J Wood Sci (2003) 49:65–72

ORIGINAL ARTICLE

Musrizal Muin · Akio Adachi · Masafumi Inoue
Tsuyoshi Yoshimura · Kunio Tsunoda

Feasibility of supercritical carbon dioxide as a carrier solvent for preservative treatment of wood-based composites

Received: October 24, 2001 / Accepted: February 15, 2002

Abstract Supercritical carbon dioxide (SC-CO_2) was tested for its potential as a carrier solvent for preservative treatment of solid wood and wood-based composites. A preliminary trial showed that the treatability of solid wood varied with its original permeability and that the SC-CO_2 treatment was not promising for refractory timber species such a *Larix leptolepis* Gordon. In contrast, 3-iodo-2-propynyl butylcarbamate (IPBC)/SC-CO_2 treatment resulted in enhanced decay resistance without any detrimental physical or cosmetic damage in all structural-use wood-based composites tested: medium density fiberboard, hardwood plywood, softwood plywood, particleboard, and oriented strand board (OSB). Further trials under various treatment conditions [25°C/7.85MPa (80kgf/cm^2), 35°C/7.85MPa, 45°C/7.85MPa, 35°C/11.77MPa (120kgf/cm^2), and 45°C/11.77MPa] indicated that although small changes in the weight and thickness of the treated materials were noted the strength properties were not adversely affected, except for a few cases of softwood plywood and oriented strand board. The results of this study clearly indicated that the treatment condition allowed SC-CO_2 to transport IPBC into wood-based composites, and the optimum treatment condition seemed to vary with the type of wood-based composite.

Key words Supercritical carbon dioxide · Preservative treatment · 3-Iodo-2-propynyl butylcarbamate (IPBC) · Wood-based composites

M. Muin (✉) · A. Adachi · M. Inoue · T. Yoshimura · K. Tsunoda
Deterioration Control Laboratory, Wood Research Institute, Kyoto University, Uji, Kyoto 611–0011, Japan
Tel. +81-774-38-3663; Fax +81-774-38-3664
e-mail: musrizal@yahoo.com

Part of this work was presented at the 51st Annual Meeting of the Japan Wood Research Society, Tokyo, April 2001; and the 32nd Annual Meeting of the International Research Group on Wood Preservation, Nara, May 2001

Introduction

The technique for pressure treatment of wood with liquid has not changed in principle over the last 160 years since the full-cell (Bethell) process was commercialized during the nineteenth century. Although some modifications have been made to improve treatability and permeability, pressure treatment is not always environmentally sound. Because of increasing concern about the disposal of waste materials and effluents from treatment plants, the development of new methods for environmentally sound preservative treatment of wood products is urgently needed. One of the approaches currently attracting scientific and commercial interest is the use of supercritical carbon dioxide (SC-CO_2) as an alternative to conventional liquid carrier solvents. Because of its physicochemical characteristics, which fall between those of liquids and gases, SC-CO_2 is expected to be able to solubilize a wide variety of biocides for transport into wood materials.

Treatment with SC-CO_2 and tebuconazole has been used to produce clean, dry decay-resistant wood products.[1] SC-CO_2 treatment also did not cause any unfavorable chemical interactions with the cell wall components of treated wood.[2] However, the optimum conditions for SC-CO_2 treatment with the incorporation of biocides must be investigated further. At a pressure of up to 4500psi (31.03MPa), SC-CO_2 treatment did not cause any physical damage to wood-based composites.[3] In contrast, treatment of refractory wood species such as white spruce, western red cedar, and Engelmann spruce resulted in collapse and splitting even though the SC-CO_2 was applied at low pressure.[4,5] In addition, treatment at a pressure of 31.03MPa and at temperatures over 45°C with an elevated pressure of more than 1800psi (12.41MPa) decreased the retention of biocides.[3,6] These results were consistent with the finding that SC-CO_2 at an elevated temperature initially resulted in increased retention at a constant pressure because of density reduction, whereas further temperature increase adversely decreased retention as volatility increased.[7]

It has been thought that successful treatment with SC-CO_2 may be associated with the permeability of wood products as well as pressure and temperature, based on treatment defects and biocide retention. Hence two series of experiments were conducted in the current investigation. First, the susceptibility of wood-based composites to 3-iodo-2-propynyl butylcarbamate (IPBC) treatment using SC-CO_2 was compared to the susceptibility of solid wood. Various temperature and pressure conditions around critical points were then examined to determine their physical and mechanical effects on each type of wood-based composite.

Materials and methods

Preliminary test

Five commercially available structural-use wood-based composites [medium density fiberboard (MDF), hardwood plywood, softwood plywood, particleboard, oriented strand board (OSB)] made from unknown wood species and three timber species (*Pinus densiflora* Sieb. et Zucc., *Cryptomeria japonica* D. Don, *Larix leptolepis* Gordon) were used for SC-CO_2 treatment. Specimens measured 210 × 30 mm × thickness for the wood-based composites and 15 mm (R) × 15 mm (T) × 120 mm (L) for both sapwood and heartwood of *P. densiflora* and *C. japonica* and heartwood of *L. leptolepis*. The characteristics of the wood-based composites and solid wood are presented in Table 1. The wood-based composites were double-coated with epoxy resin on each cut end to simulate the penetration of SC-CO_2 through surface areas of practically sized composites. All specimens were conditioned at 60°C for 72 h prior to SC-CO_2 treatment.

