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Science du bois et de fibres

Par

Charlotte GROSSE

DEVELOPMENT OF INNOVATIVE BIO-BASED TREATMENTS FOR WOOD MODIFICATION WITH BIO-POLYESTERS

Sous la direction du Pr. Philippe Gérardin et du Dr. Marion Noël

Le 10 Septembre 2018

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A ma sœur.

« Les folies sont les seules choses que l'on ne regrette jamais. »

Oscar Wild

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Main abbreviations

ASE – Anti-Swelling Efficiency
EMC – Equilibrium Moisture Content
DP – Degree of Polymerisation
HTT – Hygro-thermal Treatment
LA – Lactic Acid
MEE – Moisture Exclusion Efficiency
MOE – Modulus Of Elasticity
MOR – Modulus Of Rupture
OBS – Oligomers of Butylene Succinate
OLA – Oligomers of Lactic Acid
PBS – Poly(Butylene Succinate)
PLA – Poly(Lactic Acid)
PT – Post-Treatment
WL – Weight Loss
WPG – Weight Percentage Gain
WU – Weight Uptake

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Introduction

Societies evolution generally aims to increase well-being of populations, with development of consumption goods to facilitate the daily life. In the competitive present world, industries have to be innovative and cost-efficient, and products must respond to a need to find a place in the market. However, in the race for profit, the environmental impact was too often overlooked, with regards to natural resources, recycling and populations real needs. The progressive increase of the world consumption and standardisation of single use products engendered global issues concerning resources and waste management. Since the end of the 20th century, global concerns regarding societies impact on the environment promoted the development of alternative sustainable bio-based materials.

Because the attention on the exploitation of natural sustainable materials is rising, the scientists' efforts should focus even more on the improvement of drawbacks inherent to the few bio-friendly resources available. In this framework, wood properties enhancement becomes a very up-to-date topic for modern technology. Wood is an outstanding natural material combining several advantages such as high and easy availability, sustainability, pleasant organoleptic properties, good workability, high specific strength and relatively low price. However, wood exhibits some drawbacks as well, two of them being most significant in construction engineering: limited dimensional stability and limited biological resistance.

In former times, biocidal solutions were used: creosote first, then chromate-copper-arsenate (CCA), were dominating the market warranting very long service life. More recently, restrictions on the use of these wood preservatives have focused public and government attention on technological developments in the wood protection area. The regulation 1907/2006 of the European Union has already banned every formulation containing arsenic (e.g. CCA) and also restricted the concentration for boron (directive 2008/58/EC and 2009/2/EC) that is often used to replace arsenic as fungicide in the most common metal-based inorganic formulations (CCB). Thus, the availability and use of environmentally friendly wood preservation methods is nowadays strictly required.

Because wood affinity with water is responsible for its dimensional variations and wood moisture content linked to its biological resistance, several non-biocidal techniques have been developed to protect wood from water and air relative humidity variations over the past decades. Among them, thermal modification, chemical modification and impregnation modification can be distinguished.

Thermal modification of wood has been widely studied and has introduced many brand names of processes or products on the market such as: Retification®, Plato® or Thermowood®. Hygroscopic behaviour of thermally modified wood is improved compared to untreated wood but decay resistance is not good enough for wood to be used in ground contact. Furthermore, mechanical properties are degraded by thermal treatment making the material not suitable for load-bearing applications.

Chemical modification and/or *in situ* polymerisation studies allowed considering a high number of chemicals. However, only a very few have been successfully transposed on the market. Accoya® is a typical example of commercial modified wood based on wood acetylation. The process consists of the esterification of wood hydroxyls groups with acetic anhydride. In terms of wood impregnation, Kebony® is the most common example. The process consists in wood impregnation with monomeric furfuryl alcohol followed by polymerisation within the wood structure. Both techniques are able to impart a significant degree of decay resistance to wood and the strength properties are not significantly affected, but they are restricted to only three species of pine. Thereby, development of treatments applicable to other species locally available, like beech, is still needed.

Moreover, no satisfying product based on chemical grafting in the wood cell wall coupled to *in situ* polymerisation in the lumens of totally bio-based chemicals has ever been reported. Biodegradable polyesters, such as poly(lactic acid) (PLA) and poly(butylene succinate) (PBS), attract much attention from both academia and industries because of their potential to efficiently replace non-degradable thermoplastic polymers derived from fossil-based resources. Their monomers can be manufactured from biomass, starch or cellulose-based materials, and they polymerise in a range of temperature where wood thermal degradation is limited. Therefore, they were both considered as candidates for wood modification treatments.

This research focused on the development of processes for wood modification with PLA and PBS oligomers and was running along two axes:

- Efficient development of processes designed for rapid industrial implementation.

- Analyse and comprehension of phenomena involved in the wood modification processes, primarily wood thermal degradation, oligomers polymerisation and wood/oligomers interactions.

This work is undertaken in the framework of two R&D projects coordinated by the BFH-AHB. The WoodWisdom Net+ project BioCoPol (Joint Call 4), was dedicated to the development of new bio-based formulations for wood treatment, with focus on several main market applications: railway wood sleepers, facade wooden pieces, outdoor furniture as well as internal structures, to promote the use of indigenous species, like beech, not enough exploited mainly because of their limited biological resistance. The idea was based on the combination of former research projects separately conducted in partners' labs, which led to promising wood preservation technologies considering the complementary properties of the homo-polymers. Co-polymerisation of those compounds within the wood structure was expected to improve wood performance by benefiting from actual properties of each separated treatment.

The project BioThermoWood, funded by the Swiss national body of COST (European cooperation in science and technology) under the COST Action FP1303 theme (Performance of bio-based building materials) targeted the combination of chemical modification of wood by

bio-based polyesters (PLA and PBS) and thermo-treatment, in order to manufacture an end-product suitable as bio-based building material. Based on former results, emphasis was given to optimisation of PBS oligomers diffusion in the wood structure and fixation of PLA and PBS oligomers in the cell wall.

This manuscript is arranged as follows:

- The first part is a "Literature review" presenting a brief description of wood and wood/water interactions, the wood modification techniques and the PLA and PBS synthesis methods, properties and degradation.

- The second part "Wood modification with lactic acid" describes processes development and optimisation for wood modification with lactic acid based treatments and the mechanism of wood protection. (Paper 1 to Paper 5)

- The third part relates to wood modification with poly(butylene succinate) oligomers and wood-polymer interactions. (Paper 6 to Paper 8)

- The fourth part relates to the processability of the modified wood. (Paper 9)

- The general conclusions and perspectives.

Introduction

Le développement durable est au cœur des problématiques sociétales actuelles et concerne tous les domaines d'activité. Etant une ressource renouvelable et bio-sourcée, le bois est déjà largement utilisé et promu en tant que matériau de construction (charpente, structure de bâtiment en ossature bois, bardage, lames de terrasse, fenêtres, etc…). Cependant, les essences locales largement disponibles, telles que le Hêtre, n'ont pas toujours les propriétés requises pour permettre leur utilisation en extérieur. L'hygroscopie du matériau constitue un désavantage majeur lorsque celui-ci est utilisé dans des environnements humides ou lorsque l'humidité relative subit de grandes variations. La forte affinité du bois avec l'eau peut être la cause de variations dimensionnelles et du développement de moisissures et champignons altérant les propriétés du matériau. Jusqu'à présent, la majorité des traitements de préservation font appel à l'utilisation de finitions permettant une protection de surface jouant le rôle de barrière physique vis-à-vis des agents de dégradation ou à l'imprégnation de substances biocides à l'intérieur du matériau. Cependant, on assiste depuis le début des années 2000 à des changements importants dans la plupart des pays industrialisés suite à une prise de conscience collective pour la protection de l'environnement et à la mise en place de régulations de plus en plus contraignantes sur l'utilisation de biocides telles que la Directive Biocide 98/8/CE. Il en résulte un développement de nouvelles alternatives dites « non biocides » impliquant la modification de la structure chimique des macromolécules constitutives du bois. La modification thermo-chimique est un procédé qui consiste à modifier la matière à cœur, avec pour objectif d'améliorer les propriétés du bois, en particulier la résistance fongique. Pour ce faire, conférer au bois un équilibre hygroscopique inférieur à la limite basse de développement des champignons est une approche qui permet en sus de limiter les variations dimensionnelles dues à l'humidité de l'air. Limiter les variations dimensionnelles augmente logiquement la durabilité des assemblages et des revêtements de surface, ce qui améliore encore les performances du matériau.

Les constituants du bois possèdent des groupements hydroxyles (-OH) qui rendent le matériau hydrophile. Les modifications thermochimiques envisagées dans ces travaux de recherche consistent principalement à limiter l'accès à ces groupements et/ou à réduire leur nombre, par imprégnation de monomères/oligomères bio-sourcés (oligomères d'acide lactique (OLA) ou de polybutylene succinate (OBS)) suivie de leur polymérisation *in situ* par traitement thermique. L'ajout dans le système d'imprégnation d'un biocide naturel (devant être fixé, chimiquement ou physiquement) ou d'un catalyseur de la polymérisation peut être envisagé.

Les traitements finaux devront présenter un impact réduit sur l'environnement. Pour cela, l'origine des constituants de base, les éventuelles émissions créées pendant le traitement, l'énergie consommée par le procédé, ainsi que les éventuelles pollutions provoquées en service devront être évaluées.

Ce sujet de recherche conjugue les sciences du bois et la chimie des polymères. Outre la synthèse elle-même des produits de traitement, les principales caractérisations et analyses qui seront menées sont répertoriées dans la liste ci-dessous :

- Caractérisation du produit de traitement :
    - Evaluation du degré de polymérisation (DP) avant imprégnation par chromatographie d'exclusion stérique (SEC)
    - Evaluation du DP après polymérisation hors du bois par SEC
    - Evaluation de la cinétique de polymérisation hors du bois par suivi par spectroscopie infrarouge a transformée de Fourier (FTIR)

- Caractérisation du traitement :
    - Mesure des taux d'imprégnation et taux d'imprégnation résiduel
    - Evaluation de la persistance du produit d'imprégnation dans le bois
    - Appréhension des interactions bois-polymère par analyse thermique mécanique dynamique sous diverses conditions d'humidité si nécessaire (DMTA)
    - Suivi de la polymérisation dans le bois par analyse thermogravimétrique (TGA)

- Caractérisation des propriétés du bois modifié :
    - Durabilité : évaluation de la résistance fongique à plusieurs souches de champignons lignivores
    - Hygroscopie
    - Stabilité dimensionnelle
    - Caractérisation mécanique
    - Résistance à l'exposition extérieure naturelle et artificielle
    - Adhésion des revêtements de surface
    - Collage

Ce sujet de thèse s'est développé autour de deux axes :

- L'analyse et la compréhension des phénomènes intervenant dans le traitement du bois au moyen des produits bio-sourcés choisis, favorisant ainsi l'optimisation constante du procédé.
- Le développement efficace et orienté vers la pratique de produits de traitement destinés à une implémentation rapide dans l'industrie.

Cette thèse a été financée par l'intermédiaire de deux projets de recherche coordonnés par la Haute Ecole Spécialisée Bernoise, Département Architecture Bois et Génie Civil (BFH-AHB), co-laboratoire d'accueil. D'une part le projet BioCoPol (WoodWisdom Net+ Joint Call 4, financements nationaux de consortia Européens), focalisant sur les traitements à base d'acide lactique, réalisé en partenariat avec trois laboratoires (l'unité BioWooEB du CIRAD, le LERMaB de l'Université de Lorraine, et l'Université de Sciences Appliquées de Salzbourg) et deux partenaires industriels. D'autre part un projet national financé par l'antenne Suisse du COST (European cooperation in science and technology) sous la thématique de l'Action COST FP1303 (Performance of bio-based building materials) focalisant sur le traitement PBS, et en particulier sur les conditions de traitement et de post-traitement, en partenariat avec plusieurs laboratoires européens.

Etat de l'art

Les propriétés du bois sont, en majeure partie, déterminées par son anatomie et sa composition chimique. Ainsi, les méthodes non biocides permettant d'améliorer les performances du bois sont généralement liées à la modification de la composition chimique du matériau. Les méthodes de modification du bois peuvent être regroupées en quatre catégories : modification chimique, modification thermique, modification de la surface et modification par imprégnation (Hill 2006, Sandberg *et al.* 2017, Gérardin 2016). Le bois acétylé est un exemple typique de bois modifié actuellement commercialisé. Le procédé de modification fait intervenir un traitement chimique et consiste en une estérification des groupements hydroxyles par l'anhydride acétique. Des traitements similaires existent à partir d'autres anhydrides ou d'autres réactifs capables de réagir avec les groupements hydroxyles du bois (Rowell 2005). En ce qui concerne les méthodes d'imprégnation du bois, l'exemple le plus commun est celui du bois furfurylé. Le bois est imprégné avec des monomères d'alcool furfurylique polymérisés *in situ* (Lande *et al*. 2004, Gérardin 2016).

Une méthode hybride a été développée par Noël *et al*. (2009a, 2009b, 2015a) basée sur des oligomères d'acide lactique (OLA). Le traitement se déroule en deux étapes : l'imprégnation d'OLA suivie de leur polymérisation *in situ* initiée par traitement thermique. Ce procédé a été étudié par Noël *et al* (2009a/b, 2015a/b/c) sous différents aspects et selon plusieurs méthodes de traitement. L'influence des conditions du traitement thermique a d'abord été évaluée en présence de catalyseurs (0.6% d'acide sulfurique ou 5% d'octanoate d'étain) (Noël *et al* 2009a/b). Deux cycles de chauffage ont permis de révéler l'importance des conditions du traitement thermique sur les propriétés du bois modifié. Après imprégnation, le bois subit soit un cycle de chauffage court (120°C / 1h), soit un cycle de chauffage long (120°C / 1h + 103°C jusqu'à stabilisation de la masse). Le taux de lessivage passe de 90% pour le chauffage court, à 20% pour le chauffage long (Noël *et al*. 2009a/b). Cependant, les propriétés mécaniques du bois modifié sont fortement diminuées. Dans la mesure où cette dégradation du bois pourrait être attribuée aux catalyseurs, et où le bois modifié a une efficacité anti-gonflement prometteuse de 60% à 100% d'humidité relative, Noël *et al*. (2015a) ont poursuivi leurs recherches sans catalyseur mais avec une étape de traitement thermique à 120°C plus longue (6h). Ce traitement conduit à un taux de lessivage de 80%. La répartition de masse molaire des OLA extraits du bois après traitement a été évaluée par chromatographie d'exclusion stérique, analyse thermogravimétrique et calorimétrie différentielle à balayage. Ces analyses ont prouvé que la polymérisation *in situ* avait bien lieu, mais qu'elle n'était probablement pas suffisamment importante pour fixer le produit dans la structure du bois (Noël *et al.* 2015b/c).

Les recherches ont ensuite été étendues à d'autres bio-polyesters, en plus de l'acide polylactique (PLA), sélectionnés pour leur potentielle compatibilité avec le bois : PGA (acide polyglycolique), PBS (polybutylène succinate), PBA (polybutylène adipate). Des co-oligomères (PLA/PGA et PBS/PBA avec des ratios respectifs de 3:1, 1:1 et 1:3) ont été synthétisés (Noël *et al*. 2014a/b/c, 2015a/b). Le comportement en sorption du bois traité a été étudié par Vitkeviciute *et al.* (2014), et Vitkeviciute (2015). Les résultats démontrent des comportements très variés selon le système. Deux catégories de traitements apparaissent en

fonction de leur capacité à diffuser dans le bois: le PLA et le PGA qui diffusent facilement dans les parois cellulaires durant la phase de polymérisation par traitement thermique d'une part, le PBS et le PBA qui restent dans les lumens d'autre part. Les traitements à base de PGA ont des résultats comparables aux traitements à base de PLA, bien que le taux d'imprégnation soit plus élevé (jusqu'à 150% de prise de masse sous vide). De plus, lorsque le traitement thermique n'est pas assez long (6 heures), les plus courtes chaînes de PGA plastifient les parois cellulaires, ce qui conduit à un ramollissement du matériau. Lorsque l'étape de traitement thermique est allongée (48 heures), il semble que la polymérisation *in situ* compense la perte de résistance du matériau, et il en résulte une certaine fragilité du bois modifié dans la majorité des cas. La co-polymérisation du PLA avec le PGA ne permet pas d'améliorer le traitement. Il est probable que la formation du co-polymère soit plus difficile à maitriser pendant la synthèse, en particulier *in situ*, et qu'elle ne soit pas favorable à la diffusion du co-polymère, ni à ce qu'il interagisse avec le bois. Les mêmes observations ont été faites concernant les co-polymères PBS/PBA. En tant qu'oligomères purs, le PBS et le PBA donnent des résultats similaires, bien que les résultats du bois traité avec du PBS soient légèrement plus prometteurs en ce qui concerne la stabilité dimensionnelle.

Literature review

Wood is a natural material combining several advantages such as high and easy availability, sustainability, pleasant organoleptic properties, good workability, high specific strength and relatively low price. Beech (*Fagus sylvatica*) is abundantly available in Europe. But because it exhibits limited dimensional stability and limited biological resistance, its usage is for now restricted to indoor furniture, wooden items (toys, kitchen utensils, musical instruments) or flooring. Thereby, development of protection treatments applicable to beech is needed for a better valorisation of this local resource.

1. The structure of wood

1.1. From the tree to the cell

During their life, trees are in competition for sunlight on the one hand and the access to water and minerals from the soil on the other hand. Plants have to grow high to escape the shadow of the others, and the trunk connecting the roots. Besides, the crown of a tree needs to be light and rigid, but to some extent flexible in order to bear the crown against adverse weather conditions (Teischinger 2016).

The tree trunk is made of heartwood, surrounded by sapwood then bark (Figure 1). Differentiation is made between those three main parts because they have different functions, therefore different constitutions. The heartwood is the inner part of the trunk and insure only the mechanical support. It is made of dead cells, formerly created in the life of the tree. The sapwood is the living part of the tree insuring the raw sap conduction from the roots to the leaves and the nutrient storage. The conduction cells are found in the longitudinal direction. The storage cells, parenchyma, are found in the radial direction. Finally, the elaborated sap is conducted from the leaves to the roots through the bark.

Trees grow in two directions. Because most cells are elongated and vertical (i.e. aligned parallel to the tree trunk), wood shows extreme anisotropy. Between wood and bark, the cambium ensures the growth in circumference by producing new cells during the growing season. During their life, those cells are progressively building cell wall outside the plasma membrane, which act as a supportive framework. Wood structure, i.e. wood lignocellulosic material, consists in the cell wall.

The cell wall is a very efficient structure consisting of interconnected network of cellulose (45%), hemicellulose (30%) and lignin (25%) (Stevanovic *et al.* 2009). It is formed of several layers created at different stage of the cell life (Figure 2) (Jeney 2011).

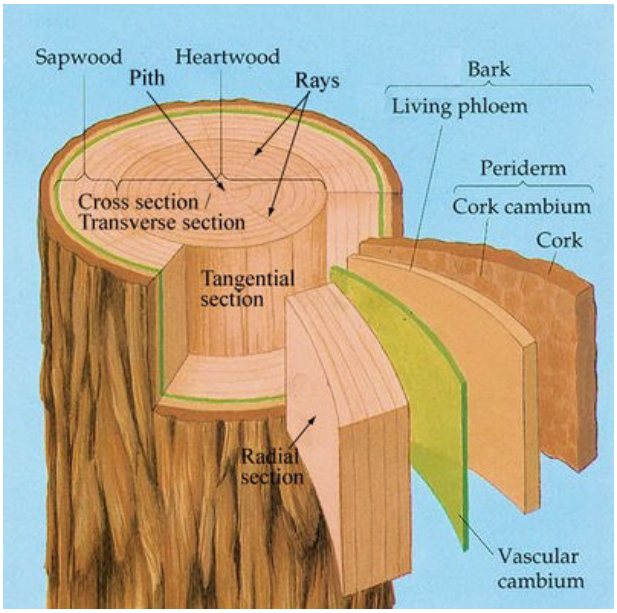


Figure 1 : Scheme of trunk transverse cut. Copyright University of Cambridge, DoITPoMS, 2008.

The middle lamella (M) connects the cell walls together. It has a high content of lignin and is in principle free of cellulose. Its thickness varies from 0.5 to 1.5 µm and is smaller in sapwood than in heartwood. The primary wall (P) is a thin layer of 0.1 µm, made of cellulose microfibrils, randomly orientated to allow further expansion of the cell to occur. They are embedded in a matrix of lignin and hemicelluloses. The secondary wall (S) is thick, dense and stiff and made of three layers (S_1, S_2, S_3). Because of the high content of cellulose microfibrils, the secondary wall confers most of the wood mechanical properties (Hout Info Bois 2012). Chemical composition and polymers orientation varies in the three layers (Table 1).

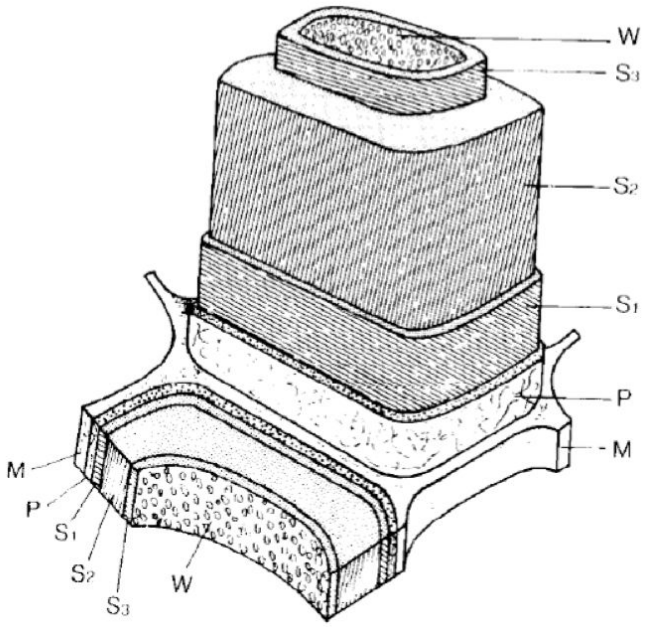


Figure 2 : Layered structure of cell wall. M: middle lamella; P: primary wall; {S_1, S_2, S_3}: secondary wall; W: warty layer (Jeney 2011).

Table 1 : Secondary cell wall structure (Hout Info Bois 2012)

	S_1	S_2	S_3
Microfibrils orientation	Variable alternate helical winding	Parallel helical winding	Parallel helical winding
Microfibrils angle to the cell axis	60 to 80°	5 to 30°	60 to 90°
Layer thickness	0.1 to 0.35 µm	1 to 10 µm	0.5 to 1.1 µm

The space between microfibrils is partially occupied by hemicelluloses and lignin. Because of the incomplete filling of the intermicrofibrillar region, the cell wall can be considered as a porous matrix. Micropores (or microvoids) in the cell wall have diameters of the order of nanometres. Their size varies with wood moisture content. They collapse when the wood is drying (Hill *et al.* 2001).

Wood is a fibre-composite material (cellulose fibres in a lignin matrix) with complex overall structure (Figure 3). The material final properties are depending on the chemical and physical properties of each wood component and also on the way they are organised together within the wood structure.

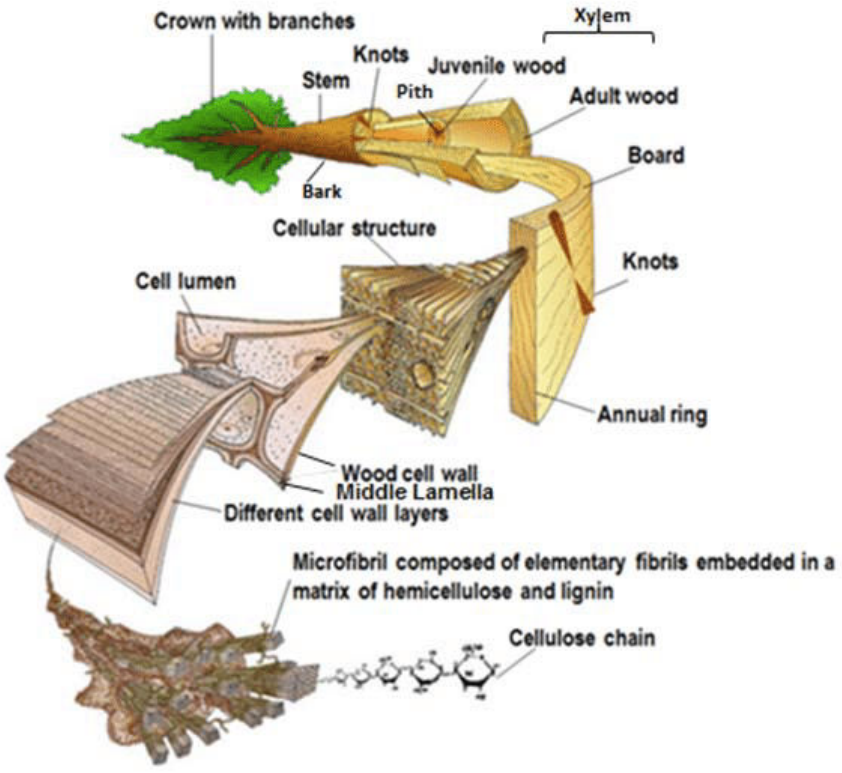


Figure 3 : Scheme of the hierarchical structure of coniferous wood (softwood). Copyright University of Canterbury, 1996. Artwork by Mark Harrington, slightly changed and extended.

1.2. Cellulose microfibrils

Cellulose is the structural basis of the cell wall and consists of anhydroglucopyranose units which are joined by β-(1→4)-glycosidic linkages to form a linear molecular chain. Two adjacent glucose units are linked by elimination of a molecule of water between their hydroxyl groups (-OH) at carbon 1 (C1) and carbon 4 (C4). Because of the β position of the OH-group at C1, the anhydroglucose units must be alternatively turned around the C1-C4 axis. Thus, the repeating unit of cellulose chain is a cellobiose unit. Figure 4 describes the structure of cellulose (Klemm *et al.* 1998).

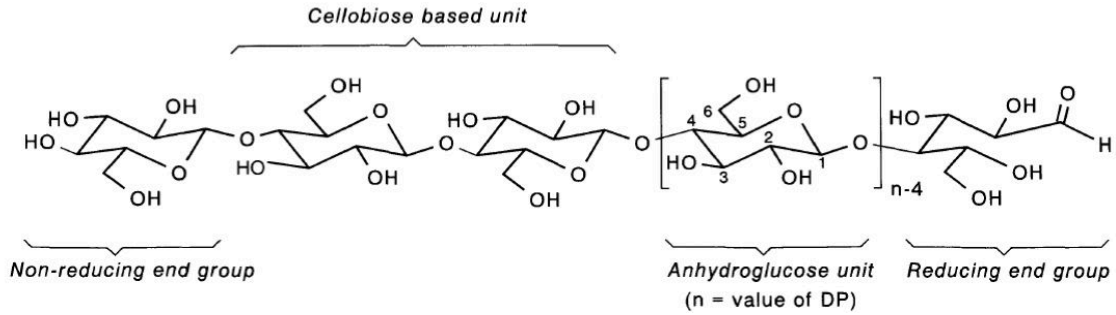


Figure 4 : Molecular structure of cellulose (Klemm et al. *1998).*

The OH-groups of cellulose molecules can form two types of hydrogen bonds. Intramolecular linkages between adjacent glucose units in the same cellulose molecule give a certain stiffness to the single chains. Intermolecular linkages between adjacent cellulose molecules are responsible for the formation of supramolecular structure (fibrils). Cellulose microfibrils have a diameter of ca. 5 to 30 nm. Cellulose degree of polymerisation (DP) in wood has been estimated at ca. 100 000 glucose units.

1.3. Hemicelluloses

Hemicelluloses are ramified heteropolysaccharides with molecular chains shorter than those of cellulose (DP of ca. 200-300). They are often divided in two categories according to their sugar unit composition: mannans (mainly made of hexose units mainly in softwoods) and xylans (mainly made of pentose units mainly in hardwoods) (Fengel *et al.* 1984). Main structural units of hemicelluloses are given in Figure 5. Hemicelluloses act as a matrix for cellulose and are a link between the fibrous cellulose and the amorphous lignin. They form H-bonds with the surface of the microfibrils and covalent linkages with the lignin matrix (Koshijima *et al.* 2003). The role of hemicelluloses in wood viscoelastic properties is determining as their degradation results in wood becoming brittle and rigid.

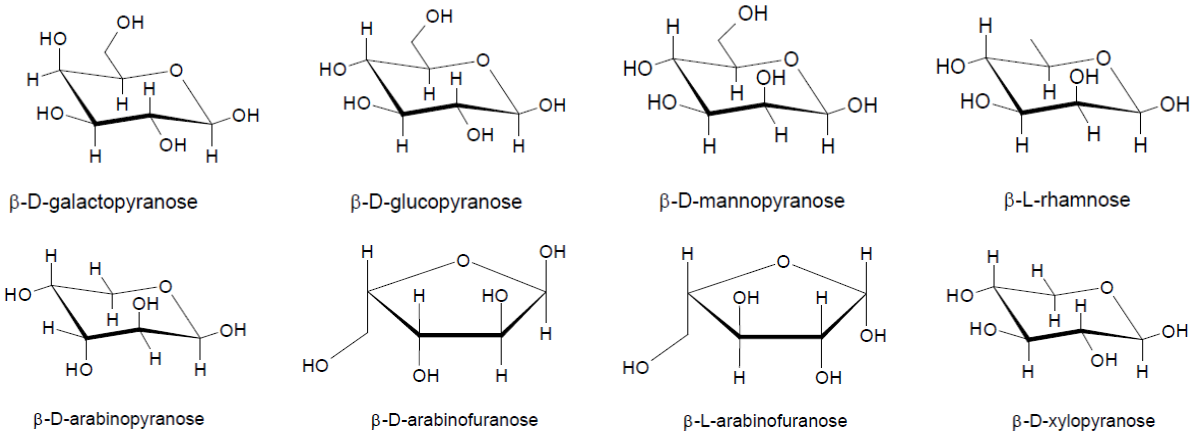


Figure 5 : Structural units of hemicelluloses (Fengel et al. *1984).*

1.4. Lignin

The lignin is a polyphenolic compound acting as a cement between cellulose fibres. It is linked and associated to at least part of the cell wall carbohydrates and is not simply deposited between. Lignins are the results of oxidative polymerisation of three phenolic alcohols (Figure 6). Their polymeric structure cannot be precisely figured out as the alcohol units are randomly bounded by several kinds of chemical linkage (Fengel *et al.* 1984).

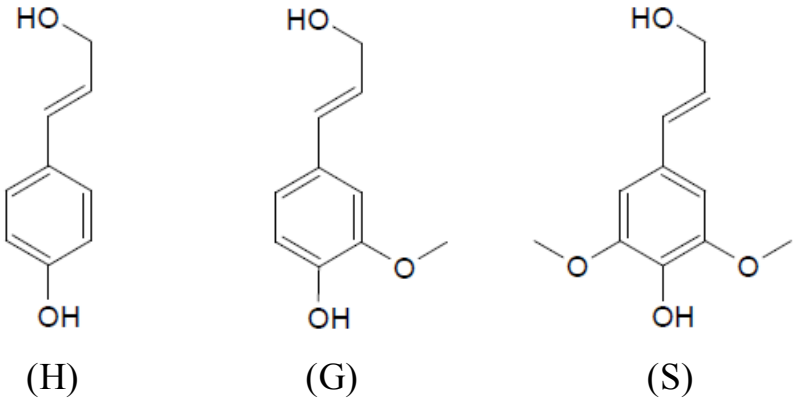


Figure 6 : Building units of lignin: coumaryl alcohol (H), coniferyl alcohol (G) and sinapyl alcohol (S) (Fengel et al. 1984).

2. Wood-water interactions

Many of the wood properties depend upon the presence of OH-groups and in particular, hydrogen bonding interactions between the molecular components of the cell wall. Moreover, the OH groups are also responsible for absorption of moisture. Wood-water interactions have been widely studied over the past century. A state of the current knowledge was done for a

recent review from Thybring *et al*. (2013) in which the physics of wood-water interactions has been discussed.

2.1. State of water

Water can be found in wood in two different states: the free water within the cell lumen (assumed to be capillary water) and the bound water which interacts with wood polymers (Nakamura *et al.* 1981). Because of its chemical and structural constitution, wood is hydrophilic and hygroscopic. Wood polymers OH-groups are the main chemical component in terms of attracting water molecules. As cellulose is organised in microfibrils, two-thirds of the hydroxyl groups are not available to interact with water as they are bound between and within cellulose chains. Mostly the ones on the surface of the microfibrils are possible sorption sites. Thus, most sorption sites are found in the hemicelluloses as their OH-groups are more accessible (Rautkari *et al.* 2013).

2.2. Moisture sorption and desorption

The sorption and desorption behaviour of wood is studied by determining the relationship between wood equilibrium moisture content (EMC) and air relative humidity (RH) at constant temperature. The sorption or desorption isotherms of wood have the same sigmoidal shapes, but differs however, producing a phenomenon of hysteresis (Figure 7). When dry wood absorbs moisture, water molecules can directly be associated with OH-groups of wood polymers, or when a layer of water molecules already occupies the wood polymers sorption sites, they can be associated with other water molecules formerly absorbed. The energy needed to create those two types of hydrogen bonds is different (giving the sigmoidal shape), and a different energy is needed to break those bonds (giving the hysteresis). Temperature influences wood EMC, which decreases with increased temperature level for a given constant RH (Merakeb *et al.* 2009, Shi *et al.* 2017).

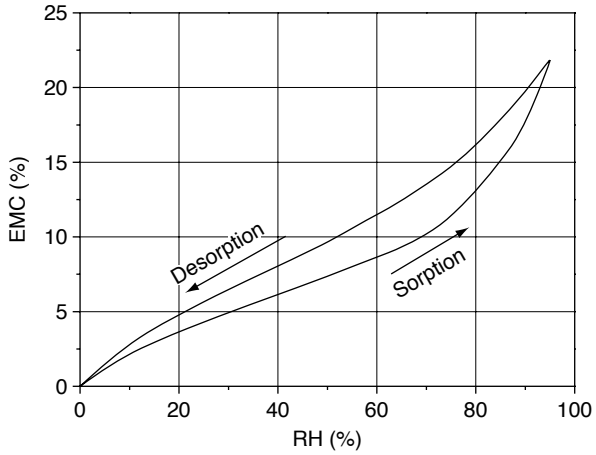


Figure 7 : Sorption and desorption isotherm of wood (Hill 2006).

2.3. Influence of moisture on wood properties

Absorption of moisture leads to dimensional instability and permits biological attack of the material. On a molecular level, the cell wall OH-groups represent the most important component influencing the performance of wood.

Dimensional variations of wood result from changes in wood moisture content. Swelling is caused by water entering the cell wall and occupying space between the cellulose microfibrils, and thereby forcing them apart. However, around a certain moisture content (from about 30 to 40%), the cell walls reach a saturated state and the swelling of wood is maximal (Murata *et al.* 2006).

Mechanism of fungal decay has been widely studied (Thybring *et al.* 2013, Srebotnik *et al*. 1988, Goodell *et al.* 1997, Hill 2002) and is the result of different chemical actions. Fungi use enzymes to degrade wood polymers. Those enzymes are not able to diffuse in the cell wall because of their size. For this purpose, fungi first release small molecules able to react with wood polymers to increase their accessibility to enzymes. However, even those small molecules need water to diffuse in the wood structure. Thus, efficient protection against fungal decay could be provided by treatments reducing the wood equilibrium moisture content.

Therefore, a strategy to improve wood dimensional stability and biological resistance could be to reduce wood hygroscopicity by limiting the accessibility of OH-groups.

Wood moisture content also influences mechanical properties. A reduction of cell walls moisture content results in an increase of the modulus of elasticity (MOE), and an increase in strength (Dinwoodie 2000). Creep deformation is also influenced by cell wall moisture content, although the relationship is more complex, and especially if wood is subjected to cyclic humidity changes (Norimoto *et al.* 1992).

3. Wood cell wall swelling

Cellulose is primarily responsible for wood swelling. Mantanis *et al.* (1994) found apparent similarities between cellulose and wood maximum swelling. Also, wood tangential swelling is stronger than the radial and longitudinal swelling. This is due to the microfibrils orientation in the secondary wall (Table 1 : Secondary cell wall structure (Hout Info Bois 2012)).

Several organic molecules can enter the cell wall and act as swelling agents. The maximum swelling of wood in organic solvents is mainly influenced by solvent properties such as the molar volume (Figure 8) and the hydrogen bonding capability (Figure 9) (Mantanis *et al.* 1994).

