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

Novel hydrophobization of wood by epoxidized linseed oil. Part 1. Process description and anti-swelling efficiency of the treated wood

Abstract: The known method of wood modification by epoxidized linseed oil (ELO) has a limiting practical application due to the rapid polymerization of ELO in the presence of acetic acid (AA) needed as a catalyst. The present study was designed to develop an alternative method by means of a two-step process to avoid the rapid polymerization. The treatment options were tested on Scots pine sapwood, with the dimensional stability (DS) of the treated samples in focus. The new method provided an anti-swelling efficiency (ASE) in the range of 40–57%, which was even better than the thermally modified (TM) reference samples with 40% ASE. The developed two-step process is a feasible and practical approach for ELO treatment of wood.

Keywords: dimensional stability, epoxidized linseed oil, modified wood, Scots pine sapwood, two-step process

Introduction

The positive effects of many wood treatment methods lie frequently in water repellency rather than in the fungicidal properties of the chemicals (Paajanen and Ritschkoff 2002; Alfredson et al. 2004; Kartal et al. 2006; Gregorova et al. 2009; Panov et al. 2010). If wood is treated with plant oils, it is important to understand the mechanisms and modes of action in order to select the best technology.

*Corresponding author: Mohamed Jebrane, Department of Forest Products/Wood Science, Swedish University of Agricultural Sciences, Box 7008, SE-750 07 Uppsala, Sweden, 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

Linseed oil is classified as drying oil, which means that the liquid is polymerizing by oxidation into a relatively hard (though elastic) solid in contact with air. Linseed oil improves the dimensional stability (DS) and protects wood against decay fungi by means of its water-repellent (hydrophobic) properties (van Eckeveld et al. 2001). However, polymerization by oxidation takes a long time during which the oil can easily be leached out from the treated wood when exposed to outdoor conditions (Koski 2008). Linseed oil can be chemically modified by epoxidation leading to epoxidized linseed oil (ELO), which is a basic polymer for the production of various plastics worldwide. Chen et al. (2002) reported that ELO can be obtained via peracetic acid, dioxirane, or hydrogen peroxide as a catalyst, while hydrogen peroxide seems to be the most efficient oxidizing agent.

There are only a few publications dealing with ELO for wood protection (Panov et al. 2010; Terziev and Panov 2011; Temiz et al. 2013). For example, Terziev and Panov (2011) reported the anti-swelling efficiency (ASE) of pinewood in the range of 50–60%, with oil retentions of only 80–120 kg m^{-3}. The authors also found a moderate improvement of wood durability in laboratory decay test performed according to the EN 113 (1997). The growth of brown rot fungi (*Coniophora puteana*, *Postia placenta*, and *Gloeophyllum trabeum*) and white rot fungi (*Trametes versicolor*) was significantly inhibited. Wood mass loss (ML) was in the range of 10–15% compared to 20–30% ML for the untreated control samples. This efficiency improvement is not enough in-ground use. Temiz et al. (2013) carried out a test with larvae of the house longhorn beetle (*Hylotrupes bajulus*) and concluded that ELO (at 200 kg m^{-3} retention) could increase the growth and survival rate of larvae.

Panov et al. (2010) studied the hydrophobic properties of linseed oil, ELO, tall oil ester, and epoxidized tall oil esters in combination with ELO and acetic acid (AA) as catalyst mixed at a ratio of 7:3 (by wt.). A significant drawback of the tested methods was the short "pot life" of the mixture, because polymerization starts immediately after ELO and AA are mixed and the viscosity of the mixture increases linearly with time. This instability

hampers practical applications (e.g., polymerization of the mixture in the treatment cylinder, pipes, pumps, etc.) that can result in the serious clogging of impregnation systems. Despite this drawback, the DS, hydrophobicity, and mechanical properties of the treated samples were significantly improved (Panov et al. 2010; Terziev and Panov 2011).

The main objective of the present study was to shed light on the DS and leachability of wood impregnated with ELO obtained by means of a two-step process consisting of impregnation with ELO or AA (first step) followed by impregnation with the other component (second step). The expectation was that the rapid polymerization of ELO can be avoided in a system where ELO and AA are mixed inside the wood; thus, the clogging of the impregnation reactor will not take place. Various treatment solutions should be tested. The analytical part of the study is aiming at the observation of ELO polymerization in wood cell walls.