Wood and wood-based composites were separately treated at 50°C and 9.81 MPa (100 kgf/cm^2) to obtain six replicates. Pure CO_2 has critical temperature and pressure points of 304 K (30.84°C) and 73 atm (7.40 MPa), respectively.[8] The SC-CO_2 treatments were conducted either with CO_2 (99.5% purity) (Kyoto Teisan, Kyoto, Japan) only or with the incorporation of 4 g IPBC (99.1% a.i.) (Arch Chemicals, Cheshire, CT, USA) dissolved in 20 ml ethanol (99.5% purity) (Nacalai Tesque, Kyoto, Japan). The concentration of IPBC in SC-CO_2 was calculated based on the weight of the CO_2 used for treatment.

The apparatus used for treatment is shown in Fig. 1. Six specimens of each type of solid wood or two specimens for each wood-based composite were placed in the treatment vessel (100 mm diameter, 300 mm high) at a time. The vessel was immersed in a temperature-controlled waterbath and preheated to the desired temperature. Liquefied CO_2 was introduced into the treatment vessel until the pressure in the vessel became equal to that of the source bomb. The pressure was raised to the target level by pumping liquefied CO_2 with a double pump at a rate of 9 ml/min. The pressure and temperature inside the vessel were monitored by a pressure gauge and a thermocouple inserted into the vessel at the center and connected to a digital recorder. The treatment vessel was maintained under the test conditions for 30 min to allow SC-CO_2 to circulate inside the vessel. At the end of treatment the pressure was released to ambient atmospheric pressure, and the treated materials were recovered for subsequent tests.

Physical defects were visually inspected just after treatment. Specimens of treated solid wood [15 (R) × 4 (T) ×

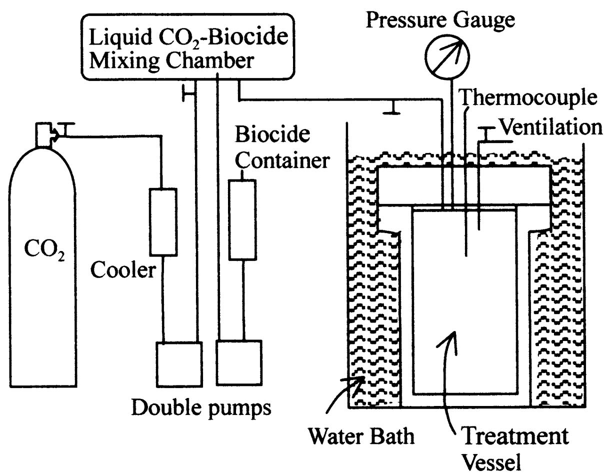

Fig. 1. Apparatus used for supercritical-carbon dioxide (SC-CO_2) treatment

Table 1. Specimens of wood and wood-based composites used for preservative treatment with supercritical carbon dioxide

Material	Component	Oven-dried density (g/cm^3)	Thickness (mm)
Medium density fiberboard	Hardwood	0.67	11.9
Plywood	Hardwood	0.56	12.1
Plywood	Softwood	0.56	11.7
Particleboard	Mixed species	0.75	11.7
Oriented strand board	Hardwood	0.62	12.2
Pinus densiflora	Heartwood	0.50	–
Pinus densiflora	Sapwood	0.50	–
Cryptomeria japonica	Heartwood	0.36	–
Cryptomeria japonica	Sapwood	0.26	–
Larix leptolepis	Heartwood	0.57	–

120 (L) mm] were cut from each original wood specimens for the strength test, and those of wood-based composites (28 × 208 mm × thickness) were obtained by sawing off the resin coating on the treated specimens. Specimens of the same size were also prepared from untreated solid wood and wood-based composites. Prior to the strength tests, all specimens were conditioned at 25°C and 75% relative humidity for 3 weeks.

Single-point bending tests with a loading speed of 10 mm/min were carried out using a Series IX Automated Materials Testing System (Instron, Canton, MA, USA) to determine the modulus of elasticity (MOE) and modulus of rupture (MOR) of the treated and untreated specimens. Span lengths of 100 and 180 mm were used for the strength tests of solid wood and wood-based composites, respectively. The results of all strength tests before and after treatment were compared by a paired Student's *t*-test, with $P < 0.01$ considered statistically significant.