There is a strong correlation between hydrogen bonding capability of the swelling solvent and the wood swelling. Because liquids with a strong hydrogen bonding capability swell the wood

to the greatest extent, the inter- and intra-microfibrils hydrogen bonds breaking mechanism is most likely involved in the wood swelling process. However, some solvents with high hydrogen bonding capability make exception and result in a low wood swelling. Mantanis *et al.* (1994) showed that wood maximum swelling decreases when the solvent molecules become bulkier. Parameters such as molar volume, solvent basicity, steric hindrance or molecular branching must also be considered.

Generally, solvent with low molar volume, high hydrogen bond capability and/or strong basic nature are efficient wood swelling agents. Water, formamide, ethylene glycol, methanol, pyridine, formic and acetic acid and butylamine induce substantial wood swelling.

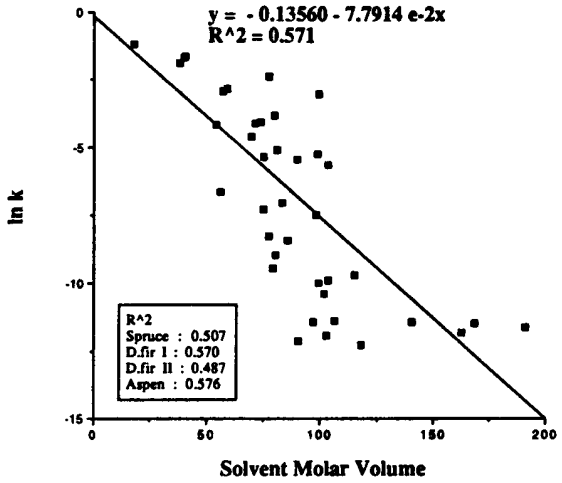


Figure 8 : The logarithm of the rate of swelling of maple plotted against the solvent molecular volume (Mantanis et al. 1994).

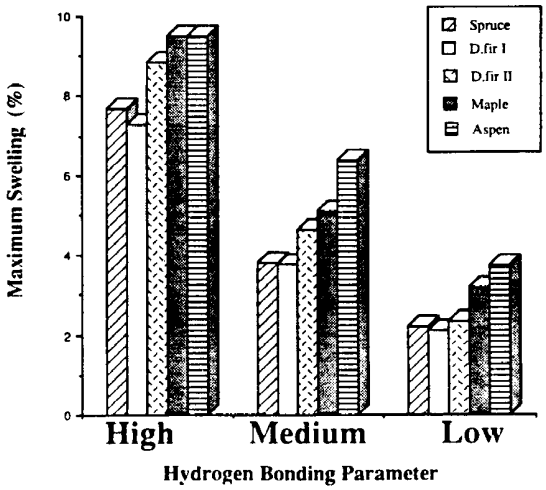


Figure 9 : The effect of the solvent hydrogen bonding capability on the maximum tangential swelling of wood (Mantanis et al. 1994).

The cell walls swelling influence the wood structure accessibility to other entities. The space between microfibrils is partially occupied by hemicelluloses and lignin. Because of the incomplete filling of the intermicrofibrillar region, the cell wall can be considered as a porous matrix. When the wood is dry (not swollen), the micropores are closed. But if the cell walls are fully swollen, the micropores are open and the interior of the cell walls is accessible to entities that are smaller than the micropores. The maximum probe diameter for cell wall penetration is 4 nm (Hill *et al.* 2005).

4. Wood preservation

During its service-life, wood is susceptible to be degraded by various agents such as mould, rots and insects. Use classes have been defined in EN 335 standard (BS EN335:2013) according to the risk of biological degradation.

Table 2 : Summary of use classes and relevant attacking biological agents for wood and wood-based products (BS EN 335:2013)

Use Class	**General use situation**[a]	**Biological agents**[b]				
		Disfiguring fungi	Wood destroying fungi	Beetles	Termites	Marine borers
1	Interior, dry	-	-	U	L	-
2	Interior, or under cover, not exposed to the weather. Possibility of water condensation	U	U	U	L	-
3	Exterior above ground, exposed to the weather. **3.1** limited wetting conditions **3.2** prolonged wetting conditions	U	U	U	L	-
4	Exterior in ground contact and/or fresh water	U	U	U	L	-
5	Permanently or regularly submerged in salt water	U[c]	U[c]	U[c]	L[c]	U
U = ubiquitous in Europe and EU territories L = locally present in Europe and EU territories						
[a] Border line and extreme cases of use of wood and wood-based products exist. This can cause the assignment of a use class that differs from that defined in this standard. [b] It may not be necessary to protect against all biological agents listed as they may not be present or economically significant in all service conditions in all geographic regions, or may not be able to attack some wood-based products due to the specific constitution of the product [c] The above water portion of certain components can be exposed to all of the above biological agents						

In former times, biocidal solutions were used to protect wood: creosote first, then chromate-copper-arsenate (CCA), were dominating the market warranting very long service life (Richardson 1993, Ruddick 2011). More recently, restrictions on the use of these wood preservatives have focused public and government attention on technological developments in the wood protection area. The regulation 1907/2006 of the European Union has already banned every formulation containing arsenic (e.g. CCA) and also restricted the concentration for boron (directive 2008/58/EC and 2009/2/EC) that is often used to replace arsenic as fungicide in the most common metal-based inorganic formulations (CCB) (Evans 2003, Schlutz *et al.* 2007).

Thus, the availability and use of environmentally friendly wood preservation methods is nowadays strictly required (Gérardin 2016). New non- biocidal preservation techniques are needed to keep using using wood outdoor (Use class 3 and 4) where it is exposed to high humidity variations and various biological agents (Table 2).

5. Wood modification techniques

5.1. Wood properties and wood modification

As defined by Hill (2006), "the term "wood modification" applies to the application of a process that alters the properties of the material such that during lifetime of a product no loss of the enhanced performance of the wood should occur". In other terms, it means that the changes in wood properties observed after treatment have to be permanent, on the contrary of a coating that may fail by cracking, and due to a modification of inherent material properties, on the contrary of a treatment with a substance biocidal in nature. In addition, the modified wood should itself be nontoxic and should not release any toxic substance during service and at the end of life.

Wood modification can be active or passive considering if they involve changes at a chemical level or not (Sandberg *et al.* 2017). Passive techniques generally entail lumen and/or cell wall filling. But, because many properties of wood are determined by its chemical constitution, wood modification methods are often active and seek to alter wood chemical constitution. OH-groups of cellulose and hemicelluloses have the potential to react with varied chemicals which could form single chemical bond with one OH-group or cross-linking between two or more OH-groups. Finally, partial degradation of the cell wall is also often involved in wood modification techniques (Figure 8). Most of those wood modification methods require accessibility of the cell wall, which will influence the choice of chemicals and processes.

Many processes for wood modification have been investigated over the past decades (Sandberg *et al.* 2017, Gérardin 2016) and the research in this field has introduced many brand names of processes or products on the market such as: Retification®, Plato® or Thermowood® for thermo-treated wood (Esteves *et al.* 2009, Boonstra *et al.* 1998, Viitaniemi *et al.* 1997), Accoya® for acetylated wood (Hill *et al.* 2005, 2009, Mohebby 2003), or Kebony® for furfurylated wood (Lande *et al.* 2004).

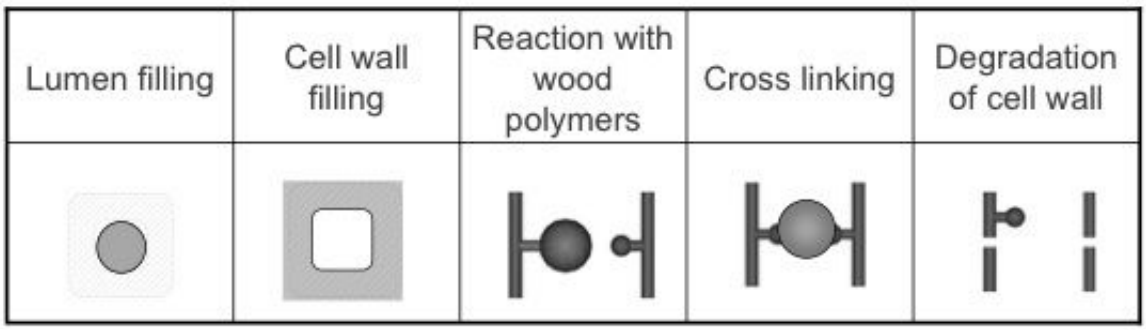


Figure 10 : Different types of wood modification at the cellular level (courtesy: Emil Engelund Thybring, University of Copenhagen, Denmark)

With chemical modification of wood, it is necessary to determine how much chemicals are in the wood and if they remain in the lumens or if they diffuse in the cell walls. One simple test involves determining the weight and dimensions of wood before and after modification (Hill, 2006). Weight gain due to modification is commonly reported in the wood modification literature as weight percentage gain (WPG), which is calculated as follows:

$$\text{WPG}\ (\%) = \frac{w_m - w_u}{w_u} \times 100 \qquad \text{Eq.1}$$

where w_m is the oven-dry mass of the modified wood and w_u is the oven-dry mass of the unmodified wood. Similarly, the volume change or bulking coefficient (BC), can be reported as a percentage increase compared to the original volume. It is calculated as follows:

$$\text{BC}\ (\%) = \frac{V_m - V_u}{V_u} \times 100 \qquad \text{Eq.2}$$

where V_m is the volume of the oven-dry modified wood sample and V_u is the volume of the oven-dry unmodified wood sample. Since these volumes are invariably determined by measuring the external dimensions of the wood sample, it cannot be assumed that BC is related to bulking of the cell wall, but only to the gross wood structure.

If a weight gain and bulking is observed after modification, this most likely indicates that the chemical has penetrated the cell wall. However, this is not enough to prove that there is any chemical reaction between the wood polymers and the chemical. If the wood is subjected to rigorous solvent extraction after modification and/or leaching in water, and a weight gain and swelling of the material are still observed, then this indicates that the modification is persistent, but does not prove the existence of a chemical bond (Hill, 2006).

Bulking and crosslinking modification have a direct impact on wood dimensional stability. As explained before (3. Wood cell wall swelling), wood swelling is limited. The principle of bulking modification is to enduringly bulk the wood cell walls with persistent entities, so the swelling due to water absorption is reduced (Figure 11). However, the final dimensions of the fully swollen wood remain the same for unmodified ($V_{u,w}$) and modified wood ($V_{m1,w}$). Crosslinking modification reduce ability of cellulose microfibril to be forced apart as they are linked through covalent bonding. The cell walls are permanently bulked as well when the wood is dry, limiting the swelling capability of water, and the fully swollen volume of wood is reduced (Figure 11).

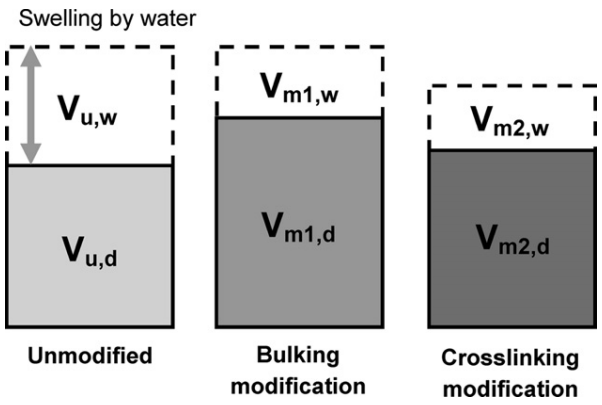


Figure 11 : illustration of dry (index d) and water-swollen (index w) volumes of unmodified (index u) and modified (index m) wood (Thybring 2013).

The modified wood hygroscopic behaviour is generally the first indicator of treatment efficiency. Anti-swelling efficiency (ASE) and moisture exclusion efficiency (MEE) respectively characterise the reduction of swelling and moisture content. They are measured after stabilisation in a moist environment and calculated as follow:

$$\mathrm{ASE}\ (\%) = \frac{S_u - S_m}{S_u} \qquad \text{Eq.3}$$

$$\mathrm{MEE}\ (\%) = \frac{EMC_u - EMC_m}{EMC_u} \qquad \text{Eq.4}$$

where $S_{u/m}$ and $EMC_{u/m}$ stand for the unmodified (index u) and modified (index m) swelling and EMC respectively.

When the treatment pre-swell wood, it is important to deduct the volume increase from modification from the dry volume, to be able to measure only the wood swelling and compare ASE with other modification techniques. Thus, for bulking and crosslinking modification, the corrected ASE (ASE*) can be calculated based on the corrected swelling (S_t^*) according to Thybring (2013):

$$S_t^*\ (\%) = \frac{V_{t,w} - V_{t,d}}{V_{u,d}} \times 100 \qquad \text{Eq.5}$$

where $V_{t,w}$ stands for the treated sample water-swollen volume, $V_{t,d}$ for treated sample dry volume, $V_{u,d}$ for untreated sample dry volume.

EMC is commonly calculated as the mass ratio of moisture to dry substance as follows:

$$\mathrm{EMC}(\%) = \frac{m_{water}}{m_{wood}} = \frac{m_w - m_d}{m_d} \qquad \text{Eq.6}$$

where m_w and m_d stand for sample wet (index w) and dry (index d) mass. In the case of modified wood, EMC can be underestimated if calculated this way because of the added mass of modification agent (Figure 12). The reduced EMC (EMC_R) allows comparison between treatments as the mass of modification agent is deducted from the dry mass.

$$EMC_R(\%) = \frac{m_{water}}{m_{modified} - m_{agent}} = \frac{m_{t,w} - m_{t,d}}{m_{u,d}} \qquad \text{Eq.7}$$

where $m_{t,w}$ stands for the treated sample wet mass, $m_{t,d}$ for treated sample dry mass, and $m_{u,d}$ for untreated sample dry weight.

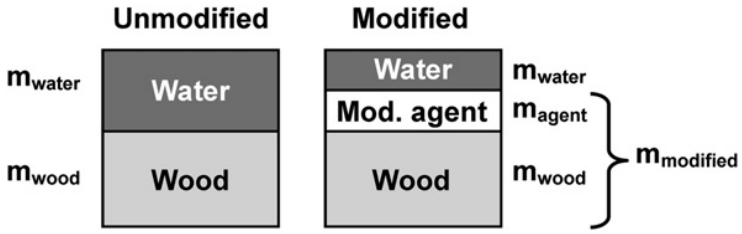


Figure 12 : illustration of different masses of moist unmodified and modified wood (Thybring 2013).

5.2. Thermal modification

Thermal modification results in hemicelluloses degradation, thus in associated decrease in moisture sensitivity. However, mechanical properties are affected due to the relative increase in wood crystallinity that contributes to decreased impact and bending resistance. This has hindered the thermo-treated wood market development (Boonstra *et al.* 2006a, 2006b, Beall 1971) until recent years when the combined effect of a decreasing production of durable timber, an increasing demand for sustainable building materials and developing regulations on the toxic chemicals use renewed the general interest in wood thermo-treatment (Esteves *et al.* 2009).

The influence of thermal treatment on wood components and the relation with the resulting wood weight loss is well known and was extensively reported. The drying region between 20°C and 150°C is followed by the first chemical transformations in the range of 180-250°C and carbonization processes above 250°C. The hemicelluloses are the first affected compounds, more degraded than cellulose because of the latter's crystalline nature. In the meantime, polycondensation reactions with other cell wall components results in further crosslinking of lignin, contributing to the increase in its apparent content. In the process, most of the wood extractives disappear (Esteves *et al.* 2008, 2009, Tjeerdsma *et al.* 2005).

Thermal treatment is one of the most efficient process to improve dimensional stability, increase the durability and reduce the wood EMC (Candelier *et al.* 2014). Even with a wide range of thermo-process conditions (temperature, duration, relative humidity, wood moisture content before treatment) and the resulting wood mass loss, the reduction in EMC was always observed, from low to high temperature (100°C to 220°C), in different extents (from 1% to ca. 15%, according to the wood species and treatment conditions according to the references). Along with EMC decrease, high anti-swelling efficiency (ASE) was always observed, with a maximal deformation reduction at 100%RH of 75% for beech wood for instance with an optimised process (Burmester 1973). Because of the decreased EMC and the chemical

transformation of wood components, the thermo-treated wood durability is also significantly improved.

However, the major drawback of the thermal process is the substantial decrease in wood mechanical properties that could not be overcome so far. The two main properties impacted are the static bending strength (MOR) and the impact bending, in a different extent according to the process conditions. Generally, thermo-treatment leading to high ASE also results in important decrease in bending strength: 20% loss in MOR for a process leading to 40% ASE were already reported by Stamm *et al.* (1946) for instance. Even if improvements were achieved since then, with optimised treatment conditions or heating under nitrogen, and even if some examples of thermo-treated wood used in construction were reported (Boonstra *et al.* 2007), the challenge of the mechanical properties decrease still has to be overcome.

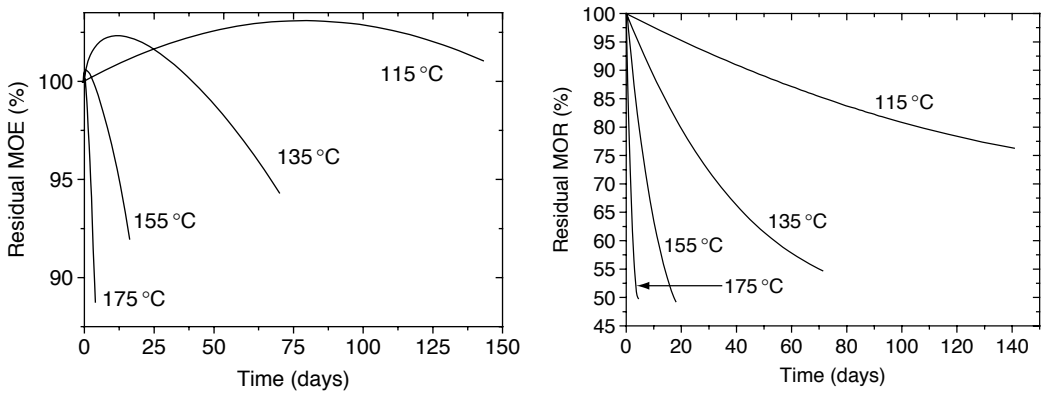


Figure 13 : Heat treatment temperature influence on wood modulus of elasticity (MOE) and static bending strength (MOR) (Hill 2006).

5.3. Chemical modification

For chemical modification, covalent bonding between chemical reagent and reactive part of wood is expected. A very large number of chemicals have been considered for their potential use for wood modification (Chang *et al.* 2003, Dawson *et al.* 1999, Gérardin *et al*. 1995, Kumat *et al.* 1991, Rowell *et al.* 1986, Timar *et al.* 2004, Thiebaud *et al.* 1997). However, most processes studied involved products that would present problems if handled in the quantities necessary for commercial operations (Hill 2006).

Wood acetylation by means of acetic anhydride is the best-known procedure. It is an esterification of hydroxyl groups in the cell wall, forming acetic acid as by-product (Figure 9) (Rowell 2005, 2007, Rowell *et al.* 2005)

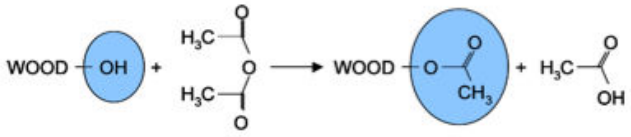


Figure 14 : Reaction of an anhydride with wood (Artwork: Accoya®).

Wood acetylation is a very efficient process to improve dimensional stability, increase the durability and reduce the wood EMC. It was evidenced that performances of acetylated wood are proportional to the WPG, i.e. the amount of chemicals remaining within the wood at the end of the process. Acetylation is found to provide decay resistance, 60-70% ASE and 40-50% MEE at ca. 20% WPG to various wood species. WPG of ca. 20% corresponds roughly to a wood swelling of ca. 7% only due to the presence of chemicals within the cell wall (Thybring *et al.* 2013).

Enhancement of wood hygroscopic behaviour is due to the cell wall bulking more than the OH-groups substitution. Mechanism of decay protection is due to a combination of factors. In addition to reducing the cell wall moisture content below decay threshold, acetylation provides a physical barrier to degradative agents and changes the substrate nature. Recent studies (Beck 2018) showed that decay of acetylated wood might only be delayed because of the moisture reduction which decreases diffusion of degradation agents in the cell walls, but eventually occurs after de-acetylation of the polysaccharides.

Strength properties of acetylated wood are not significantly affected by the process for treatment temperature of 120-140°C.

5.4. Impregnation modification

The principle of impregnation modification is to "impregnate the cell wall of wood with a chemical, or a combination of chemicals, that then react to form a material that is 'locked' into the cell wall" (Hill 2006). Many processes consist in an *in situ* polymerisation of monomers in the lumen or in the cell wall, with or without chemical grafting. Numerous chemicals have been reported since long ago: phenol-formaldehyde, melamine-formaldehyde, urea-formaldehyde resins (Hill 2006), DMDHEU (Evans *et al.* 2002), maleic anhydride with polyglycerol (Hill 2006), methyl methacrylate and/or styrene (Hill 2006), HEMA/MMA or PGMA polymers, epoxy resins (Chang *et al.* 2001), silicone, PEG. More recently, tannin-hexamine formulations have demonstrated high crosslinking properties which bring to high performance wood preservative against fungal and termite attacks, to be polymerised in-situ. Moreover, these products have shown strong mechanical and fire resistance as well as a considerable water resistance (Tondi *et al.* 2012a, 2012b).

The most-known process is furfurylation (polymerisation of furfuryl alcohol in wood, Figure 10), giving high dimensional stability and improvement of decay resistance. It is believed to be a safe process for environment (Gérardin 2016). Several reactions are likely to happen within the wood structure. The most favourable reaction leads to the formation of methylene bridge (Figure 10 (a)), but with higher reaction temperatures and furfuryl alcohol concentrations reaction, scheme (b) occurrence increases resulting in formation of ether bridges. However, the ether bridge is unstable and it is believed that it undergoes further reaction, as shown in scheme

(c). A three-dimensional polymeric network formation within the cell wall is possible if further cross-linking reactions occur (Hill 2006).

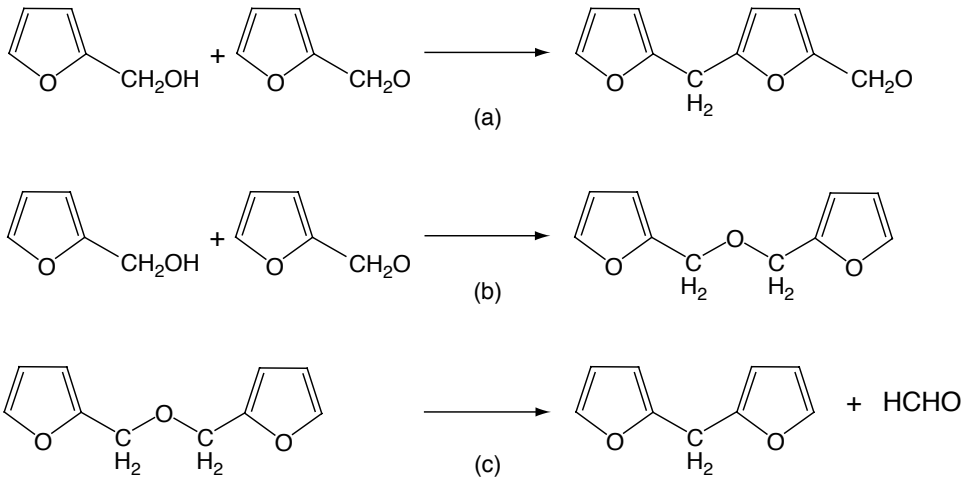


Figure 15 : Polymerisation of furfuryl alcohol within the wood (Westin et al. 2003).

Several process conditions have been evaluated over the past decades. Direct impregnation of polymerised resin did not provide satisfactory results for dimensional stabilisation because the molecules were not able to diffuse in the cell wall. Impregnation with furfuryl alcohol followed by *in situ* polymerisation with catalysts at low temperature (100-120°C) allows improvement of wood performance. The modified wood properties depend on the resin content. A WPG of 50% led to the maximal dimensional stabilisation of wood (ASE of ca. 70%) (Stamm *et al.* 1977). A WPG of resin of around 100% provided excellent performance regarding the modified wood biological resistance (Westin *et al.* 2004).

Resin treatment resulted in a decrease in MOR, abrasion resistance and impact toughness. However, an increase in wood hardness was observed as the amount of resin within the wood increased. An increase in MOE was attributed to acidic degradation of the wood by some of the catalysts used (Stamm *et al.* 1977, Westin *et al.* 2003, 2004). Finally, the colour change of wood varied from dark brown at lower resin contents to black at higher resin contents.

6. Wood modification with lactic acid

Lactic acid (2-hydroxypropanoic acid, abbreviated LA in the following) is an organic acid abundantly present in nature as animals, plants and microorganisms can produce it. Industrially, it can be obtained by fermentation of renewable resources, such as dextrose from corn or sugar beet, which is a process with low energy-cost energy and producing few coproducts (Mecking 2004) or through petrochemical synthesis.

LA is a bifunctional hydroxy acid with carboxylic acid group at one end and hydroxyl group at the other end. Two enantiomers naturally exist (L(+) and D(-), Figure 12). The L(+) lactic acid

is used as food grade acidifying agent as it also has antimicrobial activity. LA is also widely used in the cosmetics, pharmaceutical and chemical industries.

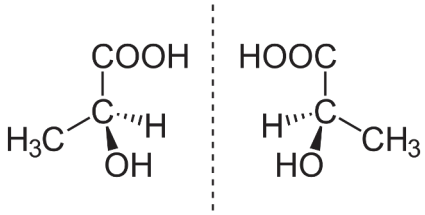


Figure 16 : Lactic acid enantiomers: L(+) (left) and D(-) (right).

6.1. Polymerisation of LA

LA leads to poly(lactic acid) (PLA) production, following a polycondensation reaction. However, to reach high molecular weights, ring opening polymerisation (ROP) of lactide cyclic di-esters is usually preferred (Figure 13) (Alba 2009, Lopes *et al.* 2014, Auras *et al.* 2004). Direct polycondensation of LA consists in creation of ester linkage between two molecules of LA, with removal of one molecule of water.

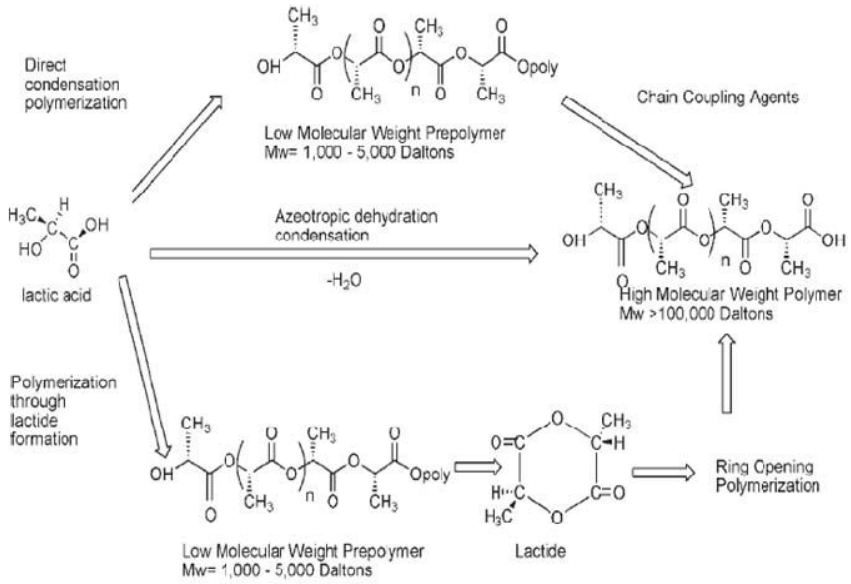


Figure 17 : Polymerisation routes for PLA (Auras et al. 2004).

The reaction is a reversible step-growth polymerisation mechanism. The reversible nature of the reaction limits the extent of conversion of lactic acid to PLA and hence the degree of polymerisation if special care is not taken to completely remove the produced water.

Polycondensation of lactic acid is strongly influenced by temperature. Even with extended curing time, the DP obtained at a certain temperature is limited. Only an increase of the temperature level allows significant further polymerisation (Figure 14) (Harshe *et al.* 2007).

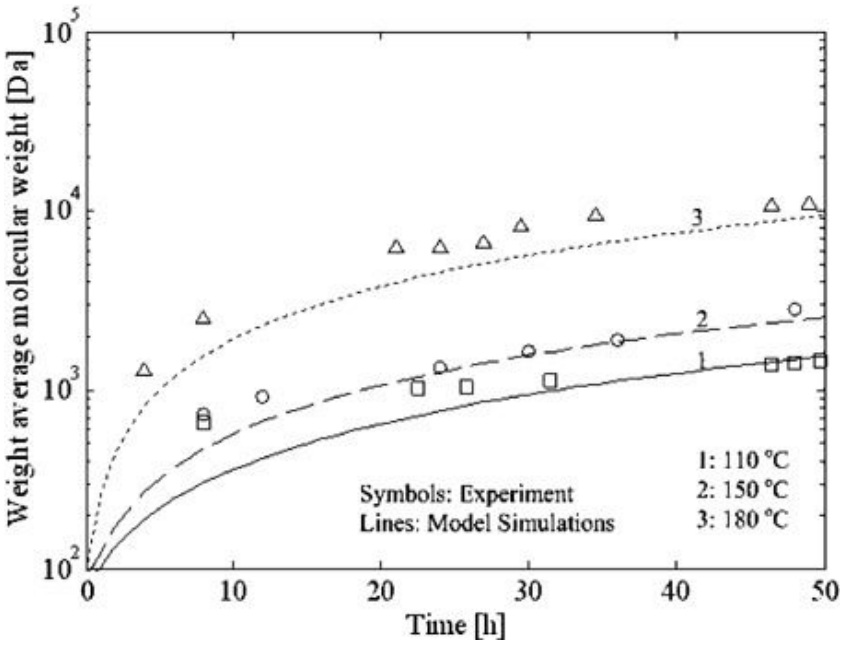


Figure 18 : Influence of temperature on LA polycondensation (Harshe et al. 2007).

6.2. Properties of PLA

Among the biopolymers, PLA has been widely studied because of its many advantages (low-cost, bio-based, biocompatible and biodegradable) and attractive properties (thermoplastic, good mechanical properties). The relatively low price and commercial availability of LA are important reasons for PLA development. It is today the most commercially produced biopolymer, mostly for the manufacture of medical grade sutures, implants and controlled drug release applications, but also for polystyrene (PS) or polyethylene terephtalate (PET) replacement. Among the main producers, Cargill Dow LLC and Mitsui Chemicals are leaders of the worldwide PLA production (Flieger *et al.* 2003).

PLA is a thermoplastic polar polymer, amorphous or crystalline. Properties of PLA are strongly dependent on the L(+)/D(-) enantiomers ratio. Usually, the glass transition and melting temperatures are around 60°C and between 130 and 180°C, respectively. Thermal stability of PLA is limited because of the carbonyl linkage sensitivity at high temperature. Thermal degradation of PLA starts around 290°C (Hwang *et al.* 2012, Chen *et al.* 2002). It can be due to thermolysis, depolymerisation, thermo-oxydative degradation or transesterification reactions (Södergard *et al.* 2002).

PLA is also sensitive to hydrolysis, which consists in the reverse reaction of polycondensation. The first step of this degradation mechanism is the water absorption, followed by random dissociation of ester linkages. Crystallinity of PLA influences the water absorption and thus, the polymer resistance to hydrolysis. Because crystalline PLA absorbs less water than amorphous PLA, it will degrade in several months instead of several weeks. In a biological environment, enzymes produced by micro-organisms catalyse PLA degradation through

hydrolysis (Södergard *et al.* 2002). Biodegradability of PLA is crucial for many applications and a strong advantage considering products end of life (Mahalle *et al.* 2014).

6.3. Use of LA for wood modification

The use of lactic acid oligomers for wood stabilization was considered because of two main properties: with a suitable catalyst carboxylic end groups expected to be grafted on wood structure blocking absorption sites for water in the cell wall, and the feasibility of *in situ* polymerisation in the lumen for mechanical properties maintain via density increase.

The solid wood impregnation with oligomers of lactic acid was first reported in 2009 (Noël *et al.* 2009a, 2009b, 2011). Noël *et al.* achieved oligomers of LA (OLA) polymerisation within wood structure and attempted grafting of polymer chains on wood OH-groups. The bulk impregnation of oligomers in wood lumens was revealed to be easily achieved under vacuum and was followed by significant diffusion of the oligomers in the cell wall during the heat treatment carried out successively in a ventilated oven to induce the *in situ* polymerisation.

Treatment carried out without chemical catalyst conferred very promising properties to wood, in terms of dimensional stability, good biological resistance and increased surface hardness, together with no decrease in the mechanical properties when the heat treatment is carried out for a long enough time at low temperature (100-120°C). However, even if a significant improvement of wood properties was observed, fixation of oligomers within the wood was not completely achieved.

The addition of several catalysts, such as sulfuric acid or stannous octoate, in the oligomers mixture successfully increased the degree of polymerisation achieved within wood, but caused a substantial degradation of the wood components, especially lignin. This resulted in very softened and malleable materials, also darkened by the process. As a matter of fact, under chemical polymerisation catalysis, a study of the influence of heat treatment conditions, at relatively low temperature, revealed the possibility to improve product persistence in wood. The total leaching did decrease from 90% for a curing at 120°C for 1h, to 20% when followed by a second curing at 103°C until constant weight. Because of a promising 60% ASE at ca. 100% relative humidity (RH) obtained with long heat treatment, and because wood degradation was attributed to the chemical catalysts, a treatment with a longer stage at higher temperature (120°C/6h) was carried out, with no chemical catalysis, which led to a total leaching of ca. 80%.

7. Wood modification with poly(butylene succinate) (PBS)

Poly(butylene succinate) (PBS) is a half-crystalline thermoplastic which could substitute polyolefines. It has mechanical properties similar to polyethylene (PE) or polypropylene (PP). This poly(alkylene dicarboxalate) biodegradable aliphatic polyester produced via

polymerisation reaction of 1,4-butanediol and dimethyl succinate was historically developed by Showa Highpolymer and Denko under the trade name "Bionolle". Nowadays, the synthesis of fully biobased PBS is possible since the implementation of bio-based succinic acid on the market (Endres *et al.* 2009).

Succinic acid is a carboxylic diacid naturally produced by plants, animals or micro-organisms (Zeikus *et al.* 1999). It is commercially available and widely used as a platform molecule (Xu *et al.* 2010a, Willke *et al.* 2004). Most part of the succinic acid world production is produced from petrochemical resources (Figure 15, Delhomme 2011). However, several bacterial strains are able to produce succinic acid (Song *et al.* 2006, Xu *et al.* 2010a, Bechthold *et al.* 2008, Xu *et al.* 2010b) from biomass and the first industrial productions were developed in 2008 (Xu *et al.* 2010b).

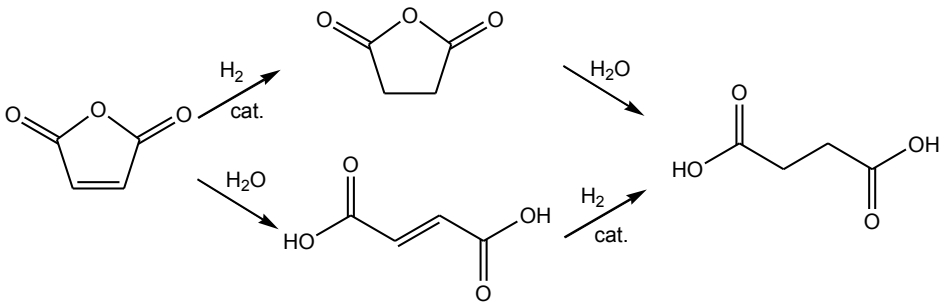


Figure 19 : Succinic acid synthesis from maleic anhydride (Delhomme 2011).

Nowadays, 1,4-butandiol (BDO) is industrially produced only from fossil resources (Mueller *et al.* 1989, Tanabe *et al.* 1977, Weitz *et al.* 1982, Fischer *et al.* 1999). It is involved in the production of many other polymers, such as polyurethanes or polyethers. Nevertheless, BDO has the potential of being bio-based because it is produced from molecules which could be produced from succinic acid (Yim *et al.* 2011).

7.1. Synthesis

Direct reaction between succinic acid and BDO is the simplest way to produce PBS. The polymerisation reaction is a two-step process (Figure 16). First, an esterification reaction occurs in a range of temperature between 150 and 200 °C. Then, the polycondensation reaction under vacuum at high temperature (220-240°C) consists in a transesterification releasing methanol (Xu *et al.* 2010a, Zeikus *et al.* 1999). Reaction catalysts and other ways of synthesis have also been investigated (Jacquel *et al.* 2011, Garin 2012).

