EFFECTS OF SUPERCRITICAL FLUID TREATMENTS ON PHYSICAL PROPERTIES OF WOOD-BASED COMPOSITES[1]

Menandro N. Acda
Graduate Research Assistant

Jeffrey J. Morrell
Associate Professor

Department of Forest Products
Oregon State University
Corvallis, OR 97331

and

Keith L. Levien
Associate Professor

Department of Chemical Engineering
Oregon State University
Corvallis, OR 97331

(Received June 1996)

ABSTRACT

The effects of supercritical fluid (SCF) impregnation on physical properties of composites were investigated at various pressures, temperatures, and treatment times with carbon dioxide as the fluid and tebuconazole as a biocide. In general, within the ranges tested, SCF treatment had no negative effects on modulus of rupture, (MOR), modulus of elasticity, (MOE), or dimensional stability of particleboard, flakeboard, or medium-density fiberboard; in some instances, SCF treatment appeared to be associated with slight property improvements in some panel types. Shear tests of plywood suggested a similar lack of treatment effect. Results indicate that, despite the elevated pressure employed during the process, SCF impregnation does not adversely affect the mechanical properties of various wood-based composites.

Keywords: Composites, preservative treatment, supercritical fluid, plywood, medium-density fiberboard, particleboard, flakeboard, strength properties.

INTRODUCTION

Supercritical carbon dioxide (CO_2) represents an attractive alternative to conventional liquid solvents for impregnating wood-based materials with biocides. The pressures employed with these processes exceed 7 MPa, and are approximately 7–10 times those used for conventional impregnation processes (Hunt and Garratt 1967; American Wood-Preservers' Association 1994). Previous studies with conventional liquid treatments of solid wood suggest that considerable losses in mechanical properties can occur at these elevated pressures (Walters 1967; Walters and Whittington 1970). Similar trials of small beams of spruce and ponderosa pine treated with supercritical CO_2 under various pressure and temperature regimes suggest that these processes have no negative effects on wood properties (Smith et al. 1993 a, b). The effects of such processes on composites, with their differing particle geometrics, voids, and wood/resin interfaces, however, remain unknown. The de-

[1] This is Paper 3147 of the Forest Research Laboratory, Oregon State University, Corvallis, OR.

Wood and Fiber Science, 29(2), 1997, pp. 121–130

TABLE 1. *Modified dimensions of samples used for evaluation of mechanical properties of supercritical fluid treated and untreated panels (ASTM D 1037).*

Test	Replications	Sample dimensions
Static bending	9	38 mm × 305 mm × panel thickness
Internal bond	4	38 mm × 50 mm × panel thickness
Moisture absorption	6	38 mm × 203 mm × panel thickness
Thickness swelling	6	38 mm × 203 mm × panel thickness

lineation of these effects is an important aspect of the development of impregnation processes. In this report, we describe trials to define the potential effects of treatment with tebuconazole in supercritical CO_2 on various physical properties of 4 wood-based composites.

MATERIALS AND METHODS

Commercial plywood, particleboard, flakeboard, and medium-density fiberboard (MDF) were cut into specimens with dimensions 38 mm × 150 mm × panel thickness. These specimens were edge-coated with epoxy and conditioned to a constant weight (nearest 0.01 g) at 65% relative humidity and 21°C. Panel thickness was then measured at 3 points along each sample (nearest 0.25 mm). Panel samples were impregnated in a high-pressure vessel as described previously (Acda 1995). Briefly, the samples were placed in a treatment vessel, which was screwed closed. Liquid CO_2 with 3.5 mole % methanol as a cosolvent was flowed over a packed bed of the biocide tebuconazole (α{2-(4-chlorophenyl)ethyl}-α-(1,1-dimethyl)-1H-1,2,4-triazole-1-ethanol), which has been shown to have excellent activity against a variety of wood-degrading fungi. The mixture flowed through the bed at 12 ml/min, a rate which previous trials suggested would produce a saturated biocide solution (Sahle-Demessie 1994). The biocide-laden mixture was then introduced into the treatment vessel and pressure was increased to 12.41, 24.81, or 31.02 MPa temperatures of 45, 60, or 75°C for 5, 15, or 30 min. Once the desired treatment conditions were met, the pressure was released and the specimens were removed from the treatment vessel.

Panel assessment after treatment

At the conclusion of treatment, the panels were carefully inspected for evidence of collapse, splits, delamination, or other treatment defects. The presence and morphology of precipitated particles of biocide were also noted. Thickness swelling, calculated as the difference between initial and final thickness after treatment and expressed as a percentage of the initial thickness, was measured at 3 points along the length of the panel with a digital sliding caliper. Weight gain (nearest 0.01 g) was determined as the difference between the pre- and post-treatment weights.

