10°C/min heating rate was measured every 0.5 s relative to the reference chemical Al_2O_3. Temperature and the differences in heat flow (μv) were recorded as a function of furnace temperature according to the principles explained by Wesley (1964). Aluminum is used as a sample pan. These analyses were conducted at the Thermal Analysis Station 100 (TAS 100), Rigaku Company, at the Industrial Technology Center of Wakayama Prefecture (Japan).

RESULTS AND DISCUSSION

Weight gain (WG) and dimensional stability of CWPC

The weight gain of CWPC due to monomer loading is given in related tables in the following sections. Dimensional stability of CWPC in relation to the obtained WPG levels and fixation mechanism of compressive deformation by the CWPC process have been discussed elsewhere (Yalinkilic et al. 1998a). Compression of monomer-treated wood successfully stabilized the dimensions and reduced monomer consumption consistent with the earlier premise.

Weight gain due to BA impregnation of CWPC was 3.54% and 7.0% for treatments conducted with 1.0 and 2.0% aqueous solutions, respectively.

Decay resistance

Mass loss of CWPC after exposure to the two decay test fungi is presented in Table 1. CWPC exhibited considerable resistance to both the decay fungi representing brown- and white-rot fungi. The good decay resistance obtained with the CWPC at about half the level of monomer loading of WPC suggested that the amount of monomer in the cell lumen is of minor importance in terms of decay resistance. Therefore, further reduction of monomer load located in the lumen can be tried. Boric acid pretreatment imparted further resistance to CWPC so that it became totally resistant to the test fungi. These results are consistent with the high level of decay resistance of BA-pretreated WPC obtained with the same monomers (Yalinkilic et al. 1998b). The remarkably good decay resistance of CWPC even without BA-pretreatment can be explained by its high moisture exclusion efficiency (MEE) value acquired by effective in situ polymerization of the monomers under hot-compression. This in situ treatment kept the water-holding capacity (WHC) below

TABLE 1. *Mass loss levels of WPC and CWPC obtained with vinyl monomer styrene (ST) and methylmetacrylate (MMA) at 90°C and 50% compression set after exposure to decay test fungi for 12 weeks.*

Treatment	Monomer load (% w/w)	Mass loss (%)	
		Tyromyces palustris mean ± SD	*Coriolus versicolor* mean ± SD
Untreated-Not compressed	—	38.6 ± 1.9^{a}	44.1 ± 2.8^{a}
Untreated-Compressed	—	39.6 ± 3.9^{a}	40.3 ± 3.9^{a}
ST-Not compressed	225.3	2.4 ± 0.3^{c}	0.5 ± 0.1^{b}
ST-Compressed	130.1	2.5 ± 0.3^{c}	0.5 ± 0.1^{b}
MMA-Not compressed	212.8	15.7 ± 2.1^{b}	1.3 ± 0.4^{b}
MMA-Compressed	142.6	5.0 ± 1.2^{c}	4.2 ± 1.0^{b}
ST+MMA-Not compressed	210.5	10.7 ± 3.0^{b}	3.1 ± 0.7^{b}
ST+MMA-Compressed	164.0	3.0 ± 0.3^{c}	2.6 ± 0.1^{b}
BA-ST-Compressed	123.0	0.4 ± 0.2^{c}	0.3 ± 0.1^{b}
BA-MMA-Compressed	118.4	1.1 ± 0.1^{c}	0.5 ± 0.2^{b}
BA-(ST+MMA)-Compressed	109.1	0.3 ± 0.1^{c}	0.1 ± 0.01^{b}

Note: Small letters given as superscript over mass loss values represent HG obtained by statistical analysis with similar letters reflecting statistical insignificance at the 95% confidence level. SD: Standard deviation. BA: Boric acid; weight gain of wood due to BA pretreatment was 3.54% (w/w).