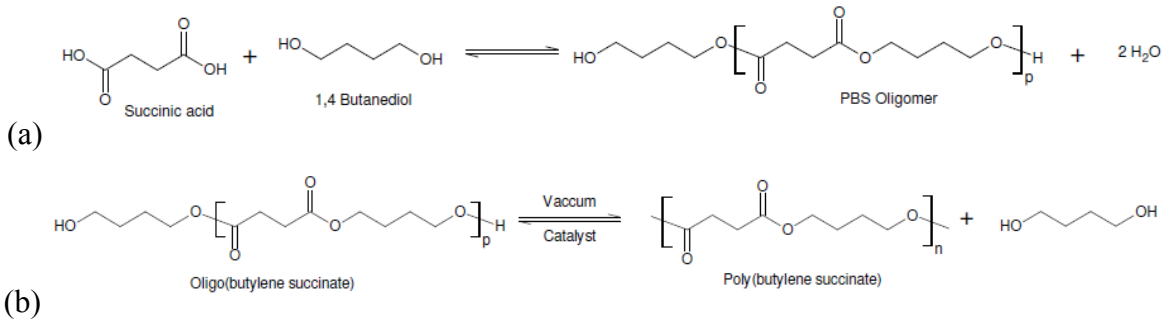


Figure 20 : PBS synthesis from direct reaction of succinic acid and BDO (a) esterification, (b) transesterification (Jacquel et al. 2011).

7.2. Properties of PBS

In comparison to PLA, PBS has a much more flexible structure (glass transition temperature of -32°C) and shows a higher toughness (Tachibana *et al.* 2010). Properties of PBS are influenced by the molecular mass and crystallinity. In general, it has a good resistance in trension (Gigli *et al.* 2016). Its fusion temperature is around 115°C depending on the DP (Garin 2012, Yoo *et al.* 1999). PBS has a better thermal stability than PLA (Georgousopoulou *et al.* 2016). Thermal degradation starts around 260°C and involves chain scission reactions, but significant degradation occurs at ca. 390°C. Thermo-oxidation occurs in the range of 170°C, involving a significant reduction of DP (Rizzarelli *et al.* 2009). Similarly to PLA, PBS is susceptible to hydrolysis due to the ester linkage (Gigli *et al.* 2016, Phua *et al.* 2011, Kim *et al.* 2008). Amorphous PBS is more sensitive to hydrolytic degradation because water can diffuse more easily than in crystalline PBS (Garin 2012, Yoo *et al.* 1999).

7.3. Use of PBS for wood modification

The use of PBS oligomers (OBS) for wood stabilization has been considered before (Noël *et al.* 2015a, 2015b). Noël *et al.* managed the impregnation modification of wood with OBS, with a major DP of 15 and decreasing amount of chains up to DP50. Because smaller oligomers could not be produced, the impregnation had to be achieved at 90°C with the solid wax-like OBS mixture in order to reduce enough the treatment viscosity. Even at this temperature, oligomers diffusion in wood cell wall was not observed. Because there was no interaction between the oligomers and the cell wall components, no anti-swelling efficiency was noticed, as well as no influence on mechanical properties. Wood acidity was also not impacted. However, a good retention of the oligomers into the wood lumen was observed, with only ca. 20% loss of the impregnated polymers during water leaching. The OBS lumen-filling treatment also allowed a substantial decrease of the wood hygroscopicity, and no undesirable increase in hydrophilicity at high relative humidity, as it was observed with PLA treatment. It was observed that the water leaching stage did allow a partial penetration of the oligomers into the cell wall suggesting that water was able to swell the cell wall and induce the shorter oligomers diffusion into the wall, conferring very promising ASE by doing so (ASE = 40%).

Carrying out the heating stage under wet conditions (saturated steam) is expected to help the diffusion of OBS into wood cell wall, thus to induce good anti-swelling efficiency. Moreover, because first pre-results indicated that a curing stage at higher temperature (160°C) leads to ASE values up to 55% according to heating duration, the combination of chemical impregnation with thermo-treatment step that would modify wood components and induce the *in situ* polymerisation simultaneously, seems to be very promising. For that reason, it would be of high scientific and technical interest to deeply investigate and develop an optimised treatment process with OBS, as this chemical revealed to confer both good dimensional stability to wood under certain conditions, and to avoid the usual severe decrease in mechanical properties observed with thermo-treatment performed at higher temperature, or chemical treatment in the presence of organic acid.

PART A: Wood modification with lactic acid

1. Process development

In this part, wood modification with lactic acid is approached on the basis of previous work from Noël *et al*. (2009a, 2009b, 2011). Wood was impregnated with lactic acid based products then heat treated to further polymerise the oligomers within the wood (Figure 21). Impregnation yield (IY) and weight percentage gain (WPG) indicate the amount of oligomers within the wood and swelling (S) and bulking coefficient (BC) are indicators for the product diffusion in the wood cell walls.

At first, only oligomeric treatments were considered. The reason was to produce a viscous but liquid OLA mixture in order to limit wood degradation during curing by decreasing acidity of the impregnation product, but keep an effective diffusion in the wood structure.

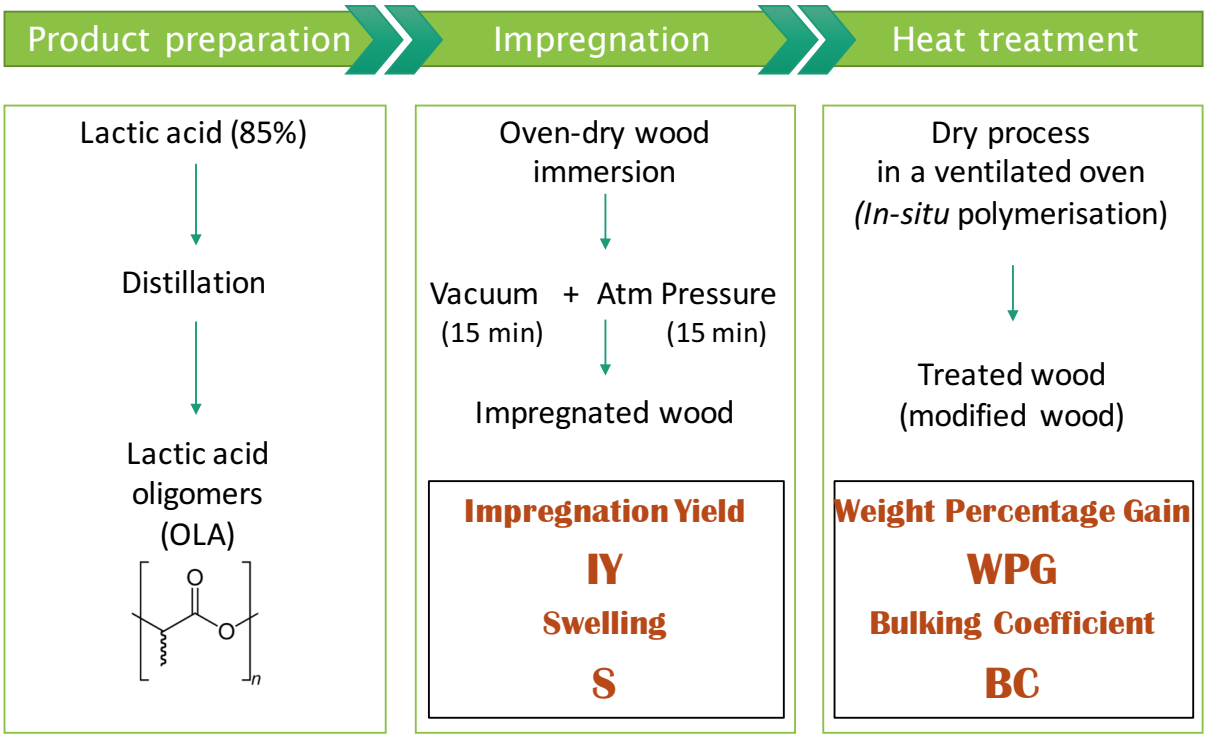


Figure 21 : Three steps process of wood modification with lactic acid oligomers.

LA curing temperature determines the extent of polymerisation (Harshe *et al.* 2007). Properties of OLA and further *in situ* polymerised OLA depend on their DP, especially their stability in moist environments (Södergard *et al.* 2002, Mahalle *et al.* 2014). First, the influence of heat treatment parameters (temperature and duration) on OLA curing and modified wood properties has been studied. Then, in order to approach more realistic treatment process conditions, the influence of water and humidity in different steps of the process was evaluated for the best performing variants. Finally, additives were considered for improvement of particular properties of modified wood: tannins for biological resistance and maleic anhydride for OLA

fixation. The results were presented in four deferent papers listed below. An overview of materials and methods of the four papers presented in this chapter is given in Table 3.

Paper 1: Optimizing wood chemical modification with oligomeric lactic acid by screening of processing conditions (Grosse *et al.* 2018a, submitted in: *J. Wood Chem. Technol.*).

Paper 2: Influence of water and humidity on wood modification with lactic acid (Grosse *et al.* 2017, published in: *J. Renew. Mat.*)

Paper 3: Optimizing wood chemical modification with lactic acid oligomers by screening of processing conditions and chemical additives (Grosse *et al.* 2016, in: *proceedings of IRG WP 47*).

Paper 4: Improvement of modified wood properties with addition of chestnut tannins in lactic acid based treatments (Grosse *et al.* 2018b, accepted in: *J. Wood Chem. Technol*.).

Table 3 : Overview of materials and methods of the four papers presented in this chapter.

Materials and Methods			**Characterisation of…**	**Paper**
Infrared Spectroscopy	FTIR ATR	Solid wood and Oligomers	OLA polymerisation	1
	FTIR ATR Golden Gate	Solid wood and Oligomers	OLA polymerisation kinetic	1
Chromatography	GPC	Oligomers and Extracted oligomers	OLA molecular mass repartition	1
Thermo gravimetric analysis	Isotherms at curing temperature	Impregnated wood	OLA polymerisation kinetic	1
Anti-swelling efficiency	Stabilisation at ca. 100% RH at 23°C	Solid wood (15x15x10 mm^3)	Treatment efficiency Wood dimensional stability	1 to 4
Equilibrium moisture content	Stabilisation at ca. 100% RH at 23°C		Treatment efficiency Wood sorption behaviour	1 to 4
Short water leaching	NF X 41-569	Solid wood (15x5x25 mm^3)	Treatment persistence OLA fixation within the wood.	1,3
	EN84	Solid wood (25x15x50 mm^3)		2, 4
Long water leaching	3 weeks immersion in water at 23°C	Solid wood (15x15x10 mm^3)	Polymer stability Influence of hydrolysis	1,3
Fungal exposure	Screening test	Solid wood (15x5x25 mm^3)	Treatment efficiency Biological resistance	1,3
	EN113	Solid wood (25x15x50 mm^3)		2, 4

1.1. Influence of heat treatment parameters

This part reports the systematic characterisation of wood treated with lactic acid oligomers under varying conditions of heat treatment (Table 4). Selection of the best treatment is done regarding the modified wood property enhancements (dimensional stability and decay resistance), and treatment persistence in wood. The extent of OLA polymerisation achieved out of and within the wood has been studied by Fourier Transform Infra-Red (FTIR) spectroscopy and thermogravimetric analysis (TGA).

1.1.1. OLA diffusion

Beech (*Fagus s.*) sapwood samples of 15x15x10 mm^3 (RxTxL) were prepared as described by Noël *et al.* (2015b). Oven-dried (103°C – 48h) samples were immersed in liquid oligomers at 20°C. Containers were then placed in a vacuum oven under reduced pressure (150 mbar) for 20 to 30 min, then atmospheric pressure over 20 to 30 min. Impregnated samples were then wiped.

Weight uptake (WU_i) and swelling (S_i) after impregnation have been calculated according to Eq.8 and Eq.9. The WUi corresponds to the IY often used in the literature (Hill, 2006).

$$IY = WU_i\ (\%) = \frac{w_i - w_{u,d}}{w_{u,d}} \times 100 \qquad \text{Eq.8}$$

$$S_i\ (\%) = \frac{V_i - V_{u,d}}{V_{u,d}} \times 100 \qquad \text{Eq.9}$$

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 dry weight and volume.

Weight uptake (WU_t) and swelling (S_t) after complete treatment respectively correspond to the WPG and the BC often used in the literature (Hill, 2006) and were calculated as followed:

$$WPG = WU_t\ (\%) = \frac{w_{t,d} - w_{u,d}}{w_{u,d}} \times 100 \qquad \text{Eq.10}$$

$$BC = S_t\ (\%) = \frac{V_{t,d} - V_{u,d}}{V_{u,d}} \times 100 \qquad \text{Eq.11}$$

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

Table 4 summarises the wood physical properties during treatment: weight uptake and swelling after impregnation and after complete treatment. After impregnation, WU_i is similar for treatments T1 to T7 since the same impregnation process was used. In all cases, less than 1% swelling is observed, showing that the product does not penetrate the cell wall at this stage. As shown in Table 4 (T1 to T4) the temperature shows a limited influence on S_t between 120°C and 140°C and S_t decreases with the temperature increase above 140°C. Shrinkage was observed with heated references treated above 160°C (T10). However, it is not enough to be the only reason for about 15% decrease of impregnated wood swelling after curing.

Table 4 : Heat treatment conditions and mean values on 10 replicates of weight uptake after impregnation (WU_i), swelling due to impregnation (S_i), weight uptake after curing (WU_t) and swelling after curing (S_t) of samples treated according to treatments T1 to T10.

N°	Treatment conditions			Wood physical properties			
	Product	Temperature (°C)	Duration (h)	WU_i (%)	S_i (%)	WU_t (%)	S_t (%)
T1	OLA	120	48	73.2± 1.9	0.3± 0.1	47.5± 0.9	19.2± 0.8
T2		140	48	70.2± 2.0	0.2± 0.2	47.4± 2.1	22.5± 0.6
T3		160	48	67.1± 4.3	0.8± 0.1	28.7± 1.8	15.3± 0.8
T4		180	48	74.8± 2.8	0.6± 0.2	15.9± 0.8	5.4± 0.3
T5		140	72	72.7± 3.8	0.3± 0.2	26.5± 1.2	17.8± 0.9
T6		140	96	70.6± 5.0	0.7± 0.1	23.8± 1.4	14.7± 0.5
T7		140	120	69.3± 4.3	0.5± 0.2	22.2± 1.1	13.8±0.8
T8	None	120	48	-	-	0.1± 0.1	0.0± 0.2
T9		140	48	-	-	-0.1± 0.1	0.03± 0.2
T10		160	48	-	-	-2.4± 0.1	-1.8± 0.1

Two hypotheses are formulated to explain lower samples swelling after heat treatment at higher temperature:

- Fewer oligomers penetrate the cell walls because above 160°C the polymerisation kinetics is too fast to allow the oligomers diffusion to the cell walls. In this case oligomers polymerise in the lumen.

- Or the oligomers penetrate the cell walls but the extended further polymerisation leads to a shrinkage of the oligomers in wood and subsequent cell wall shrinkage. OLA polymerisation at 160°C for 48h in a graduated cylinder showed 16.7 % shrinkage of the polymer when cooling down to 23°C.

To challenge the second hypothesis, a heat treatment at 140°C for 48h (S_{t1} = ca. 22%) was followed by a second step at 160°C for 48h (S_{t2} = ca. 17%). The shrinkage observe after the second step is consistent with the idea that OLA diffuse in the cell walls also at 160°C but that the swelling measured smaller because of the polymer shrinkage within the wood structure.

Moreover, transversal sections of untreated (Figure 22) and treated (Figure 23 and Figure 24) samples were observed with light microscope (Leica, DM750 M) directly after treatment. Dry samples surface was planned with a blade. Usual pre-treatment for microscopy samples preparation were avoided on purpose to ensure persistence of the oligomers in the wood structure. Cell walls swelling is observed after treatment at 140°C (Figure 23) and 160°C (Figure 24) and no significant difference can be noticed regarding the diffusion of OLA to the wood structure during curing. This observation is consistent with the second hypothesis. Reduction of swelling at higher temperature is most likely due to the shrinkage of oligomers within the cell walls when cooling.

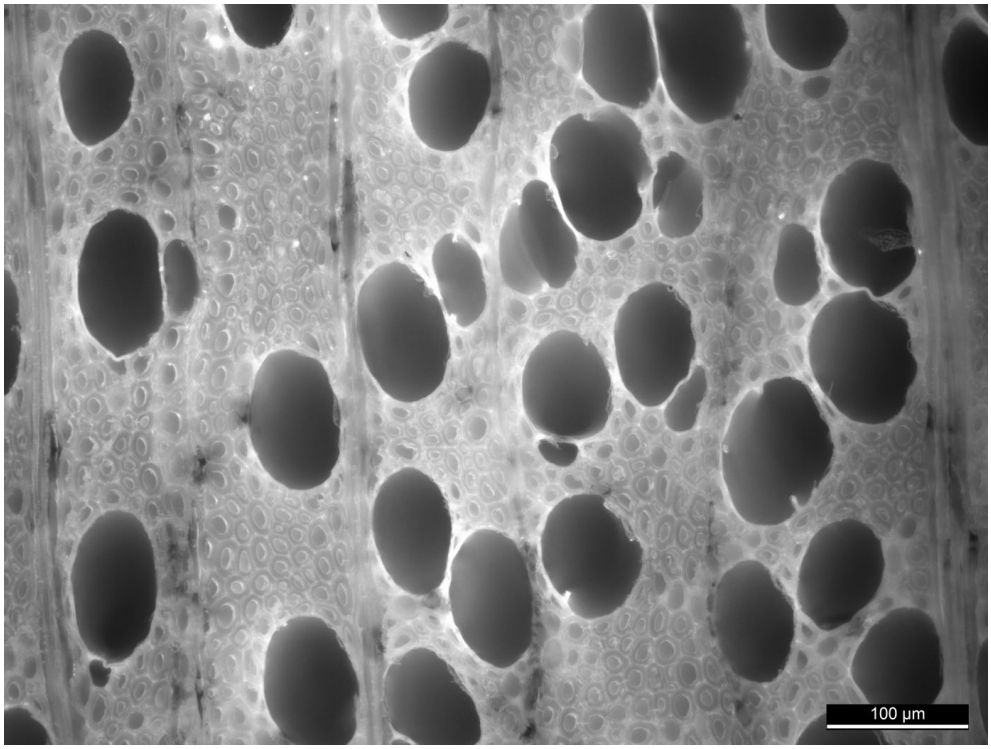


Figure 22 : Transversal section of untreated wood.

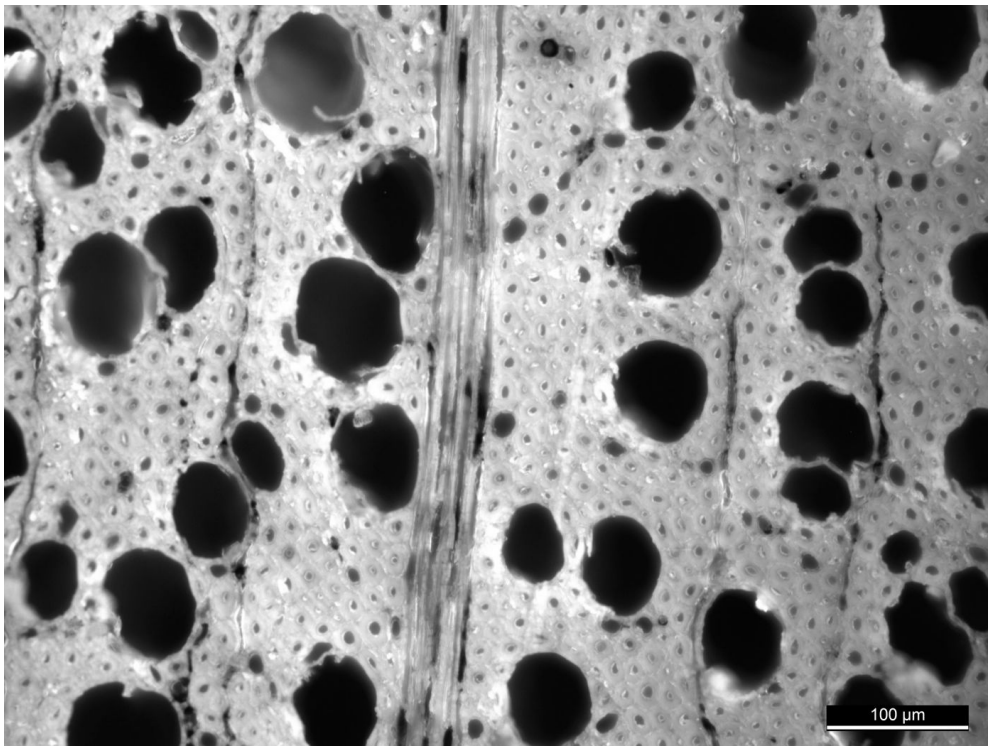


Figure 23 : Transversal section of treated wood after T2 treatment.

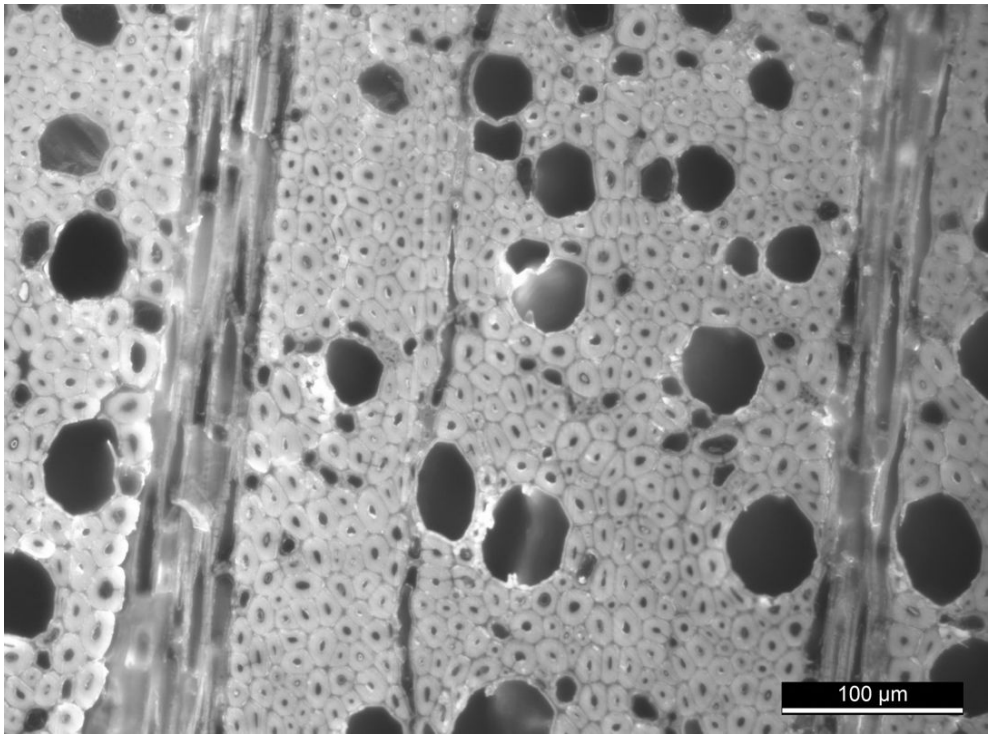


Figure 24 : Transversal section of treated wood after T3 treatment.

1.1.2. OLA polymerisation and modified wood properties

LA curing temperature determines the extent of polymerisation (Harshe *et al.* 2007). Properties of OLA and further *in situ* polymerised OLA depend on their DP, especially their stability in moist environment (Södergard *et al.* 2002, Mahalle *et al.* 2014). The influence of heat treatment parameters (temperature and duration) on OLA curing and modified wood properties has been studied. The effect of temperature and time on the extend of OLA cure was determined by Gas Permeation Chromatography (GPC), Fourier Transformed Infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). Dimensional stability of modified wood was examined by swelling and hygroscopicity measurements, and decay resistance by laboratory biological resistance evaluation.

The results are presented in details in **Paper 1:** Optimizing wood chemical modification with oligomeric lactic acid by screening of processing conditions (Grosse *et al.* 2018a, submitted in: *J. Wood Chem. Technol.*).

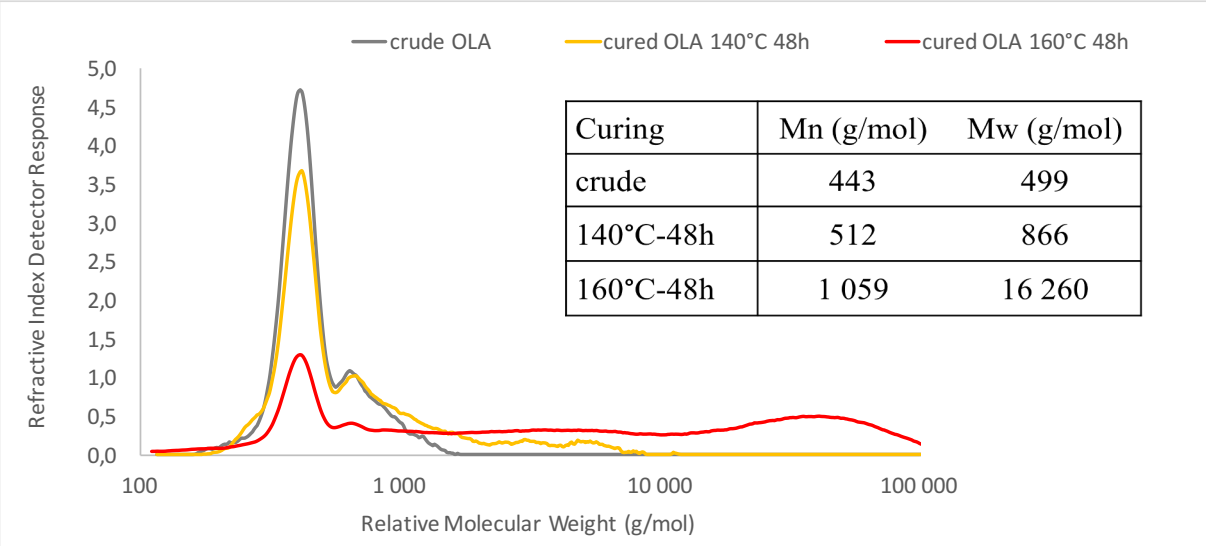
The heating step temperature and duration determine the polymerisation advancement - by increasing the temperature, longer oligomers are obtained - but also impact the wood polymers degradation.

Out of wood, a curing at 140°C for 48 h does not lead to substantial increases in OLA average molecular weight compared to curing at 160°C at a similar time. At 160°C, OLA curing is more effective than at 140°C as similar increases to OLA average molecular weight were obtained after 2h at 160°C. Relative molecular weight distributions of products are shown in Figure 25.

During curing at 160°C for 48h, oligomer chains up to 100 000 g.mol^{-1} were created. However, there appeared a significant portion of OLA which did not significantly polymerize even after 48 h at 160°C. The main component of the cured OLA remains the raw oligomers which were present in the crude OLA product.

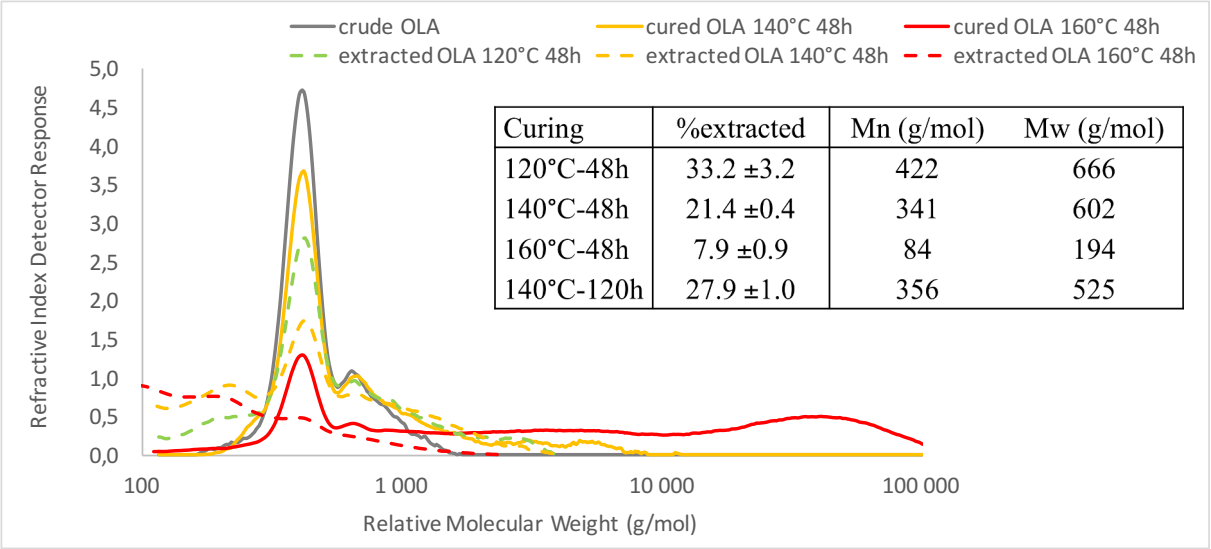
The relative molecular weight distributions of OLA products extracted from treated wood are shown in Figure 26. This reveals the average molecular weight of the solubilized, extracted products were relatively lower than for the OLA oligomer products cured outside of wood when curing below 160°C. Whereas the molecular weight of extracted products was significantly lower when curing at 160°C. However, it is also recognized the extracted products from OLA modified wood is not representative of what cannot be extracted. Physical retention of long oligomers is possible together with OLA products which are chemically bounded with wood polymers may not be extractable in this extraction process. Moreover, it is also possible that the very long oligomers shown in Figure 25 were not able to dissolve into the solvent during their extraction from wood.

In respect to temperature and duration of OLA treatments, the main component of extracted, cured oligomers from treated wood remained the raw oligomers from the crude product. This was particularly the case for the two lower temperature treatments (120°C and 140°C). Even though extended *in situ* polymerisation was evidenced by the presence of OLA oligomers longer than those from the impregnation product, it appeared impregnated OLA only partially reacts (Figure 25). At 160°C, neither small nor large OLA oligomers dominate the extracted products removed from the treated wood. This may imply an effective fixation and higher degree of OLA *in situ* polymerisation was achieved at this higher curing temperature. For curing time, a longer heat treatment at 140°C do not lead to significant extension of OLA polymerisation (Figure 26). Moreover, the extended curing times may also be disadvantageous as depolymerisation may also be promoted by the high acidity of the treated wood.



Curing	Mn (g/mol)	Mw (g/mol)
crude	443	499
140°C-48h	512	866
160°C-48h	1 059	16 260

Figure 25 : Relative molecular weight distribution, number average molecular weight (Mn) and weight average molecular weight (Mw) of oligomers produced from OLA.



Curing	%extracted	Mn (g/mol)	Mw (g/mol)
120°C-48h	33.2 ±3.2	422	666
140°C-48h	21.4 ±0.4	341	602
160°C-48h	7.9 ±0.9	84	194
140°C-120h	27.9 ±1.0	356	525

Figure 26 : Relative molecular weight distribution of oligomers cured out of wood and extracted from treated wood, percentage of oligomers extracted (%extracted), number average molecular weight (Mn) and weight average molecular weight (Mw) of extracted oligomers.

Temperature has a significant influence on the modified wood hygroscopic behaviour which could be either due to a more extended *in situ* polymerisation or wood polymers partial degradation.

For the two most common examples of commercial wood modification processes (acetylation and furfurylation), the WPG can be representative of the level of modification and an indicator of the treatment efficiency. In the case of acetylation, a WPG of 28.6% leads to an ASE* of ca. 66% when a WPG of 13.6% leads to an ASE* of ca. 38%. Similary to acetylated wood, furfurylated wood ASE* decreases with WPG decrease (Thybring, 2013). In the case of OLA treated wood, WPG and ASE* are not correlated. On the one hand, ASE* of ca. 65% is constantly reached for all curing temperatures, when on the other hand WPG significantly decreases with temperature increase (Figure 27). In contrast, the curing duration increase at 140°C demonstrate a negative influence on ASE* with gradual decrease from ca. 65% to ca. 50% after 120h and simultaneously with a WPG decrease, that might indicate wood polymers degradation by and extended reaction (Figure 27). The weight loss during heat treatment is due to three phenomena: wood polymers degradation (inducing a weight loss up to 4% at 180°C), OLA polymerisation (releasing water) and the smallest oligomers and monomers evaporation (lactic acid has a boiling temperature of 122°C).

In comparison to acetylated wood (ASE* of 38% for a WU_t of 13.6% and ASE* of 66% for a WU_t of 28.6% (Thybring, 2013)), the OLA treatment undertaken here performed promisingly, especially the treatments at 160°C and 180°C. The strong influence of curing temperature on modified wood moisture content (Figure 28 : Reduced moisture content development in time at ca. 100% RH) could be due to an extended *in situ* polymerisation or that wood polymers partially degrade. The curing temperature also had a strong influence on the hygroscopic behaviour of the heated reference samples. Their EMC decreased to 23% after curing at 160°C/48h, for ASE values up to 17%.

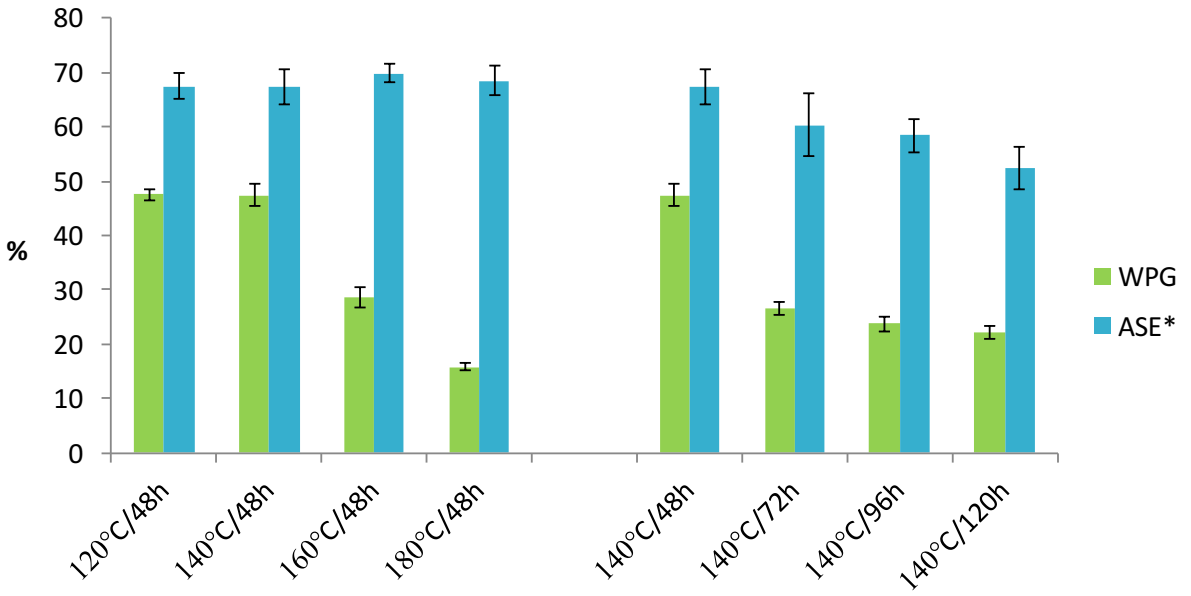


Figure 27 : Average samples Weight Percent Gain (WPG) and corrected Anti-Swelling Efficiency (ASE) of treatments.*

A possible explanation of the stable ASE* despite decreasing EMC_R may be due to micro-cracks occurring in cell walls during treatment and creating free spaces for water to penetrate without impacting the dimensions. Such cell wall degradation due to *in situ* polymerization treatments was observed by Noël *et al.* (2015). Moreover, another explanation is shown in Figure 28 : Reduced moisture content development in time at ca. 100% RH, where moisture content of wood treated at 120°C and 140°C was unstable after 500h of exposure to ca. 100% RH. This may indicate a possible oligomers hydrolysis, increasing the relative hydrophilicity of the treated wood. As the cell walls are saturated, no additional swelling is observed which explains the similar ASE* values for treatments carried out at higher temperature despite their substantial increases in moisture content. In addition, Figure 28 : Reduced moisture content development in time at ca. 100% RHshows a longer curing time at 140°C has no impact on moisture uptake development with time of treated wood samples. If a longer heat treatment at 140°C resulted in extended polymerisation, then treatment at 140°C for 120h would be expected to be more stable than one at 160°C for 48h. Therefore, a high temperature (160°C) is needed to stabilise OLA within the wood structure.