Materials and methods

Scots pine (*Pinus sylvestris* L.) sapwood was kiln dried and free of defects. The samples were sawn along the grain and paired specimens with strict radial-tangential (RT) orientation of the year rings (25×25×500 mm³). After planning, the final dimensions of the specimens were 23×23×35 mm³ and submitted to leaching and DS tests.

The samples were oven dried at 105°C to constant dry weight, and their dimensions and weights were recorded. The samples were then reconditioned to constant mass at 20°C and 65% relative humidity (RH), and their dimensions and weights were recorded again. In addition, thermally modified (TM) and acetylated (AC) wood samples were added to the DS test for comparative purposes. TM wood (W_{TM}) was treated at 210°C by steam and the AC wood (W_{AC}) had a weight percent gain (WPG) of 24%. ELO with an initial iodine number of >160 was used. AA of 99% purity served as a catalyst.

For comparative purposes, the traditional ("standard") impregnation was also conducted by means of a mixture of ELO/AA (7:3 by wt.) according to Panov et al. (2010) and Terziev and Panov (2011). This treatment is designated as SE (Table 1). In the two-step process (Table 1), the first step consisted of either AA impregnation at different concentrations or ELO impregnation in an autoclave under vacuum and pressure. In the second step, the samples were alternatively treated with either ELO or AA. An additional treatment was carried out using AA-saturated samples after adsorption of AA vapor from a saturated atmosphere over 16 days at room temperature (r.t.). For oil impregnation, ELO was first preheated in a separate cylinder and then the samples were impregnated at 70°C and 4 bar pressure. In all cases, the samples were subjected to pre-pressure of 1.5 bar prior to impregnation to avoid high oil/catalyst uptake. Wood samples were then left in the hot linseed oil after impregnation to avoid exudation. Target retention in all trials was always in the economically justified range of 80–150 kg m⁻³. Impregnated samples were cured to facilitate polymerization of ELO at 70°C for 14 days. After curing and prior to

Table 1 Treatments, additives and abbreviations.

No. of steps	Code	Chemicals added in the steps		n[b]
		1st Step	2nd Step	
1	SE[a]	ELO+AA (70:30)		18
2	AAD	Adsorbed AA	ELO	18
2	A10	AA at 100%	ELO	18
2	A7	AA at 70%	ELO	18
2	A5	AA at 50%	ELO	18
2	A3	AA at 30%	ELO	18
2	EA	ELO	AA at 70%	14

[a]Traditional one step process according to Panov et al. 2010; Terziev and Panov 2011; [b]Number of samples.

characterization tests, the samples were conditioned at 20°C and 65% RH. Table 1 outlines the treatments performed, the treatment codes, and the number of samples for each treatment.

Data available for W_{TM} and W_{AC} were limited; thus, only the DS could be tested. Chemical retention was calculated after complete treatment, and retention is expressed as kg m⁻³. WPG was calculated after complete treatment before and after leaching. Leaching and DS were tested by subjecting five samples from each treatment and corresponding control samples to four cycles of water soaking and oven drying (WS-OD). Each cycle involved WS and OD phases.

Prior to testing, the samples were oven dried, and their weights and dimensions were recorded. After 5 days in water, the samples were removed, their surfaces were wiped gently with absorbent paper, and their weights and dimensions were recorded again. To avoid any hydrolysis, the mild drying phase consisted of air drying for 3 days at r.t. followed by OD at 70°C for 2 days. After drying, the samples were placed in a desiccator, and after cooling, their weights and dimensions were recorded.

Leached formulation (LF) was calculated as the leached chemical in the WS-OD cycles divided by the impregnated chemical before leaching according to the formulas of Panov and Terziev (2009).

The ASE and ASE′ were calculated according to the methodology of Ohmae et al. (2002); see equations (1) and (2), respectively. ASE is based on the volumetric swelling of the treated samples on the basis of the oven-dried dimensions after treatment, while ASE′ is based on the volumetric swelling of the treated samples on the basis of the oven-dried dimensions before treatment. The higher the ASE is, the higher DS is achieved by the treatment.

$$ASE(\%) = \left(1 - \frac{V_s}{V_u}\right) \times 100 \quad (1)$$

$$ASE'(\%) = \left(1 - \frac{V_{s'}}{V_u}\right) \times 100 \quad (2)$$

where V_u is the volumetric swelling coefficient of untreated wood and V_s and $V_{s'}$ are the coefficients of treated wood calculated on the basis of the oven-dried dimensions after and before treatment, respectively.