Evaluation of physical and mechanical properties

The potential effects of exposure to high pressure and elevated temperature under supercritical conditions on the dimensional stability and mechanical properties of each panel type were evaluated according to test methods described in ASTM Standard D 1037 (American Society of Testing and Materials 1995a). Some modifications in specimen size were necessary because of constraints imposed by the size of the treatment vessel (Table 1). Prior to testing, all samples were conditioned to a constant moisture content in a chamber maintained at 21°C and 65% relative humidity.

Particleboard, flakeboard, and MDF were tested for static bending (ASTM D 1037; American Society for Testing and Materials 1995a). Modulus of elasticity (MOE), modulus of rupture (MOR), maximum load, and deflection were determined for each specimen by applying the load at the rate of 6 mm/min on a 280–330-mm span, depending on panel thickness, with an Instron Universal Testing Machine. Load and deflection were recorded continuously with Workbench PC (Strawberry Tree, Inc. 1991) running on a personal computer. Specimens for testing internal bond, thickness swelling, and water absorption were cut from the undamaged portion of the failed bending strips.

Internal bond tests (ASTM D 1037) were performed by gluing specimens to aluminum blocks with a hot-melt adhesive. A uniform load was applied perpendicular to the surface at the rate of 1mm/min with an Instron. The maximum load necessary to pull the specimens apart was recorded continuously. Load at failure for each sample was reduced to pounds per unit cross-sectional area of the sample.

Tests for water absorption and thickness swelling were performed by submerging specimens horizontally in water at room temperature (23–25°C) for 2 and 22 hours. Samples were drained of excess water after each submersion period, and measured for changes in amount of water absorbed and thickness. The water was changed after the 2-h submersion. Thickness swelling (nearest 0.01 mm) was measured from 3 marked points along the length of each sample with a digital sliding caliper. Water absorption and thickness swelling were expressed as a percentage of the original weight and thickness, respectively.

Plywood samples were tested for shear strength and wood failure following the U.S. Product Standard 1-83 (American Panel Association 1983). Each sample was cut to shear specimen geometry and grooved ⅔ through the core. All specimens were boiled in water for 4 h, dried at 63°C for 20 h, boiled again for another 4 h, and finally cooled in water prior to testing while wet. Shear strength was measured with an Instron Universal Testing Machine and load was recorded continuously as described for earlier bending tests. Orientation of the lathe checks was ignored in all tests. Percentage wood failure was assessed by two persons after the specimen dried.

Results of all mechanical tests were subjected to regression analyses or analyses of variance (ANOVA), and the means were compared to similar tests of untreated, unexposed samples with Tukey's Highly Significant Difference (HSD) test (Statistical Graphics Systems Corp. 1993) ($\alpha = 0.05$) to determine if treatment induced significant strength losses.

RESULTS AND DISCUSSION

Effects of supercritical conditions on physical properties

No signs of splits, collapse, delamination, or other treatment defects were observed in any of the panel types tested. The lack of treatment defects suggests that significant pressure gradients that affect structural integrity were absent during treatment. In comparison, previous trials of high-pressure liquid treatments of coniferous woods induced collapse and other structural changes (Walters and Whittington 1970). Most treated samples were dry and clean, with no marked changes in appearance. As a result, supercritical fluid-treated panels could be used immediately after treatment. Some samples, however, contained tebuconazole crystals at the ends. Crystals ranged in size from very fine to up to 1 mm in diameter. This suggests that variations in biocide solubility caused uneven deposition near the vessel outlet during the rapid expansion stage (venting) at the conclusion of the impregnation process. Further trials will be required to identify treatment schedules that control surface deposition.

No significant changes in specimen thickness were noted after treatment, although sample weights increased slightly (Table 2). In some instances, samples exhibited small weight losses and slight thickness compression. Weight losses may have resulted from the removal of wood extractives or resin components during exposure to supercritical CO_2 (Tillman and Lee 1990; Ritter and Campbell 1991; Larsen et al. 1992; Kumar and Morrell 1993). Particleboard, flakeboard, and MDF exhibited greater weight losses than did plywood (Table 2). This could be the result of the larger

TABLE 2. *Effect of supercritical fluid impregnation of tebuconazole on thickness swell and weight gain of various panel types under varying combinations of pressure, temperature and treatment time.*

Variable	Statistic	Plywood	Particleboard	Flakeboard	MDF
Thickness swell[a] (%)	Mean	1.17	0.68	2.78	1.04
	Std. Dev.	0.80	1.09	1.49	0.70
	Minimum	−0.336	−2.01	−0.98	−0.38
	Maximum	3.439	4.17	6.19	2.82
Weight gain (%)	Mean	1.52	0.43	0.86	−0.32
	Std. Dev.	1.11	0.58	0.70	0.37
	Minimum	−0.05	−0.65	−0.72	−1.14
	Maximum	4.97	2.29	2.86	0.62

[a] Difference between thickness before and after treatment as a percentage of initial thickness.

surface area available for extraction, because these panels are composed of wood fibers, small particles, or flakes. The slight decrease in thickness in some samples may have resulted from the compression of void spaces within the panels during exposure to high pressure. In contrast, excessive and unrecoverable thickness swelling can result from conventional liquid treatment of wood-based composites (Deppe 1970; Hall et al. 1982).

