Micro-distribution, Water Absorption, and Dimensional Stability of Wood Treated with Epoxidized Plant Oils

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Samples of Scotch pine sapwood were treated with epoxidized linseed and soybean oils *via* an empty cell process to improve the hydrophobic properties of wood. Boric acid was included to introduce fungicidal properties into the oils. Two retention levels (80 to 140 kg/m^3 and 170 to 270 kg/m^3) were targeted for oil treatments. Both an empty cell method and emulsion techniques were used to combine epoxidized oils and boric acid in a one-step treatment. Iodine number changes, Fourier transform infrared spectroscopy (FTIR), water absorption (WA), anti-swelling efficiency (ASE), and scanning electronic microscopy (SEM) analyses were used to characterize the wood after treatment. High iodine number changes that indicated a reduction the amount of unsaturated double bonds were determined. The FTIR analysis of epoxidized oils revealed a peak at 820 cm^{-1}, which indicated that epoxide moieties (C-O-C) were present. All of the oil treatments resulted in statistically significant lower water absorptions than the control sample. The lowest water absorption values were obtained from wood treated with epoxidized oils. The highest ASE result (70%) was observed on samples treated with epoxidized soybean oil at low retention (108 kg/m^3). It was also determined that most of the latewood tracheids were filled with oils when compared to the earlywood tracheids.

Keywords: Epoxidized plant oils; Wood modification; Dimensional stability; Water absorption

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INTRODUCTION

Copper-based wood preservatives are widely used in traditional wood protection industries. Copper is the primary biocide in the wood protective formulations due to its excellent fungicidal properties as well as industrial feasibility. However, the treatment of wood and biobased products with natural substances is of increasing interest due to environmental concerns (Freeman and McIntyre 2008; Singh and Singh 2012). Research and the wood industry have focused on developing alternative protection methods based on green technologies that use natural products and processes with no toxicity or adverse environmental effects (Temiz *et al.* 2010, 2013; Singh and Singh 2012).

Developing and commercializing new fungicides or insecticides requires years of evaluation and is extremely expensive due to issues such as discrepancies between laboratory and field performance of natural products alternatives, the wide range of fungicides and insecticides, variations in the exposure conditions of wood materials, and differences among countries' regulation systems (Singh and Singh 2012; Stirling and Temiz 2014).

For centuries, plant-derived oils and tars have been used to enhance the appearance and extend the service life of wood products. Derivatives from plants, including bark, wood, leaves, seeds, and fruits, have been studied for wood protection properties. Among the plant-derived oils (either plant or essential oils), linseed, palm, and tung seed oils, as well as cinnamon and citrus peels, have been tested as potential wood protection agents (Macias *et al.* 2005; Lin *et al.* 2007; Temiz *et al.* 2010; Singh and Singh 2012; Temiz *et al.* 2013; Jebrane *et al*. 2015a,b). However, the use of plant oils for wood protection has some limitations, such as the amount of oil needed for reliable protection and the oil's tendency to exude from wood (Temiz *et al.* 2008; González-Laredo *et al.* 2015). One way to improve oil's performance as a protectant is its emulsification (Hyvönen *et al*. 2006) together with oxidation and polymerization of oils (González-Laredo *et al.* 2015; Cai 2016).

Linseed oil (LO), also known as flaxseed oil, is derived from seeds of the flax plant, *Linum usitatissimum*. It is classified as a drying oil, and it polymerizes through oxidation (Fernández-Cano 2013; Jebrane *et al.* 2015a). It is reported that linseed oil can protect wood against fungi by providing hydrophobic properties that prevent water uptake (Temiz *et al.* 2008; Jebrane *et al.* 2015a). However, LO polymerization *via* oxidation requires extensive time and is subject to exudation in outdoor conditions (Koski 2008). Plant oils contain unsaturated fatty acids that can be chemically modified by epoxidation processes using peracetic acid, dioxirane, or hydrogen peroxide as a catalyst (Chen *et al.* 2002). Some studies have tested the ability of modified LO to protect wood (Panov *et al.* 2010; Terziev and Panov 2011; Fernández-Cano 2013; Temiz *et al.* 2013; Jebrane *et al.* 2015a, 2015b; Cai 2016). Improvements in the anti-swelling efficiency (ASE) and wood durability in a laboratory decay test of samples treated with modified LO at low retention levels have been reported (Terziev and Panov 2011; Cai 2016). The modified LO with low retention reduced the water absorption and swelling of wood. Plant oils have no fungicidal effect but protect wood against decay through increased hydrophobicity. Furthermore, the protective effect can be boosted through the addition of boron for additional decay and termite resistance. Applied oil may also prevent the leaching of boron.

The main objective of the present study was to evaluate epoxidation of LO and soybean oil (SO) for wood modification with the aim to improve the hydrophobicity of wood by using low retention levels. Boric acid was combined with oils to improve their performance against fungi and insects.

EXPERIMENTAL

Materials

Scots pine *(Pinus sylvestris* L.*)* sapwood samples were used in the study. The LO and SO were purchased from Traditem GMBH Company (Hilden, Germany) and Sancar Chemical Company (İstanbul, Turkey). Boric acid was purchased from Merck (Darmstadt, Germany).

Synthesis of epoxidized oils

The oil (80 g) was placed in a three-neck round glass balloon (1 L) with a thermometer, cooler, and mechanical stirrer. The balloon was heated to the desired temperature (40, 50, and 60 °C), and kept at a constant temperature using a water tank. The required amount of acetic acid was introduced as catalyst, followed by hydrogen peroxide (16%, 210 g), which was added into the balloon to open the epoxy rings. The resulting reaction was stirred at pre-determined durations (60, 120, 180, 240, or 360 min) vigorously. After the reaction was completed, the water and organic layers were separated. The epoxidation process was carried out according to Chen *et al*. (2002).

Wood treatment processes and curing

The LO, SO, epoxidized linseed oil (ELO), epoxidized soybean oil (ESO), and their combinations with boric acid (BA) were used for wood impregnation. In ELO and ESO treatments, the epoxidized oils were dissolved in pure acetic acid at a ratio of 70:30 (w/w). Two retention levels (80 to 140 kg/m^3 (A) and 170 to 270 kg/m^3 (B)) were targeted for oil treatments. An empty cell method was used for oil treatments. The oils were heated to 80 °C to decrease their viscosity. Various pre-pressure, vacuum, and pressure times were applied to different oil treatments in order to get similar retention levels within the same sets. This variation was necessary due the chemical characteristics and viscosity differences of oils (Table 4). For the boric acid treatment, a full cell method, comprised of 20 min vacuum at 90% and 40 min pressure at 10 bar, was used. An emulsion technique was used for the combination of epoxidized oils and boric acid for one-step impregnation.

