



This is an author produced version of a paper published in *Holzforschung*.

This paper has been peer-reviewed and includes the final publisher proof-corrections and journal pagination.

Citation for the published paper:

Mohamed Jebrane, Víctor Fernández-Cano, Dmitri Panov, Nasko Terziev and Geoffrey Daniel. (2015) 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*. Volume: 69, Number: 2, pp 179-186. <http://dx.doi.org/10.1515/hf-2014-0030>.

Access to the published version may require journal subscription.

Published with permission from: De Gruyter.

Epsilon Open Archive <http://epsilon.slu.se>

Mohamed Jebrane*, Víctor Fernández-Cano, Dmitri Panov, Nasko Terziev and Geoffrey Daniel

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

Abstract: Scots pine samples were impregnated with epoxidized linseed oil (ELO) by means of a two-step process, and the effect of treatments has been studied concerning the Fourier transform infrared (FTIR) spectra, mechanical properties, moisture uptake, and field test performance. FTIR analysis of ELO-treated samples revealed that part of the ELO epoxy reactive group was chemically bound to the hydroxyl groups of wood. ELO-treated samples have improved dimensional stability, while the mechanical properties were slightly reduced and the moisture uptake was significantly lowered. The field performance of lap joints treated with ELO (90 kg m⁻³) after 60 months' exposure showed great improvements in performance, as the average annual moisture content (MC) was maintained at the level of 19.3% compared to 34.6% for lap joints treated with linseed oil (LO). The lap-joint area was not stained, and less discoloration by staining fungi on the external surfaces was observed in ELO-treated samples compared to samples treated with LO.

Keywords: epoxidized linseed oil, mechanical properties, modified wood, moisture uptake, Scots pine sapwood, SEM, two-step process of modification

DOI 10.1515/hf-2014-0030

Received January 31, 2014; accepted June 12, 2014; previously published online July 5, 2014

***Corresponding author: Mohamed Jebrane**, Department of Forest Products/Wood Science, Swedish University of Agricultural Sciences, Box 7008, SE-750 07 Uppsala, Sweden, Phone: +46 18 67 24 75, Fax: +46 18 67 34 90, e-mail: mohamed.jebrane@slu.se

Víctor Fernández-Cano, Nasko Terziev and Geoffrey Daniel: Department of Forest Products/Wood Science, Swedish University of Agricultural Sciences, Box 7008, SE-750 07 Uppsala, Sweden
Dmitri Panov: Department of Nature and Technology/Institute of Chemistry, University of Tartu, Tartu, Estonia

Introduction

The mechanical properties of modified wood depend on the modification agent, weight percent gain (WPG), the chemical reaction, curing parameters, and the wood species. Well studied are woods acetylated with acetic anhydride in terms of dimensional stability and mechanical properties (Goldstein et al. 1961; Rowell et al. 1989; Singh et al. 1992; Beckers and Militz 1994; Larsson and Simonson 1994). While the majority of acetylated woods do not show significant changes in modulus of rupture (MOR) and modulus of elasticity (MOE) (Larsson 1993), the hardness is significantly increased (Larsson 1993) or remained unchanged (Papadopoulos and Tountziarakis 2011) in comparison with untreated wood.

The static bending strength of epoxide modified wood with ethylene oxide (gas) at 20% WPG was not essentially changed (McMillin 1963). According to Akitsu et al. (1993), epoxide oligomers of propylene and butylene oxides can bulk the cell wall without significant change on the mechanical performance of wood. This is in contrast with findings of Rowell et al. (1982), who reported a reduction in the bending characteristics of wood modified with the same oxides at 24% WPG and interpreted the results as a manifestation of microcracks in the cell corners and middle lamella (ML) regions.

The epoxidation of wood with epoxidized linseed oil (ELO) takes place through a reaction between the hydroxyl groups of the main structural polymers and the three-membered rings of the oil's epoxy groups. With acetic acid (AA) as a catalyst, the degree of polymerization of the polysaccharides in wood polymers may decrease. On the contrary, the formation of new covalent carbon-oxygen bond between the epoxide groups and wood may improve the physical properties.

Terziev and Panov (2011) found increasing MOE and MOR in the range of 10–21%. The impact bending strength and hardness of ELO-treated wood were also improved at oil retention levels between 100 and 200 kg m⁻³. The

correlation between the oil retention and property increments was good. The hardness increment with 83% was remarkable.