A decay test was conducted according to JIS K 1571[9] using unweathered specimens. Untreated and treated specimens were cut into blocks (24 × 28 mm × thickness); their oven-dried weights at 60°C were measured, and they were then sterilized with gaseous ethylene oxide before the decay test. Three wood blocks were exposed to a monoculture of either the white-rot fungus *Trametes versicolor* (L.: Fr.) Pilat (fungal accession number of the Forestry and Forest Products Research Institute, Tsukuba, Japan: FFPRI 1030) or the brown-rot fungus *Fomitopsis palustris* (Berk. et Curt.) Gilbn. and Ryv. (FFPRI 0507) in a glass jar at 26° ± 2°C for 12 weeks. Three decay jars were used to test nine replicates of each treated material against the two decay fungi. The percent mass loss was calculated from the difference in oven-dried weights of each block before and after the decay test. The results were compared by Tukey's test with $P < 0.01$ considered statistically significant.

Other trials with wood-based composites

Although treatment with SC-CO_2 was considered feasible for wood-based composites, it has limited applicability to solid wood, as serious physical damage was incurred during the preliminary treatment. In fact, even the response of wood-based composites under various treatment conditions was questionable. Therefore, in further trials we investigated the physical and mechanical properties of wood-based composites treated at various SC-CO_2 conditions.

The CO_2, the wood-based composites tested, and the method used to prepare the specimens were the same as those for the preliminary test. In addition, the weight and thickness of the specimens were measured before and after SC-CO_2 treatment with a digital balance and a sliding caliper, respectively. The thickness was measured at three marked points along the specimen length.

Treatments were conducted at a subcritical point [25°C/7.85 MPa (80 kgf/cm^2)] and four supercritical points [35°C/7.85 MPa, 35°C/11.77 MPa (120 kgf/cm^2), 45°C/7.85 MPa, and 45°C/11.77 MPa] with a holding time of 30 min. The subcritical point was selected at *low temperature* with the same interval as the supercritical points (based on the finding that the chemical solubility measurement near the critical point using a continuous quasiequilibrium method resulted in more consistent values at lower temperatures[10]) and at *high pressure* (equal to the minimum pressure of the supercritical treatments) to achieve a more liquid-like state and to increase the CO_2 density and solvating power.

Two specimens of each wood-based composite were placed in the treatment vessel for each run. Treatments were conducted five times under the same treatment conditions to produce 10 replicates for each treatment condition. To understand the profile of the process parameters, temperature and pressure were carefully controlled every 5 min during the SC-CO_2 impregnation.

Following each treatment, physical cosmetic damage and strength properties of the treated wood-based composites were determined by the same method as described for the preliminary test. The results of the strength tests were compared by Tukey's test, with $P < 0.01$ considered statistically significant.

Results and discussion

Feasibility of SC-CO_2 for preservative treatment of wood and wood-based composites based on the preliminary test

Table 2 shows that SC-CO_2 treatment had no detrimental effect on the MOE or MOR of the treated materials, except for the refractory species *L. leptolepis*. The average MOE and MOR of *L. leptolepis* decreased to approximately 83% and 72% of the original values, respectively. As physical observations on the treated materials showed that the SC-CO_2 treatment cause collapse and splits in the refractory species *L. leptolepis* and the splits generally ran longitudinally and along an annual ring boundary, they might partly account for the decrease in strength. The present results suggest that the treatability of solid wood with SC-CO_2 varied significantly with the original permeability of the timber species, although SC-CO_2 has been reported to penetrate the wood matrix promptly and cause no pressure gradients when smaller specimens are treated.[11]

Based on the quantities of IPBC and CO_2 introduced into the treatment vessel, the IPBC concentration in SC-CO_2 at 50°C and 9.81 MPa was approximately 0.48% (w/w). Statistical analyses showed that the IPBC/SC-CO_2 treatment significantly improved the decay resistance of all wood-based composites (Fig. 2). However, the treatment did not always result in enhanced decay resistance of solid wood (Fig. 3). The results indicated that the effectiveness of treatment with IPBC using SC-CO_2 as a carrier solvent varied with the material treated. Surprisingly, the decay-resistance effect of treatment on heartwood was sometimes more significant than that on sapwood, as found in *C. japonica*. This fact was probably associated with the absorption of fungicide by heartwood after simultaneous removal of its extractives by SC-CO_2.[12]

Mass losses caused by the white-rot fungus *T. versicolor* were higher than those by the brown-rot fungus *F. palustris*

Table 2. Strength properties before and after supercritical-carbon dioxide treatment of wood and wood-based composites at 50°C and 9.81 MPa