For the emulsion technique, the epoxidized oil was heated to 40° C in a beaker, and then polyoxyethylene (100) stearyl ether (Brij® S100) (2.5% for ELO and 4% for ESO by wt.) and sorbitane monooleate (SPAN 80), a nonionic surfactant (6.2% for ELO and 9.2% for ESO by wt.), were added into the beaker. Boric acid (2.025 g by wt.) and acetic acid (7.5% by wt.) were mixed in deionized water (67.5% by wt.) in a separate beaker. The two solutions were then mixed by stirring for 15 min and by adding SDS, providing to bond the water to the oil (1.5% for ELO and 3% for ESO by wt.).

After the impregnation, the epoxidized oils were cured at 70 °C for 14 days in the presence of acetic acid to facilitate the polymerization process. The samples were conditioned at 20 °C and 65% relative humidity (RH) after curing. The treatment processes and variations used for wood impregnation are shown in Table 1.

Table 1. Wood Treatment Process and Variations

Variations	**Treatment Parameters**	**Polymerization** 70 °C, 14 days
3% BA + ELO	1st impregnation with BA, 2nd impregnation with ELO (Empty cell process)	+
3% BA + ESO	1st impregnation with BA, 2nd impregnation with ESO (Empty cell process)	+
3% BA + LO	1st impregnation with BA, 2nd impregnation with LO (Empty cell process)	-
3% BA + SO	1st impregnation with BA and then 2nd impregnation with SO (Empty cell process)	-
3% BA	Only impregnation with BA (full cell process)	-
ELO/ 3% BA emuls.	Emulsion technique with ELO and BA	+
ESO/ 3% BA emuls.	Emulsion technique with ESO and BA	+
ELO	Only impregnation with ELO (Empty cell process)	+
ESO	Only impregnation with ESO (Empty cell process)	+
LO	Only impregnation with LO (Empty cell process)	-
SO	Only impregnation with SO (Empty cell process)	-

ELO: Epoxidized linseed oil; ESO: Epoxidized soybean oil; LO: Linseed oil; SO: Soybean oil; and BA: Boric acid.

Methods

Iodine number changes in oils

The iodine number indicates the number of unsaturated double bonds in plant oils and reveals the rate of the epoxidation reaction after an epoxidation process. Iodine numbers of epoxidized and non-epoxidized oils were determined by the Hanus method (Hanus 1901). The iodine number was calculated according to Eq. 1,

$$\text{Iodine number (IN)} = ((V_2 - V_1) \times 0.01269 \times 100) / m \qquad (1)$$

where V_2 is the volume (mL) of thiosulfate solution consumed for the control, V_1 is the volume (mL) of thiosulfate solution consumed for the test, and m is the amount of oil used in analysis (g).

The rate of iodine number changes was calculated according to Eq. 2,

$$\text{Change Rate (CR)} = ((IN_0 - IN_1) / IN_0) \times 100 \qquad (2)$$

where IN_0 is the iodine number of non-epoxidized oil and IN_1 is the iodine number of epoxidized oil.

Fourier transform infrared (FTIR) spectra

The FTIR spectra of oils were determined by using a Bruker Tensor 37 spectrophotometer (Bruker, Billerica, Massachusetts, US) in the range of 4000 cm^{-1} to 400 cm^{-1}, with a 4 cm^{-1} resolution over 32 scans, using Diamond ATR (Bruker, Billerica, Massachusetts, USA).

Water absorption (WA) and anti-swelling efficiency (ASE)

The WA and ASE tests were performed according to the American Wood Preservers' Association AWPA E4-03 (2003) standard method. Treated and untreated wood samples (15 × 25 × 50 mm (R × T × L)) were conditioned to 12% moisture content before testing. Then, the treated and untreated samples were placed into beakers filled with deionized water. The water was refreshed after 30, 60, 120, 240, and 360 min on days 1 and 2, and then every 2 days for a total of 14 days. The weights and dimensions of the samples were recorded after every time interval. Experiments were conducted at room temperature. The WA and ASE were calculated according to Eqs. 3 and 4 after each water replacement,

$$\text{WA} = [(W_2 - W_1) / W_1] \times 100 \qquad (3)$$

$$\text{ASE (\%)} = ((V_u - V_t) / V_u) \times 100 \qquad (4)$$

where W_1 and W_2 are the weight (g) of the wood specimens before and after test, and V_u and V_t are the volumetric swelling coefficients of untreated and treated wood, respectively.

Micro-distribution of oils

Scanning electron microscopy (SEM Zeiss Evo LS 10; Zeiss, Oberkochen, Germany) was performed to visualize the micro-distribution of oil into the wood structure. Wood samples were cut by microtome to a thickness of approximately 15 µm, oven-dried at 30 °C, and then coated with gold by using an Emitech SC7620 device (Quorum Technolologies LTD, Lewes, East Sussex, UK).

Statistical analysis

The statistical package program of IBM SPSS 22.0 (IBM Corp., Armonk, NY, US) was used for the statistical analyses of the data. A one-way analyses of variance test (ANOVA) was conducted at a 95% confidence level, to determine statistically significant differences between the control and treated samples.

RESULTS AND DISCUSSION

The rates of iodine number changes for epoxidized and non-epoxidized oils are given in Table 2.

Table 2. Iodine Number Changes in Oils

Oil Type	Rate of Iodine Number Changes (%)
ELO/LO	92.88
ESO/SO	95.78

By epoxidation, the carbon-carbon bonds in the structure of unsaturated double bonds in LO and SO were opened by reacting with active oxygen. Thus, high iodine number changes indicated a small amount of unsaturated double bonds that remained in the plant oil when the epoxidation reaction was successful. High iodine number changes (over 90%) in this study showed that the epoxidation process was successful.

FTIR Spectra of Oils

The FTIR spectra of epoxidized and non-epoxidized oils are shown in Fig. 1. The spectra were collected over the range of 4000 cm^{-1} to 400 cm^{-1}. The assignments of characteristic IR absorption peaks are listed in Table 3.

Table 3. Assignments of Absorption IR Spectra Bands

IR (cm^{-1})	Assignments
820	Epoxy rings
1243	C-O stretching vibration
1728 to 1745	Carbonyl groups
2855 to 2928	C-H stretching vibration
2950 to 3000	Alkyl groups

The intense C-H bands at 2925 cm^{-1} and 2855 cm^{-1}, the strong C=O stretching vibration at 1740 cm^{-1} and the epoxide ring at 820 cm^{-1} were visible on FTIR peaks. The band at 1740 cm^{-1} is characteristic for carbonyl groups. This band is broad due to two carbonyl groups (Jebrane *et al.* 2015b). Epoxidized oils (ELO and ESO) were characterized by the stretching vibration of the epoxide moieties (C-O-C) at 820 cm^{-1}, which was not seen on the FTIR spectrum of non-epoxidized oils.