OLA treatment provides a significant biological resistance to wood, due to the combined action of the oligomers impregnation and the heat treatment.

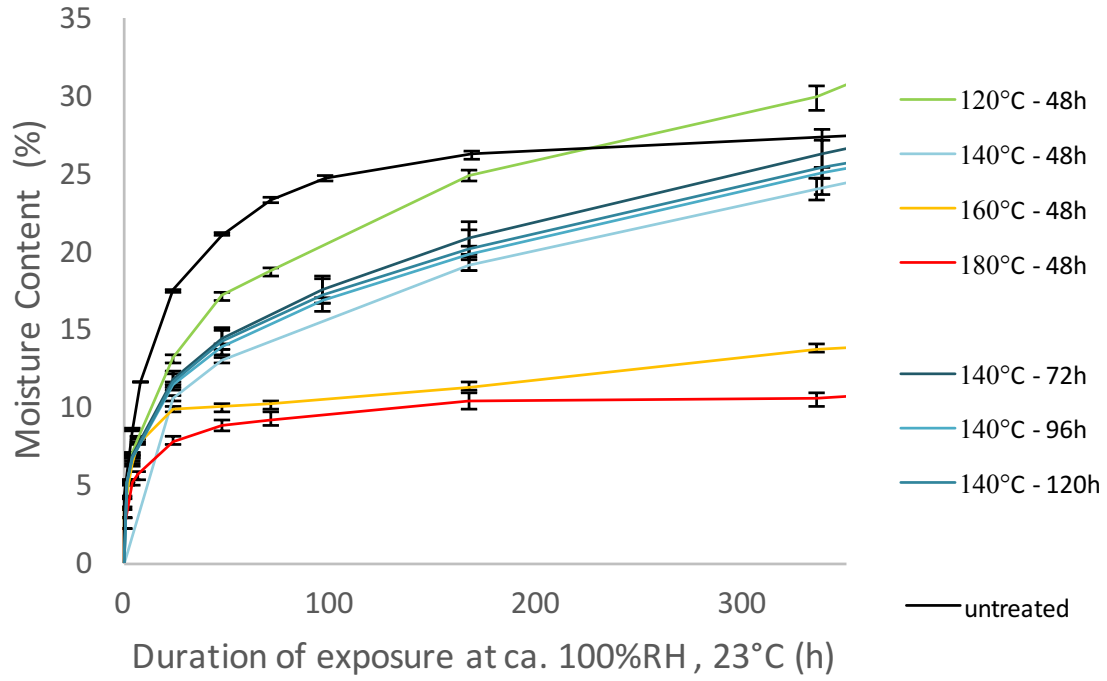


Figure 28 : Reduced moisture content development in time at ca. 100% RH

1.1.3. OLA fixation in wood

OLA polymerisation degree can also influence the product persistence in wood. Because the modified wood developed should not release product during its service life, the water leaching resistance of the treatment should be evaluated.

Wood thermal degradation is more intense at high temperature and generates water soluble products like acetic and formic acids (Chaouch *et al.* 2013, Altgen *et al*. 2016). Consequently, the %leached of heated references (T9 to T11) increased with temperature of heat treatment (Table 5). However, %leached did not increase with temperature for the modified wood. Long term leaching shows that an increase in temperature improves significantly the OLA persistence in wood. Increase in temperature or in duration of heat treatment is expected to lead to an extended in-situ polymerisation. The extended polymerisation is in turn expected to lead to better fixation of the product within the wood structure.

At temperature below 160°C, wood polymers should not be significantly affected by heat treatment (Chaouch *et al.* 2010, Werner *et al*. 2014, Yang *et al.* 2007, Shen *et al*. 2010, Heigenmoser *et al.* 2013, Grønli *et al*. 2002), but acidic conditions due to OLA impregnation could catalyse degradation reactions of wood polymers during heat treatment and make them possible even below 160°C. Tjeerdsma *et al.* (1998) suggested that products from wood thermal degradation re-condensate within wood with remaining wood polymers. Additionally, they could interact with OLA. Both processes would lead to hold them back within the wood and this could explain lower $\%leached_{31h}$ for modified wood (T3 and T4) than for heated references (T10 and T11). Fixation of OLA within the wood structure could also be due to physical entanglement because of extended polymerisation. OLA matrix might mechanically retain

wood thermal degradation products in wood, with resulting lower $\%leached_{31h}$ for modified wood than for heated references at high temperatures.

The gap between short and long-term leaching values raises the question of OLA hydrolysis in time, especially for low temperatures. Two phenomena are involved in OLA degradation. First, hydrolysis of ester bonds causes an increase of the number of carboxylic chain ends which autocatalyse the hydrolysis reaction. Second, some oligomers could become soluble in water and be leached out (Södergard *et al.* 2002). Leaching is most likely easier in the outer layers of the modified wood. Then degradation of OLA could be more advanced in the core of the samples because of the autocatalyse effect from the smaller oligomers (Grizzi *et al.* 1995). If OLA is initially less polymerised because of the low curing temperature, leachable oligomers represent most likely a higher percentage.

Table 5 : Mean values on 5 to 12 replicates of OLA persistence ($\%leached_{504h}$ and $\%leached_{31h}$) for samples treated according to treatments T1 to T7.

N°	Treatment conditions			OLA persistence	
	Product	**Temperature [°C]**	**Duration [h]**	**$\%leached_{31h}$**	**$\%leached_{504h}$**
T1	OLA	120	48	6.3± 0.1	29.2± 1.3
T2		140	48	4.1± 0.2	7.3± 0.04
T3		160	48	1.2± 0.2	5.0± 1.2
T4		180	48	5.0± 0.2	5.7± 1.0
T5		140	72	-	12.2± 1.2
T6		140	96	-	12.4± 0.7
T7		140	120	-	10.7± 2.0
T9	None	140	48	1.2± 0.2	1.9± 0.03
T10		160	48	2.5± 0.1	5.9± 0.1
T11		180	48	7.4± 0.3	-

1.1.4. Conclusion

OLA treatment is easy to impregnate in beech wood, with no dilution necessary, no pressure needed and at room temperature. Oligomers diffuse and polymerise in the cell wall only during heat treatment. This heating step temperature and duration define the polymerisation advancement, but also impact the wood polymers degradation. Temperature has a significant influence on the modified wood hygroscopic behaviour which could be either due to a more extended *in situ* polymerisation and wood hemicelluloses partial degradation. At 140°C the influence of the duration is not significant on %leached. OLA treatment provides a significant biological resistance to wood (Grosse *et al.* 2018a), due to the combined action of the oligomers impregnation and the heat treatment. OLA treatment persistence has been increased compared to Noël *et al.* (2009a) and curing at higher temperature (160°C) decreases significantly OLA %leached.

1.2. Influence of water and humidity in the process

Evaluation of wood treatment with OLA at 160°C following a dry process gives very promising insight for a further development as modified wood for outdoors applications. However, in industrial conditions, wood logs are never dried to the anhydrous state before treatment for most common applications (impregnation or heat treatment). Moreover, wood drying induces additional costs, duration and storage capacity to the process.

For wood thermal treatment, steam is usually used to convey heat. Thermal modification of wood is often carried out under saturated vapour in order to avoid cracks and mechanical properties decrease (Altgen *et al*. 2016, Cheng *et al*. 2007).

For those reasons, influence of water in the system during every step of the treatment process should be investigated to evaluate how water interferes with the process. This chapter reports three approaches where water might be present in the process: (1) utilisation of non-dried wood samples before impregnation (12%MC OLA, 32%MC OLA), (2) OLA water dilution (simulating repeated impregnation steps) (OLA50% and OLA25%), (3) curing under varying relative humidity (RH) (several combinations of temperature and RH). In comparison to the usual OLA treatment, performance of treatment carried out in presence of water is evaluated against ASE and MEE, leaching resistance according to EN84 and biological resistance according to EN113. The performance of wood directly impregnated with lactic acid was also evaluated (LA, 12%MC LA, 32%MC LA).

The results are presented in details in **Paper 2**: Influence of water and humidity on wood modification with lactic acid (Grosse *et al.* 2017, published in: *J. Renew. Mat.*).

Wood initial moisture content and OLA concentration in water have a major influence on treatment performance (Figure 29 : Influence of water in the process regarding the weight percentage gain (WPG), anti-swelling efficiency (ASE), weight loss after fungal exposure (WL) and treatment persistence (%leached).). The presence of water in wood before curing has an influence on wood biological resistance, dimensional stability and water leaching resistance. Modified wood obtained with the dry process performed better than the one obtained when water or humidity was introduced in the process. However, if heat treatment temperature is as high as 160°C, decrease of performance is not significant, especially regarding the biological resistance and ASE. While moisture serves as carrying agent of OLA/LA into wood structure by swelling the cell walls to help oligomers 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 performing well 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.

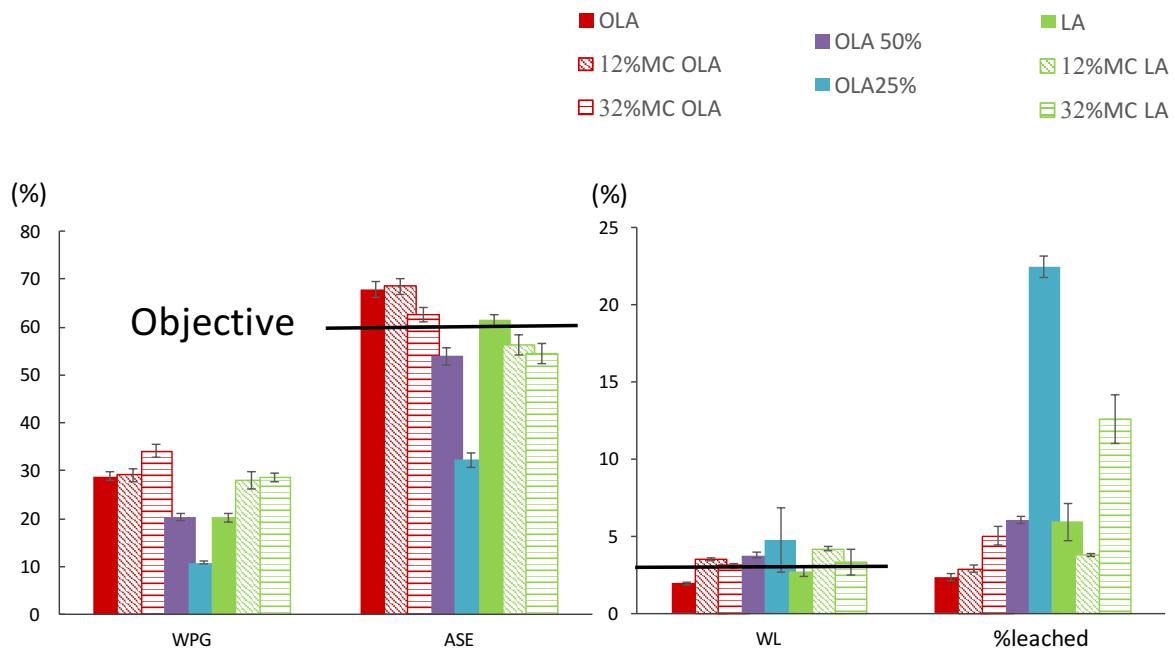


Figure 29 : Influence of water in the process regarding the weight percentage gain (WPG), anti-swelling efficiency (ASE), weight loss after fungal exposure (WL) and treatment persistence (%leached).

1.3. Treatment optimisation by screening of chemical additives

Additives were considered for the improvement of particular properties of the modified wood: hydrolysable and condensed tannins for the biological resistance and maleic anhydride, citric and tartaric acids for OLA fixation (Figure 30).

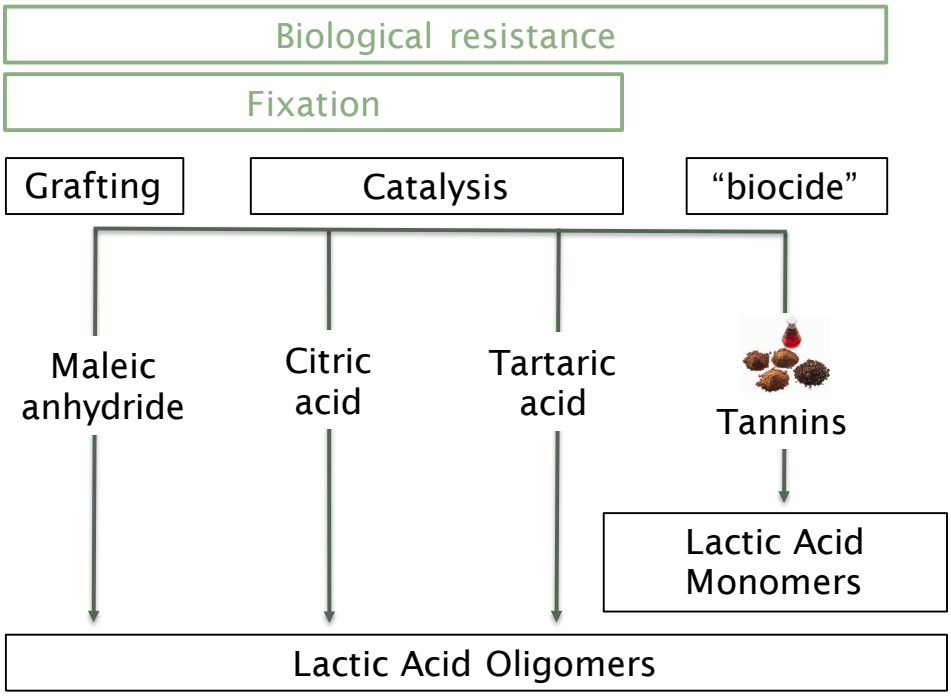


Figure 30 : Treatment optimisation by screening of chemical additives

1.3.1. Maleic anhydride and condensed tannins

The possible enhancement of performance thanks to maleic anhydride used as a grafting agent between OLA and the wood polymers was evaluated (M-OLA). The results were reported in **Paper 3:** Optimizing wood chemical modification with lactic acid oligomers by screening of processing conditions and chemical additives (Grosse *et al.* 2016, in: *proceedings of IRG WP 47*). The same global performances are observed with M-OLA, with an improvement for the persistence in the wood which is globally better for M-OLA than OLA, which confirms the relative efficiency of this approach.

1.3.2. Citric and tartaric acid

Citric and tartaric acids have been considered as potential catalysts of the polymerisation in wood during heat treatment. Because they are polyacids, their addition in the OLA mixture is expected to help OLA fixation by creating ramifications in oligomeric chains. Citric acid (CAc-OLA) or tartaric acid (TAc-OLA) have been added to OLA (1% w/w). They were progressively poured in the OLA mixture while stirring until complete dissolution.

The hygroscopic behaviour of modified wood is presented in Table 6. Citric and tartaric acids addition to OLA does not negatively impact the impregnation. However, none of the two acids improved performance of the modified wood.

Table 6 : Mean values on 10 replicates of weight uptake after impregnation (WU_i), swelling due to impregnation (S_i), weight uptake after curing (WU_t) and swelling after curing (S_t), and reduced equilibrium moisture content (EMC), reduced anti-swelling efficiency (ASE*) and reduced moisture exclusion efficiency (MEE*) of modified wood after 504h exposure at 100% RH at 23°C.*

Treatment	WU_i [%]	S_i [%]	WU_t [%]	S_t [%]	$EMC^*_{(504h)}$ [%]	$ASE^*_{(504h)}$ [%]	$MEE^*_{(504h)}$ [%]
OLA 140	64.5 ±1.9	0.3 ±0.2	33.1 ±1.5	16.0 ±0.9	16.3 ±0.2	61.1 ±3.2	39.4 ±0.7
OLA 160	60.0 ±1.0	0.0 ±0.2	28.9 ±1.0	15.7 ±0.8	13.8 ±0.2	67.8 ±1.8	48.6 ±0.7
CAc-OLA 140	65.3 ±1.8	0.3 ±0.3	38.5 ±1.3	18.9 ±0.4	18.5 ±0.4	54.3 ±1.9	31.1 ±03
TAc-OLA 140	64.0 ±3.6	-0.8 ±0.2	42.2 ±2.9	14.8 ±0.6	20.1 ±0.5	49.2 ±4.2	25.2 ±1.9

1.3.3. Condensed tannins (Mimosa tannins)

The possible enhancement of performance thanks to mimosa tannins or acetylated mimosa tannins added at 0.5, 5 or 15% in weight in the OLA mixture used as natural preservation agents was evaluated. The results were reported in **Paper 3:** Optimizing wood chemical modification with lactic acid oligomers by screening of processing conditions and chemical additives (Grosse *et al.* 2016, in: *proceedings of IRG WP 47*). Mimosa tannins addition showed interesting results but no significant durability increase was observed. Other sources of tannins should be investigated.

1.3.4. Hydrolysable tannins (Chestnut tree tannins)

The effect of Chestnut tree tannins addition on OLA modified wood biological resistance was assessed. The results were reported in **Paper 4**: Improvement of modified wood properties with addition of chestnut tannins in lactic acid based treatments (Grosse *et al.* 2018b, accepted in: *J. Wood Chem. Technol*.). Tannins addition is almost inconsequential with oligomeric based treatment but improved the monomeric based treatment. In this case, modified wood biological resistance and product persistence were increased.

1.4. Treatments selection

Treatment for wood modification with lactic acid was developed to enhance beech dimensional stability and biological resistance. Industrial implementation needs have been kept in mind at each step of the process development. Table 7 summarises the process parameters which were evaluated and indicates how they influence the modified wood properties in comparison to the best performing treatment, i.e. dry wood impregnated with OLA, followed by dry curing at 160°C for 48h (OLA 160).

OLA 160 allowed considerable improvement of beech properties regarding its hygroscopic behaviour and fungal resistance. According to the laboratory scale results, this treatment seems to be suitable for up-scaling evaluation. Wood can be impregnated at fibre saturation point or at a lower moisture content with no detrimental effect on modified wood properties.

The same treatment process using LA (LA 160) instead of OLA also appeared to be a candidate for up-scaling. It could avoid the pre-polymerisation step of the process and the diffusion of LA is more homogeneous than OLA in the length of long samples (Grosse *et al*. 2018b). However, LA modified wood performances are slightly lower than OLA modified wood.

Any of the additives used seem to allow a decrease in curing temperature (Grosse *et al*. 2016, Grosse *et al*. 2018b). However, addition of Chestnut tannins in LA (CT-LA 160) lead to performance similar to OLA modified wood (OLA 160).

Three variants were selected for processability and up-scaling: OLA 160, LA 160 and CT-LA 160. In the following, understanding of the OLA treatment wood protection mechanism is attempted with study of wood-OLA interactions and biological resistance mechanism (PART B), and processability of the material is investigated as well as process up-scaling (PART C).

Table 7 : Summary of treatment parameters influence on modified wood performances in comparison to OLA 160 treatment carried out on dry wood ((+): improvement; (-): detrimental; (=): no significant influence).

Treatment	EMC*$_{(504h)}$ [%]	ASE*$_{(504h)}$ [%]	MEE*$_{(504h)}$ [%]	%leached [%] (EN84)	Durability class (EN113)
OLA 160 Anhydrous wood	13.8 ±0.2	67.8 ±1.8	48.6 ±0.7	2.3 ±0.2	1
Influence of water and moisture in the process					
Wood initial moisture content for impregnation (up to 30%)	(=)	(=)	(=)	(=)	(=)
OLA 25% dilution in water	(=)	(=)	(=)	(=)	(-)
Curing in humid atmosphere (100% RH)	(-)	(-)	(-)	(-)	(-)
Influence of pre-polymerisation					
Impregnation with LA	(=)	(=)	(=)	(=)	(=)
Influence of chemical additives					
Maleic anhydride	(=)	(=)	(=)	(=)	(=)
Citric acid	(-)	(-)	(-)	(-)	(-)
Tartaric acid	(-)	(-)	(-)	(-)	(-)
Mimosa tannins	(=)	(=)	(=)	(-)	(-)
Chestnut tannins	(=)	(=)	(=)	(+)	(=)

2. Mechanism of wood protection

Because beech (*Fagus sylvatica*) was used for this wood modification process, one would expect that the modified wood would be more sensitive to white-rot (*Coriolus versicolor*) than brown-rot (*Coniophora puteana*). However, the weight loss after exposure to *C. puteana* was higher than after exposure to *C. versicolor* for similar virulence of both fungi with control samples (Grosse *et al.* 2018b). Furthermore, the modified wood resistance to *C. versicolor* is less affected by the treatment temperature than in the case of *C. puteana*.

Because PLA is a biodegradable polyester, one should consider that it can also be degraded by some of the stains used to evaluate wood biological resistance (Lee *et al.* 2014, Irbe *et al.* 2014). White and brown-rot have different wood degradation pattern and different enzymes (Schlosser *et al.* 1997, Schmidhalter *et al*. 1992). To better understand the mechanism of wood protection, the chemical changes occurring in the modified wood during exposure to *C. puteana* were monitored by FTIR-ATR spectroscopy.

The results are presented in **Paper 5**: FTIR-ATR monitoring of chemical changes of thermo-chemically modified beech wood degraded by brown-rot fungus (Grosse *et al*. 2018e, in: *proceedings of IRGWP 49*).

In this study, changes in modified wood chemistry following decay by brow-rot fungus were assessed by FTIR spectroscopy. Treated and untreated specimens were degraded according to the guidelines of EN 113 standard: after water leaching (EN84), samples were sterilized with gamma rays and consecutively exposed to *Coniophora puteana* for 16 weeks. Decay was assessed through weight loss: values for treated samples were in the range of 2.69% to 3.76% for modified wood and 29.7% for unmodified beech. The ratios of the areas of the lignin/carbohydrates FTIR peaks were determined before and after exposure. Analyse of the way of degradation of modified wood, in comparison with unmodified wood, shows the effect of treatment on fungi mode of action regarding the attack selectivity on modified wood components (lignin, carbohydrates and OLA).

Wood carbohydrates, as well as OLA, are decayed by *C. puteana*. However, OLA most likely postpone the cellulose degradation. In this way, OLA treatment may allow to maintain longer the wood mechanical properties. More research is being carried out on wood modification with OLA and treatment preservation mechanism.

PAPERS

Paper 1: Optimising chemical wood modification with oligomeric lactic acid by screening of processing conditions

Optimising chemical wood modification with oligomeric lactic acid by screening of processing conditions

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Abstract

When exposed to moisture, wood undergoes swelling and is susceptible to fungal degradation. Chemical modification via oligomeric lactic acid (OLA) treatment has been found to be a promising environmentally friendly solution to this disadvantage. In this study, wood was impregnated with OLA and then variously heat treated to polymerize the OLA *in-situ*. The effect of temperature and time on OLA cure and polymerization has been determined chemically. Dimensional stability was examined by water immersion and hygroscopicity measurements and biological decay resistance evaluated. OLA impregnation followed by heat treatment enhanced wood properties, with higher curing temperature at 160°C resulting in treated wood with greater dimensional stability and biological resistance.

Keywords: beech, chemical modification, lactic acid, curing, optimisation

1. Introduction

Despite being one of the main and best performing materials for construction and building industry, wood suffers two well-known limitations: its hygroscopicity impacting dimension stability; and in many applications its limited durability. As current concerns for environment protection and global sustainability encourage the use and development of natural, biodegradable and carbon sink materials, wood has an increasingly major role to play in global markets, particularly if these two drawbacks can be overcome. For these reasons, many methods for wood modification have and continue to be developed over the past decades. Most wood properties are determined by its chemical constitution [1]. In this way, wood modification often seeks to make changes at this level. Four main types of methods can be distinguished: chemical modification, thermal modification, surface modification and impregnation modification [1]. Acetylated wood is a typical example of commercial modified wood based on an active chemical treatment consisting of the esterification of wood hydroxyls groups with acetic anhydride [2]. Other similar treatments have also been made with other anhydrides, aldehydes or methylation reactions [2]. In terms of wood impregnation, the most common example is wood furfurylation which consists of monomeric furfuryl alcohol impregnation followed by its polymerization within the wood structure [3]. More recently a hybrid method has been developed by Noël *et al.* [4-6] using oligomeric lactic acid (OLA). The treatment includes a two-step process: bulk impregnation of OLA into wood and a subsequent *in situ* polymerization step performed by curing via thermally heating. These wood modifications have been investigated by Noël *et al.* under several aspects following different treatment methods [4-8].

For example, under chemical polymerization catalysis, the influence of heat treatment conditions at relatively low curing temperatures revealed the possibility to improve the polymerized product persistence in wood. The amount of product leached with water decreased from 90% for a curing at 120°C for 1 h to 20% when followed by a second, extended curing at 103°C [4, 5]. Because of promising 60% anti-swelling efficiency (ASE) at high humidity and some wood degradation can occur with some catalysts, a treatment with a longer stage at high temperature (120°C/6 h) was conducted without a chemical catalyst but led to 80% product leaching [6]. A combined analysis with size exclusion chromatography (SEC), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) revealed the molecular mass distribution of OLA oligomers solvent-extracted from wood after treatment showed *in situ* polymerization occurring, but was not sufficient to fix the OLA content in wood structure [7, 8]. This article reports the systematic characterization of wood treatments with oligomeric lactic acid under varying conditions of heating (temperature and duration). Oligomeric lactic acid polymerization was first studied without wood to determine any effects of temperature and time on OLA cure using FTIR-ATR spectroscopy and gel permeation chromatography (GPC). *In situ* polymerization within wood was then evaluated in conjunction with TGA and impregnated wood uptakes assessing the degree of OLA polymerization and that extractable from the modified wood. Treated wood performance also assessed the modified wood dimensional stability, decay resistance and treatment persistence in wood. An overall aim of this study is to find a range of curing conditions for *in situ* polymerization of OLA to ensured retention and efficacy of OLA as a sustainable modification treatment for wood.

2. Materials and methods

2.1. Materials

Wood samples (15x15x10 mm^3 and 15x5x25 mm^3, RxTxL) were cut from beech (*Fagus sylvatica L.*) (700 ±0.10 $kg.m^{-3}$) and oven-dried to constant weight prior to impregnation. L(+)-Lactic acid solution (≥ 85% w/w) was sourced from Sigma-Aldrich (Switzerland).

2.2. Oligomeric lactic acid (OLA) preparation and characterization

2.2.1. OLA preparation

OLA was prepared following the method described by Noël *et al*. [7]. Oligomeric polyesters were synthesized by their direct polymerization under vacuum, using a four-necked flask (500mL or 1L) fitted 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 (0.015MPa). The temperature was first gradually increased to 90°C as an initial distillation step of 1h. The initial oligomerisation step involved gradually increasing the temperature to 140°C for 2.5h.

2.2.2. FTIR-ATR Golden Bridge

FTIR spectra of OLA were recorded for samples during curing at 120°C, 140°C, 160°C and 180°C, using Perkin Elmer Frontier MIR system spectrometer, Specac Golden Gate and the attenuated total reflectance (ATR) method, at a resolution of 4 cm^{-1} in the range of 700 to 4000 cm^{-1}. First, the background was done at set temperature, and then liquid samples were placed on the diamond crystal of the ATR device. During the first hour, measurements have been made every 5 minutes, and then after 2h and 3h. For each sample, 32 scans were conducted and averaged. Mean spectrum were analysed using Spectrum software (Perkin Elmer).

2.2.3. Gel Permeation Chromatography (GPC)

OLA (ca. 1 g) was cured in open vials in an oven at 103°C (48 h), 140°C (48 h) and 160°C (6 h and 48 h). Vials were sealed directly after curing prior to analysis. Molecular weight (Mw) profiles of the original OLA oligomers and cured oligomers were evaluated by GPC using a Polymer Labs system and a mixed-C column (Polymer Labs). Elution was with chloroform solvent. All samples were dissolved in GPC solvent (40 mg/mL) and run on the GPC employing both refractive index (RI) and UV detectors. Molecular weight profiles were calculated according to polystyrene calibration standards.

2.3. Wood treatment

Wood samples were oven-dried at 103°C to constant weight prior to treatment. Samples untreated anhydrous weight and volume were measured ($w_{u,d}$ and $V_{u,d}$ respectively). As described by Noël *et al*. [6-8], wood samples were immersed in the pure OLA mixture, liquid 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 of product. Dry curing was carried out in a ventilated oven for temperatures from 120°C to 180°C for 48h (treatments T1 to T4 in the following), and for durations from 48h to 120h at 140°C (treatments T2 and T5 to T7 in the following).

2.4. OLA *in situ* polymerization

2.4.1. Weight variations

Weight uptakes and swelling after impregnation (WU_i and S_i) and after treatment (WU_t and S_t) were calculated according to Noël *et al*. [8] on a dry wood basis. The swelling characterizes the diffusion of oligomers into the cell walls. The weight uptake after curing (WU_t) represents the remaining oligomers weight in wood after heat treatment. Weight loss during curing (WL_c) was calculated as followed:

$$WL_c\ (\%) = \frac{w_i - w_{t,d}}{w_i - w_{u,d}} \times 100 \qquad (1)$$

where w_i , $w_{t,d}$, and $w_{u,d}$ stand for the impregnated, treated and untreated samples dry weight respectively.

2.4.2. Thermogravimetric analysis (TGA)

Weight losses due to OLA polymerization was also monitored with thermogravimetric analysis (TGA). Wood impregnated with OLA and not cured, from one wood sample, was exposed to a controlled thermo-treatment with a final temperature step under inert atmosphere (N_2). A Netzsch STA 449 F1 Jupiter, equipped with an autosampler with 20 sample positions and top-loading system with the balance in the bottom of the instrument, was used. Samples of initial mass of ca. 9 mg (±10%), were placed in concaves aluminium crucibles. Crucibles were then closed with a lid and 5 holes were made in the lid with a needle. For each temperature program, one run was made with 2 empty crucibles and used as correction file in the following. Furnace was pre-heated at 100°C. The temperature program used for TGA consists in a ramp of 10K/min from 45°C to the final temperature (120°C, 140°C or 160°C), and then 1 hour at final temperature.

2.4.3. Accelerated solvent extraction

Accelerated solvent extractions were carried out on treated wood samples (ca. 2 g, chipped samples) using a Dionex ASE 200 Accelerated Solvent Extractor. Two cycles were done with a 5-min heating step to 100°C followed by a 10-min static step at 100°C and 10 MPa in 100% chloroform. After extraction, residual samples were oven-dried (103°C) to constant weight. Molecular weight (Mw) profiles of extracted oligomers were evaluated by GPC using the method described above.

2.5. Anti-swelling efficiency (ASE)

ASE was measured following the method described by Noël *et al.* [6] on 10 replicates of 15x15x10 mm^3 (RxTxL). Treated samples were placed in a desiccator, partially filled with water to set RH at ca. 100%, at a constant temperature of 23°C. Samples volume was measured anhydrous before exposure and regularly until weight is stabilized, after 504h.
Swelling (S) of non-impregnated samples (references and heated references), was calculated as follows:

$$S\ (\%) = \frac{V_{100\%} - V_d}{V_d} \times 100 \qquad (2)$$

where V_d and $V_{100\%}$ stand for samples dry volume and volume after stabilisation at ca. 100% RH respectively. Comparison of the swelling of treated wood and untreated wood via ASE has been used to evaluate the treatment efficiency. For heated references, ASE was calculated as:

$$ASE\ (\%) = \frac{S_r - S}{S_r} \times 100 \qquad (3)$$

where S_r and S_t stand for the references and heated references swelling respectively.

Because OLA treatment pre-swell wood, it is important to deduct the volume increase from modification from the dry volume, to be able to compare ASE with other modification techniques [10]. Thus, for impregnated wood, the corrected ASE (ASE*) calculation was based on the corrected swelling calculation (S_t^*) according to Thybring [10]:

$$S_t^*\ (\%) = \frac{V_{t,100\%} - V_{t,d}}{V_{u,d}} \times 100 \qquad (4)$$

where $V_{t,100\%}$ stands for the treated sample volume after stabilisation at ca. 100% RH, $V_{t,d}$ for treated sample dry volume, $V_{u,d}$ for untreated sample dry volume.

2.6. Equilibrium moisture content (EMC)

Moisture content (MC) of non-impregnated but heated wood samples and the reduced MC of impregnated samples (MC*) have been determined on samples used for ASE determination. They are defined as follows in Eq.5 and Eq.6 [10]:

$$MC(\%) = \frac{w_{t,w} - w_{t,d}}{w_{t,d}} \times 100 \qquad (5)$$

$$MC^*(\%) = \frac{w_{t,w} - w_{t,d}}{w_{u,d}} \times 100 \qquad (6)$$

where $w_{t,w}$ stands for the wet treated sample weight, $w_{t,d}$ for treated sample dry weight, and $w_{u,d}$ for untreated sample dry weight. EMC and reduced EMC (EMC*) values were obtained after stabilization at ca. 100% RH.

2.7. Biological resistance

A preliminary determination of the conferred durability has been carried out according to an accelerated biological resistance screening test (according to the guidelines of Bravery [11]). Samples of dimensions 15x5x25 mm^3 (RxTxL), treated and leached according to the guidelines of the NF X 41-569 standard [12], were sterilized with gamma rays and consecutively placed in culture flasks on inoculated growing medium (40g malt and 20g agar/L) with *Coriolus versicolor* (L. Quelet, strain CTB 863A) for 6 weeks (at 22°C, 70% RH). Samples weight loss (WL) was determined as the ratio between the weight loss due to fungal exposure and the initial treated dry weight according to Eq. 7:

$$\mathrm{WL}\ (\%) = \frac{w_{t,l,d} - w_{t,exp,d}}{w_{t,l,d}} \times 100 \qquad (7)$$

where $w_{t,l,d}$ is the specimen weight after treatment, leaching and drying, and $w_{t,exp,d}$ is the treated specimen weight after exposure at dry state. The final MC of the samples in culture flasks at the end of exposure was calculated according to Eq. 5. A second exposure of selected samples has been carried out after the first exposure, according to the same procedure, starting from sterilization step, to evaluate the treatments long-term efficiency.

2.8. Leaching

2.8.1 Short-term leaching

Samples of dimensions 15x5x25 mm^3 (RxTxL) were leached according to the guidelines of NF X 41-569 standard [11]. The samples were immersed in water (5 volume water/1 of wood) at room constant temperature (23°C) and with constant shaking, in separated containers according to the treatment. Three immersion periods of 1h, 2h and 4h were followed by an air-drying period of 16h and then two more immersion periods of 8h and 16h. The water was changed between each immersion period. The immersion was stopped after the 5^{th} period (31h of immersion in total), and samples were air-dried for 2h before oven-drying at 103°C until stabilization of the weight. The leaching rate was calculated according to Eq. 8 and will be labelled $\%leached_{31h}$ in the following:

$$\%\mathrm{leached} = \frac{w_{t,d} - w_{t,l,d}}{w_{t,d} - w_{u,d}} \times 100 \qquad (8)$$

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

2.8.2 Long-term leaching

Treated samples (15x15x10 mm^3, TxRxL) were immersed in water at room constant temperature (23°C) for *ca.* 500 hours, in separated containers according to the treatment procedure undergone by the samples. The %leached was calculated according to Eq. 8, and will be labelled $\%leached_{504h}$ in the following.

3. Results and Discussion

3.1. OLA polymerization

3.1.1. OLA polymerization out of wood

Fourier transform infrared (FTIR) spectra of OLA samples after 3h curing at 120°C, 140°C, 160°C and 180°C, are shown Figure 1. Key peaks in the fingerprint region are assigned [4, 13-15]: 1738/1748 cm^{-1} (a) for C=O stretching, 1185 cm^{-1} (b) for C-O *sym* stretching, 1122 cm^{-1} (c) for C-O stretching, 1086 cm^{-1} (d) for C-O-C stretching and 1041 cm^{-1} (e) for C-O *anti-sym* stretching. Significant changes in IR spectra can be seen after curing for 3h, showing OLA polymerization, the extent of OLA polymerization and a temperature dependence. The C-O peak intensity decreases and the C=O stretching peak (a) was shifted to a higher wavenumber showing ester formation on OLA polymerization [4]. Furthermore, the carbonyl band *ca.* 1738 cm^{-1} reduces after curing indicating the acid groups are disappearing to the benefit of ester groups resulting from OLA polymerization. All these described changes in spectra are more pronounced for the higher temperatures employed (Figure 1) and also occur at shorter timeframes (Figure 2). For example, during the first hour, spectra (at 5 min intervals) reveal greater changes to OLA observed with an increase in temperature. This suggests for the same wood treatment impregnation uptake and duration, the degree of OLA polymerization will most likely be greater with higher temperature. This suggests a possible reduction of OLA curing time within wood using higher temperature.