Material	Modulus of elasticity (GPa)[a]			Modulus of rupture (MPa)[a]		
	Before treatment	After treatment	*t*-value	Before treatment	After treatment	*t*-value
Medium density fiberboard	5.24 (0.99)	5.71 (1.11)	−6.28	40.53 (2.89)	42.95 (3.60)	−3.84
Plywood (hardwood)	5.22 (1.08)	4.96 (0.83)	1.10	31.61 (9.14)	32.12 (5.90)	−0.14
Plywood (softwood)	7.99 (1.22)	7.12 (1.81)	1.29	54.26 (7.58)	53.18 (13.80)	0.16
Particleboard	5.00 (0.92)	4.85 (0.77)	1.09	19.69 (1.25)	20.66 (2.42)	−1.22
Oriented strand board	6.39 (0.78)	5.80 (1.74)	0.85	29.84 (5.70)	32.65 (6.63)	0.84
Pinus densiflora						
Heartwood	13.44 (2.64)	13.60 (1.28)	−0.11	123.30 (15.98)	123.02 (8.94)	0.03
Sapwood	10.24 (1.43)	11.61 (2.62)	−1.08	104.55 (18.56)	115.18 (15.59)	−1.09
Cryptomeria japonica						
Heartwood	7.37 (1.03)	6.49 (1.14)	1.32	71.67 (7.60)	65.17 (14.00)	0.84
Sapwood	5.29 (0.36)	5.29 (0.36)	0.36	45.71 (2.05)	47.73 (3.46)	−1.05
Larix leptolepis						
Heartwood	11.98 (1.09)	9.99 (0.87)	3.28*	104.42 (8.95)	75.00 (11.43)	5.25*

[a] Mean of six specimens, with standard deviation in parentheses
* Statistically significant difference before and after treatments, by paired Student's *t*-test ($p < 0.01$)

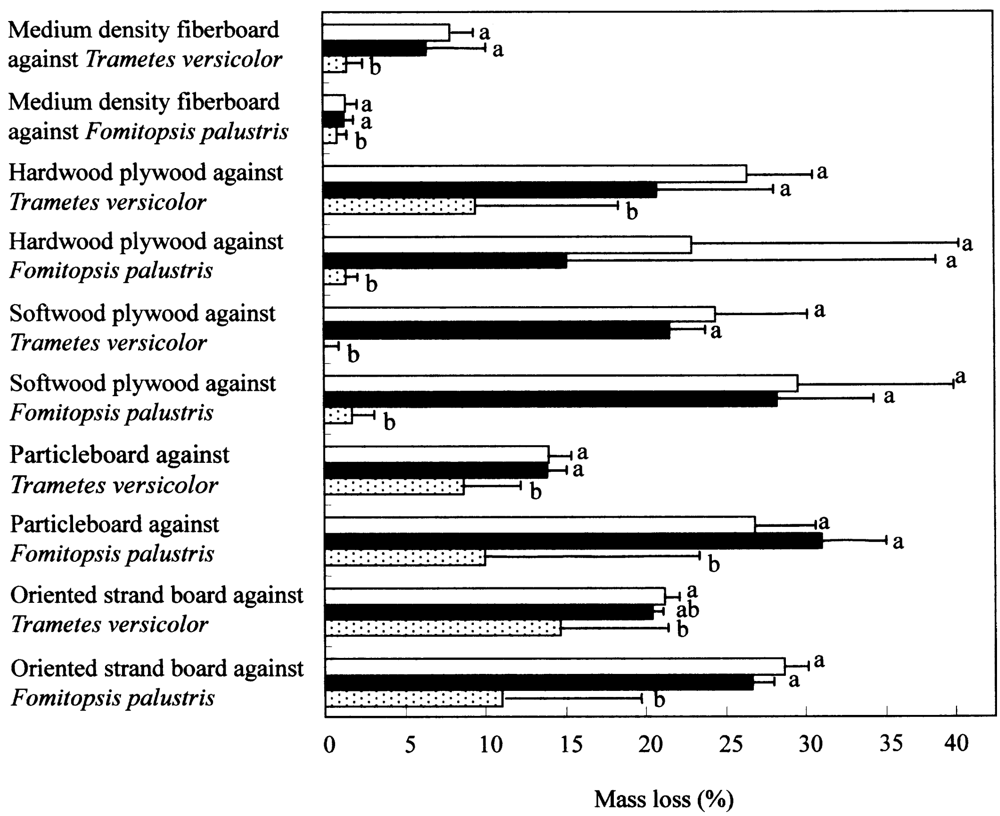

Fig. 2. Effect of SC-CO_2 treatment with and without 3-iodo-2-propynyl butylcarbamate (IPBC) on decay resistance of wood-based composites. *Open bars*, untreated controls; *filled bars*, treatment with SC-CO_2 only; *dotted bars*, treatment with SC-CO_2 and IPBC. Bars in a group of treated materials with different letters are statistically different by Tukey's test ($P < 0.01$)

in the untreated controls of MDF and hardwood plywood but lower in untreated softwood plywood, particleboard, and OSB (Fig. 2). The IPBC/SC-CO_2 treatment proved to decrease the mass loss of MDF, hardwood plywood, softwood plywood, particleboard, and OSB up to 81%, 64%, 100%, 38%, and 31%, respectively, against the white-rot fungus and up to 36%, 94%, 94%, 63%, and 62%, respectively, against the brown-rot fungus. As white-rot fungi are able to degrade both cellulosic substances and lignin, these findings were consistent with the fact that syringyl elements of hardwood lignin were more readily degradable than guaiacyl lignin of softwood.[13,14] The different effectiveness of IPBC/SC-CO_2 treatment with the type of treated wood-based composites may also be associated with the type of constituted particles and glue used, sustaining different resistance to the uptake of moisture necessary for microbial attack.[15]