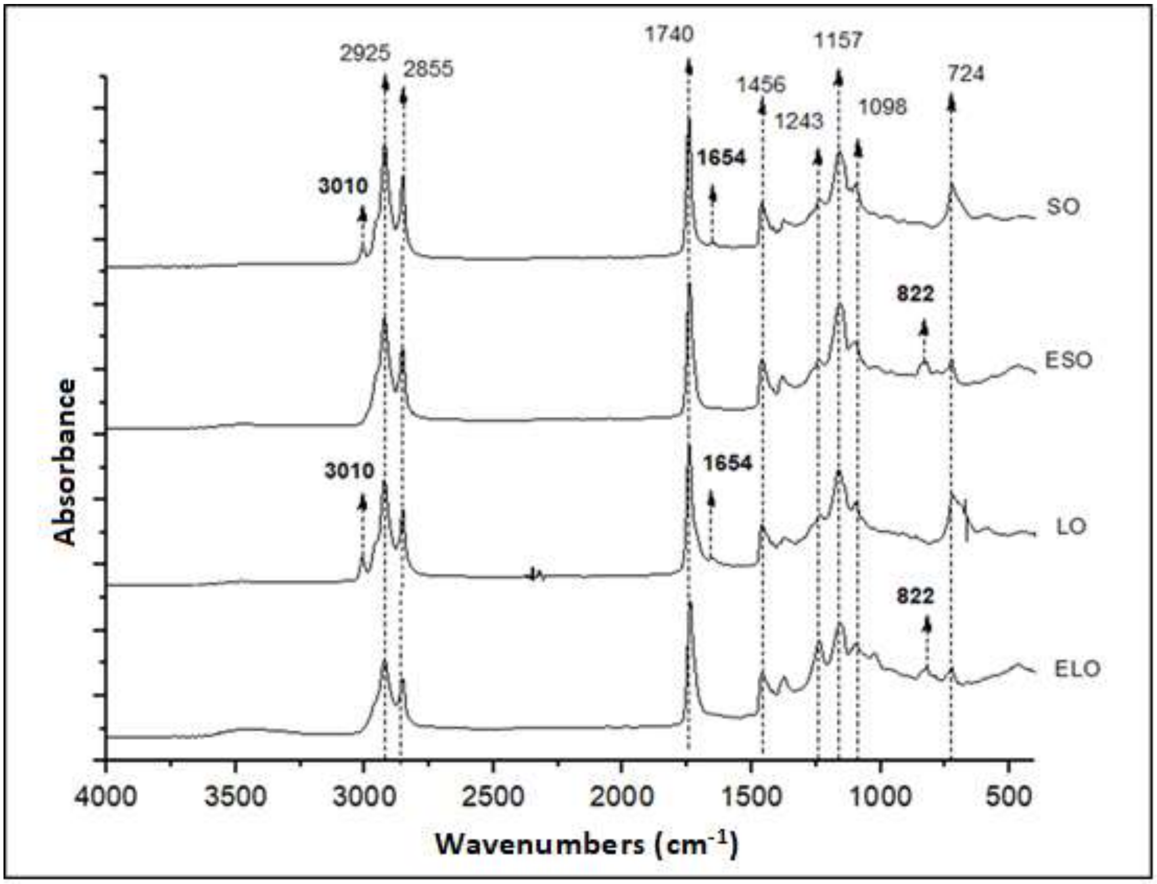

Fig. 1. FTIR spectra of oils

Water Absorption and Anti Swelling Efficiency

The retentions and treatment parameters of the impregnations are listed in Table 4. The WA and ASE results are shown in Tables 5 and 6, respectively.

Water absorption (WA) of untreated wood ranged from 30% after 30 min of water exposure to 85% after 14 days. All oil treated sets had significantly reduced WA rates when compared to that of the control samples. However, the BA treatment alone resulted in water absorption similar to that of the control due to the hydroscopic characteristic of boron.

As expected, Ret B (higher oil retention) had lower water absorption values than Ret A (lower oil retention). Both ELO and ESO showed lower WA values than those of non-epoxidized LO and SO for both Ret A and Ret B after 14 days of water exposure. It was concluded that the epoxidation process statistically significantly reduced the water uptake.

The second impregnation with BA slightly increased the WA in the treated wood samples due to the hydroscopic behavior of boron. The use of an emulsion technique, which allowed for the one-step treatment with oils and boron, also increased WA when compared to single oil treatments.

Table 4. Treatment Parameters and Retention Values

Variations	Ret.	Retention (kg/m^3)		Parameters for treatment
		1st treatment (with 3% BA)	2nd treatment (with oil)	
3% BA + ELO	A	22.65 (0.47)*	85.74 (5.79)	pp 2 bar/ 20’, p 4 bar/30’, ho/20’, vac 5’
	B	20.69 (2.24)	217.71 (17.51)	p 2 bar /30’, ho/ 20’, vac/ 5’
3% BA + LO	A	22.91 (0.40)	142.82 (18.17)	pp 2.0 bar/ 20’, p 4 bar/ 40’, ho/ 20’, vac 5’
	B	23.00 (0,27)	236.85 (21.52)	p 2.6 bar/ 40’, ho/20’, vac 5’
ELO/ 3% BA emuls.	A	124.89 (6.13)		p10 bar/ 40’
	B	174.21 (7.69)		pp 684 mmHg/ 5’, p 9 bar/60’, vac 5’
ELO	A	106.06 (17.07)		pp 0.75 bar/ 20’, p 2 bar/ 40’, ho/ 30’, vac 5’
	B	211.31 (34.92)		p 3.0 bar/ 40’, ho/20’, vac 5’
LO	A	10726 (25.43)		pp 2.0 bar/ 20’, p 4 bar/ 40’, ho/ 20’, Vac 5’
	B	239.77 (51.16)		p 2.6 bar/ 40’, ho/20’, vac 5’
3% BA	-	22.44 (0.81)		pp 684 mmHg/20’, p 10 bar/40’, vac 5’
3% BA + ESO	A	22.52 (0.63)	105.83 (20.68)	pp 0.75 bar/20’,p 2.0 bar/40’ ho/ 30’, vac 5’
	B	23.14 (0.77)	182.57 (21.05)	p 3.0 bar/ 40’ ho/ 20’, vac/5’
3% BA + SO	A	22.97 (0.79)	98.97 (13.94)	pp 0.75 bar/ 20’, p 2.2.5 bar/60’, ho/ 30’, vac 5’
	B	22.59 (0.74)	247.58 (12.65)	p 3.6 bar/ 40’, ho/20’, vac 15’
ESO/ 3% BA emuls.	A	131.18 (1.52)		p10 bar/ 35’
	B	178.92 (10.63)		pp 684 mmHg/ 10’, p 12 bar/120’, vac 5’
ESO	A	108.43 (4.82)		pp 0.75 bar/ 20’, p 2 bar/ 20’, ho/ 30’, vac 5’
	B	224.37 (32.57)		p 3.0 bar/ 30’, ho/20’, vac 5’
SO	A	128.54 (10.23)		pp 0.75 bar/ 20’, p 2.5 bar/ 60’, ho/ 30’. vac 5’
	B	222.27 (32.28)		p 3.75 bar/ 40’, ho /20’, vac 5’