ASE′ values are interpreted as follows: ASE′>0 means that the treatment has achieved chemical bonding of ELO to the wood polymers, ASE′=0 means that the treatment has only resulted in wood cell wall bulking by ELO, ASE′<0 means that the wood polymeric constituents have been damaged. The higher or lower are the ASE′ values after treatment, the greater are the mentioned effects.

Results and discussion

WPG and LF

The WPG and LF results are presented in Table 2. The amount of impregnated agent leached was probably that part of ELO that did not polymerize after curing as well as the polymerized ELO from the wood surface. The highest LF was observed when wood was impregnated first with pure AA presumably because the acid resulted in the degradation of the wood components and thereby led to an increased porosity and subsequent decrease in interaction between impregnated oil and wood polymers. The same is true for all AA treatments in the first step. However, the relatively high amount of leached substrates from the traditional one-step process (treatment SE) can only be explained by the poor penetration of the impregnating agent into the wood because of the high viscosity of the mixture. Lowest leaching was observed when ELO was impregnated in the first step, most likely because of the quasi-polymerization of the oil, and the formed long chains have a strong interaction with the wood polymers. The difference between LF cycles gives an idea about the stability of the leaching rate with the end cycle. Differences in leachability presumably reflect the level of interaction between ELO and the wood polymers.

ASE

An overview of the calculated and plotted ASE and ASE′ of all treatments is given in Figure 1. Vectors expressing dimensional changes and ASE were calculated according to the methodology of Ohmae et al. (2002) as described in the experimental section.

It can be concluded that ELO treatments ensure an improved DS of the wood comparable to (or even better

than) that achieved by thermal modification (W_{TM}). The impregnation of AA in the first step causes wood degradation, which was counteracted by subsequent polymerization of ELO. Thus, the best would be oil impregnation in the first step followed by impregnation with a catalyst in the second step to minimize degradation reactions.

With retentions of 80–120 kg m⁻³, the ASE reported by Terziev and Panov (2011) was in the range of 50–60%. In this study, the SE treatment (retention ≈160 kg m⁻³) showed ASE in the range of 42–59%. The EA treatment (retention ≈240 kg m⁻³) showed ASE in the range of 51–62%. As already observed by Panov et al. (2010), the ASE has only a small or negligible correlation with retention. Figure 1 compares the ELO treatments with the ASE and ASE′ results calculated in Table 2.

Treated samples where ELO was impregnated in the first step (EA treatment) showed significant reduction in swelling by highest ASE and high uniform ASE′ values. The reason for this is the high uptake of ELO, thus protecting the wood components from degradation by AA impregnated in the second step. This suggests that ELO has been attached to the cell walls as a cover layer to block the sorption sites in the cell wall. A similar observation was reported by Donath et al. (2006) on silane-modified wood. The results indicated also that the DS of modified samples could be improved by impregnation of a diluted AA in the first step (A5 treatment), which was demonstrated by the relatively high ASE and uniform ASE′. Impregnation of AA either at low or high concentration in the first step resulted in negative ASE′ values as well as low ASE. This was thought to be related to either insufficient amount of catalyst for polymerization of ELO (A3 treatment) or degradation of wood components by impregnation of concentrated AA (A7 and A10 treatments). Low ASE and uniform ASE′ values were observed when a catalyst was introduced by adsorption because the amount of AA inside the wood was not enough for polymerization of ELO to the wood polymeric constituents. The eventual damage caused by long exposure of the samples to an AA-saturated atmosphere seemed to be counteracted by subsequent polymerization of ELO. For SE treatment, the overall low ASE was in agreement with previous findings (Panov et al. 2010; Terziev and Panov 2011) and may be explained by the polymerization of ELO in the wood cell wall as shown by the positive trend of ASE′.

Regarding W_{TM}, it is well known that, during thermal modification, AA liberated from hemicelluloses catalyses carbohydrate cleavage and leads to a reduction in the degree of polymerization of carbohydrates and formation of new ether linkages between lignin at high temperatures (Tjeerdsma et al. 1998; Sivonen et al. 2002; Nuopponen

Table 2 Mean values of weight percentage gain after the total treatment (WPG$_T$), ASE (%) per water soaking-oven drying cycle (WS-OD) and leached formulation (LF) for each treatment.