10%, as reported previously by Yalinkilic et al. (1998a). An effective way to control decay is to keep the moisture content of wood at less than 20% (Cassens et al. 1995), since polymerized vinyl monomers have no toxic effect on fungi (Lutomsky 1975; Ibach and Rowell 1995; Yalinkilic et al. 1998b). Therefore, CWPC is degraded by fungi to a lesser extent than WPC. The ST, MMA and their mixture were similar in protection efficacy against white-rot fungus *Coriolus versicolor,* whereas WPC made of MMA and ST+MMA were significantly more susceptible to the brown-rot fungus *Tyromyces palustris* degradation than WPC obtained with ST alone and CWPC types (Table 1). Excess monomer locates in the cell lumen and offers limited contribution to decay resistance of wood by reducing water uptake of WPC (Fruno 1991; Imamura et al. 1998). That fungal degradation occurs in CWPC obtained with MMA without BA pretreatment proves the vital role of boron in decay resistance.

Termite resistance

Mass loss of CWPC with and without BA-pretreatment and mortality levels of termites after termite attacks are given in Tables 2 and 3. Mass loss of CWPC caused by termites was neglible regardless of BA-pretreatment, which denotes effective in situ polymerization. However, more than 50% of termite workers were still active after 3 weeks. Exposure of pure polymer in the starvation test resulted in quite similar levels (Table 3) and agreed with earlier results with the same termite species (Yusuf 1996; Table 2), suggesting that the monomers used became nontoxic in wood when polymerized (Yalinkilic et al. 1998b). Simply put, the mode of action of these vinyl polymers appeared to be the establishment of a physical barrier between the wood and termites. As long as the polymer covers the cell walls or stands as a barrier, CWPC is a safe product in terms of termite attack. Additionally, BA-pretreatment can totally prevent termite activity (Table 3). The apparent advantage of CWPC over WPC is total protection of wood against termites at much lower monomer loads. Seventy percent compression of wood further reduced monomer loading and had no adverse effect on termite resistance. The limited mass losses of BA-pretreated CWPC recorded were due to superficial nibbles of termites observed on the specimens' surfaces. No bore holes in the wood were detected. In situ polymerization of ST alone or the ST+MMA mixture improved resistance relative to MMA alone in terms of mass loss levels (Table 2). The negligible degree of mass loss, even for BA-pre-

TABLE 2. *Mass loss of CWPC caused by termite attack after a 3-week exposure period.*

Treatment	Compression set (%)	Polym. temp. (°C)	Monomer load (% w/w)	Mass loss Mean g Mean ± SD	Mass loss % w/w Mean ± SD
Polymer only (ST+MMA)	—	90	—	0.0001 ± 0.0	0.001 ± 0.0^{j}
Untreated-Not leached	NC	—	—	0.552 ± 0.04	25.19 ± 1.1^{a}
Boric acid (BA)-Not leached	NC	—	—	0.031 ± 0.01	1.60 ± 0.05^{ghi}
Boric acid (BA)-Leached	NC	—	—	0.233 ± 0.004	19.10 ± 0.6^{b}
ST	NC	90	225.3	0.030 ± 0.004	1.70 ± 0.05^{ghi}
ST	50	90	130.1	0.019 ± 0.004	0.91 ± 0.05^{i}
MMA	NC	90	212.8	0.110 ± 0.02	5.50 ± 0.05^{c}
MMA	50	90	142.6	0.035 ± 0.07	1.70 ± 0.6^{ghi}
ST+MMA	NC	90	210.5	0.033 ± 0.01	2.20 ± 0.1^{fg}
ST+MMA	50	90	164.0	0.018 ± 0.02	0.93 ± 0.4^{hi}
BA-ST	NC	90	212.0	0.031 ± 0.003	2.00 ± 0.1^{fgh}
BA-ST	50	90	123.8	0.035 ± 0.004	1.61 ± 0.1^{ghi}
BA-ST	70	90	63.8	0.040 ± 0.003	2.40 ± 0.04^{efg}
BA-ST	50	60	127.1	0.037 ± 0.006	1.63 ± 0.1^{ghi}
BA-ST	70	60	69.5	0.026 ± 0.006	1.69 ± 0.2^{ghi}
BA-MMA	NC	90	203.5	0.079 ± 0.005	4.00 ± 0.05^{d}
BA-MMA	50	90	118.4	0.035 ± 0.0	1.69 ± 0.01^{ghi}
BA-MMA	70	90	67.4	0.051 ± 0.02	3.27 ± 0.4^{de}
BA-MMA	50	60	119.6	0.049 ± 0.006	2.31 ± 0.01^{efg}
BA-MMA	70	60	71.5	0.038 ± 0.03	2.79 ± 0.05^{ef}
BA-(ST+MMA)	NC	90	224.2	0.020 ± 0.01	0.90 ± 0.02^{i}
BA-(ST+MMA)	50	90	109.1	0.036 ± 0.004	1.64 ± 0.1^{ghi}
BA-(ST+MMA)	70	90	65.0	0.036 ± 0.001	2.13 ± 0.1^{fg}
BA-(ST+MMA)	50	60	113.5	0.029 ± 0.003	1.36 ± 0.01^{ghi}
BA-(ST+MMA)	70	60	65.7	0.024 ± 0.03	1.49 ± 0.01^{ghi}