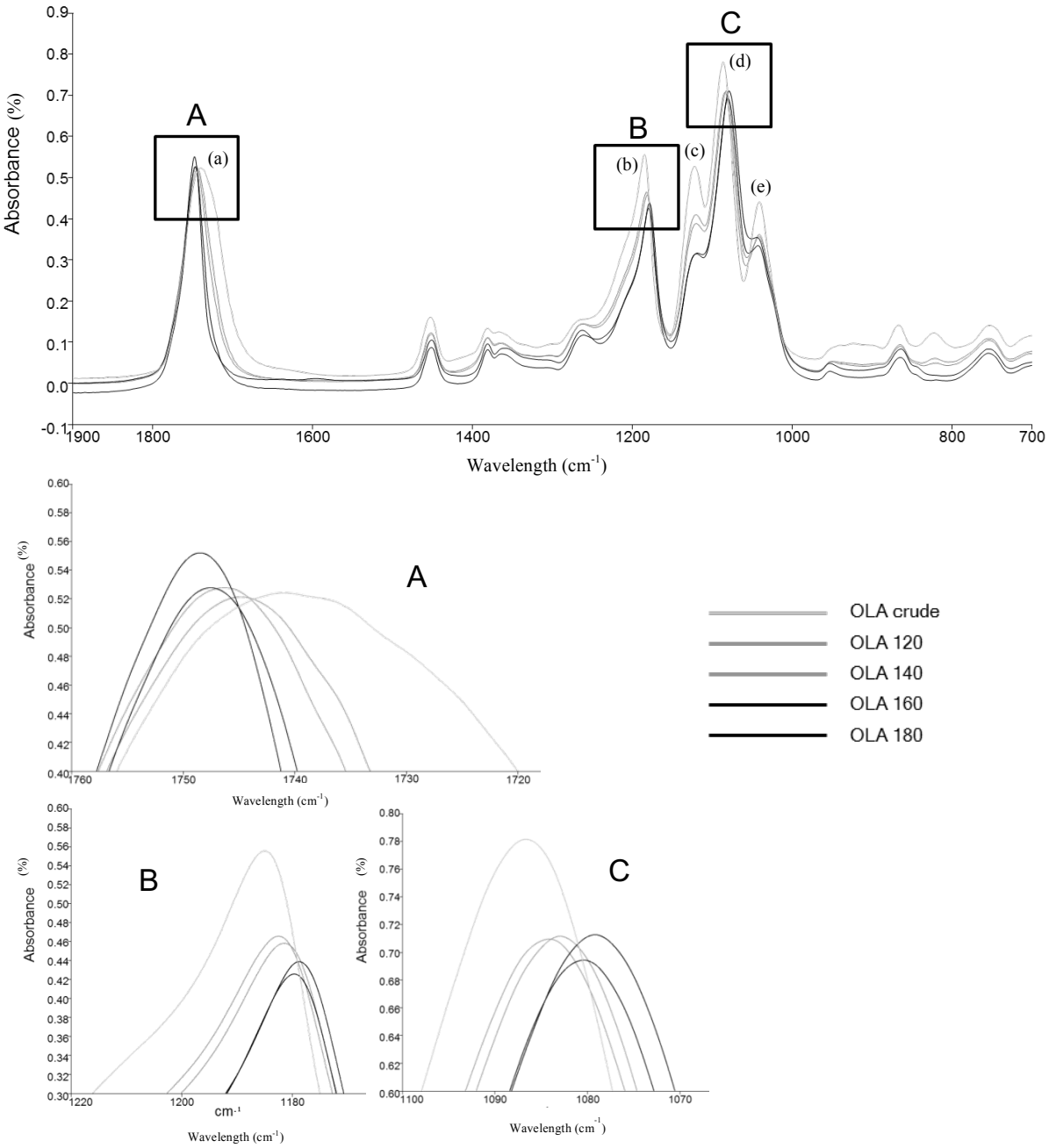


Figure 1: FTIR-ATR spectra of crude OLA and OLA after 3 hours curing at 120°C, 140°C, 160°C and 180°C

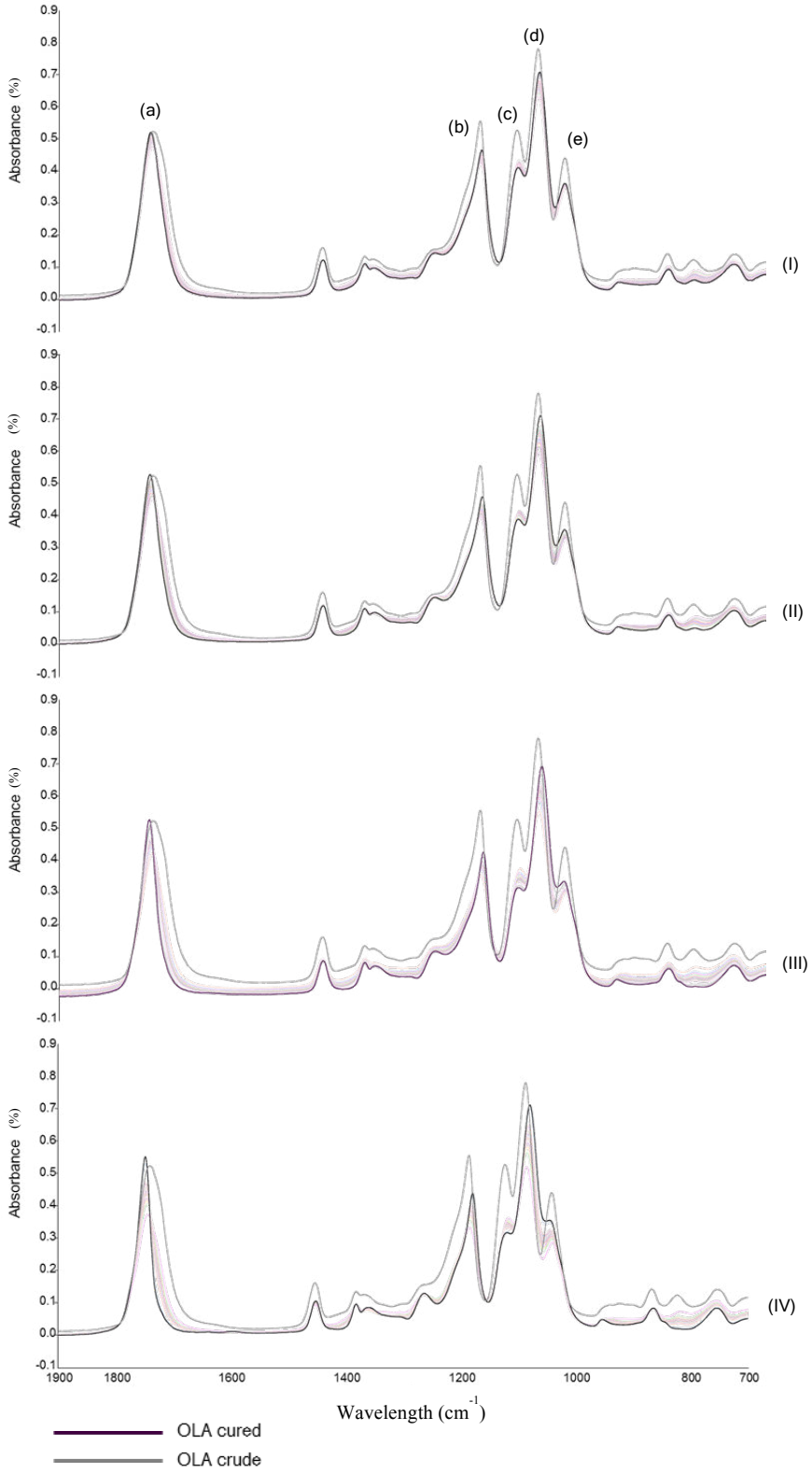


Figure 2: FTIR-ATR spectra of OLA during curing at (I) 120°C, (II) 140°C, (III) 160°C and (IV) 180°C

To provide additional complementary information on degree of OLA polymerizations, the molecular weight profiles of the crude, starting oligomers and polymerized OLA were analyzed by GPC (Table 1). Analysis found curing at 140°C for 48 h does not lead to substantial increases in OLA average molecular weight compared to curing at 160°C at a similar time. At 160°C, OLA curing is more effective than at 140°C as similar increases to OLA average molecular weight were obtained after 2h at 160°C. Relative molecular weight distributions of products are shown in Figure 3. During curing at 160°C for 48h, oligomer chains up to 100 000 $g.mol^{-1}$ were created. However, there appeared a significant portion of OLA which did not significantly polymerize even after 48 h at 160°C. The main component of the cured OLA remains the raw oligomers which were present in the crude OLA product.

Table 1: Percentage of polymer extracted (%extracted), number average molecular weight (Mn) and weight average molecular weight (Mw) of oligomers.

Product	Curing	%extracted	Mn (g/mol)	Mw (g/mol)
OLA	crude	-	443	499
	140°C-48h	-	512	866
	160°C-48h	-	1 059	16 260
	160°C-2h	-	547	1 106
Extracted OLA	120°C-48h	33.2 ±3.2	422	666
	140°C-48h	21.4 ±0.4	341	602
	160°C-48h	7.9 ±0.9	84	194
	140°C-120h	27.9 ±1.0	356	525

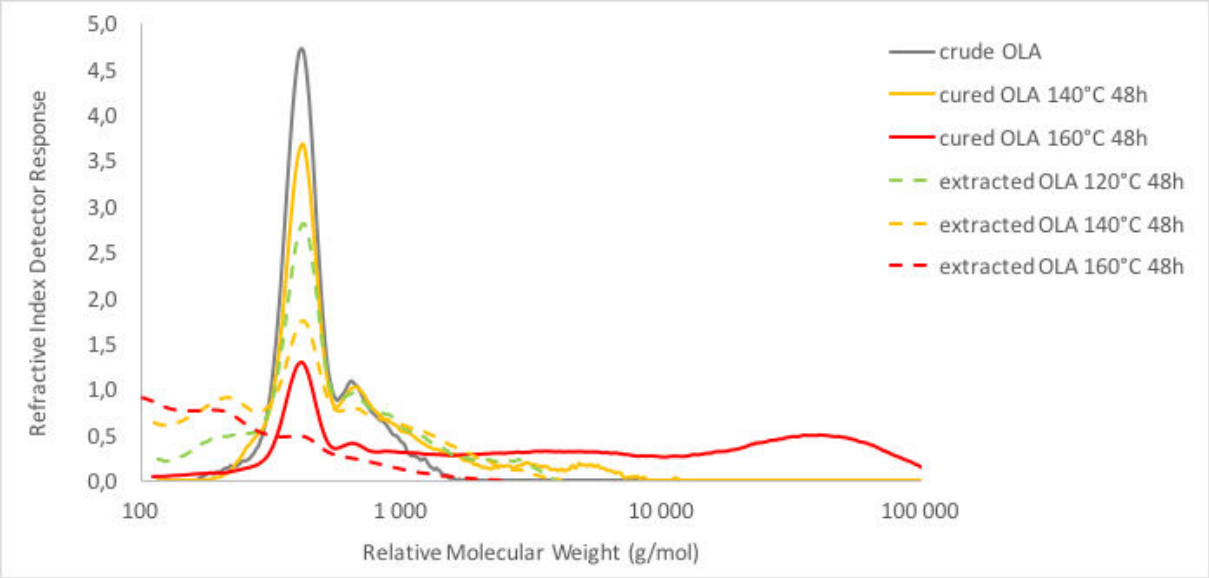


Figure 3: Relative molecular weight repartition of oligomers produced from OLA

3.1.2. OLA in situ polymerization

After OLA impregnations an average initial weight uptake (WU_i) of ca. 71% was reached for the OLA treatments (T1 to T7, Table 2). In treated samples less than 1% volume swelling was observed, indicating that the OLA oligomers do not penetrate the cell wall at this stage of treatment, but likely on OLA *in situ* curing. The weight uptakes at the end of curing (WU_t) represents the remaining oligomers in wood at the end of OLA polymerization. These WU_t values were significantly lower than WU_i. Furthermore, these losses on curing (WL_c) were greater with increasing temperature in the heating phase of the treatment i.e. from 35% at 120°C to 79% at 180°C (Table 2). This was contributed to by production and evaporation of water during polycondensation (and esterification) and may indicate an extended OLA polymerization. However, with higher temperature, the smallest oligomers may also evaporate. On this, even though the molecular weight of oligomers is targeted to generally increase, lactic acid has a boiling point of 122°C and the OLA mixture includes a substantial part of small oligomers (Figure 2) so it is not unreasonable to expect part of OLA mixture to evaporate during curing with greater temperatures. Furthermore, wood thermal degradation can also involve weight loss [16-22], particularly at the 160°C curing temperature. This was evidenced by the WU_t value (-2.4%) from heated, untreated reference samples suggesting some wood degradation from 160°C. However, this degradation may have been enhanced given the acidic nature of the OLA impregnation treatments which could promote the hemicelluloses and other wood polymers to degrade with beech susceptible to these due to a high xylan content [18, 21]. However, overall, the final WL_c is most likely to be a combination of the three phenomena – OLA polycondensation, smaller OLA oligomers evaporation and wood degradation which collectively contribute to a reduced hydroxyl groups number in OLA and in wood (Figures 1 and 2).

The relative molecular weight distributions of OLA products extracted from treated wood are shown in Figure 3. This reveals the average molecular weight of the solubilized, extracted products were relatively lower than for the OLA oligomer products cured outside of wood when curing below 160°C. Whereas the molecular weight of extracted products was significantly lower when curing at 160°C. However, it is also recognized the extracted products from OLA modified wood is not representative of what cannot be extracted. Physical retention of long oligomers is possible together with OLA products which are chemically bounded with wood polymers may not be extractable in this extraction process [7]. Moreover, it is also possible that the very long oligomers shown in Figure 3 were not able to dissolve into the solvent during their extraction from wood.

In respect to temperature and duration of OLA treatments, the main component of extracted, cured oligomers from treated wood remained the raw oligomers from the crude product. This was particularly the case for the two lower temperature treatments (120°C and 140°C). Even though extended *in situ* polymerization was evidenced by the presence of OLA oligomers longer than those from the impregnation product, it appeared impregnated OLA only partially reacts (Figure 3). At 160°C, neither small nor large OLA oligomers dominate the extracted products removed from the treated wood. This may imply an effective fixation and higher degree of OLA *in situ* polymerization was achieved at this higher curing temperature. For curing time, a longer heat treatment at 140°C do not lead to significant extension of OLA polymerization (Table 1). this was consistent with WL_c values indicating weight stabilization was observed after 72h at 140°C (Table 2). Moreover, the extended curing times may also be disadvantageous as depolymerization may also be promoted by the high acidity of the treated wood.

Table 2: Residual samples mass after curing calculated from the TGA equations (Calculated Mass), residual samples mass measured after curing in real conditions (Mass) and weight loss during curing (WL_c). Mean values on 5 to 12 replicates reduced equilibrium moisture content (EMC_t^*), corrected anti-swelling efficiency (ASE*) and leaching rates (LR_{504h} and LR_{31h}) of samples treated according to treatments T1 to T11

N°	Treatment conditions			Extrapolated from TGA	Measured from samples		Wood properties			
	Product	Temperature [°C]	Duration [h]	Calculated Mass [%]	Measured Mass [%]	WL_c [%]	EMC_t* [%]	ASE* [%]	LR_{504h} [%]	LR_{31h} [%]
T1	OLA	120	48	88.1	85.5± 0.5	35.1± 1.0	39.0± 0.7	67.4± 2.4	29.2± 1.3	6.3± 0.1
T2		140	48	79.6	87.3± 0.8	32.5± 2.1	28.7± 1.2	67.4± 3.3	7.3± 0.04	4.1± 0.2
T3		160	48	72.0	77.1± 1.1	57.2± 2.4	15.0± 0.3	69.8± 1.6	5.0± 1.2	1.2± 0.2
T4		180	48	-	65.8± 0.4	78.7± 1.6	11.9± 0.7	68.5± 2.8	5.7± 1.0	5.0± 0.2
T5		140	72	78.4	73.2± 1.1	63.5± 1.9	30.9± 2.0	60.3± 5.8	12.2± 1.2	-
T6		140	96	77.5	74.1± 1.0	66.3± 2.3	29.0± 0.6	58.4± 3.1	12.4± 0.7	-
T7		140	120	76.8	72.9± 1.2	68.0± 2.2	29.3± 2.1	52.4± 3.8	10.7± 2.0	-
T9	None	140	48	-	-	-	26.8± 0.2	7.8± 3.5	1.9± 0.03	1.2± 0.2
T10		160	48	-	-	-	22.9± 0.1	16.8± 0.6	5.9± 0.1	2.5± 0.1
T11		180	48	-	-	-	-	-	-	7.4± 0.3

Table 3: Mean values on 6 replicates of weight loss (WL), wood final humidity (H) and WL of the untreated references (R WL) after exposure to *Coriolus versicolor*

	1rst exposure			2nd exposure		
Treatment	WL [%]	H [%]	R WL [%]	WL* [%]	H [%]	R WL [%]
T1	5.81 ± 0.3	57.94 ± 1.48	16.37 ± 0.97	-	-	-
T3	0.49 ± 0.08	35.42 ± 0.03	13.92 ± 0.16	1.91 ± 0.12	44.06 ± 0.03	4.82 ± 0.20
T8	8.36 ± 1.08	56.15 ± 2.35	16.80 ± 0.78	-	-	-
T10	5.10 ± 2.38	40.14 ± 0.04	9.21 ± 0.97	11.14 ± 2.12	26.00 ± 0.04	8.72 ± 0.67

*Cumulated weight loss on the two exposure periods

Given the *in situ* polycondensation of OLA was shown to be faster at high temperatures (Figure 2), TGA evaluations were undertaken to assess the extent of OLA mass loss with temperature. Analysis showed that sample mass decreases faster at higher curing temperature (Figure 5). Weight losses of ca. 4.6%, 8.2% and 10.4% after 1 h were observed at 120°C, 140°C and 160°C respectively Extrapolation of this data was used to estimate samples mass after curing (Table 2). Results from this simulation were consistent with those obtained with treated samples (calculated mass in comparison with measured mass after curing, Table 2). This implies that, at a set temperature, the extent of polymerization may be limited, but also confirms the most influential parameter of OLA curing is temperature compared to the duration of this cure. According to Harshe *et al.* [20], most of the water is produced during the first hour of the lactic acid esterification reaction and similarly evidenced the reaction temperature strongly influences the duration of this phase, i.e. from ca. 4 hours at 110°C to less than 30 min at 170°C. At 170°C, samples were found to lose ca. 10% of their weight during the first 30 min, due only to lactic acid polycondensation, but only ca. 4% if the temperature was decreased to 110°C providing some consistency in the OLA *in situ* polymerization results obtained here.

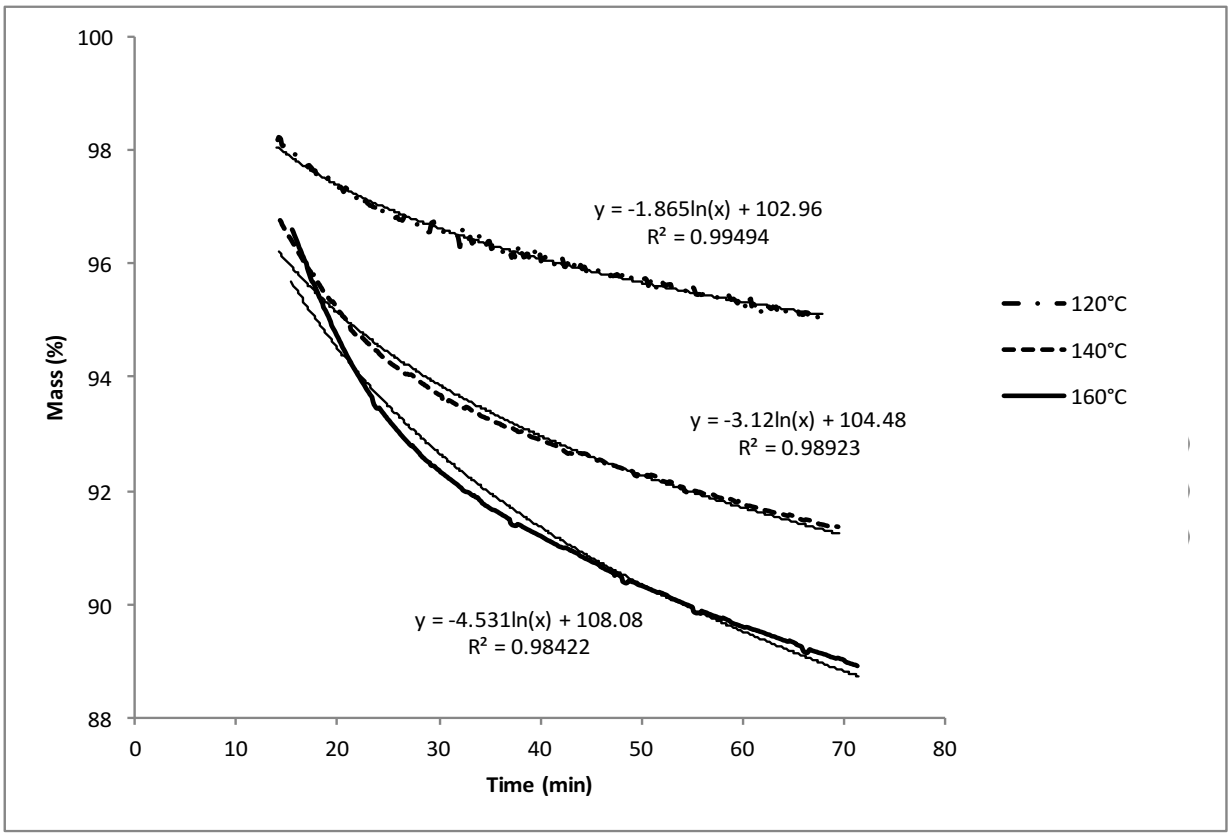


Figure 5: TGA of impregnated wood at 120°C, 140°C and 160°C

3.2. Modified wood properties

3.2.1. Hygroscopic behaviour of modified wood

In evaluating the treated wood properties, it was found the OLA treatment enhanced the wood hygroscopic behaviours (Table 2). In comparison to acetylated wood (ASE* of 38% for a WU_t of 13.6% and ASE* of 66% for a WU_t of 28.6% [10]), the OLA treatment undertaken here performed promisingly, especially the T3 and T4 treatments. Influence of treatment temperature

was not significant for wood dimensional stabilisation with similar ASE* values of ca. 68% across samples T1 to T4 (Table 2). In contrast, treatment duration demonstrated a negative influence on ASE* with a gradual decrease from 67.4% (T2 after 48 h) to 52.2% (T7 after 120h) that may indicate possible degradation of wood polymers by an extended reaction in acidic conditions at 140°C. The EMC* values also decrease substantially with an increase in curing temperature, from 39% (at 120°C) to 12% (at 180°C, T1-4, Table 2). This had a significant impact on hygroscopic properties. The strong influence of curing temperature on modified wood moisture content could be due to an extended *in situ* polymerization or that wood polymers partially degrade. As found above, the curing temperature also had a strong influence on the hygroscopic behaviour of the heated reference samples. Their EMC decreased to 23% after curing at 160°C/48h, for ASE values up to 17%.

A possible explanation of the stable ASE* despite decreasing EMC* (Table 2) may be due to micro-cracks occurring in cell walls during treatment and creating free spaces for water to penetrate without impacting the dimensions. Such cell wall degradation due to *in situ* polymerization treatments was observed by Noël *et al.* [8]. Moreover, another explanation is shown in Figure 4, where moisture content of T1 and T2 was unstable after 500 h of exposure to 100% RH. This may indicate a possible oligomers hydrolysis, increasing the relative hydrophilicity of the treated wood. As the cell walls are saturated, no additional swelling is observed which explains the similar ASE* values of T3 and T4 despite their substantial increases in moisture content. In addition, Figure 4 shows a longer curing time at 140°C has no impact on moisture uptake development with time of treated wood samples. If a longer heat treatment at 140°C resulted in extended polymerization, then T7 would be expected to be more stable than T3. Therefore, a high temperature (160°C) is needed to stabilize OLA within the wood structure.

3.2.3. Durability

In initially assessing the potential durability of treated samples, treatment with OLA provided significant biological resistance to the wood, being a combined action of oligomer impregnation and heat treatment (Table 3). *Coriolus versicolor* exposure of beech samples for 6 weeks showed 7.4% weight loss (WL). Heat treatment alone had a strong influence on wood biological resistance as evidenced by the heated reference samples (T8 and T10). After heat treatment at 120°C for 48 h (T8), WL after exposure was similarly as high as for the virulence control. However, untreated samples in the flask with treated samples were twice as degraded by the fungi. When heated at 160°C, wood biological resistance was improved and WL of heated wood was of ca. 5% (T10). With OLA impregnation and curing at 160°C, WL after exposure can be reduced to 0.5% (T3). However, on curing at 120°C and without complete fixation of OLA in wood structure (as above), oligomer leaching was observed during exposure to fungus for T1. Long term durability, assessed through a second exposure, is showing very promising resistance for OLA treated samples at 160°C. This biological evaluation gives insight for further development as a modified wood for outdoor applications. Currently, characterization is being currently carried out with standardised methods and larger samples with several fungal strains to be reported in another article [9].

3.2.4. Discussion on OLA fixation in wood

Wood thermal degradation is more intense at higher temperature and generates water soluble products like acetic and formic acids [24, 25]. Consequently, the %leached of heated references (T9 to T11) was found to increase with the temperature of heat treatment. However, %leached

did not increase with temperature for the OLA modified wood. Long term leaching (500 h) shows that an increase in temperature significantly improves the OLA persistence in wood. Increases in temperature or in duration of heat treatment is expected to lead to an extended *in-situ* polymerization. This extended polymerization is in turn expected to lead to better fixation of the OLA product within the wood structure.

At lower OLA curing temperatures, wood polymers should not be significantly affected by heat treatment [18-22], but acidic conditions due to OLA impregnation may catalyse degradation reactions of wood polymers during heating even at low temperatures (120°C). Additionally, Tjeerdsma *et al*. [25] suggest products from wood thermal degradation can re-condensate within wood and react with remaining wood polymers if the temperature is high enough and therefore also react with OLA products. Both processes would lead to their retention within the wood and explain lower $\%leached_{31h}$ values for OLA modified wood (T3 = 1.2% and T4 = 5.0%) compared to heated reference samples (T10 = 2.5% and T11 = 7.4%). Fixation of OLA within the wood structure due to extended polymerization occurs most likely through physical entanglement, similar to other polymer systems [2]. Therefore, the OLA matrix be physically retained within the wood and, when reacted with thermal degradation products, contribute to the lower $\%leached_{31h}$ values for modified wood than for heated reference samples treated at high temperatures.

Evident in Tables 2 and 3 are differences between short and longer-term leaching values suggesting the possibility of OLA hydrolysis with time, especially for samples produced at lower temperatures. Two phenomena may be involved in this OLA degradation. Firstly, hydrolysis of ester bonds creating carboxylic chain ends which further autocatalyze this reaction. Secondly, some OLA oligomers become soluble in water and become lost on leaching. If OLA was initially less polymerized due to a low curing temperature, then leachable oligomers are most likely produced (Figure 3).

4. Conclusion

The OLA treatment process is easy to impregnate in beech wood. For the extent of OLA cure, the heating step temperature and duration determine the extent and degree of polymerization. Increasing the cure temperature to 160°C produces longer OLA oligomers but will also impact wood polymer degradation and the treated wood properties. This temperature also has a significant influence on the modified wood hygroscopic behaviour and ASE and EMC values contributed by an extended *in situ* polymerization and partial degradation of wood polymers. At 140°C the influence of the curing duration was not significant. Additionally, OLA treatments provide a significant biological resistance to wood, which was also due to the combined action of OLA oligomer impregnation and the heat treatment.

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Paper 2: Influence of water and humidity on wood modification with lactic acid

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 ($15 \times 15 \times 10$ mm^3 and $15 \times 25 \times 50$ 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

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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.

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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 mm^3 (R × T × L). Treated samples (15 × 15 × 10 mm^3, 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 mm^3 (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.

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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 mm^3 (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	–	–

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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

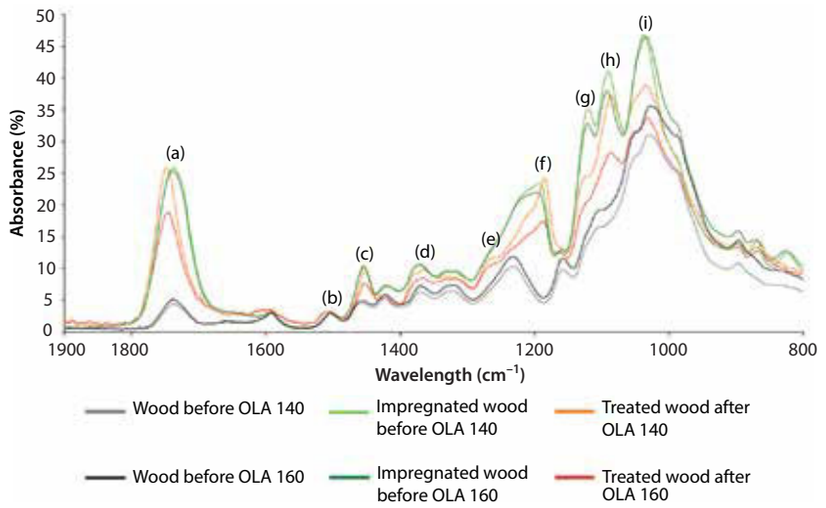


Figure 1 FTIR-ATR spectra of OLA 140 and OLA 160 before impregnation, after impregnation and after heat treatment.

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

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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

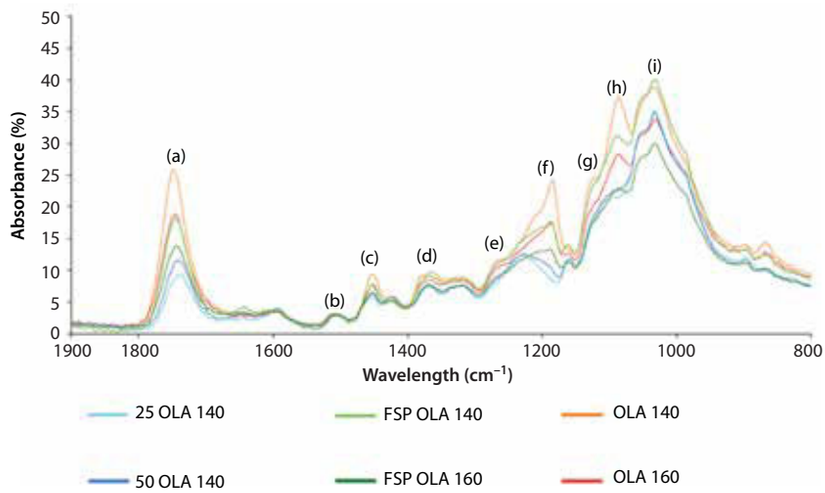


Figure 2 FTIR-ATR spectra of treated wood according to 25 OLA 140, 50 OLA 140, FSP OLA 140, FSP OLA 160, OLA 140 and OLA 160 procedures, after treatment.

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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

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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

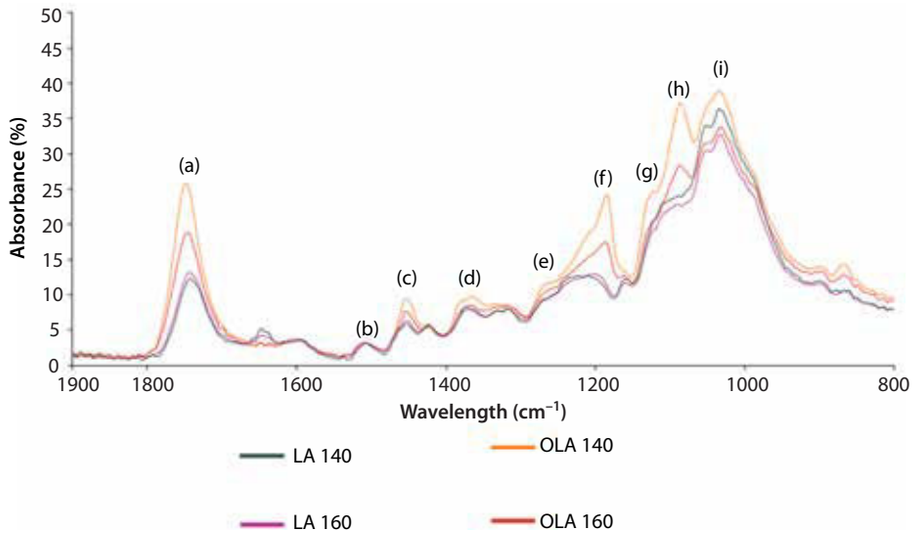


Figure 3 FTIR-ATR spectra of treated wood according to LA 140, LA 160, OLA 140 and OLA 160 procedures, after treatment.

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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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Paper 3: Optimizing wood chemical modification with lactic acid oligomers by screening of processing conditions and chemical additives

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Section 4 **Processes and properties**

Optimising wood chemical modification with lactic acid oligomers by screening of processing conditions and chemical additives

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Optimising wood chemical modification with lactic acid oligomers by screening of processing conditions and chemical additives

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ABSTRACT

Oligomer systems based on lactic acid (OLA), were impregnated in wood and polymerised *in-situ* by heat treatment to improve the properties of the treated wood especially regarding anti-swelling efficiency (ASE), hygroscopicity, water leaching resistance and durability. This article relates the optimisation of the heat treatment conditions and the consideration of selected chemicals for improvement of the treatment efficiency. Maleic anhydride has been considered as a potential additive for oligomers fixation to wood polymers and condensed tannins of Mimosa have been considered as potential additives for improvement of the biological resistance. In both cases, the additives have been mixed into the oligomers or reacted with the oligomers prior to impregnation. The heating step parameters (especially temperature) have a substantial influence on the modified wood properties. The global wood hygroscopic behaviour has been substantially improved by all treatments, with equilibrium moisture content decreased by half for ca. 70% ASE* values for the best performing treatments. The increase in temperature decreases significantly the leaching rate, down to values <5% after extended leaching periods. The treatment provides a significant biological resistance to wood, as shown by weight loss <0.6% after 6-week accelerated fungal exposure, due to the combined action of the oligomers impregnation and the heat treatment. The same global performances are observed with M-OLA, with an improvement for the persistence in the wood which is globally better for M-OLA than OLA, and confirms the relative efficiency of this approach. Treatments with added tannins are also promising as the tannins, known for their hydrophilic nature, have however no damaging effect on treated wood hygroscopic behaviour.

Keywords: wood, chemical modification, lactic acid oligomers, optimisation

1. INTRODUCTION

Despite being one of the main and best performing materials for construction and industry since ages, wood suffers, however, from two limitations: its hygroscopicity and limited durability. Because of current concerns on environment protection and global sustainability encourage the use and development of natural, biodegradable and carbon sink materials, wood has a major role to play in nowadays global markets, supposing that the two drawbacks mentioned above are overcome. For these reasons, many methods for wood modification have been developed over the past decades. Most of the wood properties are determined by its chemical constitution. In this way, wood modification often seeks to make changes at this level. Four main types of methods can be distinguished: chemical modification, thermal modification, surface modification and

impregnation modification (Hill 2006). Acetylated wood is a typical example of commercial modified wood based on an active chemical treatment which consists of the esterification of wood hydroxyls groups with acetic anhydride, but other similar treatments have been made with other anhydrides or aldehydes or methylation reactions (Rowell 2005). In terms of wood impregnation, the most common example is the wood furfurylation which consists of wood impregnation with monomeric furfuryl alcohol followed by polymerisation within the wood structure (Lande *et al*. 2004). A hybrid method has been developed by Noël *et al*. (2009a, 2009b, 2015a) using lactic acid oligomers (OLA). The treatment consists in a two-step process: bulk impregnation of OLA in wood and subsequent *in-situ* polymerization performed by heat treatment. Wood modification with OLA by impregnation and *in-situ* polymerization has been investigated by Noël *et al*. (2009a/b, 2015a/b/c) under several aspects and following different treatment methods. For instance, under chemical polymerisation catalysis (0.6% of sulfuric acid or 5% of tin octoate), the influence of heat treatment conditions had been evaluated according to two cycles (120°C / 1h, referred as SH; 120°C/1h + 103°C until constant weight referred as LH) revealing leaching rate (LR) up to 90% for SH and 20% for LH (Noël *et al*. 2009a/b). Because of a promising 60% ASE at 100% relative humidity (RH) obtained with LH, and because wood degradation was attributed to the chemical catalysts, a treatment with longer stage at high temperature (120°C/6h) was carried out, with no chemical catalysis, which led to 80% leaching rate (LR as define in the following) (Noël *et al*. (2015a). The combined analysis by SEC / TGA / DSC (size exclusion chromatography / thermogravimetric analysis / differential scanning calorimetry) of the molecular mass distribution of OLA oligomers solvent-extracted from wood after treatment showed that the *in-situ* polymerization was effective, but most likely not enough advanced to fix most of the oligomers in wood structure (Noël *et al*. 2015b/c). This article reports the systematic characterization of wood treated with lactic acid oligomers under varying conditions of heat treatment (temperature and duration). Besides, maleic anhydride, a widely used compatibilizer in the polymers industry for enhancement of the interfacial adhesion between immiscible polymers, and especially between polylactic acid (PLA) and cellulosic fibers (Hwang *et al*. 2012), has been considered as a potential additive for oligomers fixation to wood polymers. The potential of condensed tannins as plastic additives, because of antioxidant, light and thermal stability properties, has been already reported (Grigsby *et al*. 2013). Condensed tannins of Mimosa have been here considered as potential additives for improvement of the biological resistance. In both cases, the additives have been mixed into the oligomers or reacted with the oligomers prior to impregnation.

