

Furfurylation of *Pinus pinaster* Wood

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ABSTRACT

Furfurylation was tested with maritime pine wood (*Pinus pinaster* Aiton,) which is the most important pine species in Portugal. The wood was treated with a furfuryl alcohol mixture (FA 70 mix) at Kebony Products DA in Norway, in an autoclave using vacuum and pressure stages and subsequently cured and dried in a vacuum drying kiln. Both heartwood and sapwood were treated, with weight percent gains of 38% and 23% respectively. There were no significant changes on MOE and bending strength. Janka hardness increased 56% and 49%, on radial and tangential sections, respectively. Equilibrium moisture content decreased in the sapwood from 8.9 to 5.1% (at 35% relative humidity), from 12.9 to 7.3% (at 65%) and from 17.3 to 9.0% (at 85%). In heartwood the moisture decrease was very small. The dimensional stability of sapwood increased with ASE35 35.6 and 41.8%, ASE65 29.0 and 43.4% and ASE85 31.4 and 45.1% for radial and tangential directions respectively. The improvements for heartwood were smaller and only significant in the tangential direction and at the higher relative humidity values: ASE65 was 12.3 and 22.4% and ASE 85 10.5 and 24.8% for radial and tangential directions, respectively.

INTRODUCTION

Wood modification by either thermal, chemical, surface or impregnation modification processes has grown significantly in the last few years. Furfurylation is often considered an impregnation modification since it is believed, although not unanimously, that there are no chemical bonds between furfuryl alcohol and wood. Lande *et al.* (2004a) suggested the grafting between lignin and furfuryl alcohol but Venås *et al.* (2006) found no proof of such linkages on treated wood using ATR-IR spectroscopy. Alfred Stamm (1977) first suggested the use of furfuryl alcohol to modify wood but the process used zinc chloride as catalyst and was not suitable for lumber-size material due to a chromatographic separation when the catalyst solution penetrated the wood. Recently Schneider (1995) and Westin (1995) developed similar processes with new catalysts based on cyclic carboxylic anhydrides. *Pinus pinaster* is the most important forest species in Portugal and pine wood is considered as having low durability and high dimensional instability. It is commonly preserved by traditional impregnation with biocides but the increased restrictions cause apprehension on preservation companies. Furfurylation is one of the potentially more competitive wood modification processes. Because furfuryl alcohol can be obtained from furfural which is a secondary product in the production of bioethanol, its price is expected to lower considerably with increasing

bioethanol production. Another advantage of furfurylation is that the equipment is similar to the currently used in traditional preservation, thereby lowering the cost of a possible conversion.

EXPERIMENTAL

Treatment

Pine boards (*Pinus pinaster* Aiton) were treated with a furfuryl alcohol mixture (FA 70 mix) at Kebony Products (Norway). The treatment was carried out in an autoclave by a vacuum and pressure stage and subsequently cured and dried in a vacuum drying kiln.

Equilibrium moisture and dimensional stability

Treated and untreated wood samples were kept in a controlled environment at 20 °C and sequentially equilibrated at 35, 65 and 85% relative humidity for at least 4 weeks in each relative humidity and until mass variation was less than 5% in two consecutive days. Mass was determined and the equilibrium moisture content (EMC) was calculated. The samples dimensions were measured in radial and tangential directions and dimensional stability of the heat treated samples was calculated as an Anti Swelling Efficiency (ASE) for the three values of relative humidity (ASE35, ASE65, ASE85).

Mechanical properties

The mechanical properties were determined with samples of 340 x 20 x 20 mm³ (axial x radial x tangential) by a three point bending device. MOE measurements were made using a constant velocity of 0.3 mm/min and for bending strength the velocity was estimated to cause rupture in about 3 min. MOE and bending strength were determined according to NP-619 as:

$$\text{MOE(N/mm}^2\text{)} = \frac{\Delta F * L^3}{\Delta x * 4 * b * h^3} \quad \text{Bending strength (MPa)} = \frac{3 * F * L}{2 * b * h^6} \quad (1)$$

where F is the load on rupture measured in N, $\frac{\Delta F}{\Delta x}$ is the slope of the elastic zone in N/mm, L is the arm length, h the height and b the width, all expressed in mm.

Hardness was measured according to ISO 3350 standard (1975). Since untreated pine wood is soft, the force measured was that required to embed a 11.28 mm steel ball into wood to a quarter of its diameter (2.82 mm).