Note: NC: Not compressed. For other abbreviations refer to Table 1.

treated CWPC supports the fact that BA acts as a poison in the stomach of termites after digestion of wood (Yalinkilic et al. 1996, 1997b, 1998c; Su et al. 1997a; Williams et al. 1990). Consequently, vinyl monomers exhibited only a physical protection of wood from excess termite attack because degraded small pieces of BA pretreated CWPC kill the termites.

Mechanical properties

Surface hardness.—Brinell hardness values for CWPC, WPC, and untreated compressed wood are given in Table 4. CWPC was superior to WPC even at almost half the level of monomer loading. CWPC obtained with ST alone and ST+MMA had significantly higher surface hardness after polymerization at 90°C followed by the same treatments applied at 60°C. WPC obtained by ST or ST+MMA also yielded significantly higher surface hardness than untreated compressed wood. MMA imparted less hardness to wood than ST or ST+MMA, regardless of compression. However, contrary to the other treatments, in situ polymerization of MMA at 60°C under compression improved hardness. Taking the above results into account, we postulate that MMA is more appropriate than ST when VAZO is used as a catalyst. Since the hardness of wood is defined as resistance to indentation (Brown et al. 1952) and is closely related to crushing and shearing strength (Kollman and Côté 1968), CWPC that acquired more than two times the surface hardness of WPC at even lower monomer loads should compete in the

TABLE 3. *Termite mortality (TM) levels over the 3-week exposure period.*

Treatment	Compression set (%)	Polym. temp. (°C)	Monomer load (% w/w)	TM (%)		
				1st week	2nd week	3rd week
Starvation (with no specimen)	—	—	—	0.0	6.5	12.1
Polymer only (ST+MMA)	—	90	—	2.1	8.7	15.6
Untreated-Not leached	NC	—	—	6.0	8.0	11.0
Boric acid (BA)-Not leached	NC	—	—	17.0	100.0	—
Boric acid (BA)-Leached	NC	—	—	7.0	20.0	32.0
ST	NC	90	225.3	15.0	25.0	29.9
ST	50	90	130.1	7.0	15.5	28.5
MMA	NC	90	212.8	11.0	17.0	29.0
MMA	50	90	142.6	13.5	24.0	38.5
ST+MMA	NC	90	210.5	6.6	18.5	27.0
ST+MMA	50	90	164.0	25.0	34.5	40.2
BA-ST	NC	90	212.0	31.0	83.0	100.0
BA-ST	50	90	123.8	8.5	77.5	100.0
BA-ST	70	90	63.8	14.5	85.7	100.0
BA-ST	50	60	127.1	15.5	79.0	100.0
BA-ST	70	60	69.5	18.0	81.0	100.0
BA-MMA	NC	90	203.5	32.0	89.4	100.0
BA-MMA	50	90	118.4	14.0	92.5	100.0
BA-MMA	70	90	67.4	23.0	92.5	100.0
BA-MMA	50	60	119.6	12.5	86.0	100.0
BA-MMA	70	60	71.5	11.5	83.5	100.0
BA-(ST+MMA)	NC	90	224.2	23.0	88.1	100.0
BA-(ST+MMA)	50	90	109.1	16.0	63.5	100.0
BA-(ST+MMA)	70	90	65.0	19.5	88.5	100.0
BA-(ST+MMA)	50	60	113.5	19.5	93.0	100.0
BA-(ST+MMA)	70	60	65.7	19.5	94.0	100.0

Note: For abbreviations refer to Table 1.

