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# Influence of Water and Humidity on Wood Modification with Lactic Acid

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**ABSTRACT** Impregnation of dry wood with pure lactic acid oligomers (OLAs) followed by heat treatment confers promising properties to wood because of OLA's good diffusion, *in-situ* polymerization and persistence in cell walls. Treatment provides drastic reduction of the equilibrium moisture content, high dimensional stability and good durability. The presence of water during treatment has been evaluated. Curing of OLA impregnated dry wood in humid atmosphere leads to a strong and global degradation of the material. OLA treatment of wet wood only impacts the water leaching rate negatively. Treatment of dry wood with OLA diluted in water additionally decreases the biological resistance and is not efficient for decreasing hygroscopicity. Treatment of dry wood with lactic acid solution leads to a lower polymerization level but confers good properties.

**KEYWORDS:** Wood modification, lactic acid, wood impregnation, heat treatment

## 1 INTRODUCTION

Several approaches for wood protection have been extensively studied and reported. Metallic salts and creosote for long-term durability, coatings for aesthetic reasons and moisture and UV protection are the best-known procedures [1–3]. However, chemical modification is gaining more and more attention for the reduction of wood sensitivity to water, leading to an increase in durability and decrease in the dimensional instability [4, 5]. Chemical modification has been brought to the market several times. The two principal industrial processes are acetylation and furfurylation of wood, known under the trade names Accoya® and Kebony® respectively. While acetylation consists of the acetic anhydride grafting on wood hydroxyl groups, furfurylation is the *in-situ* polymerization of furfuryl alcohol. Because the cell wall is treated and hydroxyl groups accessibility drastically reduced, the dimensional stability is thus highly increased [6, 7].

In order to increase the range of efficient wood treatments by means of biobased compounds, lactic acid- based treatment has been recently reported to be a combined approach associating chemical reaction with wood hydroxyls and *in-situ* polymerization. Lactic acid oligomers (OLAs) impregnated into wood at room temperature demonstrated the ability to polymerize in wood structure by heat treatment. Besides, the polymer chains obtained were proven to be partially blocked in the wood structure. Under specific treatment conditions, wood properties were drastically improved as well [8, 9].

More specifically, the curing step was carried out under dry conditions, after impregnation of oven-dried beech wood (*Fagus sylvatica* L.) with pure OLA at 140 °C or 160 °C for 48 h. This treatment conferred promising properties to wood, in particular regarding anti-swelling efficiency (ASE), moisture exclusion efficiency (MEE), decay resistance and treatment persistence in wood [10, 11]. However, under industrial conditions, wood logs are never dried to the anhydrous state before treatment for most common applications to make them economically viable. Moreover, thermal modification of wood can be carried out under saturated vapor in order to avoid cracks and a decrease in mechanical properties [12, 13]. For that

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reason, impregnation of lactic acid (LA) and OLA with water in the system during every step of the treatment should be investigated to evaluate if water interfered with the process.

This article reports three approaches where water might be present: (1) utilization of non-dried wood samples before impregnation, (2) OLA water dilution resulting in repeated impregnation steps, (3) curing under different relative humidity (RH) (several combinations of temperature and RH). In comparison to the usual OLA treatment [10, 14, 15], performance of treatment carried out in the presence of water is evaluated against ASE [16] and MEE [16], leaching resistance according to EN84 [17] and biological resistance according to EN113 [18].

## 2 MATERIALS AND METHODS

Table 1 and Table 2 summarize wood treatment procedures and the main experimental quantities descriptions respectively.

### 2.1 Materials

Wood samples (15 × 15 × 10 $mm^3$ and 15 × 25 × 50 $mm^3$, T × R × L) were cut from beech (*Fagus sylvatica* L.) (ρ = ca. 700 $kg.m^{-3}$). L(+)-Lactic acid solution (≥ 85%) was obtained from Sigma-Aldrich (Switzerland).

### 2.2 Lactic Acid Oligomers (OLAs) Preparation

Lactic acid oligomers were prepared following the method described by Noël *et al.* [11]. Oligomeric polyesters were synthesized by their direct polymerization under vacuum, using a four-necked flask (500 mL or 1 L) equipped with a magnetic stirrer and reflux condenser linked to an inline cold trap and vacuum pump. Thermometers were used to observe the polymerization, condenser head, and heater temperatures. The solution was heated under reduced pressure (0.015 MPa). The temperature was first gradually increased to 90 °C at an initial distillation step of 1 h. The initial

**Table 1** Treatments description.

| Treatment | Conditioning | Impregnation product | Wet curing | | | Dry curing | |
|---|---|---|---|---|---|---|---|
| | | | Temperature [°C] | RH [%] | Duration [h] | Temperature [°C] | Duration [h] |
| OLA 140 | Anhydrous | Lactic acid oligomers | – | – | – | 140 | 48 |
| OLA 160 | | | | | | 160 | 48 |
| FSP OLA 140 | FSP | Lactic acid oligomers | – | – | – | 140 | 48 |
| FSP OLA 160 | | | | | | 160 | 48 |
| 50 OLA 140 | Anhydrous | Aqueous solution of OLA at 50% | – | – | – | 140 | 48 |
| 25 OLA 140 | | Aqueous solution of OLA at 25% | | | | | |
| OLA 160 RH 100 | Anhydrous | Lactic acid oligomers | 160 | 100 | 2 | 103 | 36 |
| OLA 160 RH 80 | | | | 80 | | | |
| OLA 160 RH 50 | | | | 50 | | | |
| LA 160 | Anhydrous | Lactic acid monomers | – | – | – | 160 | 48 |
| FSP LA 160 | FSP | | | | | | |
| Ref | Anhydrous | None | – | – | – | – | – |
| Ref 140 | | | | | | 140 | 48 |
| Ref 160 | | | | | | 160 | 48 |

