SUPERCRITICAL FLUID (SCF) TREATMENT: ITS EFFECT ON BENDING STRENGTH AND STIFFNESS OF PONDEROSA PINE SAPWOOD

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ABSTRACT

Adverse effects on mechanical properties from using a supercritical fluid (SCF) to increase preservative penetration of refractory woods were evaluated by treating small ponderosa pine sapwood specimens with supercritical carbon dioxide at 64 combinations of temperatures (35 to 80 C), pressure (1,000 to 4,000 psig), and time (0.5 to 2 h). Thereafter, the treated and identical untreated specimens were equilibrated to constant moisture content and tested for bending strength and stiffness. The SCF-treated and untreated specimens were not significantly different in modulus of rupture (MOR) or modulus of elasticity (MOE). Temperature, pressure, and time had no significant effect on MOR; there were interacting effects of these variables on MOE, although these interactions had no meaningful patterns.

Keywords: Supercritical fluid, bending strength, bending stiffness, pressure treatment, mechanical properties.

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INTRODUCTION

Supercritical fluids (SCF) are increasingly employed to deliver materials to or extract them from semi-porous media, including wood (Tillman and Lee 1990; Ritter and Campbell 1991; Larsen et al. 1992). SCFs have transport properties similar to those of gases and can thus penetrate deeply into materials not normally receptive to fluid treatments.

SCFs have recently been evaluated for their potential for either extracting secondary chemicals from wood chips prior to pulping (Ritter and Campell 1991) or for delivering dimensional stabilizers to solid wood (Ward 1989). In both instances, the SCF may adversely affect the mechanical properties of the residual wood. Such effects would severely reduce the value of this process for dimensional stabilization and could decrease fiber properties of pulps made from extracted chips. In this report, we describe the effects of SCF treatments on bending properties of ponderosa pine sapwood.

PROCEDURE

Small specimens (2.4 mm by 2.4 mm by 54 mm long) were cut from a ponderosa pine sapwood board. Each specimen had true radial and tangential surfaces and contained one or two latewood rings. Ten specimens were randomly selected to serve as the control group. Previous tests by the authors (data not shown) had established that a sample size of 10 specimens, strength-tested at 2% moisture with load applied to the radial or tangential face, was sufficient to estimate bending strength and stiffness to within ±10% of the mean. An additional 640 specimens were randomly selected and placed in a desiccator containing silica gel until they were SCF-treated, 10 at a time, at one of 64 combinations of temperature, pressure, and time. Factors and factor levels were chosen to represent the conditions we anticipate being used during preservative treatment with supercritical fluids. They were temperature at 35, 50, 65, or 80 C, pressure at 1,000, 2,000, 3,000, or 4,000 psig, and treatment times of 0.5, 1.0, 1.5, or 2 h. For each group of 10 specimens, a high-pressure vessel measuring 55.6 mm long and having an inside diameter of 14.9 mm was filled at a flow rate as high as 90 ml/min with pure supercritical carbon dioxide at an initial pressure of 800 psig. Pressure was then increased at a rate of approximately 2,000 psig/min to the desired value and held steady at the selected temperature and time conditions.

After treatment, the specimens were placed in a desiccator containing phosphorus pentoxide for approximately 4 days to allow the wood to reach constant moisture content. All groups were weighed; then individual specimens were tested for static bending strength and stiffness according to ASTM D-143 (American Society for Testing and Materials 1983). All specimens were stressed over a 38-mm span on an Instron testing machine by applying a load at the rate of 0.05 cm/min to the center of the radial face of each specimen. Load and deflection values were continuously collected with a Campbell Scientific, Inc. 21X micrologger.

After testing, the specimens were oven-dried at 100 C for 2 days, then reweighed; moisture content at test was computed on the basis of oven-dry weight for each group. Modulus of rupture (MOR) and modulus of elasticity (MOE) were computed for each specimen. Variances of the control and treated groups were compared according to Fisher's *F*-distribution to determine if they were significantly different, and means of the two groups were compared by a *t*-test for the same purpose. A three-factor analysis of variance (ANOVA) was used to study the effects of temperature, pressure, and time on MOR and MOE of the treated specimens.

RESULTS AND DISCUSSION

Moisture content of the groups ranged from 0.7 to 2.9% and averaged 1.7% when tested.

The mean bending strengths of the 64 groups of treated specimens ranged from 14,175 to 16,637 psi for MOR and from 1,073,800 to 1,318,944 psi for MOE. These narrow strength

TABLE 1. *Bending strengths of SCF-treated and untreated ponderosa pine sapwood.*[1]

Test values	SCF-treated	Untreated	Difference[2]
MOR, psi			
No. of specimens	631	10	
Mean	15,428	14,813	615^{ns}
Variance	3,153,643	2,092,854	1,060,789^{ns}
MOE, psi			
No. of specimens	631	10	
Mean	1,190,988	1,169,062	21,926^{ns}
Variance	2.18555E + 10	2.87504E + 10	0.68949E + 10^{ns}

[1] Specimens were 2.4-mm by 2.4-mm by 54-mm long and were tested on the radial face at approximately 2% moisture content.

[2] ns means there is no significant difference between SCF-treated and untreated specimens at the 95% significance level.

ranges suggested that there were no significant strength gains or losses. In fact, when bending strengths of the SCF-treated specimens were compared with those of controls, there were no statistically significant differences between the two samples (Table 1).