The present paper is the continuation of the work of Jebrane et al. (2014), in which a two-step process for ELO impregnation of wood was described. Here, the treated wood should be characterized by means of Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). Moreover, the physical properties of the modified woods (MOR, MOR, Brinell hardness, and compression hardness) and their moisture contents (MC) in above-ground exposure for 5 years should be tested.

Materials and methods

Kiln-dried and defect-free Scots pine (*Pinus sylvestris* L.) sapwood samples were studied. Strictly radial-tangential oriented paired specimens with dimensions of 23×23×500 mm³ served for the mechanical tests. For field testing, standard lap-joints according to ENV 12037 were prepared. Impregnation procedures were described by Jebrane et al. (2014).

FTIR spectra were obtained by the KBr technique (3 mg dried and milled wood in 300 mg KBr); Perkin-Elmer FTIR Spectrum-100 spectrometer, resolution 4 cm⁻¹, 16 scans. Three leached wood samples with dimensions of 23×23×35 mm³ from each treatment were ground and oven-dried for spectroscopy. Spectra were normalized to the band at 1505 cm⁻¹ (lignin aromatic ring vibration). The spectra of ELO and polymerized ELO were measured by distributing a film of oily sample on the surface of KBr windows; baseline-correction and normalization to the peak at 1460 cm⁻¹ (CH₂ scissors deformation vibration) were applied.

For SEM, samples were mounted on stubs by double-sided tape and coated with an approximately 6 nm layer of gold (Emitech K550X sputter coater). Instrument: Philips XL30 ESEM operated at variable kV.

The mechanical tests were performed on specimens with 12% MC (conditioning at 20°C and 65% relative humidity) with a universal testing machine (Shimadzu, AG-X 50 KN). Specimen preparation: ISO 3129 (1975). The three-point bending test was applied to determine the MOE and MOR according to ISO 3349 (1975) and ISO 3133 (1975), respectively. Static hardness (Brinell) was determined perpendicular (⊥, on the radial surface) and parallel (||) to grain according to ISO 3350 (1975). Compression stress parallel to grain was determined according to ISO 3787 (1976).

An above-ground field test according to standard ENV 12037 (1996) is still in progress in Uppsala, Sweden. The lap joints were impregnated with linseed oil (LO) or with a mixture of ELO and AA (7:3 by wt.) and cured according to the procedure (one-step impregnation) described by Jebrane et al. (2014). Only the woods with the lowest average retentions (76–96 kg m⁻³) were included in the test. The initial MC of the lap joints was measured prior to field exposure. All lap joints were weighed monthly and the current MC was calculated.

Results and discussion

FTIR spectroscopy

FTIR spectra of ELO (Figure 1) show the intense C-H bands at 2928 and 2855 cm⁻¹ and at 1370 cm⁻¹ (OME groups). Moreover, the strong C=O stretching vibration at 1740 cm⁻¹ and the epoxide ring at 820 cm⁻¹ are visible (Lligadas et al. 2006; Liu and Erhan 2010).

The heating of ELO with AA resulted in the appearance of the strong O-H band at 3465 cm⁻¹ and significant increase in intensity of the C=O band at 1740 cm⁻¹ and C-O vibration at 1240 cm⁻¹ originating from ring opening of epoxide groups by AA (Liu and Erhan 2010). The band at 1740 cm⁻¹ is broad due to two carbonyl groups (triglycerides and acetyl groups grafted to the oil). These bands

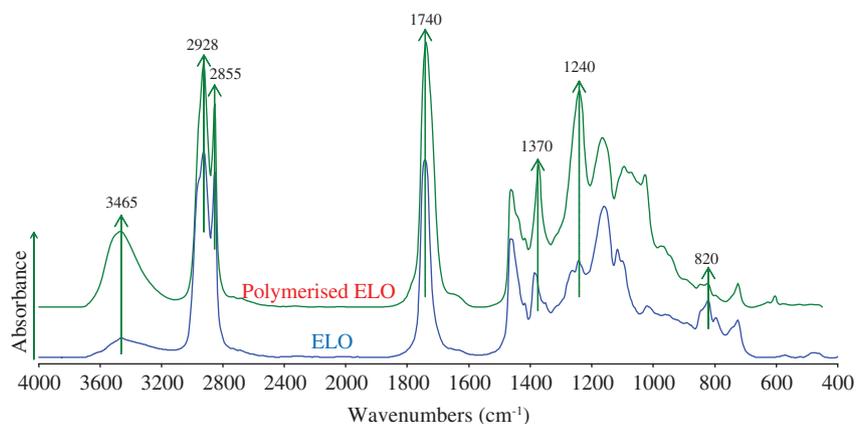


Figure 1 FTIR spectra of ELO and ELO heated with AA.

are characteristic for ring-opening products leading to hydroxyl, acetyl, and ether groups.