**Table 2** Experimental quantities description.

| Abbreviation | Description |
|---|---|
| $EMC_{FSP}$ | Wood equilibrium moisture content at fibre saturation point |
| $S_{FSP}$ | Wood swelling at fibre saturation point |
| $WU_i$ | Wood weight uptake after impregnation |
| $S_i$ | Wood swelling after impregnation |
| $WU_t$ | Wood weight uptake after treatment |
| $S_t$ | Wood swelling after treatment |
| $ASE_t$ | Anti swelling efficiency of treated wood |
| $ASE_t^*$ | Corrected anti swelling efficiency of treated wood |
| $EMC_t$ | Equilibrium moisture content of treated wood |
| $EMC_t^*$ | Corrected equilibrium moisture content of treated wood |
| $MEE_t$ | Moisture exclusion efficiency of treated wood |
| $MEE_t^*$ | Corrected moisture exclusion efficiency of treated wood |
| LR | Leaching rate |
| $S_{LR}$ | Anhydrous wood swelling after leaching |
| $WL_{exp}$ | Wood weight loss after fungal exposure |

oligomerization step involved gradually increasing the temperature to 140 °C for 2.5 h.

Diluted mixtures of OLA, at 50% and 25% weight, were prepared by addition of water into pure OLA at 20 °C while stirring.

## 2.3 Wood Treatment

### 2.3.1 Conditioning

Wood samples were oven-dried at 103 °C to constant weight prior to treatment. Samples of untreated anhydrous weight and volume were measured ($w_{u,d}$ and $V_{u,d}$).

For the selected variants (FSP OLA 140, FSP OLA 160 and FSP LA 160), wood samples were then impregnated with water at 20 °C in a vacuum oven under reduced pressure (0.015 MPa) for 10 to 15 min, then atmospheric pressure over 10 to 15 min. Air-drying was carried out at 23 °C and 60% relative humidity (RH) and the samples volume was measured every 24 h until volumetric variations were observed. Wood swelling (S) and equilibrium moisture content (EMC) at fiber saturation point (FSP) were calculated as follows:

$$EMC_{FSP}(\%) = \frac{w_{FSP} - w_{u,d}}{w_{u,d}} \times 100 \quad (1)$$

$$S_{FSP}(\%) = \frac{V_{FSP} - V_{u,d}}{V_{u,d}} \times 100 \quad (2)$$

where $w_{FSP}$ and $V_{FSP}$ stand for the sample weight and volume at FSP respectively, $w_{u,d}$ and $V_{u,d}$ for the sample untreated anhydrous weight and volume before water impregnation.

### 2.3.2 Impregnation

As described by Noël *et al*. [11], wood samples were immersed in the liquid mixtures at room temperature. Containers were then placed in a vacuum oven under reduced pressure (0.015 MPa) for 10 to 15 min, then atmospheric pressure over 10 to 15 min. Impregnated samples were then wiped to remove the excess product. Weight uptake ($WU_i$) and swelling ($S_i$) after impregnation have been calculated as follows:

$$WU_i(\%) = \frac{w_i - w_{u,d}}{w_{u,d}} \times 100 \quad (3)$$

$$S_i(\%) = \frac{V_i - V_{u,d}}{V_{u,d}} \times 100 \quad (4)$$

where $w_i$ and $V_i$ stand for the impregnated sample weight and volume respectively and $w_{u,d}$ and $V_{u,d}$ for the sample untreated anhydrous weight and volume.

### 2.3.3 Curing

Curing in humid atmosphere was carried out in a homemade reactor, provided by Aalto University, with controlled steam pressure system. Dry curing was carried out in a ventilated oven. Table 1 summarizes the different wet and dry curing conditions. Weight uptake ($WU_t$) and swelling ($S_t$) after treatment were calculated as follows:

$$WU_t(\%) = \frac{w_{t,d} - w_{u,d}}{w_{u,d}} \times 100 \quad (5)$$

$$S_t(\%) = \frac{V_{t,d} - V_{u,d}}{V_{u,d}} \times 100 \quad (6)$$

where $w_{t,d}$ and, $V_{t,d}$ and $w_{u,d}$ and $V_{u,d}$ respectively stand for treated and untreated samples anhydrous weight and volume respectively.

## 2.4 Anti-swelling Efficiency (ASE)

The ASE was measured following the method described by Noël *et al*. [11] on 10 replicates of 15 × 15 × 10 mm³ (R × T × L). Treated samples (15 × 15 × 10 mm³, T × R × L) were placed in a desiccator, partially filled with water to set RH at ca. 100%, at a constant temperature of 23 °C. Anhydrous sample volumes were measured before exposure ($V_t$), after 216 h and after weight is stabilized, after 504 h according to Grosse *et al*. [10].

Reference samples (Ref) swelling $V_r$, was calculated as follows:

$$S_r(\%) = \frac{v_{r,100\%} - v_{r,d}}{v_{r,d}} \times 100 \quad (7)$$

where $V_{r,100\%}$ stands for reference samples volume after stabilization at 100% RH and for the anhydrous reference sample volume.