The analysis of variance showed that the main effects of temperature, pressure, and time had no effect on the bending strength or stiffness of SCF-treated ponderosa pine sapwood specimens (Tables 2 and 3). A previous study at pressures up to 800 psig showed significant effects of pressure on MOR and MOE (Walters and Whittington 1970); however, these effects depended upon interactions of temperature, wood moisture, and pressure. In some instances in that study, strength increased, while other combinations of variables brought a reduction in strength.

The analysis of variance in the present study showed that the interaction of temperature by pressure was significant at the 0.041 level for MOE (Table 3). This interaction implies that the effect of temperature (averaged over all times) on MOE is different at various pressures, or conversely, that the effect of pressure is different at various temperatures (Fig. 1). Examination of the interaction failed to reveal any meaningful pattern between temperature and pressure over time. One explanation for this statistically significant but apparently meaningless interaction is that the error term was underestimated because the specimens were treated in groups of 10 rather than in-

TABLE 2. *Analysis of variance for MOR.*

Source of variation	Sum of squares	df	Mean square	*F*-ratio	Sig. level
Main effects	29,478,074	9	3,275,341	1.047	0.401
Temp.	5,118,545	3	1,706,181	0.545	0.651
Press.	4,738,667	3	1,579,555	0.505	0.679
Time	19,521,397	3	6,507,132	2.080	0.102
2-Factor interactions	105,423,188	27	3,904,562	1.248	0.182
Temp. Press.	51,701,696	9	5,744,632	1.837	0.059
Temp. Time	35,246,410	9	3,916,267	1.252	0.260
Press. Time	18,020,024	9	2,002,224	0.640	0.763
3-Factor interactions	78,007,392	27	2,889,162	0.924	0.578
Temp. Press. Time	78,007,392	27	2,889,162	0.924	0.578
Residual	1,773,476,533	567	3,127,824		
Total	1,986,789,642	630	3,153,634		

Note: 9 missing values have been excluded.

TABLE 3. *Analysis of variance for MOE.*

Source of variation	Sum of squares	df	Mean square	F-ratio	Sig. level
Main effects	177,793,878,304	9	19,754,875,367	0.918	0.509
Temp.	78,999,846,265	3	26,333,282,089	1.224	0.300
Press.	10,005,975,139	3	3,335,325,046	0.155	0.926
Time	88,374,533,386	3	29,458,177,796	2.369	0.251
2-Factor interactions	855,019,004,157	27	31,667,370,524	1.472	0.060
Temp. Press.	380,228,106,229	9	42,247,567,359	1.964	0.041*
Temp. Time	186,514,701,541	9	20,723,855,727	0.963	0.470
Press. Time	281,771,209,855	9	31,307,912,206	1.455	0.162
3-Factor interactions	529,318,084,950	27	19,604,373,517	0.911	0.596
Temp. Press. Time	529,318,084,950	27	19,604,373,517	0.911	0.596
Residual	1.2197999E + 13	567	21,513,226,152		
Total	1.3768924E + 13	630	21,855,463,377		

Note: 9 missing values have been excluded.
* Significant interaction.

dividually. Specimens treated individually would probably have more variability, thus increasing the residual mean square error, decreasing the F-ratio, and thereby resulting in a nonsignificant interaction.

Ponderosa pine sapwood was chosen for this study because it is highly permeable, and therefore would minimize the risk that significant pressure gradients might develop at the start or conclusion of the SCF treatment. This characteristic was especially important because the SCF treatment vessel initially employed pressurized all specimens to 800 psig almost immediately. This high initial pressure creates a substantial probability of unequal pressures in less permeable woods. Thus, the test evaluated the effects of SCF conditions, not the effects of differential wood permeability on strength properties after SCF treatment. A previous study of high-pressure liquid treatments of conifers, however, suggests that significant pressure gradients induce collapse and other structural changes (Walters and Whittington 1970). Slow prepressurization to achieve SCF conditions could help to minimize these effects. Further studies with larger (25.4-mm by 25.4-mm by 403-mm-long) specimens and less permeable materials are planned to explore the potential for such effects under SCF conditions. The effects of supercritical carbon dioxide with the addition of a co-solvent and biocide will also be studied. The present results, however, indicate that supercritical fluid treatment with carbon dioxide has no adverse effects on strength and stiffness of permeable wood species under the temper-

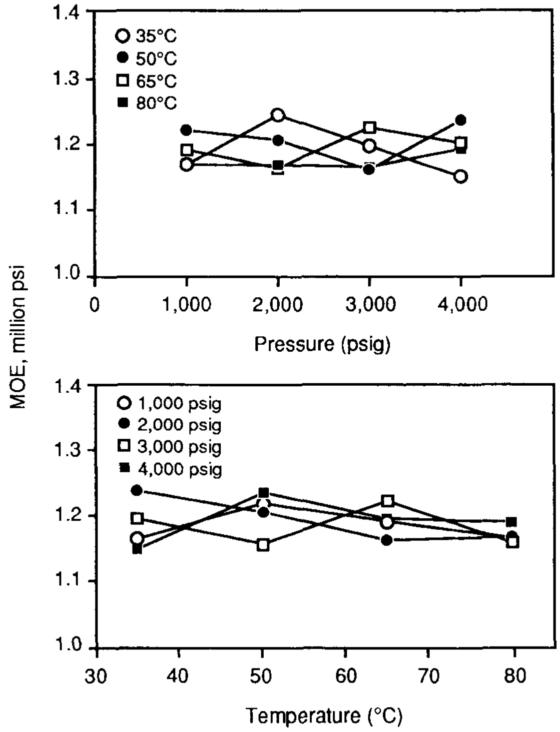

FIG. 1. Effects of pressure and temperature on MOE.

ature, pressure, and time conditions tested in this study.

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