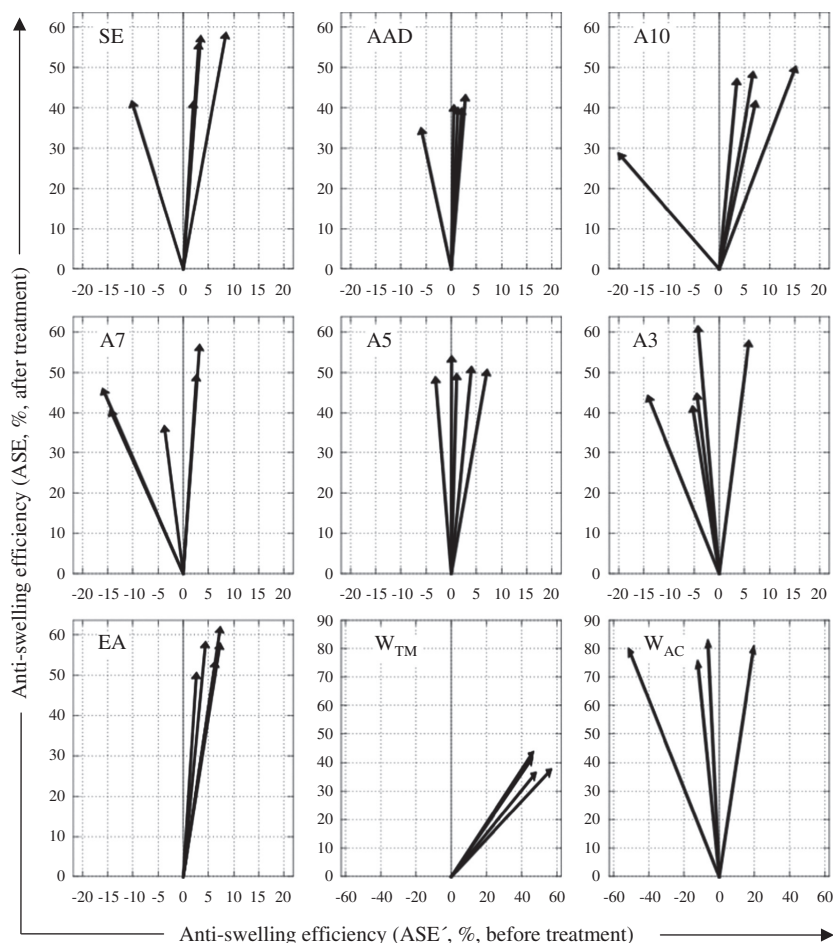| Code	WPG$_T$ (%)	Mean ASE per WS-OD cycle (%)				
		Cyc. 1	Cyc. 2	Cyc. 3	Cyc. 4	LF (%)
SE	32.3	46.4	49.9	51.8	51.2	30.2
AAD	25.5	40.0	40.0	40.7	39.8	28.0
A10	12.0	42.6	44.5	44.4	43.4	41.8
A7	22.6	43.2	45.3	46.2	46.0	28.1
A5	40.7	45.3	45.9	47.3	51.0	17.7
A3	34.7	46.1	47.6	48.4	50.0	21.8
EA	46.2	49.5	54.1	55.9	56.6	13.7

Figure 1 Results of the treatments by plotting the vectors (one for each sample) with coordinates ASE (%) and ASE' (%).

et al. 2004; Tjeerdsma and Militz 2005; Windeisen et al. 2009). Thus, the values of ASE' for TM samples do not reflect the real reactions occurring in the cell wall during thermal modification. The uniformity of ASE' for W_{TM} samples may be explained by domination of the cross-linkage reactions. However, the ASE values reflect the macroscopic changes of the samples, and in this case, W_{TM} samples have lower ASE values than the ones with best ELO treatments (e.g., EA, SE, and A5).

The W_{AC} showed the highest ASE results since a greater part of hydroxyl groups responsible for moisture adsorption would have been substituted by acetyl groups. However, it is expected that the introduction of relatively bulky acetyl groups into the wood cell wall causes significant cell wall damage. It can be concluded that the treatment with ELO provides better results than thermal modification regarding material DS. W_{AC} remains the best treatment for producing highly dimensionally stable material.

The mean values of the ASE after each cycle for the treatments are presented in Table 2. Accordingly, the EA treatment provided significant reduction of swelling with

an average ASE of 54%. The wood was less degraded by AA because the samples were first impregnated with ELO, which prevented hydrolysis of the wood components.