* Numbers in parenthesis are standard deviations.
pp: Pre-pressure; p: Pressure; vac: Vacuum; ho: Hot oil; ELO: Epoxidized linseed oil; ESO: Epoxidized soybean oil; LO: Linseed oil; SO: Soybean oil; and BA: Boric acid.

Wood treatment with oils, such as linseed, tall, soybean, rapeseed, sunflower, and coconut oils, provide hydrophobicity, which prevents water uptake into wood, and thus keeps the wood moisture content below the level at which fungi can attack (Hyvönen *et al.* 2006; Temiz *et al.* 2008). High oil retention (normally 400 to 600 kg/m^3) in wood is necessary to provide a reasonable hydrophobic effect, but may cause wood to become unreasonably expensive and heavy. In this study, two low retentions, namely 80 to 140 kg/m^3 (Ret A) and 170 to 270 kg/m^3 (Ret B)) were targeted for the oil treatments.

Table 5. Water Absorption (WA) Results

Variations	Retentions (kg/m^3)			Water Absorption (%)								
				30 min	1 h	6 h	24 h	48 h	96 h	192 h	288 h	336 h
3% BA+ ELO	A	85.74	Ave.	3.77^{bc*}	5.76^{cd}	16.59^{ef}	29.51^{hi}	35.75^{gh}	40.82^{g}	45.76^{f}	51.06^{h}	53.03^{g}
			St.D	0.38	0.54	2.89	3.33	2.97	2.75	3.02	3.47	3.70
	B	217.71	Ave.	2.51^{ab}	3.70^{ab}	7.63^{b}	15.02^{bc}	21.25^{b}	26.60^{bc}	30.39^{d}	32.77^{bc}	33.69^{ab}
			St.D	0.28	0.38	0.59	1.63	2.06	2.22	1.99	1.91	1.94
3% BA + LO	A	142.82	Ave.	5.63^{cde}	7.79^{e}	18.48^{ef}	30.17^{i}	33.51^{fg}	36.18^{e}	38.75^{e}	41.41^{e}	41.87^{de}
			St.D	1.91	2.72	5.22	2.66	1.72	1.27	1.15	1.21	1.27
	B	236.85	Ave.	5.20^{cde}	7.22^{de}	18.07^{ef}	27.83^{ghi}	29.14^{e}	30.29^{d}	31.92^{d}	33.69^{c}	33.72^{ab}
			St.D	1.15	1.89	4.70	2.34	1.60	1.61	1.79	2.03	1.98
ELO / 3% BA emuls.	A	124.89	Ave.	8.94^{h}	11.10^{gh}	19.48^{f}	29.38^{hi}	37.27^{h}	45.06^{h}	54.92^{h}	63.71^{j}	66.04^{i}
			St.D	1.42	1.53	1.74	1.83	2.03	2.19	3.05	3.66	4.90
	B	174,21	Ave.	9.40^{h}	11.17^{gh}	18.57^{ef}	25.56^{efg}	32.70^{f}	40.14^{fg}	49.73^{g}	56.84^{i}	58.51^{h}
			St.D	2.81	2.52	3.16	2.57	2.86	3.25	3.97	4.62	4.94
ELO	A	106.06	Ave.	7.68^{fgh}	8.41^{ef}	11.54^{cd}	16.85^{cd}	20.96^{b}	25.10^{b}	30.14^{cd}	34.07^{cd}	36.54^{bc}
			St.D	0.97	1.11	1.48	2.04	2.34	2.47	2.89	3.56	4.19
	B	211.31	Ave.	6.47^{efg}	7.06^{de}	9.67^{bc}	13.52^{b}	16.65^{a}	20.08^{a}	25.09^{a}	28.52^{a}	30.31^{a}
			St.D	0.53	0.56	1.38	0.80	0.96	1.14	1.29	1.35	1.43
LO	A	107.26	Ave.	3.89^{bcd}	5.66^{cd}	13.03^{d}	25.35^{efg}	32.83^{f}	37.76^{ef}	43.43^{f}	45.15^{fg}	45.68^{ef}
			St.D	0.61	0.81	1.69	3.60	2.92	3.82	6.85	5.03	5.17
	B	239.77	Ave.	2.97^{ab}	4.23^{bc}	10.77^{cd}	19.30^{d}	23.14^{bc}	26.95^{bc}	29.96^{cd}	32.20^{abc}	32.55^{ab}
			St.D	0.60	0.80	2.71	4.75	4.15	4.06	4.17	4.62	4.75
3% BA	-	22.44	Ave.	38.11^{j}	42.33^{j}	46.57^{h}	48.72^{k}	49.80^{i}	54.17^{i}	61.49^{i}	72.58^{k}	74.47^{j}
			St.D	4.89	3.65	2.81	3.01	2.96	3.64	4.26	5.84	6.26
3%BA + ESO	A	105.83	Ave.	2.36^{ab}	3.73^{ab}	9.64^{bc}	18.22^{d}	24.84^{cd}	30.91^{d}	37.25^{e}	42.22^{ef}	44.05^{e}
			St.D	1.54	2.30	6.23	7.80	7.84	7.90	8.16	9.51	10.34
	B	182.57	Ave.	1.41^{a}	2.14^{a}	4.85^{a}	9.80^{a}	15.33^{a}	21.00^{a}	26.24^{ab}	29.23^{ab}	30.11^{a}
			St.D	0.24	0.26	0.66	1.35	1.55	2.01	2.16	2.42	2.53
3%BA + SO	A	98.97	Ave.	9.18^{h}	12.72^{h}	23.66^{g}	33.21^{j}	38.07^{h}	41.67^{g}	44.27^{f}	48.21^{gh}	48.68^{f}
			St.D	2.04	3.06	3.84	2.08	2.50	2.95	3.02	3.76	3.75
	B	247.58	Ave.	5.14^{cde}	7.04^{de}	19.32^{ef}	24.18^{e}	25.55^{cd}	27.25^{bc}	29.12^{bcd}	31.11^{abc}	31.65^{a}
			St.D	1.00	1.32	3.59	2.51	2.35	2.54	2.76	2.79	2.75