Traditionally, weight gain after treatment has been used as a measure of preservative absorption. However, in this study, weight gain was poorly correlated with chemical absorption for all panel types (Fig. 1). Simultaneous extraction of wood extractives and other wood constituents by supercritical CO_2 appeared to have masked biocide absorption (Tillman and Lee 1990; Ritter and Campbell 1991). Combinations of weight gain and other process variables were also poorly correlated with chemical absorption. As a result, chemical analysis was the only reliable method for determining tebuconazole retention. Further study is needed to increase understanding of the relationship between process variables and biocide deposition for various panel types. This information will be essential for development of a controllable treatment process.

Effects of supercritical conditions on dimensional stability

Treatment pressure and temperature had no significant effects on water absorption or thickness swelling of plywood, particleboard, or MDF after a 24-h soak in water compared to untreated controls (Table 3). Flakeboard exhibited significant reductions in water absorption (39–53%) and thickness swelling (45–58%) with increasing treatment pressure or temperature (Fig. 2). This suggests that treatment under supercritical conditions may result in improved dimensional stability, apparently through reduced hygroscopicity. Release of internal stresses within and between wood particles during exposure to supercritical CO_2 may also have contributed to this effect (Halligan 1970; Hsu et al. 1989). Improved dimensional stability of flakeboard was observed at pressures from 12.41 to 31.02 MPa maintained at 60°C for 30 min.

The reduction in hygroscopicity could be the result of either pressure-heat stabilization or the bulking effect of tebuconazole on wood fibers. Heat treatment is known to impart dimensional stability to wood (Stamm 1956). This effect may be the result of thermal degradation of hemicelluloses to water-insoluble polymers that are less hygroscopic than the hemicelluloses from which they are formed (Stamm 1956). However, reductions in antishrink efficiency of about 40% required exposure to high temperatures (120–315°C) and long heating periods (Stamm et al. 1946). In addition, heat treatment was accompanied by relatively large strength losses, especially in toughness and resistance to abrasion (Stamm et al. 1946). These losses were so great that they eliminated the possibility of commerical application of this technique (Stamm 1964).

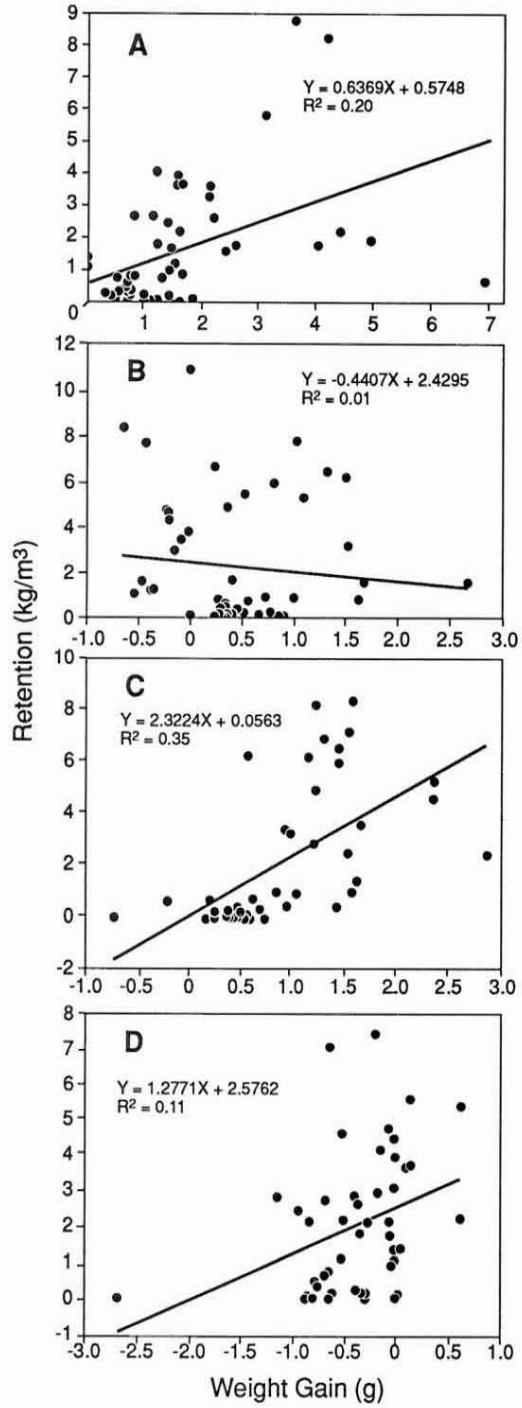

FIG. 1. Relationship between tebuconazole retention and weight gain in (A) plywood, (B) particleboard, (C) flakeboard, and (D) MDF after treatment with supercritical CO_2 at various pressures, temperatures, and treatment times.