Conclusions

The two-step process technology developed in this study showed promising results regarding wood DS. All treatments studied increased significantly the wood DS (ASE in the range of 39.8–56.6%), which was even better than that of W_{TM} (40%) reference samples. ASE' vectors and leaching results showed also that A5 and EA treatments guarantee reliable modification with less alteration of the cell walls and low loss of modifying agent. In contrast, impregnation in the first step with either low or high concentrated AA seemed to be less economically viable, as the modified samples showed more than 15% leaching after only one WS-OD cycle. The developed two-step process seems to be a feasible and practical solution for the problems of ELO treatment of wood.

References

Alfredson, G., Flaete, P.O., Temiz, A., Eikenes, M., Militz, H. (2004) Screening of the efficacy of tall oils against wood decaying fungi. In: The International Research Group on Wood Protection, IRG/WP 04-30354.

Chen, J., Soucek, M.D., Simonsick, W.J., Celikay, R.W. (2002) Epoxidation of partially norbornylized linseed oil. Macromol. Chem. Phys. 203:2042–2057.

Donath, S., Militz, H., Mai, C. (2006) Creating water repellent effects on wood by treatment with silanes. Holzforschung 60:40–46.

EN 113 European Committee for Standardization (1997) Wood Preservatives. Test Method for Determining the Protective Effectiveness Against Wood Destroying Basidiomycetes. Determination of the Toxic Values.

Gregorova, A., Wimmer, R., Hrabalova, M., Koller, M., Thomas Ters, T., Mundigler, N. (2009) Effect of surface modification of beech wood flour on mechanical and thermal properties of poly (3-hydroxybutyrate)/wood flour composites. Holzforschung 63:565–570.

Kartal, S.N., Hwang, W.J., Imamura, Y., Sekine, Y. (2006) Effect of essential oil compounds and plant extracts on decay and termite resistance of wood. Holz Roh-Werkst 64:455–461.

Koski, A. (2008) Applicability of crude tall oil for wood protection. Doctoral thesis, University of Oulu, Finland. ISBN 978-951-42-8722-0.

Nuopponen, M., Vuorinen, T., Jämsa, S., Viitaniemi, P. (2004) Thermal modifications in softwood studied by FT-IR and UV resonance Raman spectroscopies. J. Wood Chem. Technol. 24:13–26.

Ohmae, K., Minato, K., Norimoto, M. (2002) The analysis of dimensional changes due to chemical treatments and water soaking for Hinoki (*Chamaecyparis obtusa*) wood. Holzforschung 56:98–102.

Paajanen, L., Ritschkoff, A.C. (2002) Effect of crude tall oil, linseed oil and rapeseed oil on the growth of the decay fungi. In: The International Research Group on Wood Protection, IRG/WP 02-30299.

Panov, D., Terziev, N. (2009) Study on some alkoxysilanes used for hydrophobation and protection of wood against decay. Int. Biodeterior. Biodegrad. 63:456–461.

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.

Sivonen, H., Maunu, S., Sundholm, F., Jämsä, S., Viitaniemi, P. (2002) Magnetic resonance studies of thermally modified wood. Holzforschung 56:648–654.

Temiz, A., Kose, G., Panov, D., Terziev, N., Alma, M.H., Palanti, S. Akbas, S. (2013) Effect of bio-oil and epoxidized linseed oil on physical, mechanical, and biological properties of treated wood. J. Appl. Polym. Sci. 130:1562–1569.

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, Porto, Portugal. pp. 139–146.

Tjeerdsma, B., Militz, H. (2005) Chemical changes in hydroheat wood: FTIR analysis of combined hydroheat and dry heat-treated wood. Holz Roh-Werkst 63:102–111.

Tjeerdsma, B., Boonstra, M., Pizzi, A., Tekely, P., Militz, H. (1998) Characterization of thermally modified wood: molecular reasons for wood performance improvement. Holz Roh-Werkst 56:149–153.

van Eckeveld, A., Homan, W.J., Militz, H. (2001) Increasing the water repellency of Scots pine sapwood by impregnation with undiluted linseed oil, wood oil, coccos oil and tall oil. Holzforsch. Holzverwert. 53:113–115.

Windeisen, E., Bächle, H., Zimmer, B., Wegener, G. (2009) Relations between chemical changes and mechanical properties of thermally treated wood. 10th EWLP, Stockholm, Sweden, August 25–28, 2008. Holzforschung 63:773–778.