ESO / 3% BA emuls.	A	131.18	Ave. St.D	7.61^{fgh} 0.93	9.96^{fg} 0.92	18.51^{ef} 1.48	28.59^{hi} 1.97	37.09^{h} 1.94	45.90^{h} 1.97	56.35^{h} 2.25	65.11^{j} 2.37	67.89^{i} 2.53
	B	178.92	Ave. St.D	6.44^{efg} 0.50	8.61^{ef} 0.51	15.71^{e} 0.69	24.71^{ef} 1.14	32.86^{f} 1.36	41.33^{g} 1.62	50.70^{g} 1.97	57.31^{i} 2.18	59.31^{h} 2.27
ESO	A	108.43	Ave. St.D	7.90^{gh} 0.70	8.70^{ef} 0.78	12.28^{cd} 0.92	16.94^{cd} 1.10	20.88^{b} 1.29	25.43^{b} 1.72	32.43^{d} 2.31	37.41^{d} 2.83	39.56^{cd} 3.11
	B	224.37	Ave. St.D	6.41^{efg} 0.43	6.91^{de} 0.54	10.05^{bc} 0.94	14.24^{bc} 1.04	17.44^{a} 1.14	21.56^{a} 1.33	26.80^{abc} 1.63	30.44^{abc} 1.97	32.27^{a} 2.17
SO	A	128.54	Ave. St.D	5.74^{def} 1.02	7.87^{e} 1.04	17.03^{ef} 3.37	27.15^{fgh} 3.60	31.87^{f} 2.51	36.07^{e} 2.66	39.45^{e} 3.15	42.60^{ef} 3.46	43.16^{de} 3.49
	B	222.27	Ave. St.D	6.12^{efg} 0.71	8.00^{e} 0.92	16.39^{ef} 2.80	23.52^{e} 2.82	26.44^{d} 2.18	28.92^{cd} 1.98	31.41^{d} 2.45	33.41^{c} 2.66	33.98^{ab} 2.89
Control	-	-	Ave. St.D	30.30^{i} 5.55	37.03^{j} 4.56	48.72^{h} 3.61	51.94^{l} 3.00	55.99^{j} 2.98	59.48^{j} 3.08	69.79^{j} 3.46	81.81^{l} 3.95	85.55^{l} 4.03

***** Different letters denote a statistically significant difference.
ELO: Epoxidized linseed oil; ESO: Epoxidized soybean oil; LO: Linseed oil; SO: Soybean oil; and BA: Boric acid.

Table 6. Anti-swelling Efficiency (ASE) Results

Variations	**Retentions (kg/m^3)**			**Anti-Swelling Efficiency (%)**								
				30 min	**1 h**	**6 h**	**24 h**	**48 h**	**96 h**	**192 h**	**288 h**	**336 h**
3% BA+ ELO	A	85.74	Ave. St.D	86.47^{jk} 5.45	81.23^{fg} 4.50	51.47^{d} 5.88	32.62^{b} 5.63	25.05^{a} 6.22	25.47^{bcd} 6.37	24.60^{cd} 7.36	26.80^{c} 6.70	26.14^{bc} 6.34
	B	217.71	Ave. St.D	92.67^{kl} 4.52	88.59^{h} 3.02	78.72^{i} 4.77	59.86^{gh} 7.86	42.32^{cd} 8.52	42.18^{fg} 7.55	34.11^{ef} 7.46	34.17^{e} 7.14	35.46^{ef} 6.93
3% BA + LO	A	142.82	Ave. St.D	64.67^{cde} 9.14	59.29^{c} 10.35	30.96^{b} 12.23	25.74^{a} 4.86	23.40^{a} 4.59	23.31^{bc} 5.26	24.81^{cd} 5.74	26.21^{c} 5.21	26.94^{cd} 5.62
	B	236.85	Ave. St.D	70.74^{efg} 9.57	72.13^{e} 7.95	43.73^{c} 9.61	25.75^{a} 5.76	24.63^{a} 6.08	24.41^{bc} 5.69	25.04^{cd} 5.84	28.00^{cd} 5.22	27.21^{cd} 5.04
ELO / 3% BA emuls.	A	124.89	Ave. St.D	72.03^{fgh} 9.19	72.28^{e} 5.29	60.90^{gh} 5.49	45.54^{a} 6.33	31.79^{d} 5.87	31.17^{de} 5.99	30.31^{de} 6.26	33.57^{de} 7.94	32.38^{de} 8.22