TABLE 3. *Effect, mean (and standard deviation),*[a] *on water absorption and thickness swelling of plywood, particleboard, flakeboard, and MDF panels after impregnation with supercritical CO_2 at 12.41–31.02 MPa, 45–75°C for 30 min.*

	Treatment conditions						
	Pressure (MPa)				Temperature (°C)		
Panel type	Control	12.41	24.81	31.02	45	60	75
			Water absorption (%)				
Plywood	30.49 (5.01)A	33.41 (5.57)A	33.44 (9.26)	32.73 (7.26)A	34.82 (4.13)	33.41 (5.57)A	35.99 (6.22)A
Particleboard	59.96 (8.01)A	58.91 (9.42)A	56.21 (14.37)A	53.06 (9.14)A	61.69 (5.49)A	58.91 (9.42)A	60.89 (3.94)A
Flakeboard	43.96 (8.97)A	27.77 (2.79)B	20.66 (3.17)B	27.07 (11.33)B	46.65 (2.46)A	27.77 (2.79)B	29.41 (5.59)B
MDF	13.93 (1.11)A	14.82 (1.01)A	14.16 (4.73)A	14.48 (1.03)A	14.22 (1.53)A	14.82 (1.01)A	16.39 (1.06)A
			Thickness swelling (%)				
Plywood	3.65 (0.62)A	3.66 (0.62)A	3.03 (0.90)A	3.22 (0.97)A	3.55 (0.32)A	3.66 (0.62)A	3.55 (0.23)A
Particleboard	7.72 (0.71)A	6.75 (1.56)AB	5.53 (1.62)B	5.37 (1.24)B	7.65 (0.87)A	6.75 (1.56)AB	6.77 (0.58)A
Flakeboard	17.84 (0.30)A	9.81 (3.79)B	7.52 (2.01)B	10.87 (5.39)A	12.77 (1.35)AB	9.81 (3.79)B	10.77 (1.65)B
MDF	11.55 (0.99)A	10.80 (0.92)AB	8.20 (4.93)B	10.29 (1.47)AB	11.75 (0.45)A	10.80 (0.92)A	10.69 (0.70)A

[a] Means of 6 replicates per treatment. Values followed by the same letter in a given row do not differ significantly by Tukey's HSD (α = 0.05).

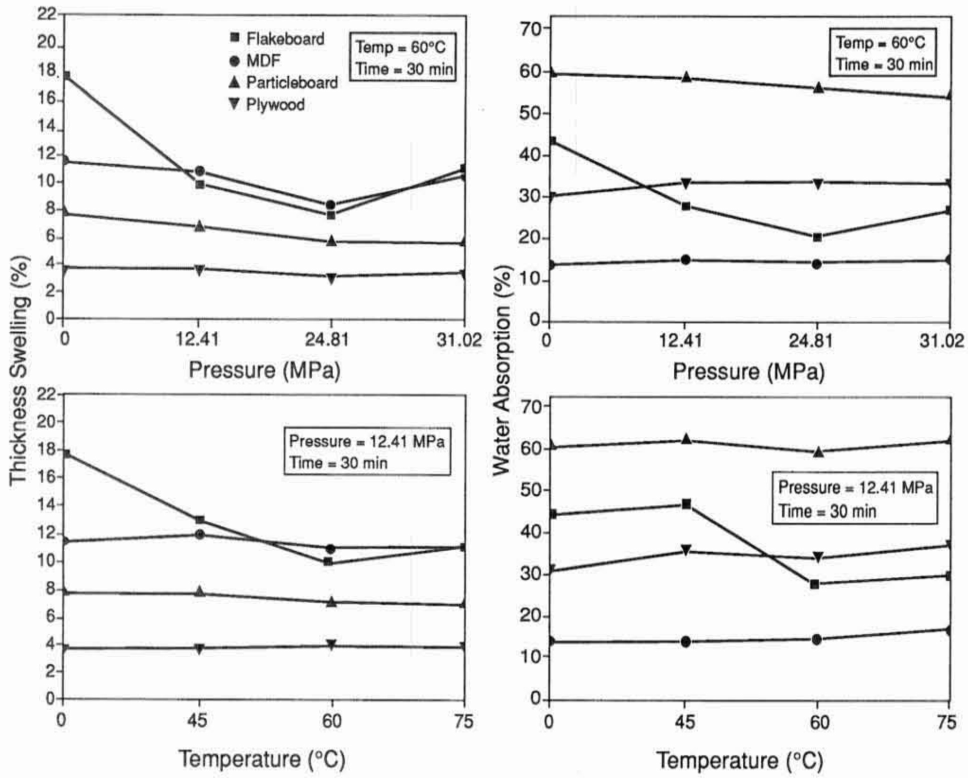

FIG. 2. Relationship between thickness swelling or water absorption (24-h soak) and pressure or temperature for various panel types following impregnation with supercritical CO_2 for 30 min.