Swelling ($S_{t,100\%}$) and ASE ($ASE_t$) of the non-impregnated samples were calculated as follows:

$$S_{t,100\%}(\%) = \frac{v_{t,100\%} - v_{t,d}}{v_{t,d}} \times 100 \quad (8)$$

$$ASE_t(\%) = \frac{s_r - s_t}{s_r} \times 100 \quad (9)$$

where $V_{t,100\%}$ stands for treated samples volume after stabilization at 100% RH and $V_{t,d}$ for treated samples anhydrous volume.

For impregnated wood, the ASE* calculation was based on the corrected swelling calculation of treated samples ($S^*_{t,100\%}$) as follows, according to Thybring [16]:

$$S^*_{t,100\%}(\%) = \frac{v_{t,100\%} - v_{t,d}}{v_{u,d}} \times 100 \quad (10)$$

$$ASE^*_t(\%) = \frac{s_r - s^*_t}{s_r} \times 100 \quad (11)$$

where $V_{t,100\%}$ stands for the treated sample volume after stabilization at 100% RH, $V_{t,d}$ for treated sample anhydrous volume, and $V_{u,d}$ for untreated sample anhydrous volume.

## 2.5 Equilibrium Moisture Content (EMC) and Moisture Exclusion Efficiency (MEE)

The EMC of non-impregnated samples ($EMC_t$) and the reduced EMC of impregnated samples ($MEE^*_t$) have been determined on samples used for ASE determination, which are defined as follows in Eqs. (12) and (13) [16, 19]:

$$EMC_t(\%) = \frac{w_{t,100\%} - w_{t,d}}{w_{t,d}} \times 100 \quad (12)$$

$$EMC^*_t(\%) = \frac{w_{t,100\%} - w_{t,d}}{w_{u,d}} \times 100 \quad (13)$$

where $w_{t,100\%}$ stands for treated sample weight after stabilization at ca. 100% RH, $w_{t,d}$ for treated sample anhydrous weight, and $w_{u,d}$ for untreated sample anhydrous weight.

The MEE of non-impregnated samples ($MEE_t$) and the corrected MEE of impregnated samples ($MEE^*_t$) were calculated as follows:

$$MEE_t(\%) = \frac{EMC_r - EMC_t}{EMC_r} \times 100 \quad (14)$$

$$MEE^*_t(\%) = \frac{EMC_r - EMC_{Rt}}{EMC_r} \times 100 \quad (15)$$

where $EMC_r$ stands for the untreated reference sample $EMC_t$ after stabilization at ca. 100% RH.

## 2.6 Leaching

Samples of dimensions 50 × 25 × 15 mm³ (L × T × R) were leached according to the guidelines of the NF EN 84 standard [17]. For each variant of treatment, samples were submerged into water (1 volume of wood for 5 volumes of water) under 4 kPa vacuum for 20 minutes and left for 2 hours. The water was changed after 2 hours, and nine times during a period of 14 days. After leaching, samples were air-dried for 6 h and oven-dried at 103 °C until weight stabilization. The leaching rate (LR) was calculated on 12 replicates according to Eq. (14):

$$LR(\%) = \frac{w_{t,d} - w_{t,l,d}}{w_{t,d} - w_{u,d}} \times 100 \quad (16)$$

where $w_{t,l,d}$ is the specimen weight after treatment, leaching and drying, $w_{t,d}$ is the specimen anhydrous weight after treatment before leaching procedure and $w_{u,d}$ is the untreated specimen anhydrous weight. LR represents the weight of leached oligomers in comparison to the total oligomers weight in the sample before leaching.

Sample swelling at dry state after leaching was calculated as follows:

$$S_{LR}(\%) = \frac{v_{t,l,d} - v_{t,d}}{v_{t,d}} \times 100 \quad (17)$$

where $V_{t,l,d}$ is the specimen volume after treatment, leaching and drying, $V_{t,d}$ and is the specimen anhydrous volume after treatment before leaching procedure.

## 2.7 Biological Resistance

Biological resistance was evaluated according to the guidelines of the EN 113 standard [18]. Samples of dimensions 50 × 25 × 15 mm³ (L × T × R) treated and leached according to the leaching procedure described above were sterilized with gamma rays and consecutively placed in culture flasks on growing medium (40 g/L malt and 20 g/L agar) inoculated with *Coriolus versicolor* (L. Quelet, strain CTB 863A) for 16 weeks (at 22 °C, 70% RH). Samples weight loss was determined on 6 replicates as the ratio between the weight loss due to fungal exposure and the initial treated anhydrous weight as follows:

$$WL_{exp}(\%) = \frac{w_{l,d} - w_{exp,d}}{w_{l,d}} \times 100 \quad (18)$$

where $w_{l,d}$ is the specimen weight after leaching and drying, and $w_{exp,d}$ is the specimen anhydrous weight after exposure. The final samples EMC in culture flasks at the end of exposure was calculated as follows:

$$EMC_{exp}(\%) = \frac{w_{exp,w} - w_{exp,d}}{w_{exp,d}} \times 100 \quad (19)$$

where $w_{exp,w}$ is the humid specimen weight after fungal exposure.