	B	174,21	Ave. St.D	80.00^{i} 9.72	74.11^{e} 6.66	67.80^{gh} 5.26	57.66^{de} 4.62	44.81^{b} 6.10	41.38^{fg} 6.10	43.74^{g} 7.18	41.22^{f} 7.28	41.84^{g} 7.80
ELO	A	106.06	Ave. St.D	51.79^{b} 8.08	58.62^{c} 7.73	60.72^{ef} 6.67	54.26^{fg} 6.86	44.12^{d} 7.06	37.74^{fg} 7.05	34.24^{ef} 7.15	34.67^{e} 8.14	34.45^{ef} 6.82
	B	211.31	Ave. St.D	62.16^{cd} 9.29	71.90^{e} 7.79	73.40^{hi} 7.50	70.69^{i} 7.57	61.94^{f} 8.64	54.95^{h} 8.66	52.05^{h} 9.10	52.17^{g} 8.79	53.90^{h} 8.65
LO	A	107.26	Ave. St.D	64.38^{cde} 4.36	65.75^{d} 6.03	54.79^{de} 6.56	37.51^{bc} 7.20	20.94^{a} 6.82	19.16^{ab} 7.89	18.14^{ab} 6.57	19.84^{b} 7.86	20.66^{b} 7.24
	B	239.77	Ave. St.D	68.26^{def} 6.79	69.90^{de} 7.03	63.74^{fg} 8.53	42.50^{cd} 14.00	26.19^{a} 9.65	23.53^{bc} 7.99	22.49^{bc} 6.19	22.88^{bc} 6.12	21.86^{bc} 6.00
3% BA	-	22.44	Ave. St.D	-33.30^{a} 9.90	-7.96^{a} 10.25	17.02^{a} 7.91	26.84^{a} 5.53	24.97^{a} 5.72	26.81^{cd} 5.60	27.05^{cd} 5.83	28.56^{cde} 5.26	26.01^{bc} 5.60
3% BA + ESO	A	105.83	Ave. St.D	88.11^{jkl} 6.59	89.64^{h} 6.17	77.96^{i} 3.91	55.59^{fg} 6.83	37.24^{c} 7.89	35.96^{ef} 8.19	35.88^{ef} 7.90	34.30^{e} 7.75	37.19^{efg} 6.83
	B	182.57	Ave. St.D	93.91^{l} 3.58	94.13^{h} 2.65	86.02^{j} 4.95	70.36^{i} 5.16	51.04^{e} 5.97	41.57^{fg} 5.95	38.92^{fg} 5.45	41.15^{f} 5.36	39.98^{fg} 6.00
3% BA + SO	A	98.97	Ave. St.D	47.70^{b} 9.31	49.09^{b} 9.68	30.04^{b} 9.20	25.83^{a} 5.23	24.04^{a} 5.56	24.41^{bc} 6.33	26.10^{cd} 7.40	25.38^{bc} 5.13	25.85^{bc} 6.20
	B	247.58	Ave. St.D	60.12^{c} 9.90	59.46^{c} 8.12	30.64^{b} 11.62	26.37^{a} 8.35	23.51^{a} 5.69	24.10^{bc} 7.16	24.75^{cd} 5.90	26.80^{c} 6.01	25.48^{bc} 8.09
ESO / 3% BA emuls.	A	131.18	Ave. St.D	78.20^{hi} 7.72	73.69^{e} 5.05	67.76^{gh} 6.16	50.86^{ef} 6.85	38.12^{c} 8.29	42.37^{g} 11.52	35.91^{ef} 8.53	34.76^{e} 8.47	36.19^{efg} 8.47
	B	178.92	Ave. St.D	82.19^{ij} 8.81	81.79^{g} 3.87	73.74^{hi} 3.17	64.10^{h} 3.76	55.94^{e} 4.63	51.78^{h} 5.51	51.34^{h} 5.87	51.21^{g} 6.31	52.35^{h} 5.45
ESO	A	108.43	Ave. St.D	71.32^{fg} 3.09	75.83^{ef} 3.25	78.96^{i} 1.71	72.79^{i} 4.22	69.93^{g} 1.87	69.09^{i} 1.56	71.15^{i} 3.86	70.01^{g} 2.01	70.0^{i} 2.01
	B	224.37	Ave. St.D	76.87^{ghi} 3.94	79.91^{fg} 4.25	80.24^{ij} 3.71	75.44^{i} 4.37	69.72^{g} 4.12	67.81^{i} 3.68	71.35^{i} 5.77	68.38^{h} 2.80	68.38^{i} 2.80
SO	A	128.54	Ave. St.D	47.56^{b} 5.07	50.87^{b} 4.13	43.58^{c} 11.02	22.24^{i} 10.21	21.83^{a} 6.20	14.57^{a} 5.31	14.06^{a} 5.03	13.98^{a} 5.25	12.70^{a} 4.84
	B	222.27	Ave. St.D	47.27^{b} 7.70	51.54^{b} 5.58	43.69^{c} 9.75	25.85^{a} 7.77	22.85^{a} 7.58	25.84^{bcd} 7.76	23.75^{bc} 7.57	22.33^{bc} 7.84	22.90^{bc} 6.80

***** Different letters denote a statistically significant difference.
ELO: Epoxidized linseed oil; ESO: Epoxidized soybean oil; LO: Linseed oil; SO: Soybean oil; and BA: Boric acid.

The ELO treatments for Ret A and Ret B showed higher ASE results compared to treatment with non-epoxidized linseed oil. The highest ASE results (70%) were obtained from ESO-treated Ret A (108 kg/m^3) while the non-epoxidized soybean oil Ret A (128 kg/m^3) resulted in 12.7% ASE. These results confirmed that the epoxidized oils bonded to the wood cell wall to decrease the possible sorption sites for water molecules. As explained above, the addition of boron as a fungicide decreased the ASE results of epoxidized oils due to the nature of boron salts.

There is some published research concerning the use of epoxidized oils for wood protection (Panov *et al.* 2010; Terziev and Panov 2011; Temiz *et al.* 2013; Jebrane *et al.* 2015a, 2015b; Cai 2016). Some of the researchers report ASE improvements in the range of 50% to 60%, with oil retentions less than 120 kg m^3 (Terziev and Panov 2011). It is also reported that ASE ranged from 42% to 59% for retentions less than 160 kg m^3. However, when retention was increased to 240 kg/m^3, ASE was 51% to 62% (Fernández-Cano 2013). The ASE values of ELO in this study were in agreement with previous results (Terziev and Panov 2011; Fernández-Cano 2013; Jebrane *et al.* 2015a). The present study showed that ASE had negligible correlation with retention, which has also been reported by several other authors, such as Fernández-Cano (2013), Jebrane *et al*. (2015a), and Panov *et al.* (2010).

SEM Observations on Oil-treated Samples

The SEM observations of the oil-treated samples are shown in Figs. 2 through 4.