Reports of dimensional stabilization by combinations of high pressure and heat are limited. Seborg et al. (1945) pressed thin veneers up to 11 MPa at 177°C sufficient to cause the flow of lignin to relieve internal stresses. The process greatly reduced the tendency of the wood to swell when wet. Dimensional stabilization of wood by exposure to inert gas at about 1.03 MPa and 200°C was also explored by Giebeler (1983).

The deposition of tebuconazole, a water-insoluble chemical, into cell walls or void spaces within the panels may have affected moisture absorption by blocking (bulking) potential water absorption sites. Similar bulking effects have been reported with such water-insoluble chemicals as polyethylene glycol and phenol-formaldehyde resin (Stamm 1956; Rowell 1983; Ward 1989). However, an ANOVA showed that various concentrations of tebuconazole, within the range obtained in this study, had no significant effect on water absorption of plywood, particleboard, flakeboard, or MDF treated from 12.41 to 31.02 MPa at 60°C for 30 min (P = 0.266, 0.269, 0.998, and 0.055, respectively) and at temperatures of 45–75°C at 12.41 MPa for 30 min (P = 0.437, 0.681, 1.000, and 0.600, respectively). The amount of chemical deposited had no significant effect on thickness swelling for plywood, particleboard, or flakeboard treated at various pressures (P = 0.306, 0.081, and 0.814, respectively) except for MDF (P = 0.042), or temperatures (P = 0.776, 0.175, 0.951, and 0.649, respectively). These results suggest that the bulking effect of tebuconazole was not responsible for improvements in the dimensional stability of treated panels. Thus, the nature of the stabilization effect of supercritical CO_2 will require further study to establish the mechanism and the potential of this technique for producing dimensionally stable panels.

TABLE 4. *Effect of treatment pressure, temperature, and duration on modulus of elasticity, mean (and standard deviation),*[a] *of particleboard, flakeboard, and MDF after impregnation with supercritical CO_2.*[b]

Treatment conditions	Modulus of elasticity (KPa)		
	Particleboard	Flakeboard	MDF
Pressure (MPa)			
0	45,875 (5,785)A	85,919 (15,228)A	96,944 (6,269)A
12.41	48,814 (2,248)A	84,877 (8,482)A	88,410 (2,406)A
24.81	51,936 (3,835)A	82,198 (9,061)A	85,205 (6,423)A
31.02	47,915 (3,542)A	88,755 (11,985)A	87,655 (2,540)A
Temperature (°C)			
0	45,876 (5,785)A	85,919 (15,228)A	96,944 (6,269)A
45	50,045 (2,245)A	106,674 (3,697)AB	103,477 (6,546)A
60	48,814 (2,248)A	84,877 (8,482)A	88,410 (2,406)A
75	51,810 (6,563)A	106,807 (11,556)B	90,460 (4,091)A
Time (min)			
0	45,876 (5,785)A	85,919 (15,228)A	96,944 (6,269)A
5	51,521 (3,410)A	99,410 (15,886)A	93,208 (3,402)A
15	52,025 (4,386)A	109,090 (6,644)A	94,607 (4,216)A
30	48,813 (2,248)A	84,877 (8,482)A	88,909 (2,406)A

[a] Means of 8–9 replicates. Values followed by the same letter in a given column within a treatment do not differ significantly by Tukey's HSD (α = 0.05).
[b] Impregnation with supercritical CO_2 at 60°C for 30 min for pressure, 12.41 MPa for 30 min for temperature, and 12.41 MPa at 60°C for duration effects.

TABLE 5. *Effect of treatment pressure, temperature, and duration on modulus of rupture, mean (and standard deviation),*[a] *of particleboard, flakeboard, and MDF after impregnation with supercritical CO_2.*[b]

Treatment conditions	Repli-cations	Modulus of rupture (KPa)		
		Particleboard	Flakeboard	MDF
Pressure (MPa)				
0	8–9	272 (36)A	482 (72)A	766 (73)A
12.41	8–9	276 (19)A	541 (40)A	733 (29)A
24.81	8–9	285 (29)A	550 (86)A	700 (47)A
32.02	8–9	244 (85)A	590 (91)A	682 (34)A
Temperature (°C)				
0	6–8	272 (36)A	482 (72)A	766 (73)A
45	8	317 (5)A	637 (46)B	819 (53)A
60	6–8	276 (19)A	541 (90)A	733 (29)A
75	6–9	282 (21)A	619 (178)B	742 (38)A
Time (min)				
0	8–9	272 (36)A	482 (72)A	766 (73)A
5	8–9	300 (13)A	558 (73)A	770 (27)A
15	8–9	309 (18)A	549 (39)A	789 (57)A
30	8–9	246 (19)A	541 (90)A	733 (29)A

[a] Values followed by the same letter in a given column within a treatment do not differ significantly by Tukey's HSD (α = 0.05).
[b] Impregnation with supercritical CO_2 at 60°C for 30 min for pressure, 12.41 MPa for 30 min for temperature, and 12.41 MPa at 60°C for duration effects.