The normalized FTIR spectra of untreated and treated wood samples can be compared in the range of 4000 to 450 cm^{-1} in Figure 2. Important changes occurred at 2928, 2857, 1738, and 1373 cm^{-1} , and the region 1300 to 1193 cm^{-1} , which are indicative of the grafting of new functional groups to the wood (Chang and Chang 2001; Pandey and Vuorinen 2008; Pandey et al. 2010; Dubey et al. 2012). All the absorption bands increased significantly after modification with ELO. The increase in intensity of bands at 1300 to 1193 cm^{-1} is indicative of an increase in ether groups as a result of reaction between wood hydroxyl groups and oil's epoxy groups (Silverstein et al. 1991; Pandey et al. 2010). Interestingly, the expected reduction of OH stretching vibration intensity at 3400 cm^{-1} cannot be seen. Probably, new hydroxyl groups originating from the reaction of AA with the oil's epoxy groups are responsible for this observation.

SEM observations on ELO-treated samples

Two samples treated according to A5 and EA impregnation schedules (Jebrane et al. 2014) were observed by SEM. There is no essential difference between the two samples. As seen by light microscopy, these samples are very difficult to cut due to their hardness, especially in the latewood (LW) region. Core subsamples with dimensions of approximately $5 \times 5 \times 5 \text{ mm}^3$ were taken from the original samples, and radial (R), tangential (T), and transverse (T) sections with approximately 1 mm thickness were cut and observed by SEM. An examination of T sections revealed that most

of the LW tracheids are filled with polymerized oil when compared to the earlywood (EW) tracheids (Figure 3a and c). Contrary to the results of Rowell and Ellis (1984), where the increase of WPG of wood treated with epoxides resulted in cell wall cracking, results obtained with ELO do not show any apparent cell wall rupture despite the high WPG of the samples observed by light microscopy.

SEM images reflect the effects of ELO impregnation, polymerization, and oil grafting. The vast majority of tracheid lumens in the EW are empty (Figure 3a–d). Polymerized oil was also found in the tips of axial tracheids (Figure 3a, head arrows) and in resin canals (Figure 3a, arrows). The penetration of ELO into the wood occurs presumably via the uniseriate and fusiform rays in particular via the ray tracheids and parenchyma cells (Figure 3b–f). These anatomical elements were often totally filled with polymerized oil and exudations were observed in some cases, that is, the polymer was exuded from ray parenchyma cells (Figure 3g, arrows). The ray tracheid and axial tracheid bordered pits can be easily recognized, the former is sealed with polymerized oil, and, in some cases, the latter is also covered with a thin film. Figure 3h shows a typical tracheid bordered pit chamber and torus, with the polymer covering the torus and part of the openings in the margo.

Due to its transparency, it was difficult to observe the presence of ELO in the wood cell by light microscopy. However, in sections viewed with SEM, the well-pronounced borders between the individual cell wall layers and ML, which are normally visible in untreated wood, were “erased” by the treatment (Figures 3c and 4). Probably, ELO penetrates the wood structure very well, and presumably the entire internal surfaces of the cell