2. MATERIALS AND METHODS

2.1. Materials

Wood samples (15x15x10 mm^3 TxRxL and 15x5x25 mm^3 TRxRTxL) were cut from beech (*Fagus sylvatica L.*) (700±0.01 $kg.m^{-3}$) and oven-dried to constant weight prior to impregnation. L(+)-Lactic acid solution (≥85%) and maleic anhydride (99%) were sourced from Sigma-Aldrich (Switzerland). Condensed Mimosa tannins were supplied by Silvachimica (Italy, trade name MIMOSA OP POLVERE).

2.2. Products preparation

2.2.1. Lactic acid oligomers (OLA) preparation

Lactic acid oligomers (OLA) were prepared following the method described by Noël *et al*. (2015b). Oligomeric polyesters were synthesized by their direct polymerization under vacuum, using a four-necked flask (500 mL or 1L) fitted 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 (150 mbar). The temperature was first gradually increased to 90°C as an initial distillation step of 1h. The initial oligomerisation step involved gradually increasing the temperature to 140°C for 2,5h.

2.2.2. Maleic anhydride grafted OLA (M-OLA)

Maleic anhydride has been grafted to OLA in presence of dicumyl peroxide as radical initiator according to the method describes by Hwang *et al*. (2012) to serve as coupling agent between the OLA and wood.

2.2.3. Tannins added OLA (T-OLA)

2.2.3.1. Tannins acetylation

Mimosa tannins have been esterified using acetic anhydride following the method described by Grigsby *et al*. (2013) in order to produce tannin esters for facilitated linkage to the OLA.

2.2.3.2. Tannins addition to OLA

Mimosa tannins, unmodified, have been added to OLA at a concentration of 0.5% (T-OLA1), 5% (T-OLA2) and 15% (T-OLA3) in weight. They were progressively poured in the OLA mixture while stirring until showing a homogenous suspension. Acetylated tannins have been added to OLA at a concentration of 0.5% (T-OLA4) following the same method.

2.3. Impregnation

As described by Noël *et al*. (2015b), wood samples were immersed in liquid oligomers (OLA) at room temperature. Containers were then placed in a vacuum oven under reduced pressure (150 mbar) for 10 to 15 min, then atmospheric pressure over 10 to 15 min. Impregnated samples were then wiped and set on aluminium foil in a ventilated oven at different temperatures for different durations. Table 1 summarises the different wood treatments, polymerisation and curing conditions.

Anhydrous sample weight was measured before impregnation, after impregnation and after heat treatment. Impregnation yield (IY) and weight percentage gain (WPG) have been calculated according to Eq. 1 and Eq. 2

$$\text{IY}\ (\%) = \frac{w_i - w_{u,d}}{w_{u,d}} \times 100 \quad (1)$$

$$\text{WPG}\ (\%) = \frac{w_{t,d} - w_{u,d}}{w_{u,d}} \times 100 \quad (2)$$

where w_i stands for the impregnated sample weight, $w_{t,d}$ for the sample weight after complete treatment (impregnated and cured), and $w_{u,d}$ the oven dried sample weight before treatment (untreated anhydrous).

Volume swelling was measured at each treatment step. Swelling after impregnation (S_i) and bulking coefficient (BC) have been calculated according to Eq. 3 and Eq. 4

$$S_i\ (\%) = \frac{V_i - V_{u,d}}{V_{u,d}} \times 100 \quad (3)$$

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

where V_i stands for the impregnated sample volume, $V_{t,d}$ for the sample volume after complete treatment (impregnated and cured), and $V_{u,d}$ the oven dried sample volume before treatment (untreated anhydrous).

For the untreated heated samples (T19 to T22), the weight uptake (WU) and swelling (S) after heat treatment have been calculated respectively according to Eq. 1 replacing w_i by w_h, the weight of the untreated sample after heating step, and Eq.3 replacing V_i by V_h, the volume of the untreated sample after heating step.

Table 1 : wood treatments and curing temperature and duration conditions

	Wood treatment conditions		
	Product	**Temperature [°C]**	**Duration [h]**
T1	OLA	120	48
T2		140	48
T3		160	48
T4		180	48
T5		140	72
T6		140	96
T7		140	120
T8	M-OLA	120	48
T9		140	48
T10		160	48
T11		180	48
T12		140	72
T13		140	96
T14		140	120
T15	T-OLA1	140	48
T16	T-OLA2	140	48
T17	T-OLA3	140	48
T18	T-OLA4	140	48
T19	/	120	48
T20	/	140	48
T21	/	160	48
T22	/	180	48

2.4. Anti-swelling efficiency (ASE)

ASE was measured following the method described by Noël *et al*. (2015a). Treated samples (15 x 15 x 10 mm^3, T x R x L) were placed at ca. 100% RH at constant temperature (23°C). Samples dimensions were measured before exposure at dry state (due to treatment process) and after weight stabilisation. Because all treatments have not been evaluated at the same time, part of the samples was measured later after stabilisation (504h of exposure in total) than the other lot (216h of exposure in total). This difference will be stated in the text. Regular weight measurements were made in order to determine the equilibrium moisture content (EMC) of samples with time.

The swelling and ASE of the heated samples (T19 to T22) was calculated according to Eq.5 and Eq.6:

$$S_h\ (\%) = \frac{V_{h,100\%} - V_{h,d}}{V_{h,d}} \times 100 \quad (5)$$

$$\mathrm{ASE}\ (\%) = \frac{S_r - S_h}{S_r} \times 100 \quad (6)$$

where $V_{h,100\%}$ stands for the untreated heated sample volume after stabilisation at 100% RH, $V_{h,d}$ for the untreated heated dry sample volume before stabilization at 100% RH and S_r the untreated unheated reference sample swelling calculated according to Eq.9. For the impregnated wood, the ASE* calculation was based on the corrected swelling calculation of treated samples (S_t^*) as defined in Eq.7 and Eq.8 according to Thybring (2013):

$$S_t^*\ (\%) = \frac{V_{t,100\%} - V_{t,d}}{V_{u,d}} \times 100 \quad (7)$$

$$\mathrm{ASE}^*(\%) = \frac{S_r - S_t^*}{S_r} \times 100 \quad (8)$$

where $V_{t,100\%}$ stands for the treated sample volume after stabilisation at 100% RH, $V_{t,d}$ for the treated dry sample volume before stabilization at 100% RH, $V_{u,d}$ the oven dried sample volume before treatment and S_r the untreated reference sample swelling

$$S_r(\%) = \frac{V_{r,100\%} - V_{r,d}}{V_{r,d}} \times 100 \quad (9)$$

where $V_{r,100\%}$ stands for the untreated unheated reference sample volume after stabilisation at 100% RH and $V_{r,d}$ for the oven dried untreated unheated reference sample volume.

EMC_t and the reduced EMC: EMC_{Rt} of treated samples exposed at 100% RH are defined as follows in Eq.10 and Eq.11 (Hill, 1998; Thybring, 2013)

$$\mathrm{EMC_t}(\%) = \frac{w_{t,100\%} - w_{t,d}}{w_{t,d}} \times 100 \quad (10)$$

$$\mathrm{EMC_{Rt}}(\%) = \frac{w_{t,100\%} - w_{t,d}}{w_{u,d}} \times 100 \quad (11)$$

where $w_{t,100\%}$ stands for the treated sample weight after stabilisation at 100% RH, $w_{t,d}$ for the treated dry sample weight before exposure to 100% RH, and $w_{u,d}$ the oven dried sample weight before treatment.

2.5. Leaching

2.5.1 Short leaching

Samples of dimensions 15 x 5 x 25 mm^3 (TR x RT x L) were leached according to the guidelines of the NF X 41-569 standard. The samples were immersed in water (5 volume water/1 of wood) at room constant temperature (23°C) and with constant shaking, in separated boxes according to the treatment. Three immersion periods of 1h, 2h and 4h were followed by an air-drying period of 16h and then two more immersion periods of 8h and 16h. The water was changed between

each immersion period. The immersion was stopped after the 5th period (31h of immersion in total), and samples were air-dried for 2h before oven-drying at 103°C until stabilization of the weight. The leaching rate was calculated according to Eq. 12 and will be labelled LR_{31h} in the following

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

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

2.5.2 Long leaching

Treated samples (15 x 15 x 10 mm^3, T x R x L) were immersed in water at room constant temperature (23°C) for 504 hours or 216 hours, in separated boxes according to the treatment procedure undergone by the samples. LR was calculated according to Eq. 12, and will be labelled LR_{504h} and LR_{216h} respectively in the following.

2.6. Biological resistance

A preliminary determination of the conferred durability has been carried out according to an accelerated biological resistance screening test (according to Bravery 1978). Samples of dimensions 15 x 5 x 25 mm^3 (TR x RT x L) treated and leached according to the short leaching procedure described in 2.5.1 were sterilized with gamma rays and consecutively placed in culture flasks on inoculated growing medium (40g malt and 20g agar/L) with *Coriolus versicolor* (L. Quelet, strain CTB 863A) for 6 weeks (at 22°C, 70% RH). Samples weight loss (%) was determined as the ratio between the weight loss due to fungal exposure and the initial treated dry weight according to Eq. 13:

$$WL\ (\%) = \frac{w_{t,l,d} - w_{t,exp,d}}{w_{t,l,d}} \times 100 \quad (13)$$

where $w_{t,l,d}$ is the specimen weight after treatment, leaching and drying, and $w_{t,exp,d}$ is the treated specimen weight after exposure at dry state. The final humidity of the samples in culture flasks at the end of exposure was calculated according to Eq. 14:

$$MC\ (\%) = \frac{w_{t,exp,w} - w_{t,exp,d}}{w_{t,exp,d}} \times 100 \quad (14)$$

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

A second exposure of selected samples has been carried out according to the same procedure after the first exposure and a second sterilization in order to evaluate the treatments long-term efficiency.

3. RESULTS AND DISCUSSION

Table 2 summarises the wood physical properties, hygroscopic behaviour and treatment persistence in wood.

Table 2 : Mean values on 5 to 12 replicates of impregnation yield (IY), swelling due to impregnation (S_i), weight percent gain (WPG), bulking coefficient (BC), equilibrium moisture content (EMC_t) and reduced EMC_t (EMC_{Rt}), anti-swelling efficiency (ASE) and corrected ASE (ASE*) and leaching rates (LR_{504h}, LR_{216h} and LR_{31h}) of samples treated according to treatments T1 to T22.

Treatment		IY [%]	S_i [%]	WPG [%]	BC [%]	EMC_{Rt} [%]	ASE* [%] After 504h	LR_{504h} [%]	LR_{31h} [%]
OLA	T1	73.2± 1.9	0.3± 0.1	47.5± 0.9	19.2± 0.8	39.0± 0.7	67.4± 2.4	-29.2± 1.3	-6.3± 0.1
	T2	70.2± 2.0	0.2± 0.2	47.4± 2.1	22.5± 0.6	28.7± 1.2	67.4± 3.3	-7.3± 0.04	-4.1± 0.2
	T3	67.1± 4.3	0.8± 0.04	28.7± 1.8	15.3± 0.8	15.0± 0.3	69.8± 1.6	-5.0± 1.2	-1.2± 0.2
	T4	74.8± 2.8	0.6± 0.2	15.9± 0.8	5.4± 0.3	11.9± 0.7	68.5± 2.8	-5.7± 1.0	-5.0± 0.2
	T5	72.7± 3.8	-	26.5± 1.2	17.8± 0.9	30.9± 2.0	60.3± 5.8	-12.2± 1.2	-
	T6	70.6± 5.0	-	23.8± 1.4	14.7± 0.5	29.0± 0.6	58.4± 3.1	-12.4± 0.7	-
	T7	69.3± 4.3	-	22.2± 1.1	13.8±0.8	29.3± 2.1	52.4± 3.8	-10.7± 2.0	-
M-OLA	T8	63.3± 3.0	0.2± 0.1	41.6± 2.0	15.8± 1.5	44.5± 1.2	52.6± 5.2	-24.2± 0.3	-4.8± 0.3
	T9	75.2± 3.8	0.3± 0.1	41.6± 2.2	20.0± 0.5	16.7± 0.3	73.0± 2.0	-6.3± 0.5	-3.4± 0.04
	T10	68.0± 2.7	0.7± 0.1	27.3± 1.2	14.0± 0.6	14.1± 0.1	70.8± 2.4	-3.7± 0.4	-0.4± 0.1
	T11	70.9± 3.0	0.8± 0.1	15.4± 1.3	4.8± 0.7	11.2± 0.3	68.7± 2.0	-6.3± 1.1	-4.8± 0.2
	T12	69.8± 3.8	-	25.8± 1.3	13.9±0.6	25.2± 0.1	62.3± 3.7	-4.4± 0.7	-
	T13	63.3± 3.6	-	20.9± 1.2	10.4± 0.8	25.7± 0.7	44.8± 3.3	-5.0± 0.6	-
	T14	64.0± 3.2	-	20.8± 1.0	10.0± 0.5	24.1± 1.2	47.8± 2.1	-4.6± 0.6	-
		IY [%]	**S_i [%]**	**WPG [%]**	**BC [%]**	**EMC_{Rt} [%]**	**ASE* [%] After 216h**	**LR_{216h} [%]**	**LR_{31h} [%]**
OLA	T2	63.1± 1.4	0.7± 0.1	33.7± 1.4	17.3± 0.4	15.8± 0.1	56.5± 4.1	-2.9± 0.1	-4.1± 0.2
T-OLA	T15	58.8± 5.0	0.4± 0.1	29.3± 3.0	15.9± 1.6	16.3± 1.5	74.2± 7.2	-2.5± 0.2	-1.1± 0.1
	T16	67.5± 2.0	0.6± 0.1	37.5± 1.2	14.5± 0.4	17.1± 0.1	53.1± 2.6	-3.2± 0.3	0.2± 0.1
	T17	57.2± 4.0	0.5± 0.1	34.5± 4.0	10.8± 1.1	20.8± 0.5	49.7± 5.2	-6.2± 0.2	-2.7± 0.4
	T18	59.6± 2.0	0.7± 0.1	29.2± 0.8	15.6± 0.9	16.4± 0.3	51.0± 5.2	-5.2± 0.1	-0.8± 0.2
Heated references		**IY [%]**	**S_i [%]**	**WU [%]**	**S [%]**	**EMC_t [%]**	**ASE [%] After 504h**	**LR_{504h} [%]**	**LR_{31h} [%]**
	T19	-	-	-	-	-	-	-	-1.2± 0.1
	T20	-	-	-0.1± 0.1	0.03± 0.2	26.8± 0.2	7.8± 3.5	-1.9± 0.03	-1.2± 0.2
	T21	-	-	-2.4± 0.1	-1.8± 0.1	22.9± 0.1	16.8± 0.6	-5.9± 0.1	-2.5± 0.1
	T22	-	-	-	-	-	-	-	-7.4± 0.3

3.1. OLA diffusion and in-situ polycondensation

In all cases, less than 1% swelling is observed after impregnation, showing that the products do not penetrate the cell walls at this stage. The impregnation yield is logically similar for treatments T1 to T7, T8 to T14 and T15 to T18 since only the heat treatment conditions differentiate the variants. However, the addition of maleic anhydride or tannins in the OLA seems to slightly lower and scatter the impregnation yield as shown by the average IY of 71.2 ± 2.6%, 67.8 ± 4.5% and 60.8 ± 4.6% for OLA, M-OLA and T-OLA treatments respectively.

The weight percent gain (WPG) represents the remaining oligomers weight into wood after heat treatment. It is logically lower than the IY, most likely because of further polycondensation into the wood structure leading to water release and weight loss. WPG decreases with the heat

treatment temperature increase: from 47.5% WPG at 120°C to 15.9% WPG at 180°C (Table 2). That might indicate a higher polymerisation rate into wood structure at higher temperature for constant duration. However, wood hemicelluloses are known to start deteriorating above 190°C (Shen *et al*., 2009) leading to mass decrease. This impacted the WPG but not substantially according to the references which have lost less than 2.5% weight at 140°C (Table 2). It is not known yet though, if the acidic condition into wood due to the shorter oligomers could promote the hemicelluloses and other wood polymers degradation. The addition of maleic anhydride or tannins to the OLA does not influence significantly the WPG, with similar influence of the heating temperature to the OLA.

The BC characterizes the diffusion of oligomers into the cell walls. As shown in Table 2 the temperature shows a limited influence on BC between 120°C and 140°C and BC decreases with the temperature increases above 140°C from 22.5% to 5.4%. Two hypotheses are formulated - above 160°C the polymerisation kinetics is too fast to allow the oligomers diffusion to the cell walls and oligomers polymerize in the lumen, or the oligomers penetrate the cell walls but the extended further polymerisation leads to a shrinkage of the oligomers in wood leading to the subsequent cell wall shrinkage. The M-OLA treatments (T8 to T14) show similar BC to the OLA treatments. The tannin addition to OLA does not influence significantly the BC either, whereas the high concentration in tannins (T17) could have hindered the oligomers diffusion to the cell wall. However, the lower BC in that case might also be due to lower IY.

Regarding the treatment duration at 140°C, it appears that WPG of OLA decreases with time from 47.4% after 48h to 22.2% after 120h (Table 2). However, it seems that after 72h at 140°C the polymerization rate slows down evidenced by WPG stabilization. After 72h at 140°C it is possible to reach the same WPG as after 48h at 160°C (T3), i.e. around 27% (Table 2). The BC of OLA treatments is decreasing with the duration of the heat treatment from 22.5% after 48h to 13.8% after 120h (T2, T5-7, Table 2). Like the WPG, it seems that after 96h at 140°C the BC is stabilizing slightly. These results are consistent with the hypothesis that there is a shrinkage due to the polymerization into the cell walls. There is no substantial difference in the physical properties of treated samples noticed between OLA, M-OLA and T-OLA treatments, which indicates that an adaptation of the treatment procedure is not necessary.

3.2. Hygroscopic behaviour of modified wood

The influence of treatment temperature is not significant on wood dimensional stabilisation according to similar ASE* values of ca. 68% for T1 to T4 (Table 2). In contrast, the treatment duration demonstrate a negative influence on ASE* with a gradual decrease from 67.4% after 48h to 52.2% after 120h that might indicate a possible degradation of wood polymers by an extended reaction. In comparison to acetylated wood (ASE* of 38% for a WPG of 13.6% and ASE* of 66% for a WPG of 28.6% as calculated by Thybring (2013) based on several literature sources (Yasuda *et al*. 1994), the OLA performs promisingly, especially T3 and T4.

On the other hand, EMC_{Rt} decreases substantially with the increase of thermal treatment temperature, from 39.0% at 120°C to 11,9% at 180°C (T1-4, Table 2), which is a significant positive impact on hygroscopic properties. One explanation of the stable ASE* despite decreasing EMC_{Rt} could be the micro-cracks occurring into the cell wall during the treatment and creating free spaces for water to penetrate without impacting the dimensions. Such cell wall degradation due to treatment was observed and reported by Noël *et al*. (2015c). Moreover, another explanation is shown in Fig. 1, where the EMC_{Rt} of T1 and T2 are not stable after 504h of exposure to ca. 100% RH. That might indicate a possible oligomers hydrolysis, increasing the global hydrophilicity of the system. As the cell walls are saturated, there is no additional

swelling observed which explains the similar ASE* to T3 and T4 despite the substantial increase of moisture content.

Besides, Fig. 1 clearly shows that the treatment temperature at constant duration has a much stronger impact on the EMC_{Rt} of treated wood than the duration at constant temperature. For a 48h heat treatment, an increase from 140°C to 160°C leads to an EMC_{Rt} decrease of 50% for instance. The strong influence of treatment temperature could be either due to a more extended *in-situ* polymerisation or wood polymers partial degradation. Indeed, the heat treated references (T20-21) reveal ASE values up to 16.8% and EMCt decreased to 22.9% after heat treatment at 160°C/48h.

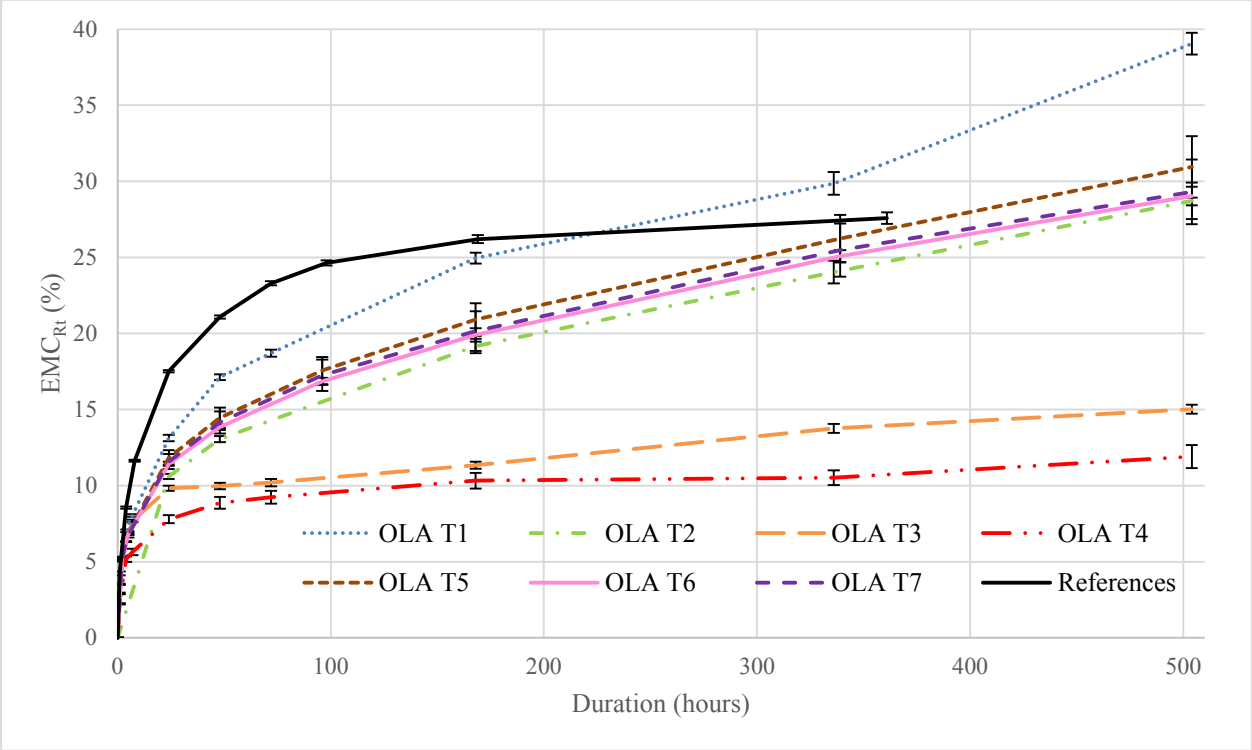


Figure 1: Reduced equilibrium moisture content (EMC_{Rt}) at 100% RH

The same global hygroscopic behaviour is observed with M-OLA, with the following differences. The increase of heat treatment duration is more detrimental to the ASE* values (T13-14 in comparison to T6-7, Table 2) which might exhibit a stronger degradation of wood due to maleic anhydride addition. But unlike the OLA treatment which sees the EMC_{Rt} decreasing from 160°C, the M-OLA treatment induces the same decrease at 140°C only (T9 in comparison to T2, Table 2). The EMC_{Rt} for longer heat treatment durations are also lower than in the case of OLA treatment.

Concerning the T-OLA treatment, it is shown in Table 2 that tannins have no damaging effect on treated wood properties in comparison to OLA treatment. The increase in tannins concentration leads however to the ASE* decrease as well as the EMC_{Rt} increase, which most likely comes from the hydrophilic nature of tannins. Acetylated tannins (T18, Table 2) induce low ASE* values, however similar to the ASE* obtained at 216h with the OLA treatment.

There is no substantially deleterious effect of maleic anhydride or tannins on the EMC_{Rt} and ASE* properties.

3.3. Treatment persistence in wood

The increase in temperature or in duration of the heat treatment is expected to lead to an extended *in-situ* polymerization, as it was proven to happen with the pure oligomers (Noël *et al*. 2009a). The extended polymerisation is in turn expected to lead to better fixation of the product into the wood structure, most likely through physical entanglement.

The long term leaching shows that the increase in temperature decreases significantly the leaching rate, while the addition of maleic anhydride is necessary to reach similar LR at 140°C for the different durations. Besides, all LR values (long and short terms) are globally lower for M-OLA than OLA, which confirms the relative efficiency of this approach.

Due to their hydrophilic character, tannins were expected to induce a higher LR. The increase in tannins concentration leads indeed to an increase in long term LR, and their acetylation does not improve this result (T18 in comparison to T15). There is no obvious tendency observed for short term leaching values of T-OLA, which are similar to those for OLA and M-OLA.

The short and long term LR of all variants can also be qualified by the LR observed on untreated references heated at different temperatures (T19-22). Further evaluations will have to be carried out to understand the combined effect of *in-situ* polymerisation and wood degradation as a function of temperature on the LR, as well as the possible hydrolysis occurring during the leaching process.

3.4. Durability

As observed in Table 3, wood treatment with OLA provides a significant biological resistance to wood, due to the combined action of the oligomers impregnation and the heat treatment (as evidenced by the untreated heated references: T21 in comparison to T19). The treatment temperature strongly impacts the performance, for OLA, M-OLA and the untreated references (with reservations due to the lower weight loss of reference samples in that latter case).

Long term durability, assessed through the second exposure, shows very promising resistance for treated samples, with a slightly better performance conferred by the M-OLA that leads to lower weight loss during the second exposure than the OLA. There is however an increase in fungal attack to take into consideration, that might reveal only a bigger inertia but no definitive protection conferred by the treatment.

Due to their fungicide role in wood, tannins were expected to induce a lower WL. The increase in tannins concentration or their acetylation does not induce a significant difference in treatment efficiency against *Coriolus versicolor* (T15 to T18). However, probably due to their hydrophilic character, the increase in tannins concentration induces an increase of samples final MC, while tannins acetylation has no impact on MC. To evaluate the most significant parameter for wood protection in between treatment conditions (temperature, duration) and additives (tannins), the assessment of control samples T2 according to the same exposure procedure is currently being carried out.

The biological evaluation gives very promising insight for a further development as modified wood for outdoors applications. Deeper characterization is being currently carried out with standardised methods on bigger samples and several fungal stems that will be reported in further articles.

Table 3: Mean values on 6 replicates of weight loss (WL), wood final moisture content (MC) and WL of the untreated references (R WL) after exposure to *Coriolus versicolor*

	1rst exposure			2nd exposure		
Treatment n°	**WL [%]**	**MC [%]**	**R WL [%]**	**WL* [%]**	**MC [%]**	**R WL [%]**
T1	5.81 ± 0.3	57.94 ± 1.48	16.37 ± 0.97	-	-	-
T3	0.49 ± 0.08	35.42 ± 0.03	13.92 ± 0.16	1.91 ± 0.12	44.06 ± 0.03	4.82 ± 0.20
T8	4.90 ± 0.10	58.64 ± 0.79	18.90 ±1.59	-	-	-
T10	0.59 ± 0.09	35.94 ± 0.01	8.37 ± 1.40	1.67 ± 0.08	38.30 ± 0.02	10.82 ± 4.49
T 15	1.95 ± 0.97	45.84 ± 3.15	12.72 ± 2.47	-	-	-
T 16	2.26 ± 1.19	50.07 ± 1.70	13.02 ± 1.90	-	-	-
T 17	1.90 ± 0.86	61.52 ± 5.56	8.24 ± 0.36	-	-	-
T 18	1.87 ± 0.13	45.95 ± 5.27	16.70 ± 2.66	-	-	-
T19	8.36 ± 1.08	56.15 ± 2.35	16.80 ± 0.78	-	-	-
T21	5.10 ± 2.38	40.14 ± 0.04	9.21 ± 0.97	11.14 ± 2.12	26.00 ± 0.04	8.72 ± 0.67

*Cumulated weight loss on the two exposure periods

The Virulence control for *Coriolus versicolor* strain on 10 replicates of Beech samples (50 x 25 x 15 mm^3, L x R x T) exposed 16 weeks showed 35.8% weight loss.

4. CONCLUSION

The OLA, M-OLA and T-OLA treatments are easy to impregnate in the wood. They penetrate and polymerise into the cell walls only during heat treatment. This heating step temperature and duration determine the polymerization advancement - by increasing the temperature, longer oligomers might be obtained - but also impact the wood polymers degradation. According to OLA treatments, the temperature has a significant influence on the modified wood hygroscopic behaviour which could be either due to a more extended *in-situ* polymerisation or wood polymers partial degradation. At 140°C the influence of the duration is not significant. The OLA treatment provides a significant biological resistance to wood, due to the combined action of the oligomers impregnation and the heat treatment. The OLA treatment persists in the wood. The increase in temperature decreases significantly the leaching rate and the OLA treatment persistence has been increased compared to Noël *et al*. (2015a). The same global performances are observed with M-OLA, with an improvement for the persistence in the wood which is globally better for M-OLA than OLA, which confirms the relative efficiency of this approach. The durability performance conferred by the M-OLA is slightly better in comparison with OLA. T-OLA treatments showed interesting results but no significant durability increase. More research is being carried out evaluating other tannins sources.

5. ACKNOWLEDGEMENT

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Paper 4: Improvement of modified wood properties with addition of chestnut tannins in lactic acid based treatments

Improvement of modified wood properties with addition of chestnut tannins in lactic acid based treatments

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Wood modification treatments based on lactic acid oligomers (OLA) and monomers (LA) enhance beech dimensional stability (up to 70%) and biological resistance (less than 3% weight loss according to EN113). Chestnut wood tannins natural biological activity might improve the modified wood durability with milder curing conditions. Treatment consisted of the impregnation of monomers or oligomers mixtures followed by curing (140°C/160°C for 48h). Tannins addition is almost inconsequential with oligomeric based treatment but improved the monomeric based treatment. In this case, modified wood biological resistance and product persistence were increased. OLA impregnated wood cured at 160°C was always the best performing treatment regarding dimensional stability and durability, but the addition of tannins in LA systems conferred promising properties to wood allowing simplification of the modification process.

Keywords: beech; chemical modification; lactic acid; optimisation; chestnut tannins

Introduction

Developing sustainable products has become a common and global concern of societies and industries. Possessing many advantages, wood is often used as raw material for the development of sustainable products. Wood is available, renewable and low cost, shows sufficient mechanical properties and its chemical constitution allows easy impregnation and reactions with other products. [1, 2] However wood hygroscopicity is a substantial drawback that affects dimensional stability and durability of the material. Most wood properties are determined by its chemical constitution and hydroxyl groups of hemicelluloses and cellulose are responsible for wood hygroscopicity [3, 4]. Several techniques have been developed to protect wood from water and humidity variations over the past decades. Wood modification methods [2], such as thermal treatment [5, 6, 7], acetylation [8, 9, 10] or furfurylation [2, 11], are aimed to modify wood chemical constitution to reduce the hydrophilic groups' availability. Technical limitations and the cost of those modification treatments often restrict the use of such modified wood for quite high added-value products.
Recently, a method using lactic acid oligomers (OLA), produced from available bio-based resources (dextrose from corn or sugar beet), has shown promising results with respect to wood

dimensional stability [12,13] and durability [13, 14]. The treatment consists of a two-step process: bulk impregnation of OLA in wood and subsequent *in situ* polymerisation initiated by heat treatment. While diffusion of OLA within the wood structure can be observed, the chemical grafting was not clearly evidenced [12, 15]. Furthermore, the *in-situ* polymerisation was proven by gel permeation chromatography (GPC) and thermogravimetric analysis (TGA) [14] but most likely not enough advanced to fix the OLA fully in the wood structure [14, 15]. Further studies showed that the heating step parameters, and especially temperature, have a substantial influence on modified wood properties [16]. By increasing the temperature up to 160°C, the performance of the material regarding moisture is improved and the product is better polymerized and retained in wood.

In industrial conditions, wood logs are never dried to the anhydrous state before treatment. Thus, influence of wood moisture content in treatment process was evaluated [17]. It appeared that water was not an issue at the beginning of the process. Wood can be impregnated at fibre saturation point with no detrimental decrease of treatment performance. Furthermore, influence of pre-polymerisation of lactic acid (LA) was studied. Properties of wood treated with LA monomers, at 160°C, are promising, with anti-swelling efficiency (ASE) higher than 60%, and substantial increase of wood decay resistance.

This article reports the systematic characterization of wood treated with lactic acid based treatments (LA or OLA) with addition of chestnut tannins (CT) aiming to improve the wood durability. LA and OLA treatments efficiency against fungal decay most likely does not involve antioxidant activity. Tannins biological activity is linked to their antioxidant property [18, 19]. In combination with LA and OLA treatments, this could be an additional mechanism improving the modified wood durability, especially for lower curing temperatures. In addition of acknowledged antifungal [20, 21] and antimicrobial [22] effect of tannins, chestnut wood tannin extract was the tannin chosen as it is the most abundant hydrolysable tannin on the market [23].

Material and Methods

Materials

Wood samples (15 x 15 x 10 mm^3, 15 x 25 x 50 mm^3, 15 x 25 x 525 mm^3 and 40 x 50 x 600 mm^3, T x R x L) were cut from beech (*Fagus sylvatica L.*) (700 $kg.m^{-3}$) and oven-dried at 103°C to constant anhydrous weight prior to impregnation. L(+)-Lactic acid solution (≥ 85%), was sourced from Sigma-Aldrich (Switzerland). Hydrolysable Chestnut Tannins (CT), extracted from chestnut wood (*Castanea sativa*), were supplied by Silvachimica (Italy, trade name FINTAN CE).

Products preparation

Lactic acid oligomers (OLA) preparation

Lactic acid oligomers (OLA) were prepared following the method described by Noël *et al.* [25]. Oligomeric polyesters were synthesized by their direct polycondensation under vacuum, using a four-necked flask (500 mL or 1L) fitted with a magnetic stirrer and reflux condenser linked to an inline cold trap and vacuum pump. Thermometers were used to observe the polymerisation, condenser head, and heater temperatures. The solution was heated under reduced pressure (0.015 MPa). The temperature was first gradually increased from 23°C to

90°C as an initial distillation step of 1h. The initial oligomerisation step involved gradually increasing temperature to 140°C for 2.5h.

OLA and LA added with hydrolysable tannins (CT-OLA and CT-LA)

Chestnut tannins were mixed with OLA or LA to lead to CT-OLA or CT-LA mixtures, respectively at a concentration of 5% in weight. They were progressively poured in the OLA or in the LA solution at room temperature while stirring until showing a homogenous suspension.

Wood treatment

Conditioning

Wood samples were oven-dried at 103°C to constant weight prior to treatment. Samples untreated anhydrous weight and volume were measured ($w_{u,d}$ and $V_{u,d}$). For the selected variants (12% OLA 160, 12% LA 160 and 12% CT-LA 160), wood samples were then stabilized at 20°C and 65% RH.

Impregnation

As described by Noël *et al.* [14], 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 of product.

Curing

Dry curing was carried out in a ventilated oven. Table 1 summarises the different curing conditions.