Effects of supercritical conditions on mechanical properties

Effective biocide protection is essential for the performance of panel products under adverse conditions, but equally important is the impact of treatment on physical and mechanical properties of the treated product. Increasing pressure from 12.41 to 31.02 MPa at 60°C, temperature from 45 to 75°C at 12.41 MPa or treatment time from 5 to 30 min produced no significant negative effects on MOE of particleboard, flakeboard, or MDF (Table 4). Flakeboard, however, exhibited a 24% increase in MOE as temperature increased from 45 to 75°C. In contrast, previous studies with liquid solvents indicated that prolonged exposure of wood to high pressures and elevated temperatures during treatment can result in considerable mechanical damage (Walters 1967; Walters and Whittington 1970; Mitchell and Barnes 1986). Our results indicate that these effects are absent in supercritical fluid-impregnated materials.

Similarly, no significant decreases in MOR were noted for particleboard, flakeboard, or MDF after exposure to the same pressures,

TABLE 6. *Effect of variations in supercritical fluid pressure, temperature, and duration on internal bond, mean (and standard deviation),*[a] *of tebuconazole-treated particleboard, flakeboard, and MDF panels.*[b]

Treatment conditions	Internal bond (KPa) Particleboard	Flakeboard	MDF
Pressure (Mpa)			
0	5.51 (0.72)A	13.34 (1.74)AB	14.36 (2.61)A
12.41	7.00 (1.45)A	10.44 (2.17)A	17.11 (3.04)A
24.81	6.24 (2.03)B	11.60 (3.48)AB	19.29 (2.03)A
31.02	7.25 (1.74)A	15.52 (3.91)B	17.98 (1.59)A
Temperature (°C)			
45	9.28 (2.75)A	10.44 (1.88)A	15.66 (0.58)A
60	6.96 (1.45)A	11.60 (3.48)A	17.11 (3.04)A
75	8.56 (1.45)A	17.40 (3.48)B	15.52 (3.91)A
Time (min)			
5	7.54 (2.03)B	11.75 (3.62)A	19.00 (1.45)A
15	7.54 (1.01)AB	12.33 (0.87)A	14.94 (4.64)A
30	6.96 (1.45)A	11.60 (3.48)A	17.11 (3.04)A

[a] Means of 5 replicates. Values followed by the same letter for all treatments within a given panel type do not differ significantly by Tukey's HSD (α = 0.05).
[b] Impregnation with supercritical CO_2 at 60°C for 30 min for pressure, 12.41 MPa for 30 min for temperature, and 12.41 MPa at 60°C for duration effects.

temperatures, and treatment period regimes (Table 5). Flakeboard, however, again exhibited a 28–32% increase in MOR as temperature increased from 45 to 75°C.

The different amounts of tebuconazole retention obtained in this study had no significant effect on either MOE or MOR of tested panels, regardless of pressure, temperature, or duration of treatment ($P > 0.05$). Previous studies indicated that treatment of wood-based composites with several conventional wood preservatives resulted in reductions in mechanical properties (Boggio and Gertjejansen 1982; Hall et al. 1982; Schmidt 1982). Our results, however, indicate that tebuconazole had no effect on the strength properties of particleboard, plywood, or MDF, probably because tebuconazole does not interact chemically to a significant extent with the wood.

The reason for the improvement in elastic and strength properties of flakeboard after impregnation under supercritical conditions re-

TABLE 7. *Effect, mean (and standard deviation),*[a] *of temperature, pressure, and duration period during supercritical fluid impregnation of plywood on shear strength and wood failure.*

	Treatment conditions						
		Pressure (MPa)			Temperature (°C)		
Time (min)	Control	12.41	24.81	31.02	45	60	75
				Shear strength (KPa)			
0	19 (3)A	—	—	—	—	—	—
5	—	19 (4)A	—	—	—	—	—
15	—	19 (3)A	—	—	—	—	—
30	—	20 (6)A	19 (4)A	19 (3)A	18 (3)A	20 (6)A	17 (3)A
				Wood failure (%)			
0	94 (4)A	—	—	—	—	—	—
5	—	97 (3)A	—	—	—	—	—
15	—	94 (4)A	—	—	—	—	—
30	—	92 (7)A	95 (4)A	95 (5)A	93 (6)A	92 (7)A	96 (4)A

[a] Means of 9–19 replicates. Values followed by the same letter for a given panel type do not differ significantly by Tukey's HSD (α = 0.05).

mains unclear. Postcuring of resin, polymerization of wood components, or direct reaction of tebuconazole with wood components may account for this effect. Further study will be required to elucidate the potential causes of this improvement.