The current results with IPBC were compared to those attained with tebuconazole, which was the only biocide tested for its fungicidal efficacy when SC-CO_2 was used

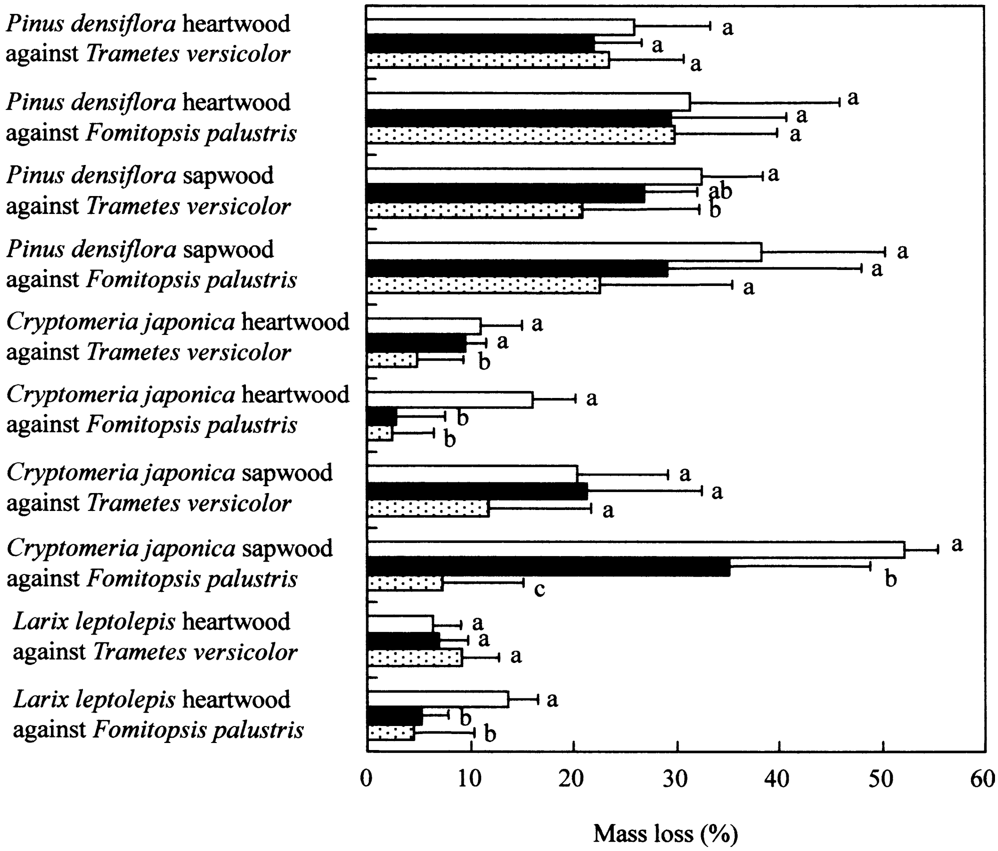

Fig. 3. Effect of SC-CO_2 treatment with and without IPBC on decay resistance of solid wood. *Open bars*, untreated controls; *filled bars*, treatment with SC-CO_2 only; *dotted bars*, treatment with SC-CO_2 and IPBC. Bars in a group of treated materials with different letters are statistically different by Tukey's test ($P < 0.01$)

as a carrier solvent. The tebuconazole/SC-CO_2 treatment showed similar results for enhancement of decay resistance of most wood-based composites, except MDF.[1] Interestingly, excellent decay resistance was achieved by IPBC/SC-CO_2 treatment at much lower pressure in this study than the pressure used for tebuconazole/SC-CO_2 treatment.[1] These facts indicated that different treatment conditions and different biocides may cause different decay-resisting effects to the same type of wood-based composites. Moreover, the current results strongly support the feasibility of SC-CO_2 as a carrier solvent for preservative treatment of wood-based composites under the present treatment conditions. The SC-CO_2 treatment therefore could overcome the limitations of conventional liquid treatments of wood-based composites associated with a redrying process. Previous studies have indicated that redrying at high temperatures after pressure treatment with liquid generally reduced the mechanical properties of treated material and may cause sheet twisting.[16] Although there were no data available on the IPBC treatment of wood-based composites using solvents other than SC-CO_2, a previous study showed no conspicuous difference in mass loss by *T. versicolor* when ponderosa pine sapwood blocks were treated at a retention of IPBC of 0.5 kg/m^3 using either SC-CO_2 or toluene solvents.[11]

Profile of process parameters (pressure and temperature)

Pressure and temperature changes during SC-CO_2 impregnation of wood-based composites are shown in Fig. 4 under five treatment conditions. In general, when liquid CO_2 was introduced, the pressure in the treatment vessel immediately increased to the equilibrium level of the CO_2 bomb. The temperature in the treatment vessel sharply dropped at the same time and recovered within 3 min. Additional liquid CO_2 pumped in to attain the desired pressure caused a slight temperature rise, and the temperature fell and became stable when the target conditions were maintained. The temperature decreased during the venting period as the pressure sharply dropped to the level of the ambient atmosphere.