TABLE 4. *Brinell hardness of CWPC at 50% compression set and WPC obtained by vinyl polymerization with and without boric acid (BA) pretreatment.*

Treatment	Polymer load (%, w/w) mean	SG (g/cm^3) mean	Hardness (MPa) mean ± SD
Untreated-Not compressed	—	0.324	7.9 ± 0.1^{g}
Untreated-Compressed at 90°C	—	0.648	26.0 ± 1.7^{f}
Untreated-Compressed at 60°C	—	0.648	28.1 ± 1.5^{f}
ST-Not compressed	188.0	1.290	89.0 ± 6.6^{d}
ST-Compressed at 90°C	92.7	1.273	177.3 ± 5.2^{b}
ST-Compressed at 60°C	91.2	1.242	137.8 ± 3.0^{c}
MMA-Not compressed	174.5	1.246	65.7 ± 8.8^{e}
MMA-Compressed at 90°C	84.3	1.204	83.7 ± 7.6^{d}
MMA-Compressed at 60°C	87.2	1.193	129.6 ± 4.5^{c}
ST+MMA-Not compressed	196.8	1.263	88.5 ± 16.3^{d}
ST+MMA-Compressed at 90°C	99.4	1.276	192.8 ± 7.9^{a}
ST+MMA-Compressed at 60°C	84.5	1.206	177.1 ± 2.7^{b}
BA-(ST+MMA)-Not compressed	191.1	1.270	79.4 ± 2.5^{d}
BA-(ST+MMA)-Compressed at 90°C	96.0	1.276	181.2 ± 5.6^{a}
BA-(ST+MMA)-Compressed at 60°C	92.1	1.250	176.9 ± 4.4^{b}

SG: Specific gravity. Note: For abbreviations refer to previous tables.

TABLE 5. *Modulus of elasticity (MOE) and modulus of rupture (MOR) of pre- or post-compressed CWPC in comparison with untreated-compressed wood and WPC.*