## 2.8 FTIR-ATR

The FTIR spectra of solid wood were recorded for samples before impregnation, after impregnation and after heat treatment, on 5 different points of the wood surface, using a PerkinElmer Frontier MIR system spectrometer and the attenuated total reflectance (ATR) method, at a resolution of 4 $cm^{-1}$ in the range of 600 to 4000 $cm^{-1}$. The solid wood samples were pressed against the diamond crystal of the ATR device. A pressure applicator with a torque knob ensured that the pressure applied was the same for all measurements. For each sample, 32 scans were conducted and averaged. Mean spectra were analyzed using Spectrum software (PerkinElmer). The baseline was first constructed by connecting the two lowest points around 1910 and 1550 $cm^{-1}$. Spectra were then normalized on the peak at 1505 $cm^{-1}$.

# 3 RESULTS AND DISCUSSION

Modified wood hygroscopic behavior is presented in Table 3; product persistence in the wood and biological resistance are presented in Table 4.

## 3.1 Dry Process Performance (OLA 140 and OLA 160)

Influence of heat treatment temperature on wood impregnated with pure OLA has been reported by Grosse *et al.* [10] and revealed a minimum temperature to treatment efficiency (between 140 °C and 160 °C). In order to study the influence of water and humidity in the process, two variants of dry heat treatment (140 °C and 160 °C for 48 h) have been selected as references for the present work (variant OLA 140 and OLA 160). For both variants, there is an improvement of wood hygroscopic properties in comparison to untreated wood, but at 160 °C the treatment is more efficient regarding all criterions (Table 3 and 4). OLAs diffuse into lumens during impregnation ($WU_i \geq 60\%$ but $S_i$ = ca. 0%) and into the wood structure during heat treatment (swelling after curing, $S_t$ = ca. 16%). $WU_T$ indicates how far the polycondensation goes: water formation and evaporation due to heat treatment induce a significant weight loss. Effective polymerization during heat treatment has been proven by Noël *et al* [8] by gel permeation chromatography of wood extracted oligomers. The FTIR spectra of untreated wood, impregnated wood and treated wood, measured by ATR method, are shown in Figure 1 and IR bands observed in the fingerprint are summarized in Table 5. The peaks in the fingerprint are assigned [8, 20–22]: 1738/1748 $cm^{-1}$ (a) for C=O stretching in hemicellulose and OLA, 1505 $cm^{-1}$ (b) for aromatic skeletal in lignin, 1455 $cm^{-1}$ (c) for –CH3 bending in OLA, 1371 $cm^{-1}$ (d) for C-H deformation in cellulose and hemicelluloses, 1267 $cm^{-1}$ (e) for C=O bending in OLA, 1195/1185 $cm^{-1}$ (f) for C-O stretching in OLA, 1122 $cm^{-1}$ (g) for aromatic skeletal and C-O stretching in wood, 1091/1087 $cm^{-1}$ (h) for C-O-C stretching in OLA and 1036/1030 $cm^{-1}$ (i) for C-O stretching of primary alcohol in OLA, cellulose and hemicellulose. Significant changes in IR spectra can be seen after each step of the process, showing the *in-situ* polymerization of OLA. After impregnation, the amount of ester and alcohol groups was logically increased by the addition of OLA into wood. After curing, C-O peaks intensity decreased as a consequence

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**Table 3** Physical properties and hygroscopic behaviour of treated and untreated wood (15 × 15 × 10 mm3).