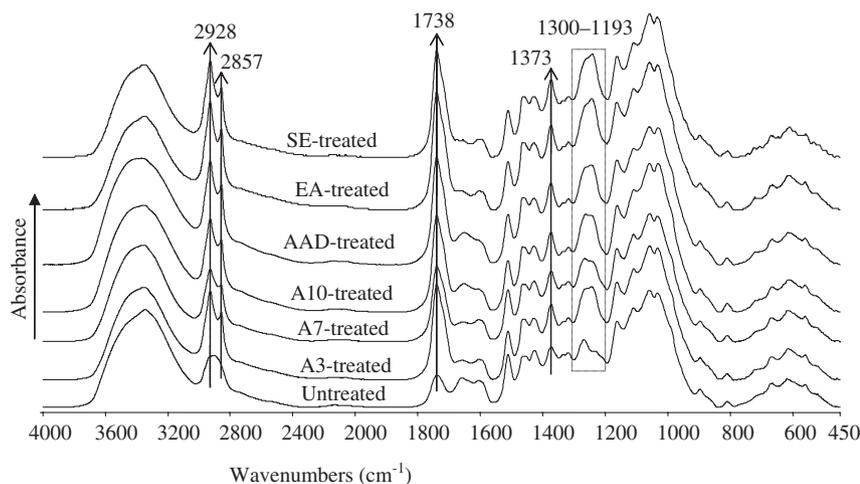


Figure 2 FTIR spectra of untreated and treated Scots pine with ELO.

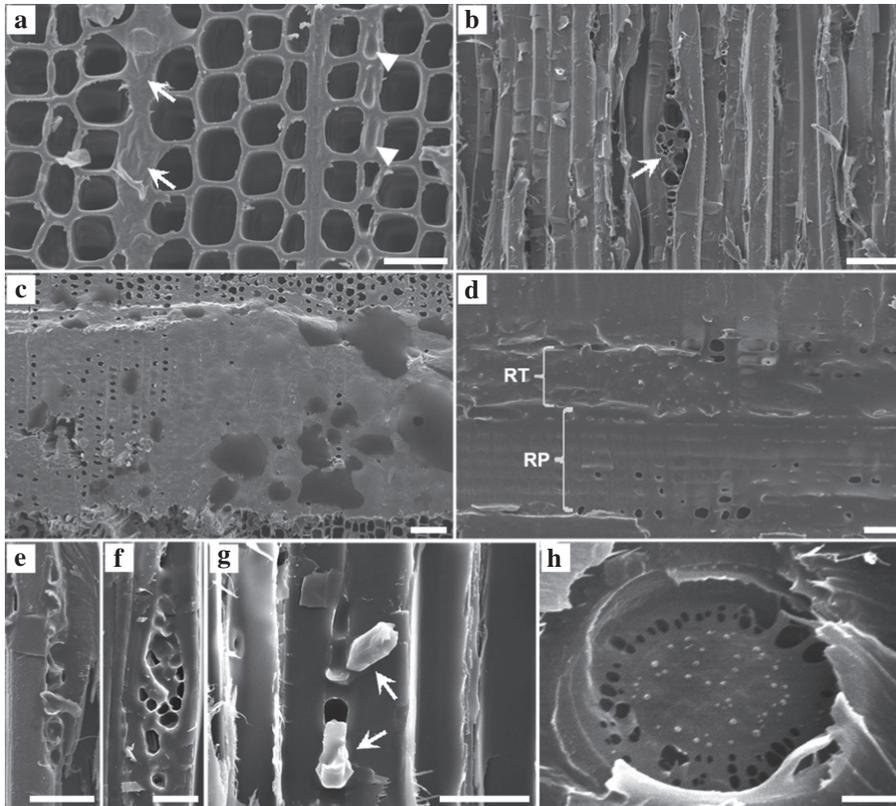


Figure 3 SEM micrographs of transverse (TS), radial (RLS), and tangential longitudinal sections (TLS) of wood treated with ELO. (a) TS of EW tracheid cell walls. (b) TLS showing empty tracheids, fusiform ray cells, and a canal with oil. (c) TS of LW tracheids almost completely filled with oil. (d) RLS showing ray canals in which both the ray parenchyma (RP) and ray tracheids (RT) showed a smooth structure covered with oil. (e and f) TLS of uniseriate rays almost completely filled with oil. (g and h) RLS showing exudation of oil from a uniseriate ray and bordered pit with indication of surface covered with polymerized oil. Scale bars, 50 mm (a–g) and 2 mm (h).