Treatment	Compress. set (%)	Polym. temp. (°C)	Monomer load (% w/w) mean	SG (g/cm^3) mean	MOE 10^3 kg/cm^2 mean ± SD	MOR kg/cm^2 mean ± SD
Control	NC	—	—	0.324	72.0 ± 1.4^{j}	661.8 ± 14.4^{j}
Control	50	60	—	0.648	115.0 ± 2.8^{h}	$1{,}148.9 \pm 63.1^{h}$
Control	70	60	—	0.782	138.3 ± 4.5^{fg}	$1{,}386.3 \pm 25.0^{g}$
Control	50	90	—	0.661	139.9 ± 5.1^{fg}	$1{,}306.8 \pm 28.7^{gh}$
BA-imp. control	NC	—	—	0.330	83.0 ± 1.7^{ij}	755.3 ± 9.9^{ij}
BA-imp. control	30	90	—	0.578	83.1 ± 1.7^{ij}	917.9 ± 27.9^{i}
BA-imp. control	50	90	—	0.631	93.0 ± 2.8^{i}	936.2 ± 18.4^{i}
Ordinary WPC						
ST	NC	90	171.0	1.117	75.6 ± 3.7^{ij}	901.4 ± 18.9^{i}
MMA	NC	90	165.4	0.907	76.4 ± 0.5^{ij}	806.2 ± 19.1^{ij}
ST+MMA	NC	90	163.1	1.005	80.8 ± 2.9^{ij}	918.6 ± 34.5^{i}
Pre-compressed CWPC						
ST	50	90	109.6	1.045	147.4 ± 3.2^{efg}	$1{,}655.0 \pm 24.2^{f}$
MMA	50	90	101.1	0.916	144.6 ± 1.5^{efg}	$1{,}681.0 \pm 18.0^{f}$
ST+MMA	50	90	107.4	1.050	156.7 ± 4.3^{cdef}	$1{,}683.7 \pm 13.8^{f}$
Post-compressed CWPC						
ST	50	60	87.8	1.090	149.7 ± 5.0^{defg}	$2{,}065.0 \pm 34.4^{de}$
ST	50	90	80.7	1.116	173.3 ± 6.5^{c}	$2{,}321.1 \pm 96.2^{c}$
ST	70	90	37.3	1.147	208.8 ± 10.2^{b}	$2{,}703.2 \pm 44.8^{b}$
MMA	50	60	73.0	1.008	136.8 ± 7.3^{g}	$1{,}965.6 \pm 77.0^{e}$
MMA	50	90	85.3	1.140	165.3 ± 9.4^{cd}	$2{,}251.1 \pm 43.8^{c}$
MMA	70	90	30.3	1.102	224.2 ± 9.2^{a}	$2{,}903.2 \pm 98.8^{a}$
ST+MMA	50	60	81.4	1.096	158.2 ± 6.0^{cde}	$2{,}160.3 \pm 44.8^{cd}$
ST+MMA	50	90	69.8	0.997	162.9 ± 5.4^{cd}	$2{,}280.2 \pm 95.7^{c}$
ST+MMA	70	90	32.8	1.143	231.6 ± 11.8^{a}	$2{,}932.9 \pm 156.3^{a}$
BA-pretreated CWPC						
BA-(ST+MMA)	50	90	84.6	1.108	168.6 ± 2.4^{cd}	$2{,}212.4 \pm 24.3^{c}$
BA-(ST+MMA)	70	90	71.1	1.183	208.8 ± 6.1^{b}	$2{,}819.2 \pm 101.9^{ab}$

Note: For abbreviations refer to previous tables.

market as an alternative material for conditions where hard surfaces are required.

Modulus of elasticity (MOE) and modulus of rupture (MOR)

The MOE and MOR results are given in Table 5. The compression process itself resulted in approximately a twofold increase in both modulus levels. Considering the almost total recovery of compression when the wood contacts water (Yalinkilic et al. 1998a), recorded improvements in MOE and MOR by compression only are of no practical importance. Moreover, higher temperatures required for permanent fixation of compressive deformation at 180°C and min 10 kg/cm^2 water vapor pressure in a closed system cause severe strength losses without any chemical treatment involved (Dwianto 1996; Dwianto et al. 1997).

Wood with WPC treatment, on the other hand, gained some bending strength, but remained similar to control specimens in elastic properties (Table 5). Compression of wood prior to monomer impregnation also did not improve elasticity, though it did improve the bending strength. Both moduli, however, were significantly improved by CWPC applied as in situ polymerization of monomers during hot-compression of wood (postcompressed CWPC) at 90°C in particular (Table 5). Re-

TABLE 6. *Summary of the changes in properties of Japanese cedar due to chemical modification and compression.*

	Change							
	CWPC (ST+MMA) 60°C		CWPC (ST+MMA) 90°C		WPC (ST+MMA) 90°C		Compressed LVL Six ply 140°C	
Property	SG	±%	SG	±%	SG	±%	SG	±%
Brinell hardness	1.21	+2,141.8	1.28	+2,340.5	1.26	+1,020.2	1.05	+800.0
MOR	1.09	+226.4	1.00	+244.5	1.26	+38.8	1.05	+257.1
			1.14	+343.2				
MOE	1.09	+119.7	1.00	+126.2	1.26	+12.2	1.05	+142.9
			1.14	+221.7				

Note: For abbreviations refer to previous tables.

sultant MOR levels of CWPC (1966 to 2933 kg/cm^2) were about 3 to 4 times higher than that of untreated control (662 kg/cm^2). MOE levels of CWPC (137,000 to 244,000 kg/cm^2) were about 2 to 3 times higher than those of untreated control specimens (72,000 kg/cm^2). They were also significantly higher than those of precompressed CWPC and WPC.