| Treatment | $EMC_{FSP}$ [%] | $S_i$ [%] | $WU_i$ [%] | $S_t$ [%] | $WU_t$ [%] | $EMC^*_{t(216h)}$ [%] | $ASE^*_{t\ (216h)}$ [%] | $EMC^*_{t(504h)}$ [%] | $ASE^*_{t\ (504h)}$ [%] | $MEE^*_{t\ (504h)}$ [%] |
|---|---|---|---|---|---|---|---|---|---|---|
| OLA 140 | – | 0.3 ± 0.2 | 64.5 ± 1.9 | 16.0 ± 0.9 | 33.1 ± 1.5 | 12.9 ± 0.2 | 62.7 ± 3.2 | 16.3 ± 0.2 | 61.1 ± 3.2 | 39.4 ± 0.7 |
| OLA 160 | – | 0.0 ± 0.2 | 60.0 ± 1.0 | 15.7 ± 0.8 | 28.9 ± 1.0 | 11.4 ± 0.2 | 68.0 ± 2.1 | 13.8 ± 0.2 | 67.8 ± 1.8 | 48.6 ± 0.7 |
| FSP OLA 140 | 33.3 ± 1.6 | 22.3 ± 0.5 | 108.7 ± 2.8 | 17.4 ± 0.5 | 36.1 ± 1.6 | 12.7 ± 0.2 | 61.5 ± 1.4 | 14.8 ± 0.4 | 59.4 ± 1.6 | 44.9 ± 1.3 |
| FSP OLA 160 | 33.7 ± 1.4 | 23.0 ± 0.3 | 109.6 ± 3.9 | 16.9 ± 0.7 | 34.2 ± 1.3 | 11.3 ± 0.2 | 65.6 ± 4.0 | 13.4 ± 0.3 | 62.8 ± 1.5 | 50.3 ± 1.0 |
| 50 OLA 140 | – | 21.6 ± 0.2 | 91.7 ± 1.8 | 15.7 ± 0.4 | 20.3 ± 0.7 | 16.7 ± 0.2 | 53.8 ± 1.7 | 21.2 ± 0.3 | 53.9 ± 1.9 | 21.2 ± 1.3 |
| 25 OLA 140 | – | 22.6 ± 0.4 | 91.6 ± 2.2 | 10.1 ± 0.4 | 10.8 ± 0.2 | 19.5 ± 0.1 | 33.4 ± 2.0 | 25.7 ± 0.5 | 32.3 ± 1.5 | 4.5 ± 1.7 |
| OLA 160 RH 100 | – | 0.2 ± 0.1 | 72.1 ± 2.1 | –12.2 ± 6.4 | –3.9 ± 6.4 | 16.8 ± 1.2 | 126.6 ± 19.2 | 26.1 ± 2.6 | 15.4 ± 12.9 | 2.9 ± 9.7 |
| OLA 160 RH 80 | – | 0.4 ± 0.2 | 73.1 ± 1.2 | 2.2 ± 3.0 | 16.5 ± 4.9 | 20.6 ± 0.8 | 37.4 ± 7.2 | 31.4 ± 1.5 | 15.9 ± 12.2 | -16.9 ± 5.5 |
| OLA 160 RH 50 | – | 0.4 ± 0.1 | 77.1 ± 2.0 | –7.0 ± 3.9 | 5.5 ± 5.1 | 20.7 ± 1.4 | 112.9 ± 7.1 | 31.0 ± 2.6 | 4.9 ± 3.5 | -15.2 ± 9.8 |
| LA 160 | – | 5.4 ± 0.3 | 71.7 ± 2.1 | 13.3 ± 0.4 | 20.3 ± 0.9 | 12.6 ± 0.2 | 62.2 ± 1.2 | 15.3 ± 0.3 | 61.4 ± 1.3 | 43.1 ± 1.0 |
| FSP LA 160 | 31.9 ± 1.3 | 24.2 ± 0.4 | 118.3 ± 1.7 | 12.4 ± 0.5 | 28.6 ± 0.8 | 13.3 ± 0.5 | 56.1 ± 2.4 | 15.3 ± 0.2 | 54.5 ± 2.0 | 43.3 ± 0.7 |
| **Treatment** | – | – | – | **$S_t$ [%]** | **$WU_t$ [%]** | **$EMC_{t(216h)}$ [%]** | **$ASE_{t(216h)}$ [%]** | **$EMCt_{(504h)}$ [%]** | **$ASE_{t(504h)}$ [%]** | **$MEE_{t(504h)}$ [%]** |
| Ref 140 | – | – | – | –1.4 ± 0.1 | –0.4 ± 0.1 | 22.2 ± 0.3 | 11.5 ± 2.4 | 24.4 ± 0.4 | 15.9 ± 3.4 | 9.3 ± 1.6 |
| Ref 160 | – | – | – | –2.0 ± 0.2 | –1.4 ± 0.1 | 19.7 ± 0.3 | 21.5 ± 3.4 | 22.0 ± 0.4 | 17.3 ± 3.8 | 18.3 ± 1.6 |
| Ref | – | – | – | – | – | 24.3 ± 0.4 | – | 26.9 ± 0.6 | – | – |

**Table 4** Physical properties, product water leaching resistance and biological resistance of treated and untreated wood (15 × 25 × 50 mm³)

| Treatment | LR [%] | $S_{LR}$ [%] | $WL_{exp}$ [%] |
|---|---|---|---|
| OLA 140 | 3.3 ± 0.2 | –4.3 ± 0.4 | 3.3 ± 0.2 |
| OLA 160 | 2.3 ± 0.2 | –3.6 ± 0.6 | 2.0 ± 0.1 |
| FSP OLA 140 | 8.3 ± 1.1 | –2.2 ± 0.2 | 4.7 ± 0.5 |
| FSP OLA 160 | 5.0 ± 0.6 | –2.3 ± 0.3 | 3.1 ± 0.3 |
| 50 OLA 140 | 6.0 ± 0.2 | –3.8 ± 0.4 | 3.7 ± 0.4 |
| 25 OLA 140 | 22.4 ± 0.7 | –2.5 ± 0.5 | 4.8 ± 4.2 |
| LA 160 | 5.9 ± 1.2 | –2.3 ± 0.2 | 2.7 ± 0.6 |
| FSP LA 160 | 12.6 ± 1.5 | –1.4 ± 0.2 | 3.3 ± 1.6 |
| Virulence control | 0.8 ± 0.1 | –0.2 ± 0.7 | 29.6 ± 2.0 |