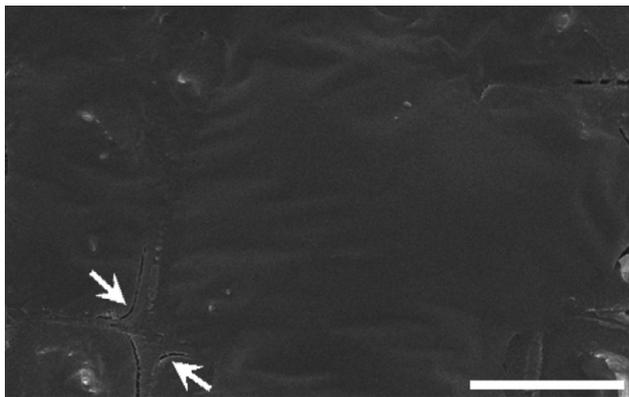


Figure 4 SEM micrograph of wood treated with ELO. TS section of LW tracheids from EA treatment with the cell wall layers and ML regions almost erased; cracks have been induced (arrows) during sectioning. Scale bar, 20 mm.

walls are impregnated, which explains the improvement of 6% volumetric swelling and 50% better anti-swelling efficiency (ASE) (Jebrane et al. 2014). Panov et al. (2010)

observed by light microscopy that ELO penetrates well the wood cell walls. The order in which ELO and AA are impregnated in wood appears to be of minor importance, and both methods ensure the reaction between the two components and grafting to the wood cell wall.

Mechanical properties

The analysis of variance (ANOVA) results (one-way) per treatment for each of the measured mechanical properties are presented in Table 1. Results are highlighted, where P is smaller than 0.05, that is, where the difference between the control and treated samples is statistically significant at the 95% level. Based on the P values, MOR is the property with the greatest effect (where significant differences are observed in five of the seven treatments) followed by hardness (\perp) and compression (in both cases determined for three of the seven treatments), then by hardness (\parallel); two out of seven treatment), and finally by MOE (in only

Table 1 Number of samples (control:treated, N:N), retention, P values (obtained by ANOVA), and relative changes ($\Delta\%$) of selected mechanical properties concerning MOE, MOR, Brinell hardness perpendicular to grain (HB \perp) and parallel to grain (HB \parallel), and compression.

Code	N:N	Retention (kg m ⁻³)	MOE		MOR		Brinell hardness				Compression	
							HB \perp		HB \parallel			
			P	$\Delta\%$	P	$\Delta\%$	P	$\Delta\%$	P	$\Delta\%$	P	$\Delta\%$
SE	11:11	107	0.415	-7	0.177	-11	0.209	-9	0.872	3	0.303	-7
AAD	12:12	90	0.549	-3	0.051	-9	0.116	-8	0.355	6	0.372	-4
A10	11:11	84	0.382	-10	0.022	-19	0.136	-11	0.210	9	0.128	-11
A7	12:12	87	0.112	-11	0.002	-18	0.035	-10	0.515	5	0.002	-19
A5	12:12	106	0.068	-12	0.000	-18	0.064	-7	0.854	2	0.118	-7
A3	12:12	101	0.029	-10	0.000	-19	0.135	-6	0.070	12	0.007	-10
EA	11:11	144	0.106	-18	0.001	-24	0.000	-21	0.184	-9	0.026	-15

^aP<0.05, statistically significant difference exists between the control and treated samples.

Bold values: P<0.05, that is, where the difference between the control and treated samples is statistically significant at the 95% level.

one treatment). Hardness (\parallel) remained unchanged for all treated samples.

The property changes were calculated by the percentage difference between the control and modified samples ($\Delta\%$); see Table 1, where the significant differences are also highlighted. Accordingly, the ELO treatments resulted in a decrease of the bending strength (MOR). The SE and AAD treatments did not show a statistically significant decrease in any of the measured properties. EA treatment caused statistically the largest decrease in MOR, HB \perp , and compression. Furthermore, EA treatment shows the highest overall decrease in the studied mechanical properties, except for compression strength. A7 treatment resulted in a decrease in the same mechanical properties as EA. In the case of A3 treatment, a decrement of MOE, MOR, and compression was observed. SE treatment leads only to the decrement of MOR and HB \perp .

In the present paper, there are some differences from the results of Terziev and Panov (2011), who studied only 20 samples in the retention range of 100 and 200 kg m⁻³. The differences are most likely due to the parameters of curing: 20 days at elevated temperature in the presents study and 16 h followed by storage at room temperature for several months in the quoted study. The way of AA introduction into the wood also plays an important role. When mixed with ELO, AA possesses less destructive properties because it is primarily involved in the opening of epoxy rings. This is confirmed by SE treatment (Table 1), which is the one-step process of Terziev and Panov (2011), and in which the overall mechanical properties are not deteriorated.