MOE is a measure of the stiffness of a material, while MOR has proved to be a more reliable measure of strength than stress at the proportional limit. This is due largely to the fact that the maximum load can be determined more precisely than the proportional limit. Also, MOR may be more constant since it is less affected by previous loads applied or by the conditions imposed in testing. Thus the importance of MOR is that it expresses the greatest load the wood will carry (Brown et al. 1952). The superiority of CWPC to WPC becomes apparent on referral to both moduli levels (Table 5). Thus the CWPC process did not only overcome the dimensional instability problem of wood (Yalinkilic et al. 1998a), but it also imparted significantly improved bending strength, elasticity, and surface hardness. BA-pretreatment of CWPC had no significant effect on mechanical properties.

In order to provide a better understanding of the mechanical performance of CWPC, a summary of the percent change in hardness, MOR, and MOE resulting from WPC and CWPC is shown in Table 6. Some mechanical properties of a phenolic resin-treated compressed laminated veneer lumber (LVL) were also included in the table as an example for comparison to Compreg. It was obtained from the sapwood of the same wood species at similar density levels and the same compression set (Kawai et al. 1991). Treated veneers of Japanese cedar were made into high density parallel-laminated panels without applying bonding resin between the plies because sufficient resin is exuded from the plies under compression at 150°C to give a good bond.

CWPC has higher hardness than all other cited products at similar specific gravity levels. Increased density resulted in significant improvement of MOR and MOR of CWPC. Therefore, high compression set can preferably be applied at much lower monomer loads so that the cell-wall structure is not destroyed.

CWPC is also expected to have higher impact resistance owing to the remarkably low process temperature (60 to 90°C) on account of the high toughness values of WPC (Meyer 1984). Therefore, the low toughness or high brittleness, which are the main disadvantages of Compreg (Kollman and Côté 1968), seemed to be improved by this newly introduced CWPC process, though that needs to be studied further. Natural color of CWPC is also worth noting.

Thermal properties

Results of the thermal analysis are given in Table 7 and Figs. 1–3. BA played an important role in reducing exothermic reaction temperatures and magnitudes for CWPC. Moreover, TG residues of BA-pretreated CWPC were significantly higher than those of monomer-

TABLE 7. *Thermal analysis results of CWPC obtained at 50% compression set and 90°C with or without boric acid (BA) pretreatment.*

Treatment	WPG of wood due to		TG residue
	BA load	Monomer load	%
Untreated	—	—	6.7
ST	—	80.7	4.6
BA-ST	7.0	77.3	20.0
MMA	—	85.3	5.4
BA-MMA	7.0	83.6	11.1
ST+MMA	—	69.8	0.0
BA-(ST+MMA)	7.0	67.0	11.2

Note: TG residue: Residual mass after combustion of test sample, calculated based on the original sample weight. For other abbreviations refer to previous tables.

only treated wood, demonstrating the protective effect of BA in combustion. These findings are consistent with earlier reports on the oxygen index and thermal properties of untreated, boron-treated, and BA-vinyl monomer combination-treated wood without compression (Su 1997b; Yalinkilic et al. 1997c, 1998b). It is worth noting that solution concentrations are usually at least 13%, compared with about 3% for preservatives; the amount of salt retained in a given volume of wood is usually 5–10 times higher than that for wood preservatives (Wilkinson 1979). Therefore, the achievement of lower peaks and magnitudes, and the increased residual mass contents on exothermic reactions in combustion of CWPC containing little BA (7%, w/w) suggest further improvements with flame-retardant boron compounds at higher loads.