Internal bond

Internal bond tests (tensile strength perpendicular to the surface) were made to assess the effect of treatment conditions on wood-adhesive integrity. The increased use of wood-based composites in which wood or other materials are glued to the boards or the cohesion of wood fibers or particles determines bond strength increases the need to evaluate internal bond strength (ASTM D 1413; American Society for Testing and Materials 1995b). Increasing treatment pressure from 12.41 to 31.02 MPa at 60°C for 30 min produced significant increases in internal bond in particleboard and flakeboard compared to untreated control panels (Table 6). Particleboard exhibited a 26–71% improvement in internal bond at 31.02 MPa, whereas flakeboard showed a 16% increase at 24.81 MPa. Increasing treatment pressure from 12.41 to 31.02 MPa at 60°C for 30 min had no effect on the internal bond of MDF.

Similar increases in internal bond were observed as temperature was increased from 45 to 75°C and pressure was maintained at 12.41 MPa. Particleboard and flakeboard exhibited a 26–68% and 50% increase in internal bond, respectively, but no significant changes were noted with MDF (Table 6). Increasing the duration of treatment from 5 to 30 min at 12.41 MPa and 60°C produced no significant effect on internal bond for flakeboard or MDF (Table 6). Particleboard, however, exhibited a 26–45% improvement.

The increased internal bond of particleboard could be associated with chemical absorption. An ANOVA of tebuconazole retention in various combinations of pressure, temperature, and duration of treatment revealed that retention had a significant effect on the internal bond of particleboard (P = 0.002, 0.043, and 0.053, respectively). This effect suggests that tebuconazole may have interacted with particleboard components, either by direct chemical reaction or a bulking effect that resulted in increased cohesion between wood particles. Further study will be required to verify this effect. Tebuconazole levels were not related to internal bond changes in flakeboard or MDF ($P > 0.05$).

Plywood shear strength and wood failure

Increasing treatment pressure from 12.41 to 31.02 MPa at 60°C, temperature from 45 to 75°C, and treatment period from 5 to 30 min had not significant effect on shear strength or wood failure in plywood compared to untreated controls (Table 7). These results suggest that supercritical conditions used in this study did not interfere with wood adhesion, and the glue–wood bond remained unchanged. Further analyses also showed that the presence of tebuconazole had no significant effect on either shear strength or wood failure ($P > 0.05$). Very high percentages of wood failures in treated samples support these results. In contrast, reductions in mechanical properties have been noted in previous studies with conventional preservative treatments of plywood (MacKay 1978; Lee 1985; Winandy et al. 1988).

CONCLUSIONS

Exposure to elevated temperatures and pressures during supercritical CO_2 impregnation with tebuconazole produced no negative effects on the physical and mechanical properties of plywood, particleboard, flakeboard, and MDF. To the contrary, supercritical fluid impregnation improved some panel properties, although the effects and their relative value are questionable. The results indicate that supercritical fluid impregnation of panel products poses little risk to panel properties, although further study on full-scale treatments would be advisable once this process is commercialized.

REFERENCES

ACDA, M. N. 1995. Supercritical fluid impregnation of wood based composites. Ph.D. dissertation, Oregon State University, Corvallis, OR. 160 pp.

AMERICAN PANEL ASSOCIATION. 1983. U.S. Product Standard 1-83 for construction and industrial plywood with typical APA trademarks. American Panel Association, Tacoma, WA.

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM). 1995a. Methods of evaluating the properties of wood-base fiber and particle panel materials. D 1037. Pages 137–166 *in* Annual book of ASTM standards. 4.09 Wood. Philadelphia, PA.

———. 1995b. Standard test method for wood preservatives by laboratory soil-block cultures. D 1413. Pages 207–213 *in* Annual book of ASTM standards. 4.09 Wood. Philadelphia, PA.

AMERICAN WOOD-PRESERVERS' ASSOCIATION. (AWPA). 1994. All timber products-preservative treatment by pressure process. Standard C1-95. Pages 17–23 *in* AWPA book of standards. Woodstock, MD.

BOGGIO, K., AND E. J. GERTJEJANSEN. 1982. Influence of ACA and CCA waterborne preservatives on the properties of aspen waferboard. Forest Prod. J. 32(3):22–26.

DEPPE, H. J. 1970. The protection of sheet material against water and decay. J. Inst. Wood Sci. 5(3):41–45.

GIEBELER, E. 1983. Dimensional stabilization of wood by moisture-heat-pressure-treatment. Holz Roh-Werkst. 41: 87–94.