The relationship between the retention of ELO and decrease of MOR was insignificant as confirmed by a low regression coefficient ($R^2=0.22$). The ELO treatments where AA was impregnated separately in two steps seem

to explain the decrease in MOR, where AA has presumably attacked the wood polysaccharides, likely hemicelluloses. The AAD treatment, for example, with very low adsorbed AA did not show any statistically relevant deterioration in mechanical properties.

The bad performance of EA may be explained by the high oil uptake compared to other treatments. Since AA was impregnated in Step 2, it remained inside the wood structure and thus may have caused a greater damaging effect on the polysaccharides. However, the retention of AA in the EA treatment exceeded significantly (50–80%) the amount of AA in the other trials (i.e., 254 kg m⁻³).

Above-ground field test

ELO-treated woods have very good hydrophobic properties (Panov et al. 2010; Jebrane et al. 2014). ELO seals pores and rays and thus eliminates the transport of free water, which is also manifested based on the 50–60% improved ASE data. The field performance of lap joints treated with LO and ELO after 60 months' exposure is presented in Figure 5. The climate in Uppsala (Sweden) is characterized by average annual precipitation and temperature of 562 mm and 7°C, respectively. In the case of the untreated wood, a median decay rate of 3.0 after 6–7 years' exposure and an average service life in the range 6.5–8.5 years were observed (Bergman et al. 2008). The above-ground field exposure of treated and reference samples demonstrated that MC fluctuations are significantly higher in the untreated samples (i.e., above 100% in winter; not shown in Figure 5) than in those impregnated with LO and ELO (Figure 5). ELO shows best performance retaining the average annual MC of 19.3% compared to 34.6% for the

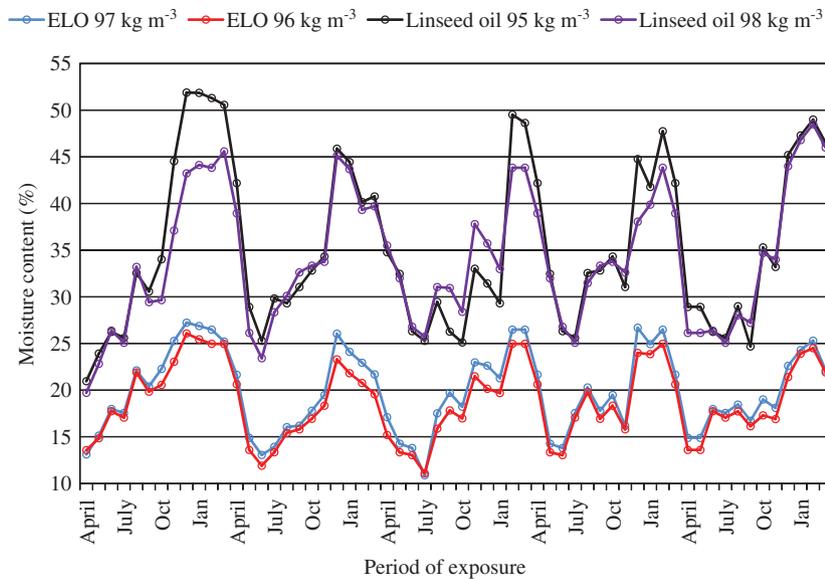


Figure 5 MC fluctuations of lap joints exposed above ground for 60 months according to the standard ENV 12037 in Uppsala, Sweden. MC of two LO-treated and two ELO-treated lap joints are shown.