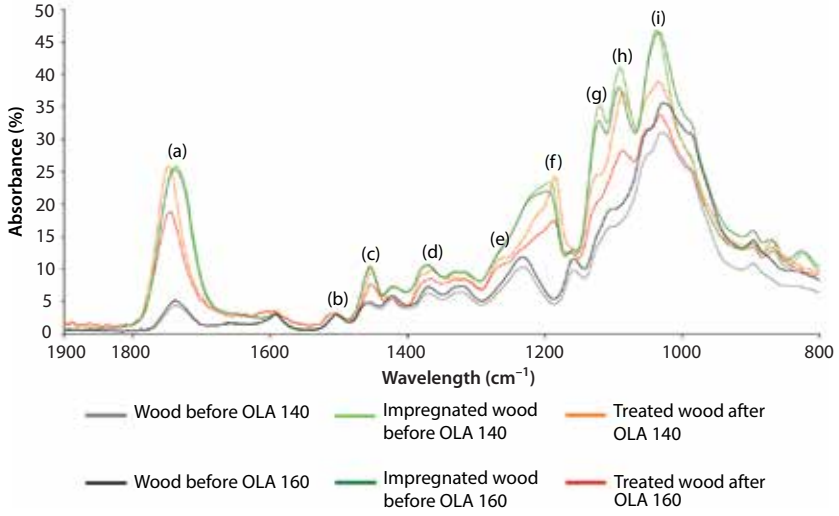


**Figure 1** FTIR-ATR spectra of OLA 140 and OLA 160 before impregnation, after impregnation and after heat treatment.

**Table 5** Absorption bands attributions

| N° | Band position | | | Assignment |
|---|---|---|---|---|
| | Beech | Impregnated wood | Treated wood | |
| a | 1738 | 1738 | 1748 | C=O stretching |
| b | 1505 | 1505 | 1505 | Aromatic skeletal vibration |
| c | – | 1455 | 1455 | $–CH_3$ bending of OLA |
| d | 1371 | 1371 | 1371 | C-H bending of cellulose |
| e | – | 1267 | 1267 | C=O bending of OLA |
| f | – | 1195 | 1185 | C-O stretching of OLA |
| g | 1122 | 1122 | 1122 | Aromatic skeletal and C-O stretching of wood |
| h | – | 1091 | 1087 | C-O-C stretching of OLA |
| i | 1030 | 1036 | 1030 | C-O primary alcohol |

of OLA polymerization. C-O stretching peaks of OLA (f and g) shifted at a lower wavenumber, probably due to the formation of hydrogen bonds between the C-O of OLA and –OH of cell wall carbohydrates [21]. C=O stretching peak (a) shifted at a higher wavenumber, showing a higher ester linkage content due to OLA polymerization [8]. Furthermore, impregnated wood band around 1738 $cm^{-1}$ is larger than the one of treated wood: acid groups disappeared and ester groups were created with OLA polymerization. All those modifications are more intense after treatment at 160 °C than after treatment at 140 °C, as a result of a more advanced polymerization, which might explain the better performance of OLA 160 in comparison to OLA 140.

## 3.2 Influence of Water on Treatment Performance

Water was introduced into the process — in the wood cell walls before impregnation (FSP OLA 140 and FSP OLA 160) and in the impregnation product (50 OLA 140 and 25 OLA 140) — in the step where reaction was carried out under humid atmosphere (OLA 160 RH 100, OLA 160 RH 80 and OLA 160 RH 50).

### 3.2.1 Diffusion and *In-Situ* Polycondensation

Impregnation of OLA was easier when cell walls were at FSP ($S_{FSP}$ = ca. 23%). Wood $EMC_{FSP}$ was ca. 33% before impregnation. Then wood was impregnated with OLA. The resulting $WU_i$ was 109%. $WU_i$ is always calculated from wood anhydrous weight before impregnation. Thus, 109% of $WU_i$ also includes the water present in cell walls before OLA impregnation. Assuming all water remains, weight uptake due to OLA is ca. 76%. Anhydrous wood had a $WU_i$ of 62%. Wood impregnation at FSP allows a significant increase of $WU_i$. After curing, OLA retention in cell walls is, however, not significantly affected ($S_t$ = 17% instead of 16% for dry wood). $WU_t$ of 36% and 34% for FSP OLA 140 and FSP OLA 160 respectively, highlights a high weight loss due to curing. Even though the presence of water might hinder polycondensation, this weight loss could indicate good polymerization. The FTIR spectra of FSP OLA 140 and FSP OLA 160 (Figure 2) are consistent with this hypothesis. Indeed, spectra of FSP OLA 140/160 and OLA 140/160 are similar. However, intensities of absorption bands resulting from OLA decreased and shifting of 1198 $cm^{-1}$ and 1736 $cm^{-1}$ from acid to ester wavenumbers are lighter. It is most likely due to excess of water, which slows down the reaction kinetics.

Dilution of OLA leads to a lower $WU_t$, indicating a reduced amount of remaining polymer in wood after curing. Despite a high $WU_i$ and $S_i$ of 92% and 22% respectively, $WU_t$ decreased with oligomer dilution down to 20% for 50 OLA 140. Impregnation is easier as dilution reduced OLA mixture viscosity, but fewer oligomers diffuse into wood as water is also absorbed. Furthermore, the FTIR spectra of 50 OLA 140 and 25 OLA 140 (Figure 2) reveal low intensity of OLA absorption bands and almost no shifting of 1198 $cm^{-1}$ and 1736 $cm^{-1}$ from acid to ester wavenumbers. OLAs are most likely less polymerized due to the excess of water.

Curing wood impregnated with OLA under humid atmosphere leads to very heterogeneous results and important wood degradation. The combination of