Weight uptake and swelling, after impregnation (WU_i and S_i) and after complete treatment (WU_t and S_t) were calculated as followed:

$$WU_{i/t}\,(\%) = \frac{w_{i/t,d} - w_{u,d}}{w_{u,d}} \times 100 \qquad (1)$$

$$S_{i/t}\,(\%) = \frac{V_{i/t,d} - V_{u,d}}{V_{u,d}} \times 100 \qquad (2)$$

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

Table 1: Treatment and curing process description

Treatment	Conditioning	Curing
OLA 140 **LA 140**	Anhydrous	140°C/48h
OLA 160 **LA 160**		160°C/48h
CT-OLA 140 **CT-LA 140**		140°C/48h
CT-LA 160		160°C/48h
12% OLA 160 **12% LA 160** **12% CT-LA 160**	12% MC (20°C/65%RH)	160°C/48h
Ref 140 **Ref 160** **Ref**	Anhydrous	140°C/48h 160°C/48h -

Anti-swelling efficiency (ASE)

ASE was measured following the method described by Noël *et al.* [14] on 10 replicates of 15 x 15 x 10 mm^3 (T x R x L). Treated samples were placed in a desiccator, partially filled with water to set RH at ca. 100%, at a constant temperature of 23°C. Samples volume was measured anhydrous before exposure ($V_{t,d}$), after 216h and after weight is stabilized, after 504h according to Grosse *et al.* [16].

Reference samples (Ref 140, Ref 160 and Ref) swelling S_r, was calculated as follows:

$$S_r(\%) = \frac{V_{r,100\%} - V_{r,d}}{V_{r,d}} \times 100 \quad (3)$$

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

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

$$S_{t,100\%}\ (\%) = \frac{V_{t,100\%} - V_{t,d}}{V_{t,d}} \times 100 \quad (4)$$

$$ASE_t\ (\%) = \frac{S_r - S_t}{S_r} \times 100 \quad (5)$$

where $V_{t,100\%}$ stands for heat-treated samples volume after stabilisation 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 [25]:

$$S^*_{t,100\%}\ (\%) = \frac{V_{t,100\%} - V_{t,d}}{V_{u,d}} \times 100 \quad (6)$$

$$ASE_t^*(\%) = \frac{S_r - S_{t,100\%}^*}{S_r} \times 100 \quad (7)$$

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

Equilibrium moisture content (EMC)

EMC of the reference samples (EMC_t) and the reduced EMC of impregnated samples (EMC_t^*) have been determined on samples used for ASE determination, they are defined as follows in equations (8) and (9) [17, 25]:

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

$$EMC_t^*(\%) = \frac{w_{t,100\%} - w_{t,d}}{w_{u,d}} \times 100 \quad (9)$$

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

Leaching

Samples of dimensions 15 x 25 x 50 mm^3 (T x R x L) were leached according to the guidelines of the NF EN 84 standard [26]. After leaching, samples were air-dried for 6h and oven-dried at 103°C until weight stabilisation. The leaching rate (LR) was calculated on 12 replicates according to equation (10):

$$LR\ (\%) = \frac{w_{t,d} - w_{t,l,d}}{w_{t,d} - w_{u,d}} \times 100 \quad (10)$$

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.

Biological resistance

Biological resistance was evaluated according to the guidelines of the EN 113 standard [27]. Samples of dimensions 15 x 25 x 50 mm^3 (T x R x L) were treated and leached according to the NF EN 84 [26] leaching procedure described above, then sterilized with gamma rays and consecutively placed in culture flasks on growing medium (40g/L malt and 20g/L agar) inoculated with *Trametes versicolor* (L. Quelet, strain CTB 863A) or *Coniophora puteana* (S. Karsten, strain BAM Ebw. 15) for 16 weeks (at 22°C, 70% RH). Sample weight loss was determined on 6 replicates as the ratio between the weight loss due to fungal exposure and the initial treated and leached anhydrous weight as follows:

$$WL_{exp}\ (\%) = \frac{w_{l,d} - w_{exp,d}}{w_{l,d}} \times 100 \quad (11)$$

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 moisture content (MC) in culture flasks at the end of exposure was calculated as follows:

$$MC\ (\%) = \frac{w_{exp,w} - w_{exp,d}}{w_{exp,d}} \times 100 \qquad (12)$$

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

FTIR-ATR

Products

FTIR spectra of impregnation products and Chestnut tannins were recorded using Perkin Elmer 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}. For each sample, 32 scans were conducted and averaged. Mean spectrum were analysed using Spectrum software (Perkin Elmer).

Treated wood

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 Perkin Elmer 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 spectrum were analysed using Spectrum software (Perkin Elmer). The baseline was first constructed by connecting the two lowest points around 1910 and 1550 cm^{-1}. Spectrum were then normalised on the peak at 1505 cm^{-1}.

Results and Discussion

Products characterization

Table 2 summarizes IR bands observed in FTIR-ATR spectra of CT, OLA, LA, CT-OLA and CT-LA.

FTIR-ATR spectrum of chestnut tannins revealed the presence of several functional groups typical of hydrolysable tannins (Figure 1). The peaks in the fingerprint are assigned [29, 30]: 3700-2900 cm^{-1} (a) for OH and aromatic CH stretching, 2972 and 2934 cm^{-1} (b) for aliphatic CH_3 and CH_2 stretching, 1721 cm^{-1} (c) for C=O stretching, 1605 cm^{-1} (d) for aromatic C=C *sym* stretching, 1513 cm^{-1} (f) for ring in plane bending, 1447 cm^{-1} (h) for aromatic C=C *antisym* stretching, 1176 cm^{-1} (k) for aliphatic C-O *sym* stretching and 1032 cm^{-1} (n) for aliphatic C-O *antisym* stretching. Absorption bands at 1605, 1176 and 1032 cm^{-1} are typical of gallic and ellagic-based compounds found in chestnut tannins [26, 27, 29].

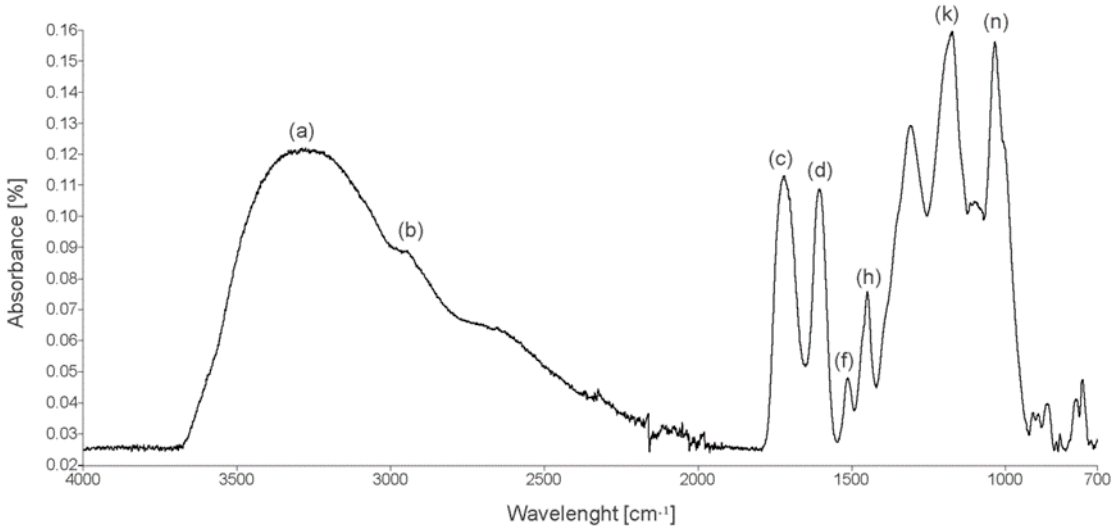


Figure 1: FTIR-ATR spectra of chestnut tannins in the middle infra-red range (4000-700 cm^{-1}). Table 2 summarizes absorption bands attribution.

Table 2: ATR-FTIR vibrational peaks attribution

N°	Band position (cm^{-1})									Assignment
	Products					Treated wood				
	TH	OLA	LA	CT-OLA	CT-LA	OLA	LA	CT-OLA	CT-LA	
a	3700-2900	3700-2900	3700-2900	3700-2900	3700-2900	3600-3050	3600-3050	3600-3050	3600-3050	OH stretching; aromatic CH stretching
b	2972; 2934	2988; 2940	2988; 2940	2988; 2940	2988; 2940	3000-2800	3000-2800	3000-2800	3000-2800	aliphatic CH_3; CH_2 stretching
c	1721	1733	1717	1734	1717	1748	1743	1747	1739	Carbonyl C=O stretching
d	1605	-	-	-	-	1601	-	1605	1604	Aromatic C=C *sym* stretching
e	-	-	1560	-	-	-	-	-	-	C-O-H deformation vibration
f	1513	-	-	-	-	-	-	-	-	Ring in plane bending
g	-	1452	1455	1453	1455	1452	1452	1452	1452	$-CH_3$ bending
h	1447	-	-	-	-					Aromatic C=C *antisym* stretching
i	-	-	-	-	-	1367	1367	1360	1361	C-H bending of cellulose
j	-	1267	-	1267	-					C=O bending of OLA
k	1176	1185	1222	1187	1208	1187	1205	1186	1197	Aliphatic C-O *sym* stretching
l	-	1123	1122	1121	1121	-	-	-	-	Aromatic skeletal and C-O stretching
m	-	1087	-	1088	1090	1084	1098	1084	1090	C-O-C stretching of OLA
n	1032	1040	1043	1040	1043	1037	1032	1035	1034	Aliphatic C-O *antisym* stretching

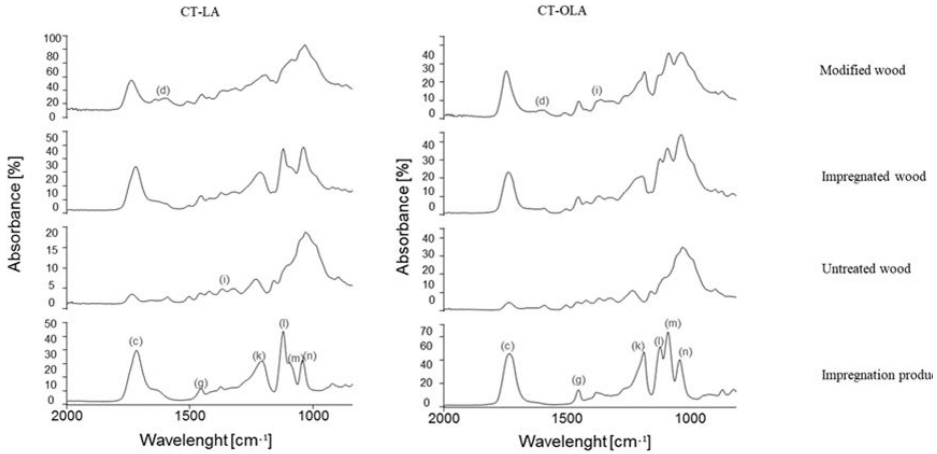


Figure 2: FTIR-ATR spectra of impregnation products (CT-LA and CT-OLA), untreated wood, impregnated wood and modified wood (CT-LA 140 and CT-OLA 140) in the middle infra-red range (2000-700 cm^{-1})

Table 3: Physical properties (swelling and weight uptake after impregnation (S_i and WU_i) and after treatment (S_t and WU_t) and hygroscopic behaviour (equilibrium moisture content (EMC) and anti-swelling efficiency (ASE) at 23°C and 100%RH) of treated and untreated wood. Average values obtained on 10 replicates of dimensions 15x15x10 mm^3 (TxRxL).

Treatment	S_i [%]	WU_i [%]	S_t [%]	WU_t [%]	$EMC_t/EMC_t^{*}{}_{(216h)}$ [%]	$ASE_t/ASE_t^{*}{}_{(216h)}$ [%]	$EMC_t/EMC_t^{*}{}_{(504h)}$ [%]	$ASE_t/ASE_t^{*}{}_{(504h)}$ [%]
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
LA 140	4.8 ±0.3	69.9 ±0.7	15.5 ±0.6	22.7 ±1.0	14.2 ±0.2	60.0 ±1.6	18.0 ±0.4	58.7 ±2.2
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
LA 160	5.4 ±0.2	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 ±1.2
CT-OLA 140	0.7 ±0.2	63.3 ±2.5	14.2 ±0.1	38.3 ±2.0	15.6 ±0.2	54.9 ±3.4	18.8 ±0.3	52.2 ±3.3
CT-LA 140	2.2 ±0.2	68.6 ±2.7	14.7 ±0.6	23.8 ±0.9	16.7 ±0.3	49.9 ±3.0	20.8 ±0.2	51.4 ±2.5
CT-LA 160	4.5 ±0.6	73.5 ±9.7	11.6 ±1.4	23.6 ±3.1	14.8 ±0.6	55.4 ± 4.8	18.4 ±0.7	55.7 ±4.5
12% OLA 160	5.9 ±0.3	104.0 ±6.8	14.0 ±0.5	29.1 ±2.5	11.7 ±0.8	67.3 ±5.0	14.9 ±1.1	68.5 ±3.2
12% LA 160	15.8 ±1.9	100.4 ±11.5	12.6 ±0.9	28.0 ±3.5	13.9 ±0.6	57.3 ±3.2	17.6 ±0.8	56.3 ±3.9
12% CT-LA 160	16.9 ±1.5	117.1 ±6.3	11.3 ±0.4	29.5 ±1.4	12.1 ±0.5	66.4 ±2.8	15.5 ±0.9	64.7 ±2.7
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
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
Ref	-	-	-	-	24.3 ±0.4	-	26.9 ±0.6	-

FTIR-ATR spectra of impregnation products (CT-OLA and CT-LA) are shown in Figure 2. The peaks in the fingerprint are assigned according to the literature [12, 32, 33, 34]: 1717/1733 cm^{-1} (c) for C=O stretching in LA/OLA, 1560 cm^{-1} (e) for C-O-H deformation vibration in LA, 1453 cm^{-1} (g) for $–CH_3$ bending in LA and OLA, 1267 cm^{-1} (k) for C=O bending in OLA, 1185/1222 cm^{-1} (l) for aliphatic C-O *sym* stretching in OLA/LA, 1122 cm^{-1} (m) for aromatic skeletal and C-O stretching in OLA and LA, 1087 cm^{-1} (n) for C-O-C stretching in OLA and 1040/1043 cm^{-1} (o) for aliphatic C-O *antisym* stretching in OLA/LA. Chestnut tannins were added in a small amount (5% w/w) in OLA and LA, thus none of the peaks which have only contribution from tannins are clearly visible. No major difference can be noticed between OLA and OLA CT spectra (Table 2). However, in CT-LA spectra, the peak at 1560 cm^{-1} (e) from C-O-H deformation vibration is no longer visible and the aliphatic C-O *sym* stretching vibration peak (l) is shifted to the lower wavelength.

Effect of tannins addition on wood modification

Table 2 and Table 3 respectively show wood weight and volumetric variations during treatment ($WU_{i/t}$, $S_{i/t}$) for samples of dimensions 15 x 15 x 10 mm^3 (T x R x L) and 15 x 25 x 50 mm^3 (T x R x L) respectively.

Effect of hydrolysable tannins addition on diffusion

OLA diffusion during impregnation is not affected by CT addition for the smallest samples (Table 3). In all cases, WU_i is between 60% and 65%, and almost no product diffuses into the walls (Si = 0%). For samples of dimensions 15 x 25 x 50 mm^3 (Table 4), impregnation is more difficult. During impregnation, tannins particles tend to gather on the wood surface, blocking the wood pores which limits diffusion. Smallest samples are most likely already saturated with OLA before pores blocking with tannins agglomerations. After heating, effective diffusion in wood cell walls can be observed with OLA and CT-OLA.

LA and CT-LA are both easily impregnated in beech wood. However, hydrolysable tannins addition in LA leads to a decrease in WU_i as well and lower diffusion in wood cell walls (S_i decreased by half), in comparison to pure LA treatment. Samples of dimensions 40 x 50 x 600 mm^3 were impregnated with LA and CT-LA, cured at 160°C for 48h and then sawed in the longitudinal direction to observe product diffusion (Figure 3). Whereas the colour of LA 160 was homogeneous, CT-LA 160 samples were lighter in the core. Because no such difference was noticed with LA 160, this can only be due to a lower product diffusion in the core of the samples.



Figure 3: Treatment diffusion in the core of samples of dimensions 40 x 50 x 600 mm^3 for LA 160 (a) and CT LA 160 (b)

Effect of hydrolysable tannins addition on OLA/LA polymerization

FTIR-ATR spectra of CT-OLA 140 and CT-LA 140 are shown in Figure 2. IR bands observed are summarized in Table 2. The peaks in the fingerprint are assigned according to literature [12, 32, 33, 34]. In addition to impregnated chemicals, wood components contributions are visible on FTIR spectra. OLA and LA polymerization and interactions with wood have been investigated in previous studies [17, 35]. Modified wood spectra being identical, influence of CT on polymerization could not be evidenced by FTIR. However, tannins might have an influence on OLA polymerization as the weight loss due to curing is lower for CT-OLA 140 than for OLA 140 (Table 2). Because the weight loss after curing was not influenced by tannins addition, polycondensation of LA was most likely not hindered by tannins.

Modified wood performance

The hygroscopic behaviour of modified wood is presented in Table 3 and product persistence and wood biological resistance in Table 4.

Table 4: Physical properties (swelling and weight uptake after impregnation (S_i and WU_i) and after treatment (S_t and WU_t), product water leaching resistance (LR) and biological resistance (weight loss after exposure to *T. versicolor* (WL_{TV}) and *C. puteana* (WL_{CP})) of treated and untreated wood. Average values obtained on 6 replicates of dimensions 15x25x50 mm^3 (TxRxL).

Treatment	S_i [%]	WU_i [%]	S_t [%]	WU_t [%]	LR [%]	WL_{TV} [%]	WL_{CP} [%]
OLA 140	-0.3 ±0.1	59.6 ±2.2	23.7 ±0.6	40.1 ±1.5	3.3 ±0.2	3.3 ±0.2	3.8 ±0.5
LA 140	6.0 ±0.5	76.9 ±6.9	20.5 ±0.5	35.5 ±3.0	9.3 ±1.5	4.5 ±0.3	-
OLA 160	0.0 ±0.2	58.7 ±1.5	19.2 ±0.8	31.2 ±1.5	2.3 ±0.2	2.0 ±0.1	2.7 ±0.2
LA 160	5.5 ±0.4	74.8 ±4.2	16.9 ±0.5	29.0 ±1.3	5.6 ±1.2	2.7 ±0.3	-
CT-OLA 140	-0.3 ±0.2	55.8 ±2.4	17.0 ±0.1	43.6 ±1.9	4.0 ±0.2	4.8 ±0.2	5.2 ±0.9
CT-LA 140	2.2 ±0.1	63.8 ±2.9	20.9 ±0.9	34.2 ±1.4	6.3 ±0.7	3.7 ±0.2	3.9 ±0.5
CT-LA 160	2.6 ±02	69.8 ±3.0	15.6 ±0.9	29.1 ±1.6	3.2 ±1.1	2.7 ±0.1	5.1 ±0.5
12% OLA 160	10.6 ±0.7	85.9 ±2.4	22.6 ±0.4	42.3 ±1.4	2.9 ±0.4	3.7 ±0.1	3.5 ±0.2
12% LA 160	18.0 ±1.0	94.7 ±3.6	19.3 ±1.2	38.4 ±1.8	3.8 ±0.2	3.6 ±0.2	4.2 ±0.2
12% CT-LA 160	14.7 ±0.7	91.0 ±3.6	18.3 ±0.5	35.4 ±1.3	2.9 ±0.4	3.0 ±0.1	4.0 ±0.4
Virulence control	-	-	-	-	-0.8 ±0.1	29.6 ±2.0	29.7 ±1.6

CT addition has a different effect depending on the treatment (OLA or LA). In both cases, the treatment efficiency regarding wood hygroscopic behaviour is reduced (Table 3). In CT-OLA 140 and CT-LA 140, the number of available hydroxyl groups might have increased in comparison to OLA 140 and LA 140, respectively. Tannins are hydrophilic and contribute to this increase, but if the polymerization was hindered, there might also be a higher amount of hydroxyl groups due to shorter oligomers.

Regarding wood biological resistance, virulence controls and controls in the flask with treated

samples had sufficient WL (> 20%) to validate the test and no sample had to be rejected. Tannins have an added value only when mixed with LA. When tannins are mixed with OLA, their biological activity does not allow to compensate the biological resistance decrease due to the lower curing temperature used for the treatment. However, hydrolysable tannins improved the modified wood biological resistance and product persistence when they were added to LA, for a curing at 140°C (CT-LA 140 in comparison with LA 140) and at 160°C (CT-LA 160 in comparison with LA 160). CT-LA 140 (WL_{TV} = 3.7%, WL_{CP} = 3.8%) showed performance similar to OLA 140 (WL_{TV} = 3.3%, WL_{CP} = 3.9%).

Because the treatment can be heterogeneous in the core of samples due to impregnation product diffusion, especially for long samples, beech samples of dimension 15 x 25 x 525 mm^3 (T x R x L) have been impregnated with OLA, LA or LA CT and cured at 160°C for 48h. They have been cut in 10 samples of dimension 50 x 25 x 15 mm^3 to evaluate resistance to *T. versicolor* in the length of the sample, according to EN113 standard (Figure 4). In the first 150 mm (sections a, b and c), no significant difference was observed between treatments. In the middle (sections d and e), a small decrease in treatment efficiency was noticed for OLA 160, but not for LA 160 and CT-LA 160. This is due to the higher viscosity of OLA in comparison with LA and CT-LA.

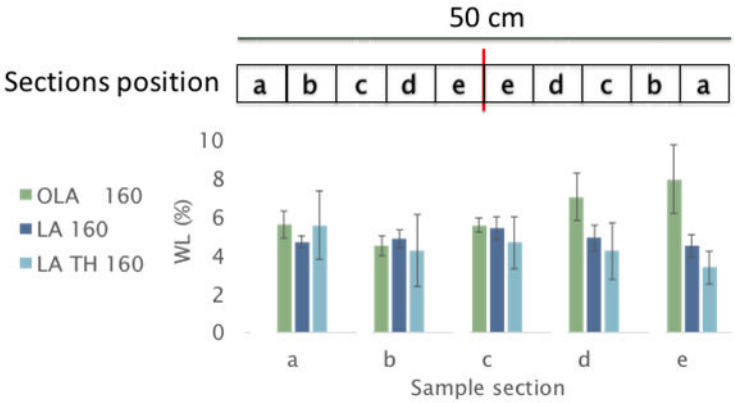


Figure 4: Weight loss (WL) after exposure to *C. versicolor* of long samples sections for OLA 160, LA 160 and CT LA 160.

Influence of wood initial moisture content

In this study, wood at 12% Moisture Content (MC) was impregnated with OLA, LA and CT-LA and cured at 160°C for 48h (referred as 12% OLA 160, 12% LA 160 and 12% CT-LA 160 respectively). Influence of wood initial moisture content on OLA and LA treatments performance has been investigated in another article for wood at fibre saturation point [17].

It was shown that moisture allows better diffusion of OLA in wood structure and has no deleterious effect on modified wood hygroscopic behaviour, but had mixed results with product persistence in wood and fungal decay. Durability of 12% OLA 160 is lower than OLA 160, but the WL after exposure to *T. versicolor* and *C. puteana* remained under 4%, showing the treatment efficiency against those two fungi (Table 4). Modified wood hygroscopic behaviour

and product persistence in wood remained the same for 12% OLA 160 and OLA 160. OLA treatment is more efficient if the wood is dry for impregnation. Depending on the targeted application, lower performance could be sufficient and wood drying before treatment could be avoided. Lower wood MC before impregnation allowed better performance for LA as well. ASE_t* decreased from 61% for LA 160 to 56% for 12% LA 160 with a higher standard deviation (Table 3). Treatment efficiency against fungal decay was lower as well, but WL after exposure to fungus remained under 5%. On the contrary, for CT-LA, wood initial moisture content increase improved hygroscopic behaviour and durability of CT-LA 160.

Conclusion

OLA 160 wood treatment performance regarding anti-swelling efficiency and durability are promising and the modified wood could be used outdoors. Enhancement of dimensional stability with OLA treatment is similar to acetylation and furfurylation treatments. For the same amount of product impregnated in wood (WU_t of ca. 30%) similar efficiency was observed (ASE* of ca. 65%) [25]. For industrial application, it is advisable to be able to decrease the curing temperature. Natural "biocidal" effect of tannins might improve the modified wood durability with milder curing conditions. Optimisation of this treatment was investigated regarding the influence of chestnut wood tannins addition to lactic acid oligomers or monomers on the treated wood properties, after curing at 160°C or 140°C. Tannins addition has a different effect depending on the treatment (OLA or LA). In both cases, the treatment efficiency regarding wood hygroscopic behaviour was reduced. However, hydrolysable tannins improved the modified wood biological resistance and product persistence when they were added to LA. Because LA is less viscous than OLA, performance of LA 160 and CT-LA 160 were more homogeneous in the length of the treated wood in comparison with OLA 160. Biological resistance of modified wood was improved by CT addition even though they do not diffuse in the core of the samples. For up-scaling, LA based treatments might be more suitable because LA diffuses better in wood and might provide sufficient resistance to fungal decay for some applications. OLA 160 was always the best performing treatment regarding dimensional stability and durability, but two other candidates of modified wood for outdoor application arose from this study: LA 160 and CT-LA 160.

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Paper 5: FTIR-ATR monitoring of chemical changes of thermo-chemically modified beech wood degraded by brown-rot fungus

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Section 4 **Processes and properties**

FTIR-ATR monitoring of chemical changes of thermo-chemically modified beech wood degraded by brown-rot fungus

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FTIR-ATR monitoring of chemical changes of thermo-chemically modified beech wood degraded by brown-rot fungus

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ABSTRACT

Wood chemical modification with lactic acid oligomers (OLA) has been reported to confer promising properties for wood outdoors applications. To better understand the lactic acid interaction with wood, chemical changes following biological degradation have been characterized with a battery of tests. Fourier transform infrared (FTIR) spectroscopy has been proved to be a valuable tool for studying fungal decay and chemical changes of degraded beech wood have been already investigated. In this study, changes in modified wood chemistry following decay by brow-rot fungus were assessed by FTIR spectroscopy. Wood specimens of beech (*Fagus sylvatica L.*) were modified by a thermo-chemical treatment process. Oligomer systems based on lactic acid, were impregnated in oven-dried wood and polymerised *in situ* by heat treatment according to a treatment process reported by Grosse *et al*. (2016). Treated and untreated specimens were tested according to the guidelines of EN 113 standard: after water leaching (EN84), samples were exposed to *Coniophora puteana* for 16 weeks. Decay was assessed through weight loss: values for treated samples were in the range of 2.69% to 3.76% for modified wood and 29.7% for native beech. The ratios of the areas of the lignin/carbohydrates FTIR peaks were determined before and after exposure. Lignin, carbohydrates and cured OLA associated bands relative intensities were used to assess wood degradation. Analyse of the degradation patterns of modified wood, in comparison with unmodified wood, shows the effect of treatment on fungal mode of action regarding the attack selectivity on modified wood components (lignin, carbohydrates and OLA).

Keywords: wood modification, lactic acid, FTIR-ATR, brown-rot.

1. INTRODUCTION

It is both an industrial and societal strong demand today to take in account the environmental impact of any new process or product to be implemented on the market. For any outdoor use, wood should be protected by means of relatively detrimental agents towards the environment. If solutions have been offered in the field of wood modification, providing significant improvements in dimensional stabilization and decay resistance, none is perfectly satisfying and

competitive (Hill 2006a, 2006b, Rowell 2005, Lande *et al*. 2004). For this reason, it is important to continue the development of new wood modification processes.

Wood chemical modification with lactic acid oligomers (OLA), developed through the WoodWisdom Net+ JC4 project BioCoPol and COST FP1303 project BioThermoWood, has been reported to confer promising properties of treated wood for outdoors applications (Noël *et al*. 2015, Grosse *et al*. 2016). While dimensional stability of the treated wood is relatively independent of treatment parameters (temperature, duration, oligomers initial polymerization degree or wood initial moisture content), its decay resistance is more variable. Fourier transform infrared (FTIR) monitoring of chemical changes occurring during this treatment and *in-situ* polymerisation of OLA were evidenced by Grosse *et al*. (2017). The FTIR spectra of unmodified wood, impregnated wood and modified wood were measured by ATR method. Significant changes in IR spectra can be observed after each step of the process, showing the *in-situ* polymerisation of OLA. After impregnation, the amount of ester and alcohol groups was increased by the addition of OLA in wood. After curing, C-O peaks intensity decreased because of OLA polymerization. C-O stretching peaks of OLA (1195 cm^{-1} and 1122 cm^{-1}) 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 (Qu *et al*. 2010). C=O stretching peak (1738 cm^{-1}) shifted at a higher wavenumber, showing a higher ester linkage content due to OLA polymerisation (Noël *et al*. 2009). Furthermore, impregnated wood band around 1738 cm^{-1} is larger than the one of completely treated wood: acid groups disappeared and ester groups were created with OLA polymerisation. FTIR spectroscopy has also been proved to be a valuable tool for studying fungal decay (Moore and Owen 2001) and chemical changes of degraded beech wood have been already studied (Faix et al. 1991, Pandey and Pitman 2003). This article reports FTIR monitoring of chemical changes in modified wood following decay by brow-rot fungus. To optimize the treatment, but also to be able to foresee durability of the material, understanding of brown-rot degradation mechanism of the modified wood is necessary. Treated and untreated specimens were degraded according to the guidelines of EN 113 standard (1996): after water leaching (EN84, 1997), samples were exposed to *Coniophora puteana* for 16 weeks. Decay was assessed through weight loss. The ratios of the areas of the lignin/carbohydrates FTIR peaks were determined before and after exposure to fungus.

2. MATERIALS AND METHODS

2.1. Materials

Wood samples (50x25x15 mm^3 RxTxL) were cut from beech (*Fagus sylvatica L*.) (700±0.01 $kg.m^{-3}$) and oven-dried to constant weight prior to impregnation. L(+)-Lactic acid solution (≥85% m/m) was sourced from Sigma-Aldrich (Switzerland).

2.2. Lactic acid oligomers (OLA) preparation

Lactic acid oligomers (OLA) were prepared following the method described by Grosse *et al*. (2017). Oligomeric polyesters were synthesized by their direct polymerization under vacuum, using a four-necked flask (500 mL or 1L) fitted 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 as an initial distillation step of 1h. The initial oligomerisation step involved gradually increasing the temperature to 140°C for 2.5h.

2.3. Wood treatment

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

As described by Noël *et al*. (2009, 2015), 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 of product. Dry curing was carried out in a ventilated oven at 140°C (OLA 140) and 160°C (OLA 160) for 48h.

Weight uptake and swelling, after impregnation (WU_i and S_i) and after treatment (WU_t and S_t) were calculated as followed:

$$WU_{i/t}\ (\%) = \frac{w_{i/t,d} - w_{u,d}}{w_{u,d}} \times 100 \qquad (1)$$

$$S_{i/t}\ (\%) = \frac{V_{i/t,d} - V_{u,d}}{V_{u,d}} \times 100 \qquad (2)$$

where w_i and V_i stand for the impregnated sample weight and volume respectively and $w_{t,d}$ 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. Leaching

Samples of dimensions 50 × 25 × 15 mm^3 (L × T × R) were leached according to the guidelines of the NF EN 84 standard (1997). 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 following:

$$LR\ (\%) = \frac{w_{t,d} - w_{t,l,d}}{w_{t,d} - w_{u,d}} \times 100 \qquad (3)$$

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

2.5. Biological resistance

Biological resistance was evaluated according to the guidelines of the EN 113 standard (1996). Samples of dimensions 50 × 25 × 15 mm^3 (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 *Coniophora puteana* (strain Bam Ebw.15) for 16 weeks (at 22 °C, 70% RH). Six untreated beech samples of the same dimensions were also used as virulence controls. 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:

$$WL_{exp}\ (\%) = \frac{w_{t,l,d} - w_{t,exp,d}}{w_{t,l,d}} \times 100 \qquad (4)$$

where $w_{t,l,d}$ is the specimen weight after treatment, leaching and drying, and $w_{t,exp,d}$ is the treated specimen weight after exposure at dry state. The final humidity of the samples in culture flasks at the end of exposure was calculated according to Eq. 13:

$$H\ (\%) = \frac{w_{t,exp,w} - w_{t,exp,d}}{w_{t,exp,d}} \times 100 \qquad (5)$$

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

2.6. FTIR-ATR

The FTIR spectra of dry solid wood were recorded for samples after heat treatment, after leaching and after fungal exposure, 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 heights of the peaks were measured from the baseline, which was constructed by the connection of the two lowest data points on either side of the peak. Drawing and measuring a vertical line to the top of the peak determined the peak height. The ratios of lignin peaks intensities against those of the carbohydrates were calculated before and after fungal exposure.

3. RESULTS AND DISCUSSION

3.1. Weight loss data

Treatment persistence in wood and biological resistance are presented in Table 1. All control samples (control beech in the flask with modified wood) had a WL above 20% and all modified wood samples had a H between 20% and 80% at the end of the test. Thus, no sample had been rejected according to EN113 specifications. Wood treatment with OLA provides a significant biological resistance to wood. 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_{exp} is below this threshold value (WL_{exp} = ca. 2.7%). However, the efficiency of the treatment decreased for OLA 140.

Table 1: Mean percentage weight uptake after treatment (WU_t), swelling after treatment (S_t), leaching rate (LR), humidity at the end of the test (H) and weight loss (WL_{exp}) of modified wood and virulence control samples). Quantities given in the parentheses correspond to values from control samples in the flask with modified wood.

Treatment	WU_t [%]	S_t [%]	LR [%]	H [%]	WL_{exp} [%]
OLA 140	40.1 ±1.5	23.7 ±0.6	3.3 ±0.2	41.8 ±2.7 (59.7 ±1.0)	3.8 ±0.5 (35.0 ±0.9)
OLA 160	31.2 ±1.5	19.2 ±0.8	2.0 ±0.1	33.2 ±1.5 (57.5 ±3.2)	2.7 ±0.3 (37.7 ±2.0)
Virulence control	-	-	0.8 ±0.1	59.2 ±4.2	29.7 ±1.6

3.2. FTIR studies

3.2.1. Unmodified and modified wood

Detailed description of the bands assignments and changes in the FTIR spectra due to treatment has been provided by Grosse *et al*. (2017). The peaks used in this study are assigned as follows

(Pandey 1999; Pandey *et al*. 2003, 2004; Qu *et al*. 2010; Naumann *et al*. 2005): 1747 cm^{-1} for unconjugated C=O in OLA, 1738 cm^{-1} for unconjugated C=O in xylan (hemicellulose), 1596 cm^{-1} and 1505 cm^{-1} for aromatic skeletal in lignin, 1462 cm^{-1} and 1425 cm^{-1} for C-H deformation in carbohydrates and lignin, 1375 cm^{-1} for C-H deformation in cellulose and hemicellulose, 1330 cm^{-1} for C-H vibration in cellulose C_1-O vibration in syringyl derivatives, 1268 cm^{-1} and 1230 cm^{-1} for C-O stretch in lignin and xylan, 1186 cm^{-1} for C-O stretch in OLA, 1158 cm^{-1} for C-O-C vibration in cellulose and hemicellulose, 1122 cm^{-1} for aromatic skeletal in lignin and C-O stretch, 1087 cm^{-1} for C-O-C stretch in OLA, 898 cm^{-1} for C-H deformation in cellulose. Table 2 summarized absorption bands attribution.

Table 2: Absorption bands attributions

	Band position (cm-1)		Assignment
	Beech	Modified wood	
a	1738	1747	C=O stretch in hemicellulose and OLA
b	1596/1505	1596/1505	Aromatic skeletal in lignin
c	1462/1425	1450/1425	C-H deformation in carbohydrates and lignin
d	1375	1375	C-H deformation in cellulose and hemicellulose
e	1330	1330	C-H vibration in cellulose and C_1-O vibration in syringyl derivatives
f	1268/1230	1268	C-O stretch in lignin and xylan
g	-	1186	C-O stretch in OLA
h	1158	-	C-O-C vibration in cellulose and hemicellulose
i	1122	1122	Aromatic skeletal in lignin and C-O stretch
j	-	1087	C-O-C stretch in OLA
k	898	-	C-H deformation in cellulose

3.2.2. Beech decayed by C. puteana

FTIR spectra of undecayed beech and beech exposed to *C. puteana* for 16 weeks are shown in Figure 1. Brown rot fungi degrade and metabolize cellulose and hemicellulose and leave the lignin almost unaltered (Enoki *et al*. 1998; Perez *et al*. 1993; Schmidt 2006). FTIR studies of the chemical changes in beech decayed by *C. puteana* has been already reported by Pandey *et al*. (2003, 2004). The intensity of carbohydrates bands at 1738, 1375, 1158 and 898 cm^{-1} decreased after exposure to the fungus and intensity of absorption bands resulting from lignin at 1596, 1505, 1462, 1425, 1330, 1230, and 1122 cm^{-1} increased. This is due to an increase in the wood lignin content resulting from polysaccharide components decay.