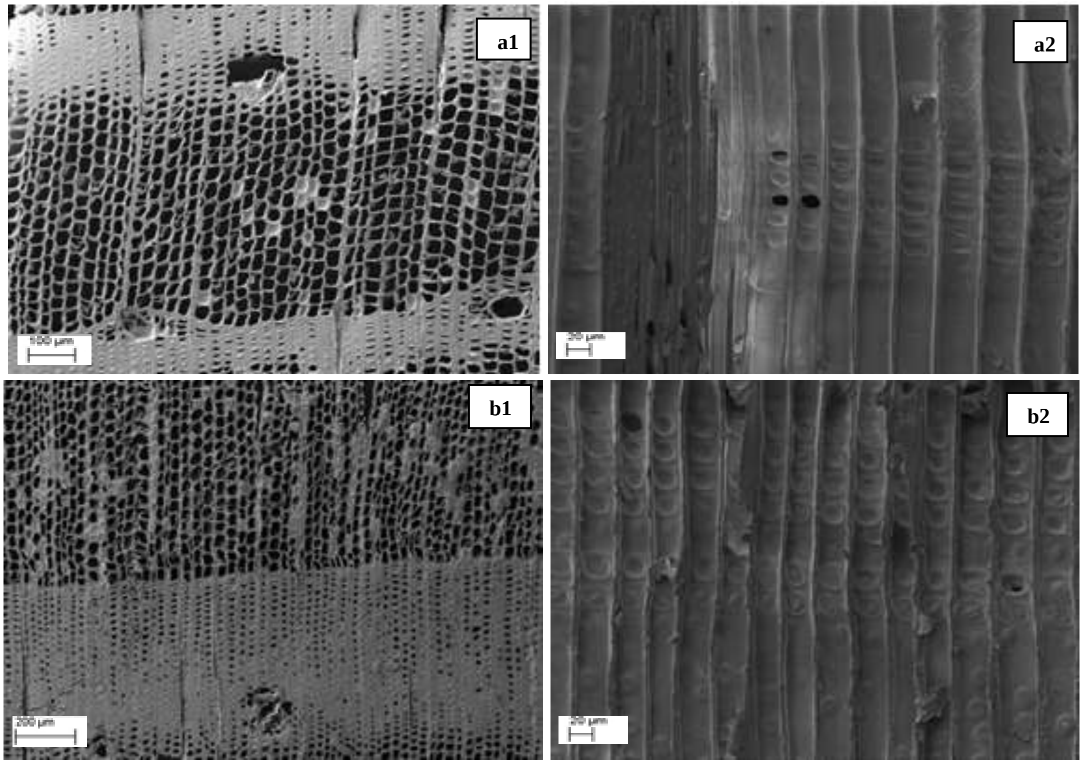

Fig. 2. SEM micrograph of treated wood (a1- ELO-treated wood: cross-section; a2- ELO-treated wood: radial section; b1- LO-treated wood: cross-section; and b2- LO-treated wood: radial section

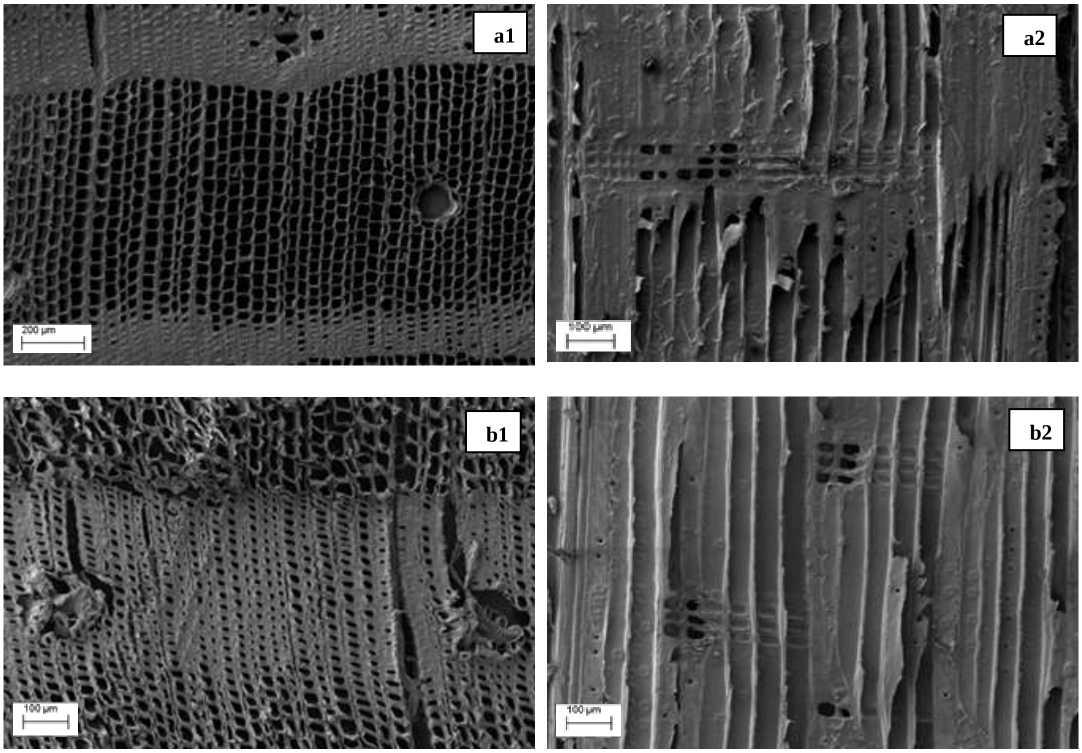

Fig. 3. SEM micrograph of treated wood (a1- ESO-treated wood: cross-section; a2- ESO-treated wood: radial section; b1- SO-treated wood: cross-section; and b2- SO-treated wood: radial section).

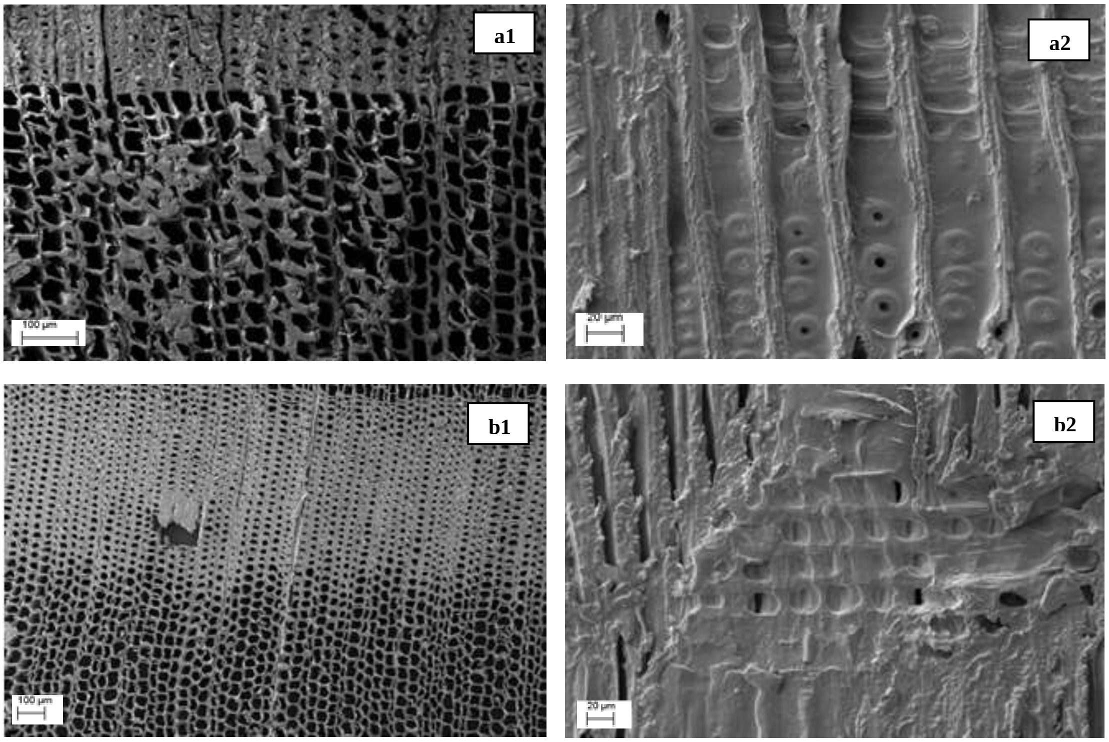

Fig. 4. SEM micrograph of treated wood (a1- ELO/ 3% BA emulsion-treated wood: cross-section; a2- ELO/ 3% BA emulsion-treated wood: radial section; b1- ESO/ 3% BA emulsion-treated wood: cross-section; and b2- ESO/ 3% BA emulsion-treated wood: radial section)

As displayed in the SEM micrographs of transversal sections, most of the latewood tracheids were filled with oils when compared to the earlywood tracheids. In addition, more of the tracheid lumens in the earlywood were filled with epoxidized oils than that of non-epoxidized oils. Rays were often filled with oils, which indicated that penetration of oils into wood structure occurs *via* these anatomical elements. Jebrane *et al.* (2015b) reported that ray tracheids and parenchyma cells are the main route for oil distribution into wood.