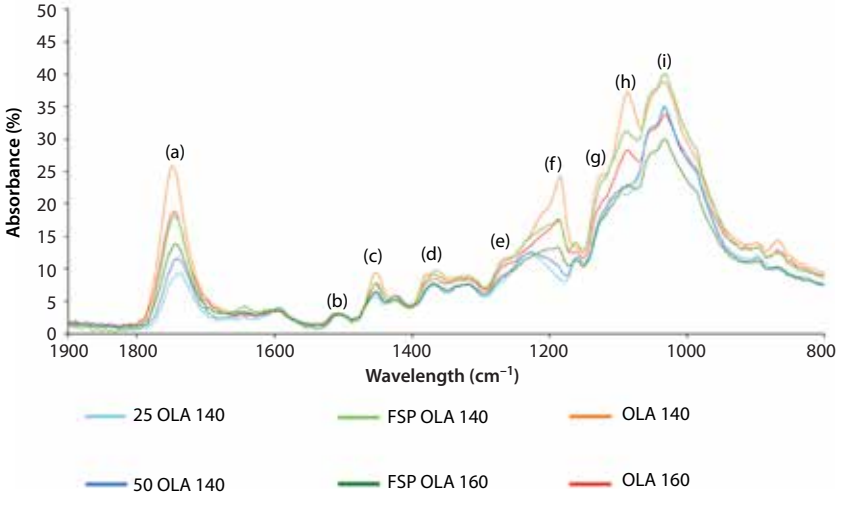


**Figure 2** FTIR-ATR spectra of treated wood according to 25 OLA 140, 50 OLA 140, FSP OLA 140, FSP OLA 160, OLA 140 and OLA 160 procedures, after treatment.

acidic, humid and warm conditions is deleterious to wood polymers [23, 24]. Densification of some samples has been observed after the whole treatment process (curing in humid atmosphere and drying) with consistent negative $S_t$ (wood shrinkage).

### 3.2.2 Hygroscopic Behavior

Hygroscopic behavior of modified wood after 216 h is not affected by wood's initial moisture content. However, after 504 h, ASE* of FSP OLA 140/160 are lower than OLA 140/160 respectively, whereas $MEE^*_t$ are higher. Thus, less water is absorbed when wood was at FSP before impregnation but dimensional stabilization is reduced. The outer layer of wood is most likely the first place where OLAs polymerize, then the core, following the heat diffusion process. If the wood was wet at the beginning of curing, free water evaporation allows slowing down of the outer layer warming when the core temperature is gradually increasing. Thus, the formation of microcracks might be reduced [10, 25], explaining why $MEE^*_t$ increased but not $ASE^*_t$.

Because less product remains in the wood structure when OLAs were diluted, and because OLAs are most likely less polymerized, more hydrophilic, $ASE^*_t$ and $MEE^*_t$ of the treatment are reduced. After 504h, $ASE^*_t$ decreased from 61% for OLA 140 (pure OLA) down to 54% and 32% for 50 OLA 140 and 25 OLA 140 respectively. $MEE^*_t$ is impacted more by oligomers dilution and decreased to 21% and 4% for 50 OLA 140 and 25 OLA 140 respectively.

Curing under humid atmosphere leads to very heterogeneous results. Because many samples shrunk during treatment, coherent $ASE^*_t$ values were difficult to obtain. However, none of the OLA 160 RH 100, OLA 160 RH 80 or OLA 160 RH 50 were dimensionally stable. Even though they were impregnated with OLA and densified, swelling after 504 h calculated from densified state, was higher than untreated samples. Furthermore, the modified wood is more hygroscopic than untreated wood. Curing conditions most likely hydrolyzed both OLA and wood polymers [23, 24]. Thus, the remaining product (most likely small oligomers and monomers), more hydrophilic than polymerized OLA, absorbs water in addition to the water absorbed by wood.

### 3.2.3 Product Persistence

Leaching rate (LR) increases for wood impregnated at FSP from 3.3% to 8.3% and from 2.3% to 5.0% for FSP OLA 140 and FSP OLA 160 respectively, in comparison with OLA 140 and OLA 160 respectively. However, volumetric shrinkage after leaching is reduced by almost half. This is consistent with the hypothesis of better oligomer diffusion into the wood structure.

Dilution of OLA is also detrimental to oligomers persistence in wood. LR increases from 3.3% with pure OLA (OLA 140), to 6.0% and 22.4% with 50% and 75% dilution respectively. This is consistent with the hypothesis of a less advanced polymerization.

Reference samples (control samples for EN113, non-treated) were leached according to the same procedure. The resulting LR of 0.8% indicates molecules and substances from wood could be leached with the oligomers. The amount of those substances can be higher for the modified wood as a thermo-treatment in acidic condition was performed. Leaching water was not analyzed. However, obtaining a low LR was the aim and a promising result in this study.

### 3.2.4 Biological Resistance

All control samples (untreated beech in the flask with treated beech) had a WL above 20% and all treated samples had an EMC between 20% and 80% at the end of the test. Thus, no sample has been rejected according to EN113 specifications.

Wood treatment with OLA provides a significant biological resistance to wood. Water in the process is always deleterious, but treatment leads to WL below 5% in all cases. To reach EN113 specifications, the average weight loss after 16 weeks of exposure must be lower than 3% (with only one sample having a weight loss between 3% and 5%). For OLA 160, which is the most efficient treatment, WL is below this threshold value (WL = ca. 2%). The same treatment with wood at FSP performs just above the limit.

### 3.2.5 OLA Treatment Global Performance

Curing in humid atmosphere at 160 °C leads to major wood degradation and most likely the competitive reaction of hydrolysis of OLA. Wood drying before impregnation allows better treatment performance. However, hygroscopic properties and biological resistance of FSP OLA 160 are promising as a better $MEE^*_t$ was obtained, $ASE^*_t$ was higher than 60% and treated wood was close to reaching EN113 specifications. For an industrial application, wood can easily be air-dried to a lower MC, which might have a lower impact on treatment performance. OLA dilution under 50% is already detrimental to all modified wood properties, but a small diffusion of water from wood to the OLA mixture during impregnation might not significantly influence the performance. Indeed, 50 OLA 140 $ASE^*_t$ is still higher than 50% and WL after exposure to *C. versicolor* is less than 4%. Treatment persistence was always reduced by water in the process. Because water hinders polycondensation, more small oligomers and monomers might remain. Those

  

are more leachable, but a second leaching would most likely show better results. However, if OLA are too diluted, there are most likely not enough oligomers in wood to allow a significant degree of polymerization. OLAs might be barely polymerized, and more than half of them were leached in the case of 25 OLA 140.