The rates of pressurization and their orders of magnitude varied with the treatment conditions. With treatment at 25°C and 7.85 MPa (Fig. 4a), the rate of pressurization was extremely slow during the initial stage of the introduction of CO_2 and then sharply increased after the pressure reached its critical point. Similar trends in the pressurization rate occurred at 35°C and 45°C with a target pressure of 11.77 MPa (Fig. 4c,e), although the higher temperature resulted in a higher rate of pressurization during the overall process. At the subcritical condition (25°C and 7.85 MPa), the rate of pressurization was 0.16 MPa/min, which was approximately 67% and 150% higher when the temperature was increased to 35°C and 45°C, respectively. The pressurization rate of SC-CO_2 appeared to be lower at a higher target pressure at a given temperature. At 35°C, for example, the average rate of pressurization was 0.26 MPa/min at a target pressure of 7.85 MPa (Fig. 4b) and was approximately 40% slower than that at a pressure of 11.77 MPa (Fig. 4c). At 45°C the difference in the pressurization rates

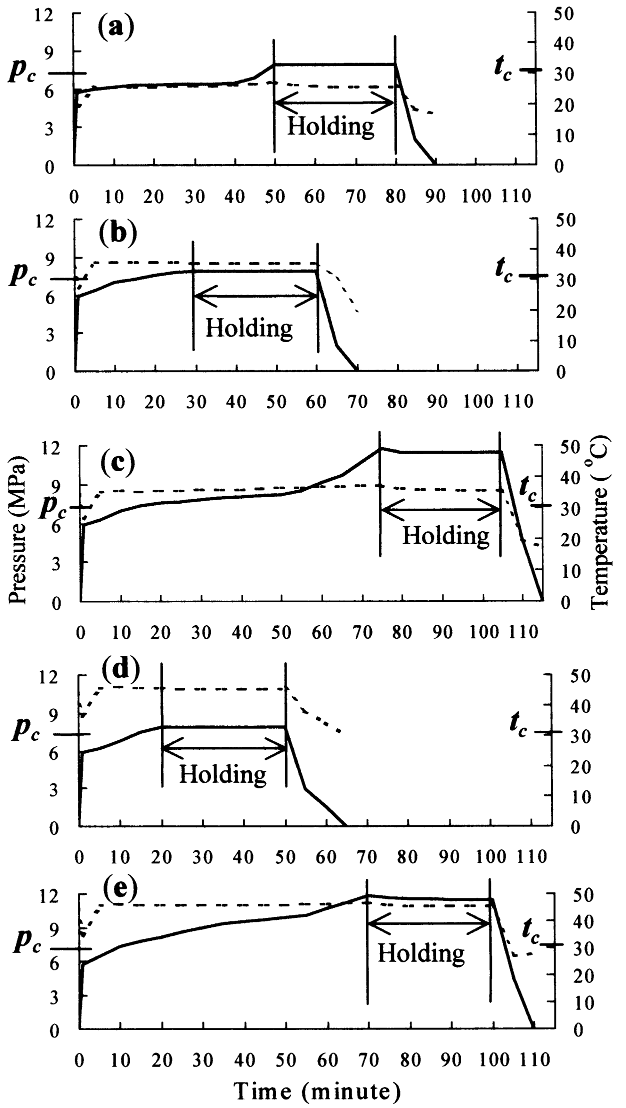

Fig. 4a–e. Pressure and temperature changes during supercritical fluid impregnation into wood-based composites at 25°C/7.85 MPa (**a**), 35°C/7.85 MPa (**b**), 35°C/11.77 MPa (**c**), 45°C/7.85 MPa (**d**), and 45°C/11.77 MPa (**e**) with a holding time of 30 min. *Solid lines*, pressure level; *dashed lines*, temperature level. CO_2 critical pressure (7.40 MPa) and critical temperature (30.84°C) are indicated by p_c and t_c, respectively

between target levels of 7.85 and 11.77 MPa (Fig. 4d,e) was approximately 58%. Pressurization rates generally vary with target temperatures and the amount of CO_2 introduced into the treatment vessel by a double pump. Unfortunately, the pressurization rates are not controllable by the present apparatus. Therefore, it is thought that treatment effects on the samples take place not only when the pressure reaches a target level but also during the holding time. One of the probable effects is extraction of the materials in the treatment vessel. If nondurable components are readily extractable, SC-CO_2 treatment tends to result in less mass loss due to decay fungi compared with that of untreated controls in most cases, as shown in Figs. 2 and 3.