HALL, H. J., R. O. GERTJEJANSEN, E. L. SCHMIDT, C. G. CARL, AND R. C. DE GROOT. 1982 Preservative treatment effects on mechanical and thickness swelling properties of aspen waferboard. Forest Prod. J. 32(11/12):19–26.

HALLIGAN, A. F. 1970. A review of thickness swelling in particleboard. Wood Sci. Technol. 4:301–312.

HSU, W. E., W. SCHWALD, AND J. A. SHIELDS. 1989. Chemical and physical changes required for producing dimensionally stable wood–based composites. Wood Sci. Technol. 23:281–288.

HUNT, G. M., AND G. A. GARRATT. 1967. Wood preservation, 3rd ed. McGraw–Hill, New York, NY. 433 pp.

KUMAR, S., AND J. J. MORRELL. 1993. Effect of fatty acid removal on treatability of Douglas-fir. Document No. IRG/WP 93-40008. International Research Group on Wood Preservation, Stockholm, Sweden.

LARSEN, A., N. A. JENTOFT, AND T. GEIBOKK. 1992. Extraction of formaldehyde from particleboard with supercritical carbon dioxide. Forest Prod. J. 42(4):45–48.

LEE, A. W. C. 1985. Effect of CCA treating and air-drying on the properties of southern pine lumber and plywood. Wood Fiber Sci. 17(2):209–213.

MACKAY, J. F. G. 1978. Kiln drying of treated plywood. Forest Prod. J. 28(3):19–21.

MITCHELL, P. H., AND H. M. BARNES. 1986. Effect of drying temperature on the clear wood strength of southern pine treated with CCA-Type A. Forest Prod. J. 36(3): 3–12.

RITTER, D. S., AND A. G. CAMPBELL. 1991. Supercritical carbon dioxide extraction of southern pine and ponderosa pine. Wood Fiber Sci. 23(1):24–44.

ROWELL, R. M. 1983. Chemical modification of wood. Forest Prod. Abstr. 6(12):363–382.

SAHLE-DEMESSIE, E. 1994. Deposition of chemicals in semi-porous solids using supercritical fluid carriers. Ph.D. dissertation, Oregon State University, Corvallis, OR. 301 pp.

SCHMIDT, E. L. 1982. Effects of a formaldehyde and sulphur dioxide treatment on the decay and mechanical properties of aspen waferboard. Int. J. Wood Preserv. 2:173–175.

SEBORG, R. M., M. A. MILLET, AND A. J. STAMM. 1945. Heat-stabilized compressed wood (Staypak). Mech. Eng. 67(1):25–31.

SMITH, S. M., J. J. MORRELL, E. SAHLE-DEMESSIE, AND K. L. LEVIEN. 1993a. Supercritical fluid treatments: Effects on bending strength of white spruce heartwood. Document No. IRG/WP 93-20008. International Research Group on Wood Presevation, Stockholm, Sweden.

———, E. SAHLE-DEMESSIE, J. J. MORRELL, K. L. LEVIEN, AND H. NG. 1993b. Supercritical fluid (SCF) treatment: Its effect on bending strength and stiffness of ponderosa pine sapwood. Wood Fiber Sci. 25:119–123.

STAMM, A. J. 1956. Thermal degradation of wood and cellulose. Ind. Eng. Chem. 48:413–417.

———. 1964. Wood and cellulose science. Ronald Press Co., New York, NY.

———, H. K. BURR, AND A. A. KLINE. 1946. Staybwood. Heat-stabilized wood. Ind. Eng. Chem. 38:630–634.

STATISTICAL GRAPHICS SYSTEMS CORP. 1993. StatGraphics users guide. Version 7. Rockville, MD.

STRAWBERRY TREE, INC. 1991. Workbench PC users guide. Version 2.0.2. Sunnyvale, CA.

TILLMAN, L. M., AND Y. Y. LEE. 1990. Pulping of southern pine under low water, alkaline conditions using supercritical carbon dioxide-sulfur dioxide mixtures. Tappi 73(7):140–146.

WALTERS, C. S. 1967. The effect of treating pressure on the mechanical properties of wood: I. Red gum. Proc. Am. Wood Preserv. Assoc. 63:166–178.

———, AND L. WHITTINGTON. 1970. The effect of treating pressure on preservative absorption and on the mechanical properties of wood. II. Douglas fir. Proc. Am. Wood Preserv. Assoc. 66:179–193.

WARD, D. T. 1989. Supercritical fluid-aided deposition of methyl methacrylate into wood. M.S. thesis, University of Southern Florida, Tampa, FL. 102 pp.

WINANDY, J. E., S. L. LEVAN, E. L. SCHAFFER, AND P. W. LEE. 1988. Effect of fire-retardant treatment and redrying on the mechanical properties of Douglas-fir and aspen plywood. USDA For. Serv. Res. Pap. FPL RP-485. Madison, WI. 19 pp.