## 3.3 Impregnation with LA

Anhydrous wood and wood at FSP were impregnated with LA and cured at 160 °C for 48 h (therefore named LA 160 and FSP LA 160 respectively).

### 3.3.1 Diffusion and *In-Situ* Polycondensation

There is an effective product diffusion into wood structure during impregnation ($S_i$ = 5% and $WU_i$ = 72% for LA 160). LA was sourced as 85% water dilution. More swelling after impregnation might be expected according to 50 OLA 140 $S_i$ of 22%. Monomers should more easily penetrate the cell walls as they have smaller volumetric dimension than OLA. Thus, in the case of diluted OLA, it was most likely water in cell walls after impregnation. For FSP LA 160, $S_i$ increased up to 24% as cell walls were water saturated before impregnation and $WU_i$ was 118%. Again, cell walls water swelling prior to impregnation makes it easier.

The $S_t$ of 13% for LA 160 shows monomers diffusion and persistence in wood structure during curing. $WU_t$ is only 20%, which can be due to a smaller amount of remaining product in comparison to OLA 160. For FSP LA 160, $S_t$ is lower but $WU_t$ is higher, most likely because of polymerization hindered by water in cell walls. Furthermore, the FTIR spectra of LA 160 and FSP LA 160 (Figure 3) reveal low intensity of OLA absorption bands and almost no shifting of 1198 $cm^{-1}$ and 1736 $cm^{-1}$.

### 3.3.2 Modified Wood Properties

In comparison with OLA 160, $ASE^*_t$ of LA 160 decreased from 68% down to 61%, $MEE^*_t$ decreased from 49% to 43%, LR increased from 2% to 5% and WL after exposure to *C. versicolor* increased from 2% to 3%. Better performance was obtained with OLA 160 but LA 160 performed as well as OLA 140. An initial moisture content of wood influences modified wood properties but only really impacts the product persistence (LR of 13% and 6% for FSP LA 160 and LA 160 respectively). Air-dried wood (MC = ca. 12%) treated with LA at 160 °C might be performant enough for some outdoor applications with limited moisture exposure.

## 4 CONCLUSION

Evaluation of wood treatment with OLA at 160 °C following a dry process gives very promising insights that can be used in the further development of modified wood for outdoor applications. Wood's initial moisture content and OLA concentration in water have a major influence on treatment performance. The presence of water in wood before curing has an influence on wood's biological resistance, dimensional stability and water leaching resistance. Modified wood obtained with the dry process performed better. However, if the heat treatment temperature is as high as 160 °C, the decrease in performance is not significant, especially regarding the biological resistance

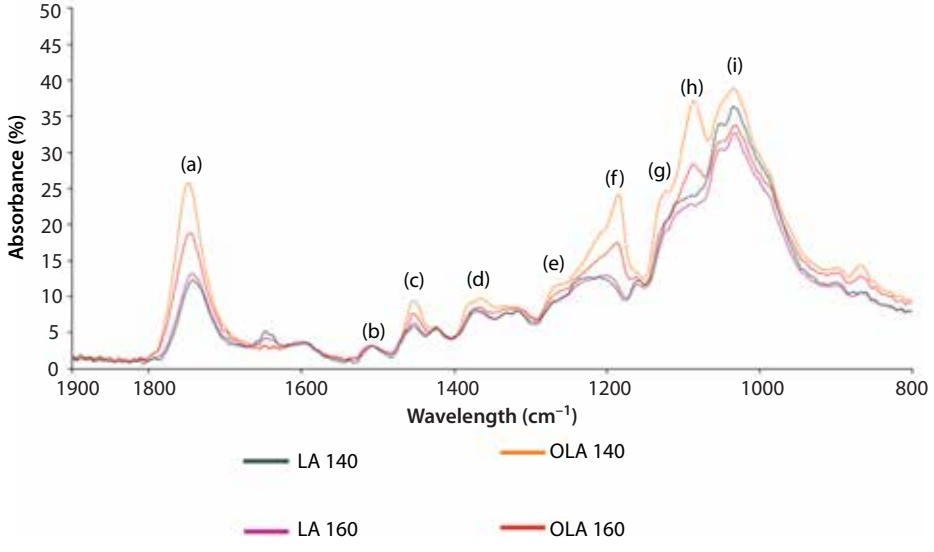


**Figure 3** FTIR-ATR spectra of treated wood according to LA 140, LA 160, OLA 140 and OLA 160 procedures, after treatment.

and ASE. While moisture serves as carrying agent for OLA/LA into wood structure by swelling the cell walls to help oligomer diffusion, the *in-situ* polycondensation of OLA/LA is most likely hindered by water in the system, as observed via FTIR analysis. However, air-dried wood (MC = ca. 12%) treated with OLA or LA at 160 °C might be performant enough for outdoor applications. Curing under humid atmosphere at 160 °C was attempted. The combination of acidity, heat and moisture leads to major material degradation.

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