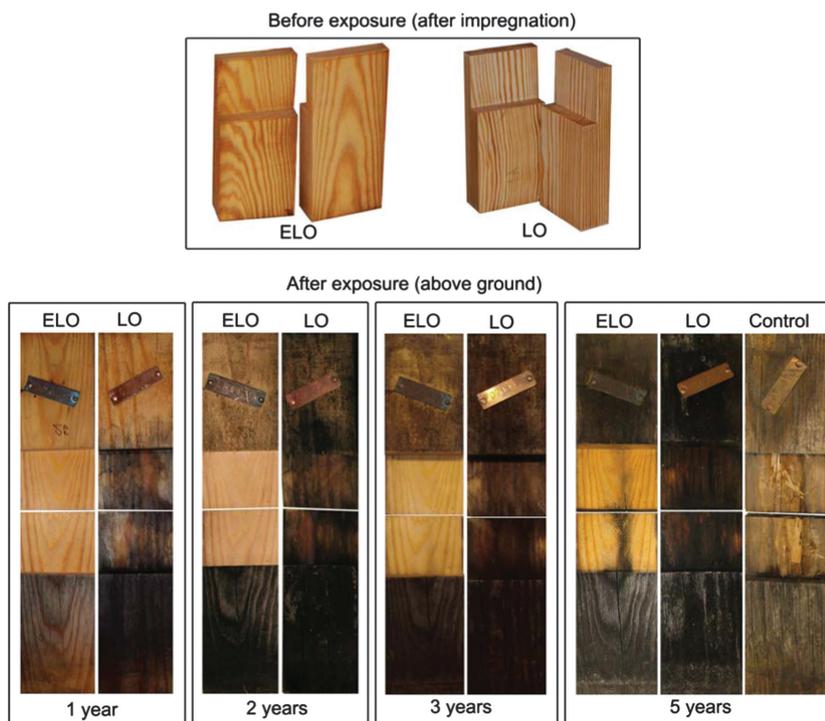


Figure 6 Photographs of lap joints impregnated by ELO and LO before and after exposure above ground for 60 months according to the standard ENV 12037 in Uppsala, Sweden.

lap joints treated with LO; the MC exceeding 25% in only eight occasions for the entire test period. In summer, the MC of the ELO-treated lap joints decreased below 15%. LO was less effective than ELO showing 10–5% more MC in summer and winter than ELO. LO-treated samples never had an MC <25%.

Both LO- and ELO-treated samples have less checks than untreated samples and no signs of decay were visible. The LO-treated samples are, however, discolored by staining fungi both externally and in the joint, while the ELO-treated samples are less discolored and totally free of stain in the joint (Figure 6). A previous polymerase

chain reaction (PCR) analysis of wood impregnated with LO and exposed above ground in Uppsala revealed that *Aureobasidium pullans* and *Epicoecum nigrum* are the most common staining fungi responsible for discoloration (unpublished observations). An assessment of exposed samples indicated that the untreated control lap joints were heavily decayed (Figure 6) after 60 months' exposure with a decay rate of "3," which is in line with previous findings for the same field (Bergman et al. 2008). These results support the conclusion that ELO-treated timber can be used for claddings with or without painting.

The above-ground field test is promising that ELO treatment could be an alternative protective formulation to creosote treatment in terms of dimensional stability, protective efficacy, unchanged or improved wood mechanical properties, and noncorrosiveness.

Conclusions

Scots pine sapwood was treated with ELO with a range of formulations and AA as a catalyst for ring-opening reaction of ELO's epoxy groups. FTIR analysis confirmed the introduction of new ether functions to wood. SEM observations proved the penetration of the oil into the wood structure and cell walls. The mechanical properties were affected by the parameters of ELO treatments. In particular, the mechanical properties were affected more when AA was impregnated separately. MOR was the most affected property with a decrease of approximately 20%. No changes were found in the MOE and hardness. The above-ground field exposure of treated and reference samples demonstrated that MC fluctuations were significantly higher for the untreated samples than those impregnated with LO or ELO. ELO exhibited the best performance, retaining the average annual MC at 19.3% compared to 34.6% for the lap joints treated with LO. The MC of ELO-treated lap joints exceeded 25% on only eight occasions for the entire test period of 60 months and the MC was always below 15% during the summer. ELO-treated samples have less checks and an improved resistance to staining fungi in the overlapping area compared to control and LO-treated lap joints.

References

Akitsu, H., Norimoto, M., Morooka, T., Rowell, R.M. (1993) Effect of humidity on vibrational properties of chemically modified wood. *Wood Fiber Sci.* 25:250–260.