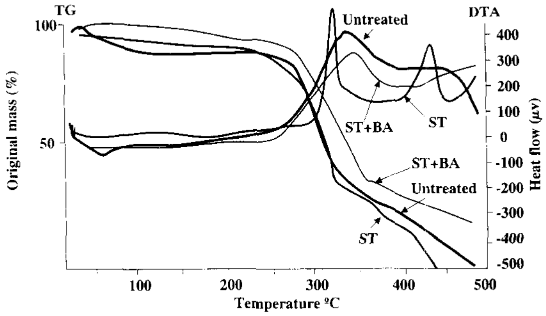

FIG. 1. Thermogravimetric curves of CWPC obtained with styrene (ST) in situ polymerized at 90°C and 50% dry set with and without boric acid (BA) pretreatment. TG (Thermogravimetry): Gravimetrical changes in sample weight during heating at 10°C per min. DTA (Differential thermal analysis): Peak temperature of exothermic reactions under heat flow. For other abbreviations refer to the tables.

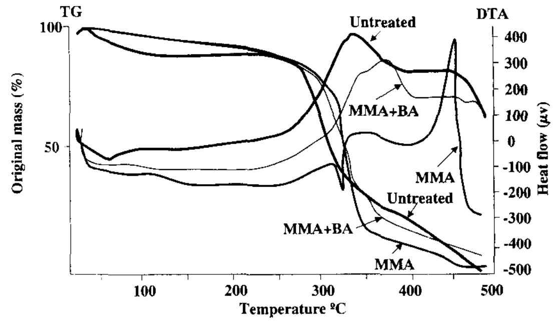

FIG. 2. Thermogravimetric curves of CWPC obtained with methylmetacrylate (MMA) in situ polymerized at 90°C and 50% dry set with and without boric acid (BA) pretreatment. For other abbreviations refer to Fig. 1 and the tables.

Absence of TG residue of the CWPC obtained with ST+MMA as compared to that from individual treatments was probably due to the presence of more polymer in the sampled part of the specimens.

CONCLUSIONS

The biological, mechanical, and thermal resistance of compressed wood polymer composite (CWPC) obtained by in situ polymerization of styrene (ST), methylmethacrylate

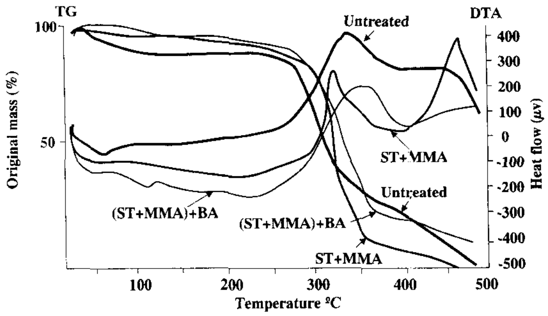

FIG. 3. Thermogravimetric curves of CWPC obtained with styrene and methylmethacrylate combination (ST+MMA, 50:50, v/v) in situ polymerized at 90°C and 50% dry set with and without boric acid (BA) pretreatment. For other abbreviations refer to the tables.

(MMA), and their combination (50:50, v/v) during hot-compression was tested. Results showed that boric acid pretreated CWPC has very good resistance to biological degradation. The amount of boron remaining even after 10 cycles of severe weathering was sufficient to protect the CWPC against decay fungi *Tyromyces palustris* and *Coriolus versicolor*, representing brown- and white-rot fungi, respectively, and against the even more destructive termite *Coptotermes formosanus*. In addition to biological performance, mechanical properties, such as surface hardness, MOE, and MOR, of CWPC were significantly improved compared with ordinary WPC and phenolic resin-treated compressed laminated veneer lumber (Compreg). The problem of low toughness or high brittleness of Compreg is likely to be alleviated by this newly introduced CWPC process, owing to the remarkably low process temperature (60 to 90°C) and improvement of these properties by WPC process. This will be studied further. BA-pretreatment of CWPC remarkably improved the combustion resistance.

In conclusion, CWPC is an alternative structural material for exterior use where high physical, biological resistance, thermal and mechanical properties are required. A number of monomers can potentially be applied to obtain new CWPC products. Studies of grafting of vinyl monomers onto wood cell-wall components and copolymerization practices are under way in association with the CWPC process, in order to diversify and improve the quality of the end product.

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