Table 3. Changes in the weight and thickness of wood-based composites treated with supercritical carbon dioxide under various treatment conditions

Treatment conditions	Changes in the weight (w) and thickness (t) of treated wood-based composites (%)[a]									
	Medium density fiberboard		Hardwood plywood		Softwood plywood		Particleboard		Oriented strand board	
	w	t	w	t	w	t	w	t	w	t
25°C/7.85 MPa	−0.37 (0.06)	−0.15 (0.05)	−0.08 (0.07)	0.00 (0.09)	−0.03 (0.13)	0.00 (0.13)	0.00 (0.17)	−0.32 (0.24)	0.00 (0.27)	−0.21 (0.26)
35°C/7.85 MPa	−0.73 (0.27)	−0.45 (0.15)	−0.71 (0.36)	−0.21 (0.16)	−0.64 (0.37)	−0.14 (0.10)	−0.46 (0.39)	−0.30 (0.14)	−1.00 (0.45)	−0.83 (0.35)
35°C/11.77 MPa	−0.70 (0.10)	−0.44 (0.04)	−0.59 (0.07)	−0.24 (0.14)	−0.64 (0.24)	−0.13 (0.09)	−0.31 (0.17)	−0.37 (0.22)	−0.66 (0.30)	−0.44 (0.17)
45°C/7.85 MPa	−0.85 (0.19)	−0.58 (0.23)	−0.83 (0.44)	−0.28 (0.10)	−0.83 (0.24)	−0.28 (0.18)	−0.51 (0.24)	−0.23 (0.18)	−0.79 (0.42)	−0.61 (0.26)
45°C/11.77 MPa	−0.72 (0.27)	−0.40 (0.18)	−1.09 (0.40)	−0.38 (0.12)	−1.11 (0.40)	−0.28 (0.09)	−0.90 (0.19)	−0.50 (0.27)	−1.13 (0.27)	−0.61 (0.31)

[a] Mean of 10 treated specimens, with standard deviations in parentheses

Table 4. Effect of supercritical-carbon dioxide treatment on the modulus of elasticity of treated wood-based composites

Treatment conditions	Modulus of elasticity (GPa)[a,b]				
	Medium density fiberboard	Hardwood plywood	Softwood plywood	Particleboard	Oriented strand board
Untreated control	3.36 (0.31) a	6.06 (0.16) a	6.12 (0.51) a	3.20 (0.10) a	4.37 (0.82) a
25°C/7.85 MPa	3.46 (0.13) a	6.22 (0.74) a	5.45 (0.41) ab	3.42 (0.09) b	2.29 (0.64) b
35°C/7.85 MPa	3.50 (0.09) a	6.12 (1.04) a	5.57 (0.30) ab	3.40 (0.03) b	2.91 (0.80) b
45°C/7.85 MPa	3.47 (0.05) a	6.29 (0.25) a	5.33 (0.48) bc	3.17 (0.13) a	2.46 (0.76) b
35°C/11.77MPa	3.38 (0.22) a	6.14 (0.06) a	5.52 (0.53) b	3.26 (0.06) ab	2.54 (0.65) b
45°C/11.77 MPa	3.49 (0.20) a	6.06 (0.17) a	4.76 (0.33) c	3.39 (0.06) b	2.72 (0.85) b

[a] Mean of 10 treated specimens, with standard deviations in parentheses
[b] Values in column with different letters are significantly different by Tukey's test ($P < 0.01$)

Table 5. Effect of supercritical-carbon dioxide treatment on the modulus of rupture of treated wood-based composites

Treatment conditions	Modulus of rupture (MPa)[a,b]				
	Medium density fiberboard	Hardwood plywood	Softwood plywood	Particleboard	Oriented strand board
Untreated control	37.43 (4.80) a	62.70 (2.56) a	52.88 (9.08) ab	15.59 (1.24) a	28.80 (5.92) a
25°C/7.85 MPa	40.47 (3.42) a	54.94 (6.29) b	51.52 (1.12) ab	17.80 (0.41) b	19.85 (5.08) ab
35°C/7.85 MPa	38.79 (1.79) a	59.27 (3.58) ab	42.75 (7.99) a	17.33 (0.84) b	26.59 (4.23) ab
45°C/7.85 MPa	38.53 (2.22) a	62.50 (2.65) a	51.66 (6.48) ab	17.48 (0.51) b	19.50 (5.10) b
35°C/11.77MPa	37.28 (3.32) a	60.64 (2.11) ab	54.23 (3.12) b	18.32 (0.54) b	20.30 (5.50) ab
45°C/11.77 MPa	39.11 (2.32) a	60.43 (4.20) ab	51.34 (7.39) ab	18.04 (0.64) b	22.14 (7.56) ab

[a] Mean of 10 treated specimens, with standard deviations in parentheses
[b] Values in column with different letters are significantly different by Tukey's test ($P < 0.01$)

Effects of treatments on treated wood-based composites

None of the SC-CO_2 treatment conditions tested in the current study caused any physical damage. Thus, it appears that no pressure gradient occurred during SC-CO_2 treatment of wood-based composites. In contrast, SC-CO_2 treatment tended to cause small changes in the weight and thickness of the treated materials (Table 3). These changes in weight and thickness may be due to the removal of resin or extractives (or both) up to 1.13% (w/w) from the treated materials and the compression of voids within the composites as the result of physical and chemical interaction of SC-CO_2 with the treated materials.