RESULTS AND DISCUSSION

Treatment

Furfuryl alcohol penetrated in both sapwood and heartwood, but the heartwood showed a whiter band in the central region of the board, where furfuryl could not penetrate, suggesting that although heartwood impregnation with furfuryl alcohol is feasible, it is only viable for small diameters. Weight percent gain (WPG) of treated wood was on average 38% for sapwood and 23% for heartwood while it was 31% for samples with sapwood and heartwood. These results suggest that this species absorbs more furfuryl alcohol than the reported earlier for other pine species (Lande *et al.* 2004b) for which the heartwood was not apt for treatment.

Mechanical properties

The static bending properties of pine wood were not significantly affected by the treatment. MOE was on average 10924 and 10833 MPa while bending strength was 166 and 176 MPa for untreated and treated wood, respectively. In relation to hardness there was a clear increase in radial and tangential surfaces of about 50% (Table 1). This increase was higher than the reported earlier for Scots pine for which Brinell hardness increased about 20% for WPG=32% and about 30% for WPG=47% (Lande *et al.* 2004b).

Table 1: Mechanical properties of untreated and treated pine wood

	Sample	MOE [MPa]	Bending strength [MPa]	Radial Hardness [N]	Tangential Hardness [N]
Untreated	Average	10924	166	4505	4363
	St.dev.	1021	14	322	668
Treated	Average	10833	176	7013	6534
	St. Dev.	907	12	416	454

Equilibrium moisture

Equilibrium moisture content decreased in the sapwood from 8.9% to 5.1% (at 35% relative humidity), from 12.9% to 7.3% (at 65%) and from 17.3% to 9.0% (at 85%), corresponding respectively to 43%, 43% and 48% improvement in relation to untreated wood. In heartwood the moisture decrease was very small and only significant for 85% relative humidity with an 11% improvement (Table 2).

Table 2: Equilibrium moisture content of untreated and treated pine wood

	Sample	Sapwood			Heartwood		
		EMC (35%)	EMC (65%)	EMC (85%)	EMC (35%)	EMC (65%)	EMC (85%)
Untreated	Average	8.9	12.9	17.3	7.4	10.9	14.5
	St. Dev.	0.1	0.2	0.3	0.3	0.3	0.5
Treated	Average	5.1	7.3	9.0	7.2	10.1	12.9
	St. Dev.	0.1	0.1	0.1	0.2	0.4	0.4

Dimensional stability

The dimensional changes between 35%, 65% and 85% relative humidity and oven dry samples are presented on Table 3. The dimensional changes decreased for all treated samples, both of sapwood and heartwood, leading to an improved dimensional stability. The improvement was higher for sapwood with ASE35 35.6% and 41.8%, ASE65 29.0% and 43.4% and ASE85 31.4% and 45.1% for radial and tangential directions respectively. The improvements for heartwood were smaller and only significant in the tangential direction and at the higher relative humidity values: ASE65 was 12.3% and 22.4% and ASE85 10.5% and 24.8% for radial and tangential directions, respectively (Table 3). The anisotropy of pinewood dimensional changes decreased with treatment mainly for sapwood: the ratio of tangential to radial dimensional changes was on average 1.7 for untreated wood and 1.4 for treated wood. The difference was smaller for heartwood decreasing from 1.6 to 1.5.

Table 3: Dimensional changes and Anti Shrinking Efficiency (ASE) of untreated and treated wood

Sample	Sapwood						Heartwood					
	Radial [%]			Tangential [%]			Radial [%]			Tangential [%]		
	35%	65%	85%	35%	65%	85%	35%	65%	85%	35%	65%	85%
Untreated	Average	1.8	2.7	3.5	2.9	4.6	6.2	1.7	2.5	3.2	2.6	4.1
	St. Dev.	0.4	0.4	0.5	0.4	0.5	0.4	0.8	0.4	0.5	0.5	0.5
Treated	Average	1.2	1.9	2.4	1.7	2.6	3.4	1.6	2.2	2.8	2.4	3.2
	St. Dev.	0.4	0.4	0.5	0.4	0.5	0.5	0.0	0.4	0.5	0.4	0.5
ASE (%)		35.6	29.0	31.4	41.8	43.4	45.1	6.3	12.3	10.5	8.1	22.4
												24.8

CONCLUSIONS

Furfurylation of *Pinus pinaster* wood improved the behaviour in relation to moisture by decreasing the wood equilibrium moisture content and increasing its dimensional stability, without significant effect on bending properties. Hardness was significantly increased by the treatment. The anisotropy of pinewood dimensional changes decreased with treatment. Furfurylation of *Pinus pinaster* wood shows an interesting potential to improve the wood quality for solid timber products. The treatment is possible in sapwood and to some extent in heartwood.

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