CONCLUSIONS

In this study, the effect of epoxidized plant oils (linseed and soybean) on dimensional stability and water absorption of wood was studied. The main findings were as follows:

1. Epoxidation processing of plant oils reduced the amount of oil treatment needed for wood protection through the epoxidation of double bonds at the fatty acid part of the triglyceride.
2. Emulsions of oil and boron were a feasible and practical solution for combining the two.
3. The wood treated with epoxidized oils noticeable reduced water absorption after 14 days exposure in water. The highest ASE (70%) was obtained from the samples treated with epoxidized soybean oils for low retention (108 kg/m^3) in 336 h soaking test.
4. The ASE had a negligible correlation with the retention of oils within the test scope of this article.
5. Most of the oils were located in the latewood tracheids.

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REFERENCES CITED

AWPA E4-03 (2003). "Standard method of testing water repellency of pressure treated wood," American Wood Protection Association, Birmingham, AL.

Cai, S. (2016). *Scots Pine (Pinus sylvestris L.) Sapwood Modification by Vinyl Acetate–Epoxidized Plant Oil Copolymer*, Ph.D. Thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Chen, J., Soucek, M. D., Simonsick, W. J., and Celikay, R. W. (2002). "Epoxidation of partially norbornylized linseed oil," *Macromolecular Chemistry and Physics* 203(14), 2042-2057. DOI: 10.1002/1521-3935(200210)203:14<2042::AID MACP2042>3.0.CO;2-0

Fernández-Cano, V. (2013). *Epoxidised Linseed Oil as Hydrophobic Substance for Wood Protection- technology of Treatment and Properties of Modified Wood*, Master's Thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Freeman, M. H., and McIntyre, C. R. (2008). "A comprehensive review of copper-based wood preservatives," *Forest Products Journal* 58(11), 6-27.

González-Laredo, R. F., Rosales-Castro, M., Rocha-Guzmán, N. E., Gallegos-Infante, J. A., Moreno-Jiménez, M. R., and Karchesy, J. J. (2015). "Wood preservation using natural products," *Madera y Bosques* 21, 63-71.

Hanus, J. (1901). "Die anwendung von jodmonobromid bei der analyse von fetten und oelen [The use of iodine monobromide in the analysis of fats and oils]," *Zeitschrift für Untersuchung der Nahrungs und Genussmittel* [*Journal for the Investigation of the Foodstuffs, As Well As the Commodities*] 4(20), 913-920.

Hyvönen, A., Piltonen, P., and Niinimäki, J. (2006). "Tall oil/water–emulsions as water repellents for Scots pine sapwood," *European Journal of Wood and Wood Products* 64(1), 68-73. DOI: 10.1007/s00107-005-0040-5

Jebrane, M., Fernández-Cano, V., Panov, D., Terziev, N., and Daniel, G. (2015a). "Novel hydrophobization of wood by epoxidized linseed oil. Part 1. Process description and anti-swelling efficiency of the treated wood," *Holzforschung* 69(2), 173-177. DOI: 10.1515/hf-2014-0029

Jebrane, M., Fernández-Cano, V., Panov, D., Terziev, N., and Daniel, G. (2015b). "Novel hydrophobization of wood by epoxidized linseed oil. Part 2. Characterization by FTIR spectroscopy and SEM, and determination of mechanical properties and field test performance," *Holzforschung* 69(2), 179-186. DOI: 10.1515/hf-2014-0030

Koski, A. (2008). *Applicability of Crude Tall Oil for Wood Protection*, Ph.D. Thesis, Faculty of Technology, Department of Process and Environmental Engineering, University of Oulu, Oulu, Finland.

Lin, C.Y., Wu, C. L., and Chang, S. T. (2007). *Evaluating the Potency of Cinnamaldehyde as a Natural Wood Preservati*ve (IRG/WP 07-30444), The International Research Group on Wood Protection, Stockholm, Sweden.

Macias, F. A., Torres, A., Maya, C. C., and Fernandez, B. (2005). "Natural biocides from citrus waste as new wood preservatives," in: *Proceedings of the 4th World Congress on Allelopath*y, *Establishing the Scientific Base*, Wagga Wagga, New South Wales, Australia, pp. 426-429.

Panov, D., Terziev, N., and Daniel, G. (2010). *Using Plant Oils as Hydrophobic Substances for Wood Protection* (IRG/WP 10-30550), in: *41st Annual Meeting of the International Research Group on Wood Protection*, Biarritz, France.

Singh, T., and Singh, A. P. (2012). "A review on natural products as wood protectant," *Wood Science and Technology* 46(5), 851-870. DOI: 10.1007/s00226-011-0448-5

Stirling, R., and Temiz, A. (2014). "Fungicides and insecticides used in wood preservation," in: *Deterioration and Protection of Sustainable Biomaterials*, American Chemical Society, Washington, DC, US, pp. 185-201. DOI: 10.1021/bk-2014-1158.ch010

Temiz, A., Alma, M. H., Terziev, N., Palanti, S., and Feci, E. (2010). "Efficiency of bio-oil against wood destroying organisms," *Journal of Biobased Materials and Bioenergy* 4(4), 317-323. DOI: 10.1166/jbmb.2010.1092

Temiz, A., Kose, G., Panov, D., Terziev, N., Alma, M. H., Palanti, S., and Akbas, S. (2013). "Effect of bio-oil and epoxidized linseed oil on physical, mechanical, and biological properties of treated wood," *Journal of Applied Polymer Science* 130(3), 1562-1569. DOI: 10.1002/app.39334

Temiz, A., Panov, D., Terziev, N., and Hafren, J. (2008). "Research on silicones and oils as hydrophobic agents," in: *V National Congress of Wood Protection*, CIDEMCO, San Sebastian, Spain.

Terziev, N., and Panov, D. (2011). "Plant oils as "green" substances for wood protection," in: *Ecowood 2010: Minimizing the Environmental Impact of the Forest Products Industries*, Porto, Portugal, pp. 143-149.

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