The effects of SC-CO_2 treatment on the strength properties varied with the treatment conditions and the type of wood-based composites (Tables 4, 5). SC-CO_2 at supercritical points generally had better effects on the strength properties of treated wood-based composites than that at a subcritical point. The treatment conditions at supercritical points had no significant negative effects on the MOE and MOR of MDF, hardwood plywood, or particleboard. In contrast, a significant decrease in MOR was noted in hardwood plywood after treatment at the subcritical point. Among the supercritical conditions, treatment at 35°C and 7.85 MPa produced the best results. Treatment at conditions far above the critical point may result in decreased strength properties, as found for treatment of softwood plywood at 45°C and 11.77 MPa. The MOE of softwood plywood dropped dramatically after SC-CO_2 treatment at all supercritical conditions except at 35°C and 7.85 MPa. The exceptional treatment condition had no significant negative effects on the MOE or MOR of all tested wood-based composites except on the MOR of OSB. One differentiation was that a significant decrease in MOR was noted in OSB after all SC-CO_2 treatments. The physical and chemical interactions thought to occur during SC-CO_2 impregnation may contribute to the changes in strength properties.

Conclusions

Preservative treatment with SC-CO_2 as a carrier solvent was more feasible with wood-based composites than with solid wood. Results of this study also suggest that the application of SC-CO_2 is limited to permeable wood species. Wood-based composites treated with IPBC using SC-CO_2 as a carrier solvent proved to be decay-resistant. Various treatment conditions resulted in different physical and mechanical effects on each wood-based composite, and treatment at slightly above the critical point produced the best results. The feasible treatment condition appeared to be associated with physical and chemical interactions between SC-CO_2 and the constituents of wood-based composites without any physical damage or unfavorable effects on the strength properties.

Because SC-CO_2 at around the critical point may be useful as a carrier solvent for preservative treatment of wood-based composites, the solubility of various biocides under the present treatment conditions must be determined to establish a reliable, practical treatment process. Further studies are underway to determine the solubility of biocides in SC-CO_2, the biocidal efficacy of other fungicides and insecticides, and the optimum preservative treatment conditions for each type of wood-based composite.

References

1. Acda MN, Morrell JJ, Levien KL (1996) Decay resistance of composites following supercritical fluid impregnation with tebuconazole. Mater U Org 30:293–300
2. Larsen A, Jentoft NA, Geibokk T (1992) Extraction of formaldehyde from particleboard with supercritical carbon dioxide. For Prod J 42(4):45–48
3. Acda MN, Morrell JJ, Levien KL (1997) Effects of supercritical fluid treatments on physical properties of wood-based composites. Wood Fiber Sci 29(2):121–130
4. Anderson ME, Leichti RJ, Morrell JJ (2000) The effects of supercritical CO_2 on the bending properties of four refractory wood species. For Prod J 50(11/12):85–93
5. Kim GH, Morrell JJ (2000) In-situ measurement of dimensional changes during supercritical fluid impregnation of white spruce lumber. Wood Fiber Sci 32(1):29–36
6. Morrell JJ, Levien KL, Demessie ES, Acda MN (1997) Impregnating wood with biocides using supercritical carbon dioxide: process parameters, performance and effects on wood properties. Proc Am Wood Preserv Assoc 93:367–384
7. Smith RM (1999) Supercritical fluids in separation science: the dreams, the reality and the future. J Chromatogr A 856:83–115
8. Kitao O, Tanabe K, Ono S, Kumakura S, Nakanishi K (1998) Theoretical studies on the cluster structure in the supercritical area. Fluid Phase Equilibria 144:279–286
9. JIS K 1571 (1998) Qualitative standards and testing methods of wood preservatives. Japanese Industrial Standard (JIS), Japanese Standards Association, Tokyo
10. Abaroudi K, Trabelsi F, Recasens F (2000) Quasi-static measurement of equilibrium solubilities in SC fluids: a mass transfer criterion. Fluid Phase Equilibria 169:177–189
11. Morrell JJ, Levien KL, Demessie ES, Kumar S, Barnes HM (1993) Treatment of wood using supercritical fluid processes. Proc Can Wood Preserv Assoc 14:6–25
12. Ritter CD, Campbell GA (1991) Supercritical carbon dioxide extraction of southern pine and ponderosa pine. Wood Fiber Sci 23(1):98–113
13. Kirk TK, Chang H, Lorenz LF (1975) Topochemistry of the fungal degradation of lignin in birch wood as related to the distribution of guaiacyl and syringyl lignins. Wood Sci Technol 9:81–86
14. Leightley LE (1984) The use of ^{13}C CP/MAS NMR in the chemical identification of decayed and undecayed tropical timber species. International Research Group on Wood Preservation, document IRG/WP/1224
15. Savory JG (1968) Microbial attack of timber and allied constructional materials. In: Walters AH, Elphick JS (eds) Biodeterioration of materials. Elsevier, Amsterdam, pp 403–407
16. Winandy JE (1987) Effects of treatment and redrying on mechanical properties of wood. In: Proceedings of wood protection techniques and the use of treated wood in construction, 47358, pp 54–62