- Beckers, E.P.J., Militz, H. (1994) Acetylation of solid wood. Initial trials on laboratory and semi industrial scale. In: *Second Pacific Rim Bio-Based Composites Symposium*, Vancouver, Canada. pp. 125–133.
- Bergman, Ö., Råberg, U., Terziev, N. (2008) Validity of above ground testing according to ENV 12037. In: *The International Research Group on Wood Protection*, IRG/WP 08-20379.
- Chang, S.T., Chang, H.T. (2001) Inhibition of the photodiscoloration of wood by butyrylation. *Holzforschung* 55:255–259.
- Dubey, M.K., Pang, S., Walker J. (2012) Changes in chemistry, color, dimensional stability and fungal resistance of *Pinus radiata* D. Don wood with oil heat-treatment. *Holzforschung* 66:49–57.
- European Committee for Standardization (1996) ENV 12037. Wood preservatives-field test method for determining the relative protective effectiveness of a wood preservative exposed out of ground contact-horizontal lap-joint method.
- Goldstein, I.S., Jeroski, E.B., Lund, A.E., Nielson, J.F., Weaver, J.W. (1961) Acetylation of wood in lumber thickness. *Forest Prod. J.* 11:363–370.
- ISO 3129 (1975) Wood-sampling methods and general requirements for physical and mechanical tests.
- ISO 3133 (1975) Wood-determination of ultimate strength in static bending.
- ISO 3349 (1975) Wood-determination of modulus of elasticity in static bending.
- ISO 3350 (1975) Wood-determination of static hardness.
- ISO 3787 (1976) Wood-test method-determination of ultimate stress in compression parallel to grain.
- Jebrane, M., Fernández-Cano, V., Panov, D., Terziev, N., Daniel, G. (2014) Novel hydrophobization of wood by epoxidised linseed oil. Part 1. Process description and anti-swelling efficiency of the treated wood. *Holzforschung* 69:173–177.
- Larsson, P. (1993) Properties of Acetylated Solid Wood. Licentiate thesis, Dept. of Forest Products and Chemical Engineering, Chalmers Technical High School.
- Larsson, P., Simonson, R. (1994) A study of strength, hardness and deformation of acetylated Scandinavian softwoods. *Holz Roh-Werkstoff* 52:83–86.
- Liu, Z., Erhan, S.Z. (2010) Ring-opening polymerization of epoxidized soybean oil. *J. Am. Oil. Chem. Soc.* 87:437–444.
- Lligadas, G., Ronda, J.C., Galià, M., Cádiz, V. (2006) Bionano-composites from renewable resources: epoxidized linseed oil-polyhedral oligomeric silsesquioxanes hybrid materials. *Biomacromolecules* 7:3521–3526.
- McMillin, C.W. (1963) Dimensional stabilization with polymerizable vapor of ethylene oxide. *Forest Prod. J.* 13:56–61.
- Pandey, K.K., Vuorinen, T. (2008) UV resonance Raman spectroscopic study of photodegradation of the of hardwood and softwood lignins by UV laser. *Holzforschung* 62:183–188.
- Pandey, K.K., Hughes, M., Vuorinen, T. (2010) Dimensional stability, UV resistance, and static mechanical properties of Scots pine chemically modified with alkylene epoxides. *BioResources* 5:598–615.
- Panov, D., Terziev, N., Daniel, G. (2010) Using plant oils as hydrophobic substances for wood protection. In: *The International Research Group on Wood Protection*, IRG/WP 10-30550.
- Papadopoulos, A.N., Tountziarakis, P. (2011) The effect of acetylation on the Janka hardness of pine wood. *Eur. J. Wood Prod.* 69:499–500.

- Rowell, R.M., Ellis, W.D. (1984) Reaction of epoxides with wood. USDA Forest Service Research Paper, FPL 451, Forest Products Laboratory, Madison.
- Rowell, R.M., Moisuk, R., Meyer, J.A. (1982) Wood polymer composites: Cell wall grafting of alkylene oxides and lumen treatments with methyl methacrylate. *Wood Sci.* 15:90–96.
- Rowell, R.M., Imarura, Y., Kawai, S., Norimoto, M. (1989) Dimensional stability, decay resistance, and mechanical properties of veneer-faced low-density particleboards made from acetylated wood. *Wood Fiber Sci.* 21:67–79.
- Silverstein, R.M., Bassler, G.C., Morill, T.C. *Spectrometric Identification of Organic Compounds*. 7th ed. John Wiley and Sons, New York, 1991.
- Singh, S.P., Dev, I., Kumar, S. (1992) Chemical modification of wood with acetic anhydride. *Journal of the Timber Development Association of India* 38:5–8.
- Terziev, N., Panov, D. (2011) Plant oils as “green” substances for wood protection. In: *EcoWood 2010, Minimizing the Environmental Impact of the Forest Products Industries*, University Fernando Pessoa, Porto, Portugal. pp. 139–146.