The ratios of the lignin/carbohydrate peak height have been calculated for undecayed and decayed beech (Table 3), according to the same method described by Pandey *et al*. (2003). Because *C. puteana* alter carbohydrates with limited lignin degradations, the ratios increased after fungal exposure. The biggest variation is observed for the peak at 898 cm^{-1} characteristics of C-H deformation in cellulose, but relative intensity of C-O-C vibrations in cellulose and hemicellulose (1158 cm^{-1}) and unconjugated C=O stretch in xylan (1738 cm^{-1}) respectively, also decreased by 4 and 3 respectively.

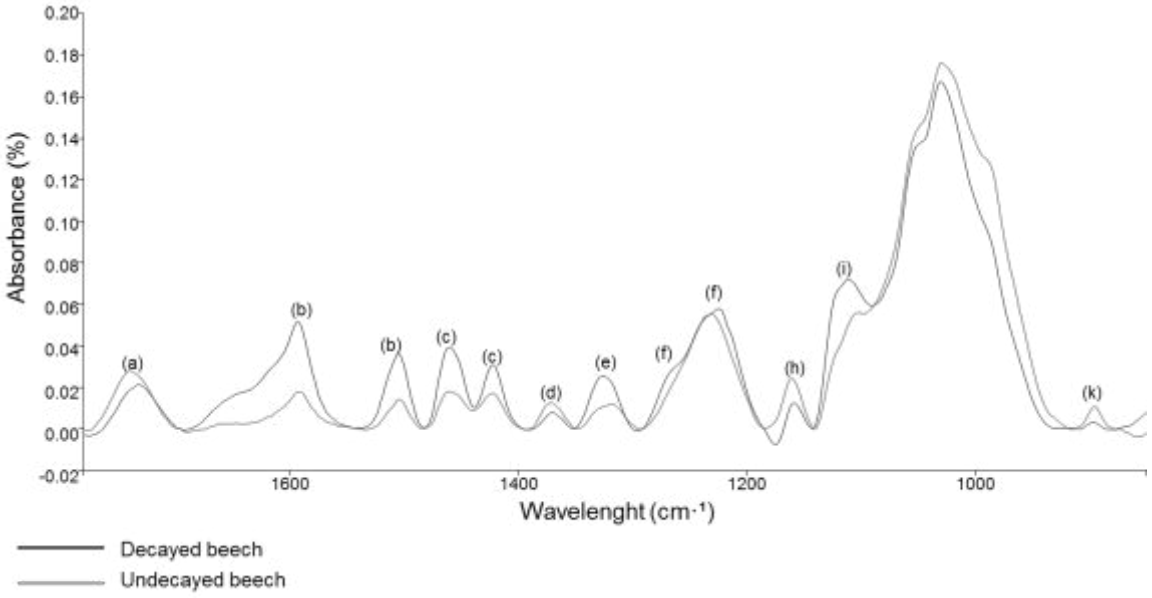


Figure 1: FTIR spectra of undecayed beech and beech decayed by *C*. *puteana* after 16 weeks

For undecayed beech, significant differences appeared for ratios involving peaks at 1158 cm^{-1} and 898 cm^{-1}, when similar values were obtained for 1738 cm^{-1} and 1375 cm^{-1}. This is most likely due to the difference in the sample's preparation method. In Pandey *et al*. (2003), wood blocks were extracted with a solution of ethanol and toluene and oven-dried at 60°C, whereas in this study, samples were leached with water and oven-dried at 103°C. Also, the samples size was different, and so was the wood surface/volume ratio. For decayed beech, it seems that fungi used in this study were less aggressive than the one used by Pandey *et al*. (2003). Indeed, after 16 weeks of exposure, samples shown WL_{exp} obtained after only 8 weeks in Pandey *et al*. (2003). However, the lignin/carbohydrate peak heights ratios progression is consistent with the WL_{exp}.

Table 3: Ratios of the intensity of the lignin associated bands with carbohydrates bands for undecayed and decayed samples

	Measured		**Pandey *et al*. (2003)**	
Relative intensities of lignin against carbohydrates typical bands	**Undecayed beech**	**Decayed beech Exposed 16 weeks WL_{exp} = 40%**	**Undecayed beech**	**Decayed beech Exposed 8 weeks WL_{exp} = 40%**
I_{1505}/I_{1738}	0.45	1.30	0.45	0.95
I_{1505}/I_{1375}	1.01	4.20	1.38	4.51
I_{1505}/I_{1158}	0.58	2.36	1.73	5.02
I_{1505}/I_{898}	1.28	10.12	2.24	17.19

Those ratios have been linearly correlated with the wood lignin content (Pandey *et al*. 2004). It can be calculated according to the following equation:

$$\text{Lignin } \% = 15.6 + 8.91 \times \frac{I_{1505}}{I_{1374}} \qquad (6)$$

Pandey *et al*. (2004) found good correlations between the lignin content and peak heights ratios for lignin/carbohydrates were obtained with 1738, 1374 and 1158 cm^{-1} for unmodified wood. However, I_{1505}/I_{1374} was used in this study to calculate the lignin content because there is no contribution of OLA in the peak at 1374 cm^{-1}. The lignin content calculated according to Eq. 6 is of ca. 24.6% for undecayed beech and 53.0% for decayed beech. Pandey *et al*. (2004) also

measured the lignin content with acetyl bromide method and found a correlation with the WL_{exp}. For undecayed beech (WL_{exp} = 0%), the lignin content was about 25% and about 55% for decayed beech with a WL_{exp} of ca. 40%. Results consistency confirms the choice of the ratio I_{1505}/I_{1374} to estimate the lignin content in this study.

3.2.3. Modified wood decayed by C. puteana

FTIR spectra of undecayed modified wood and modified wood exposed to *C. puteana* for 16 weeks are shown in Figure 2. Table 2 summarized absorption bands attribution. Like for unmodified wood, intensity of carbohydrates bands at 1747 and 1375 cm^{-1} decreased after exposure to the fungus because of hemicellulose degradations. However, the intensity of the peak at 898 cm^{-1}, characteristics of C-H deformation in cellulose, increased. This last observation is most likely due to OLA degradation and the resulting decrease of interactions between the oligomers and cellulose. OLA degradation can also be evidenced with the intensity decrease of the peak at 1087 cm^{-1}. Absorption bands resulting from lignin at 1596, 1505, 1462, 1425, 1268 and 1122 cm^{-1} have the same intensity before and after exposure to the fungus.

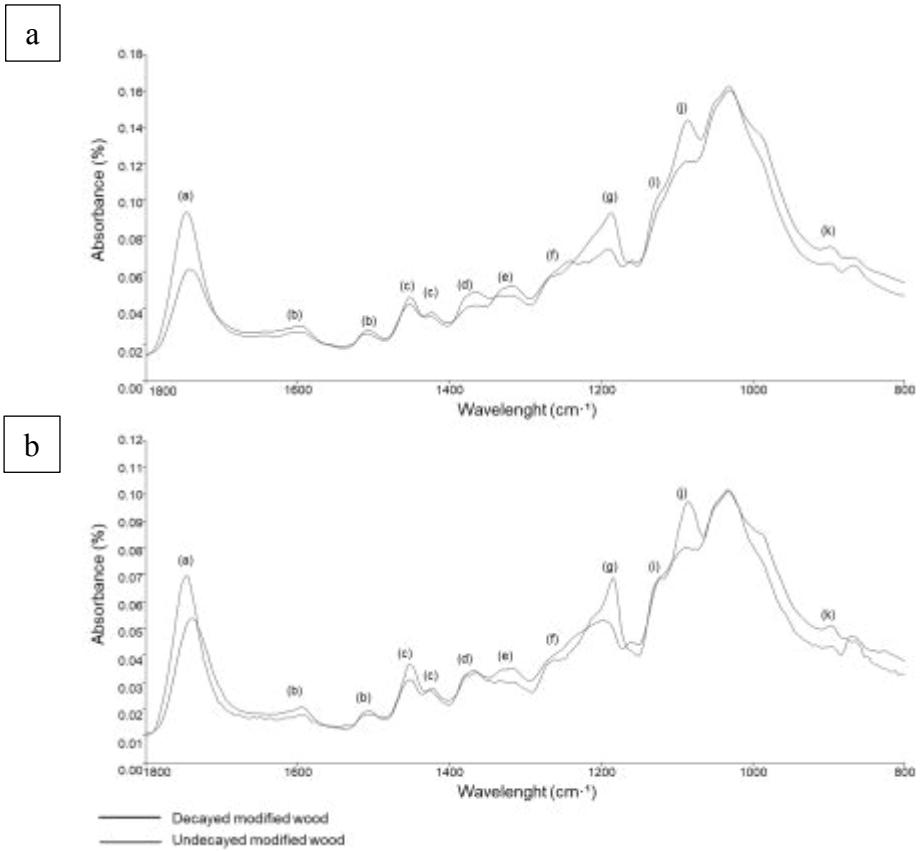


Figure 2: FTIR spectra of undecayed modified wood and modified wood decayed by *C. puteana* after 16 weeks, for treatment at 160°C (a) and 140°C (b)

The ratios of the lignin/carbohydrate and lignin/OLA peak height have been calculated for undecayed and decayed modified wood. Results are shown in Table 4. Because values of I_{1505}/I_{1747} and I_{1505}/I_{1375} increased, but less than for unmodified wood, and value of I_{1505}/I_{898} decreased, OLA treatment has most likely a protective effect for cellulose but not for hemicellulose. However, *C. puteana* could be able to hydrolyse OLA because values of I_{1505}/I_{1186} and I_{1505}/I_{1087} increased. Treatment at higher temperature is more efficient against the fungus. C-O links could be less vulnerable with a more extend polymerization. I_{1505}/I_{1087} increased more for

treatment at 140°C in comparison with treatment at 160°C, whereas it has almost no influence on the other ratios increases.

The lignin content calculated according to Eq. 6, for treatment at 160°C, is of ca. 21.1% for undecayed modified wood and 32.4% for decayed modified wood. Because it has been calculated with I_{1505}/I_{1374} ratio, the calculated lignin content takes only the wooden part of the material in account. It is in the same range as unmodified wood (between 20% and 25%). After exposure to the fungus, the lignin content increase evidenced cellulose and hemicellulose degradation, which is however, reduced in comparison with unmodified wood.

Table 4: Ratio of the intensity of the lignin associated band at 1505 cm^{-1} with carbohydrates and OLA bands for un-decayed and decayed samples.

	Modified wood cured at 160°C		**Modified wood cured at 140°C**	
Relative intensities of lignin against carbohydrates and OLA typical bands	**Undecayed**	**Decayed**	**Undecayed**	**Decayed**
$\mathbf{I_{1505}/I_{1747}}$	0.07	0.15	0.04	0.12
$\mathbf{I_{1505}/I_{1375}}$	0.62	1.88	0.35	0.80
$\mathbf{I_{1505}/I_{1184}}$	0.20	0.68	0.11	0.37
$\mathbf{I_{1505}/I_{1087}}$	0.06	0.11	0.13	0.67
$\mathbf{I_{1505}/I_{898}}$	2.32	1.88	1.39	1.60

4. CONCLUSION

Wood modification with OLA treatment increases significantly beech biological resistance. Analyse of the way of degradation of modified wood, in comparison with unmodified wood, shows the effect of treatment on fungus mode of action regarding the attack selectivity on modified wood components. Wood carbohydrates, as well as OLA, are decayed by *C. puteana*. However, OLA most likely postpone the cellulose degradation. In this way, OLA treatment may allow to maintain longer the wood mechanical properties. More research is being carried out on wood modification with OLA and treatment preservation mechanism.

5. ACKNOWLEDGEMENT

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PART B: Wood modification with poly(butylene succinate) oligomers (OBS)

1. Process development

In this part, wood modification with poly(butylene succinate) oligomers (OBS) is approached based on the previous work from Noël *et al*. (2014, 2015a, 2015b). When impregnation was followed by curing at moderate temperature (120°C/140°C), the treatment did not lead to wood dimensional stability enhancement because OBS treatment is only lumen-filling. The combination of OBS impregnation with long dry heat treatment (9 days, 160°C) appeared to lead to dimensional stabilisation up to 55% even with no diffusion of OBS in cell wall. Dimensional stability was assessed before and after water leaching test with the same samples. Because the samples cured at moderate temperature had residual swelling after water leaching and drying, and because the leached samples showed an increased anti-swelling efficiency, it seemed worthy to investigate the influence of humidity during curing. The possibility of curing in humid atmosphere would be a considerable advantage for industrial implementation of the process as steam is generally used for heat convection for the production of thermo-treated wood.

A heat treatment in humid atmosphere (hygro-thermal treatment (HTT)) has been carried out with OBS impregnated beech in a pressurised reactor. The aim of the HTT is to induce partial swelling of wood cell walls so that the OBS can diffuse into the structure. Figure 31 illustrates the three steps of the whole process.

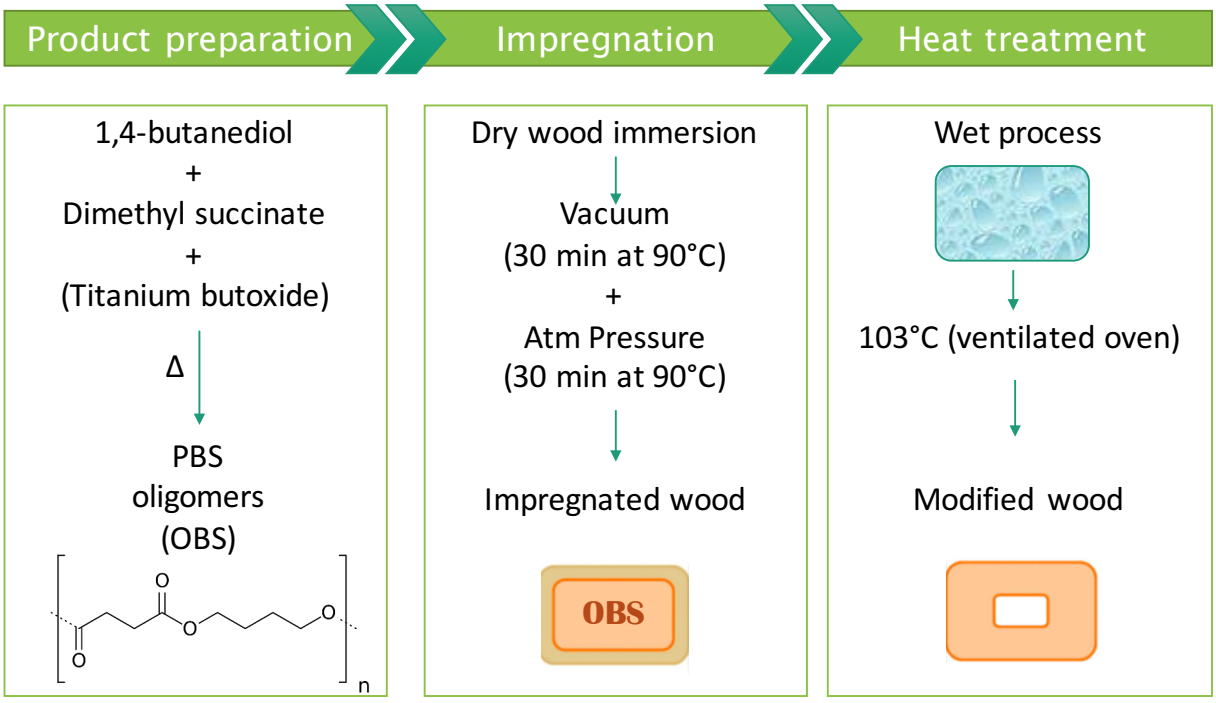


Figure 31 : Three steps process of wood modification with poly(butylene succinate) oligomers.

Impregnation yield (IY) and weight percentage gain (WPG) indicate the amount of oligomers within the wood and swelling (S) and bulking coefficient (BC) are indicators for the product diffusion in the wood cell walls. They are calculated on the wood anhydrous weight basis (according to Eq.8, Eq.10, Eq.9 and Eq.11 respectively) after impregnation and after complete treatment (Figure 32).

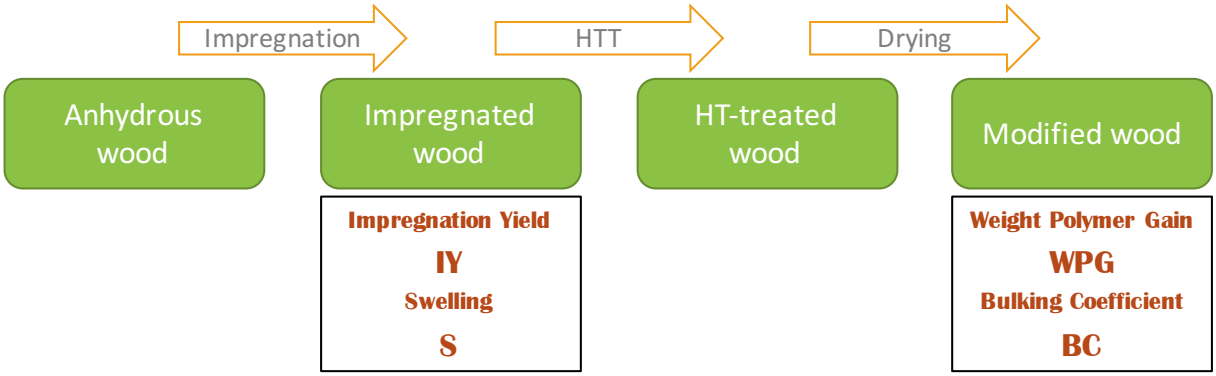


Figure 32 : Indicators of the amount of product within the wood (IY and WPG) and product diffusion in the wood structure (S and BC) calculated after impregnation and after complete treatment..

The influence of HTT duration, temperature and relative humidity in the reactor on products diffusion in the cell wall, OBS curing and modified wood performance were assessed. The results were presented in two deferent papers listed below. An overview of materials and methods of the four papers presented in this chapter is given in Table 8.

Paper 6: Wood modification with poly(butylene succinate) oligomers: influence of hygro-thermal treatment conditions. (Grosse *et al*. 2018c, submitted in: *Wood Science and Technology*).

Paper 7: Influence of hygro-thermal treatment temperature and duration on dimensional stabilisation of wood modified with poly(butylene succinate) (Grosse *et al.* 2017b, in: *proceedings of IRG WP 48*).

Table 8 : Overview of materials and methods of the two papers presented in this chapter.

Materials and Methods			**Characterisation of…**	**Paper**
Chromatography	GPC	Oligomers and Extracted oligomers	OLA molecular mass repartition	6
Anti-swelling efficiency	Stabilisation at ca. 100% RH at 23°C	Solid wood (15x15x10 mm^3)	Treatment efficiency Wood dimensional stability	7
Equilibrium moisture content	Stabilisation at ca. 100% RH at 23°C		Treatment efficiency Wood sorption behaviour	7
Long water leaching	3 weeks immersion in water at 23°C	Solid wood (15x15x10 mm^3)	Treatment persistence Polymer stability Influence of hydrolysis	6,7

1.1. OBS impregnation and curing

Despite of a mean impregnation yield of 67.4%, only ca. 1% volumetric increase is observed after impregnation, showing that OBS do not penetrate the cell walls at this stage of the process.

Characterisation of the impregnation product was carried out. Relative molecular weight distributions of oligomers mixtures are presented in Figure 33 : Relative molecular weight distribution of OBS and further polymerised oligomers produced from OBS. OBS produced in laboratory according to the method described by Noël *et al.* (2014, 2015a, 2015b), is a mixture of monomers and oligomers up to 60 units (ca. 10 000 $g.mol^{-1}$) and residual methanol from polymerisation reaction. After impregnation, the relative decrease of small oligomers amount and increase of longer oligomers amount showed that oligomers with the lowest molecular mass (lower than 900 $g.mol^{-1}$) are preferentially diffusing in wood.

Because OBS is solid at room temperature, impregnation was carried out above the melt temperature at ca. 90°C. According to the relative molecular weight distribution of oligomers mixtures cured at 103°C for 48h, oligomers do not further polymerise during impregnation. A post treatment of impregnated wood carried on at 103°C for 48h would also not lead to significant further polymerisation of OBS in the wood structure.

An effective polymerisation is observed after curing at high temperature (140° or 160°C). After 2h at 160°C, most of the smallest oligomers disappeared. A curing step combining high relative humidity and high temperature might result in partial diffusion of products in cell wall and *in situ* polymerisation of OBS.

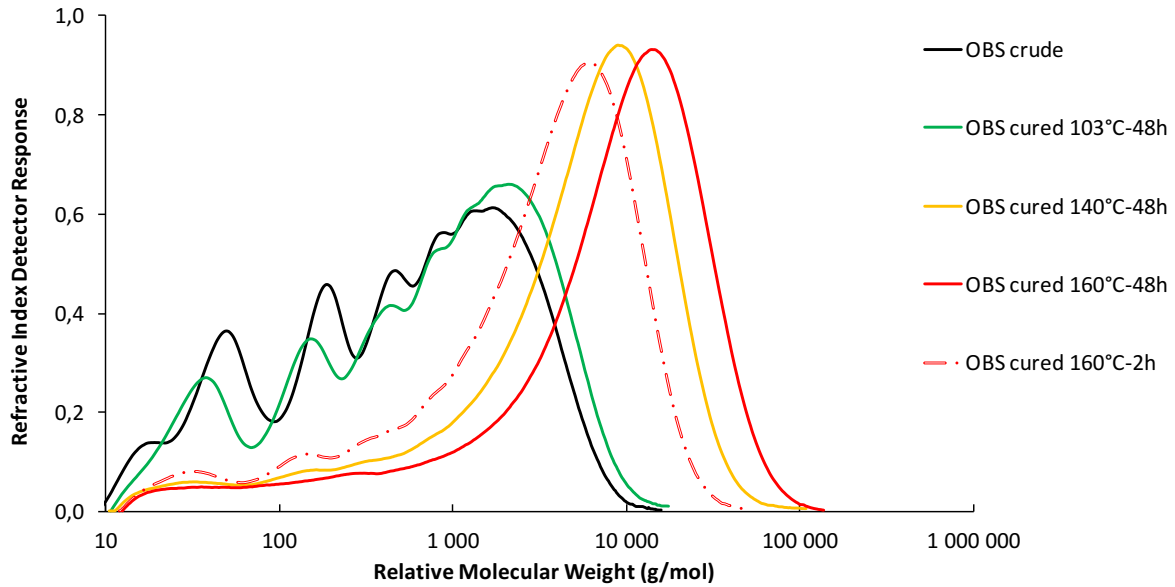


Figure 33 : Relative molecular weight distribution of OBS and further polymerised oligomers produced from OBS.

1.2. Influence of hygro-thermal treatment on OBS diffusion

Enhancement of OBS diffusion has been attempted through HTT which should induce partial swelling of wood cell walls with water so that the OBS can diffuse into the structure. HTT has been carried out with OBS impregnated beech in a pressurised reactor. HTT conditions are summarised in Table 9. Vapour pressure was regulated by increasing temperature in the external water reservoir and releasing excess pressure to ensure constant process RH. A final thermal post-treatment (103°C-48h in a ventilated oven) was carried out to dry the treated samples. The influence of treatment duration, temperature and relative humidity on products diffusion in the cell wall was assessed.

Table 9 :Hygro-thermal treatment conditions

Temperature (°C)	Relative humidity (%)	Pressure (MPa)	Duration (h)
100	100	0.10	2
100	100	0.10	0.5
130	100	0.27	2
130	80	0.22	2
130	50	0.13	2
130	100	0.27	0.5
130	80	0.22	0.5
130	50	0.13	0.5
160	100	0.62	2
160	80	0.49	2
160	50	0.31	2
160	20	0.12	2
160	100	0.62	0.5
160	80	0.49	0.5
160	50	0.31	0.5
160	20	0.12	0.5

Effective diffusion of products in the cell walls was observed after HTT (Figure 34). The BC measured after HTT is always substantially higher than the swelling obtained after impregnation (BC value for a HTT of 0h). BC variations with HTT conditions do not follow a clear pattern. However, some affirmations can be done. The diffusion is faster at 130°C and 160°C than at 100°C. A maximum BC is reached around 15% (HTT carried out for 10h at 100°C and 100% RH results in a BC of ca.15% as well). Two options appear to be competing for effective diffusion of OBS: high temperature (160°C) for short time (0.5h) or low temperature (100°C) for long time (2h).

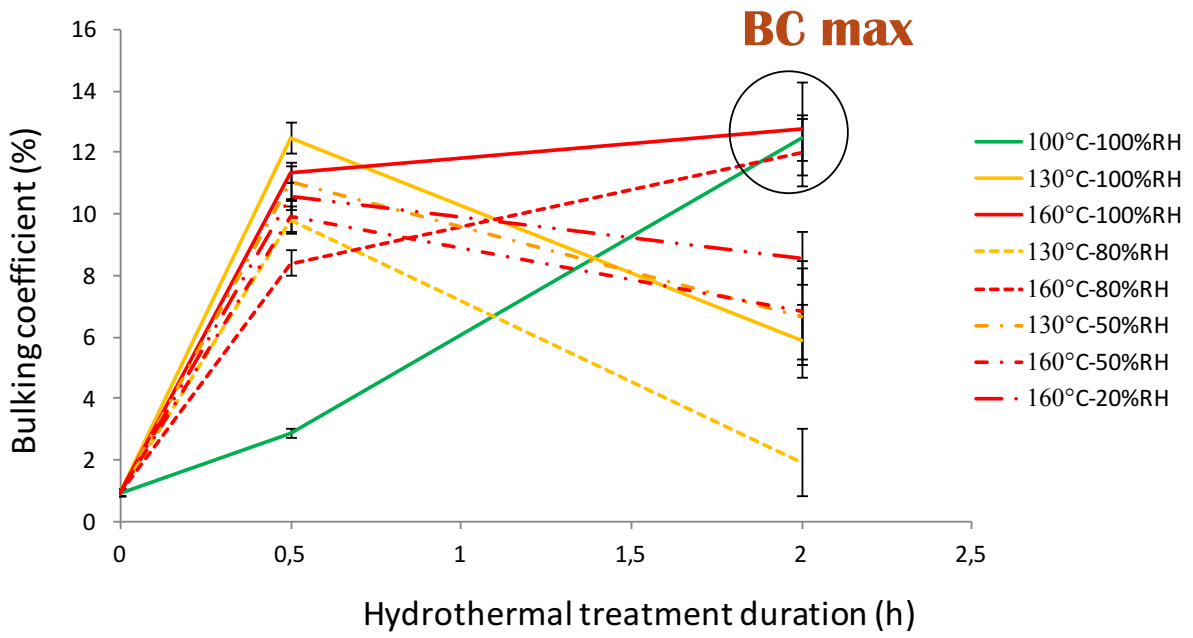


Figure 34 : Influence of hygro-thermal treatment duration, temperature and relative humidity on products diffusion in the cell wall (BC)

1.3. Mechanism of OBS diffusion during hygro-thermal treatment

BC variations with HTT conditions do not follow a clear pattern. The mechanism of OBS diffusion during HTT is most likely due to a combination of phenomena acting simultaneously. This chapter relates how OBS hydrolysis and HTT conditions might influence products diffusion in the cell walls. Due to OBS relative sensitivity to water at those high temperatures, there is a risk of oligomers hydrolysis in the process (Kanemura *et al.* 2012). Besides, the high pressure needed to get to 100% RH at high temperature could certainly influence the products flow into wood structure.

High RH in the reactor might lead to degradation of OBS during HTT (Figure 35 and Figure 36), especially in combination with high temperature. Indeed, ester groups present in OBS are sensitive to hydrolysis, leading to random ester linkage cutting along the main chain, resulting in a decrease of polymerization degree (Freyermouth, 2014). Furthermore, if the wood is saturated with moisture during HTT, further polymerization could be prohibited (Garin, 2012). Reducing RH during HTT at high temperature might allow enduring efficient OBS diffusion in the cell walls while avoiding extended oligomers hydrolysis.

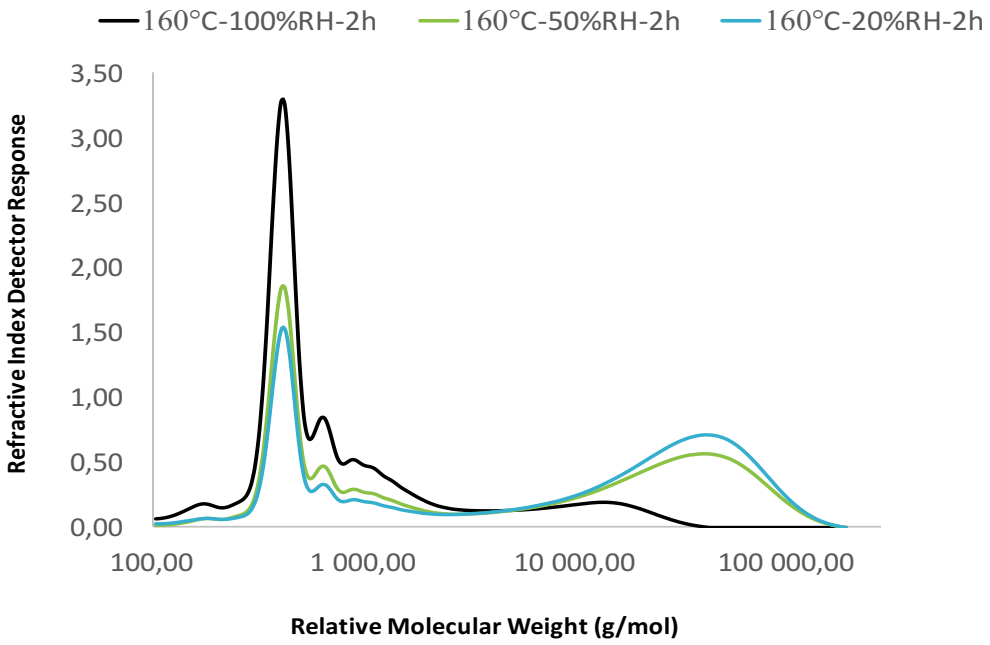


Figure 35 : Influence of relative humidity (RH) at 160°C on the OBS relative molecular weight distribution extracted from modified wood.

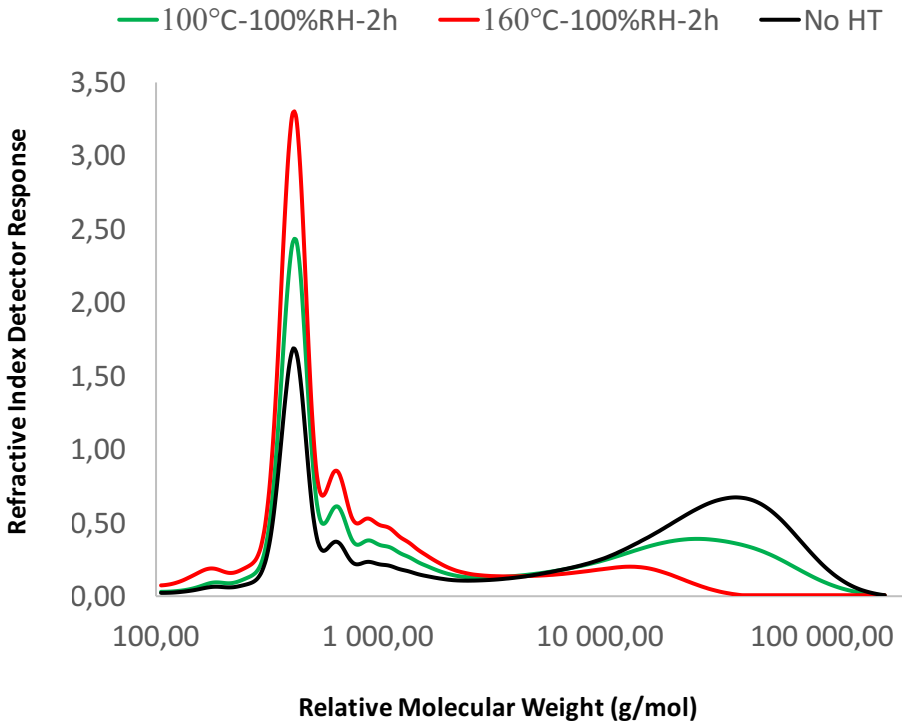


Figure 36 : Influence of temperature at 100% relative humidity (RH) on the OBS relative molecular weight distribution extracted from modified wood.

Figure 37 shows correlation between BC and pressure in the reactor, rather than temperature or process RH. Altgen *et al.* (2016) suggested that with high pressure, wood degradation products may remain within wood during hydrothermal treatment. The same conclusion could be drawn for hydrolysed OBS chains. At higher pressure, chemicals have a higher boiling point. Therefore, combination of OBS hydrolysis producing smaller molecules able to penetrate the

cell walls and high pressure reducing the leaching of chemicals and saturating the cell walls with it, can explain the increase of BC only when the pressure was high enough.

It is likely that each combination of HTT parameters leads to different modified wood properties. Therefore, evaluation of modified wood performance is reported in the next chapter.

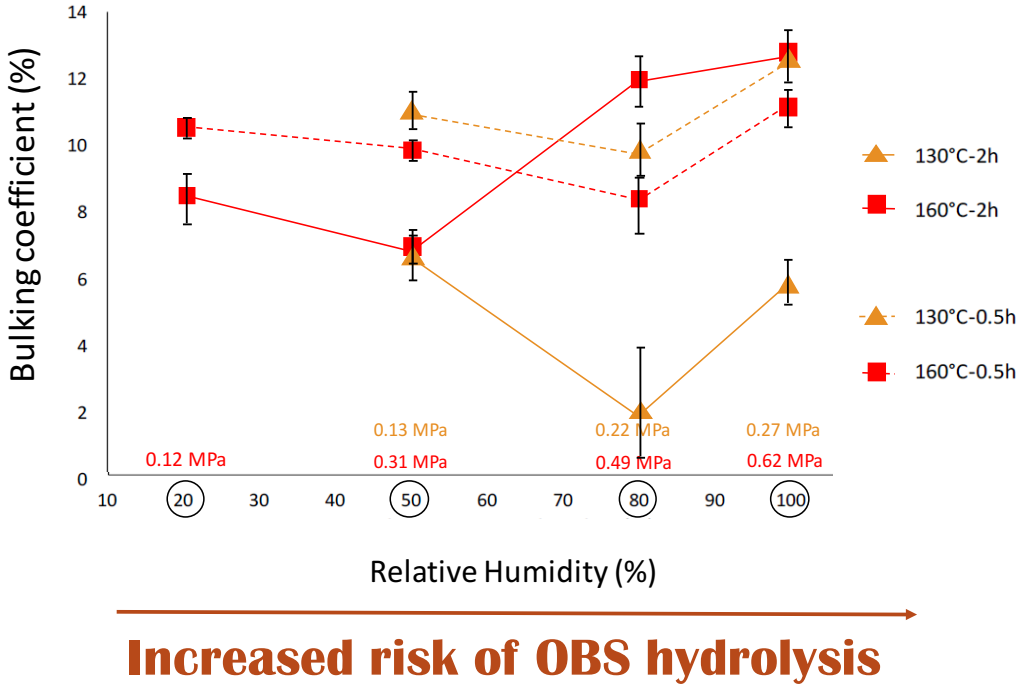


Figure 37 : Bulking coefficient according to hygro-thermal treatment conditions and increased risk of OBS hydrolysis.

1.4. Influence of treatment on modified wood properties

The impact of temperature, pressure and RH during the process on wood and OBS degradation, and wood degradation products, oligomers and water diffusion have been studied. Final WPG and swelling appeared to result from several factors that act simultaneously. In this chapter, the influence HTT conditions and OBS diffusion in wood on the modified wood properties and treatment persistence is reported.

Impregnated samples, which were not submitted to HTT, showed only limited diffusion of oligomers in the cell walls, and no dimensional stabilisation was observed. As seen in Figure 38, HTT temperature plays an essential role in treatment ASE if the treatment is carried on at 100%RH for 0.5h only. Most likely because of the limited penetration of OBS in the cell wall, HTT at 100°C-100%RH-0.5h does not provide sufficient ASE. The BC is higher at 130°C and 160°C and ca.50% ASE is reached. At high temperature (160°C), this performance regarding ASE is reached only at 100%RH (Figure 39).

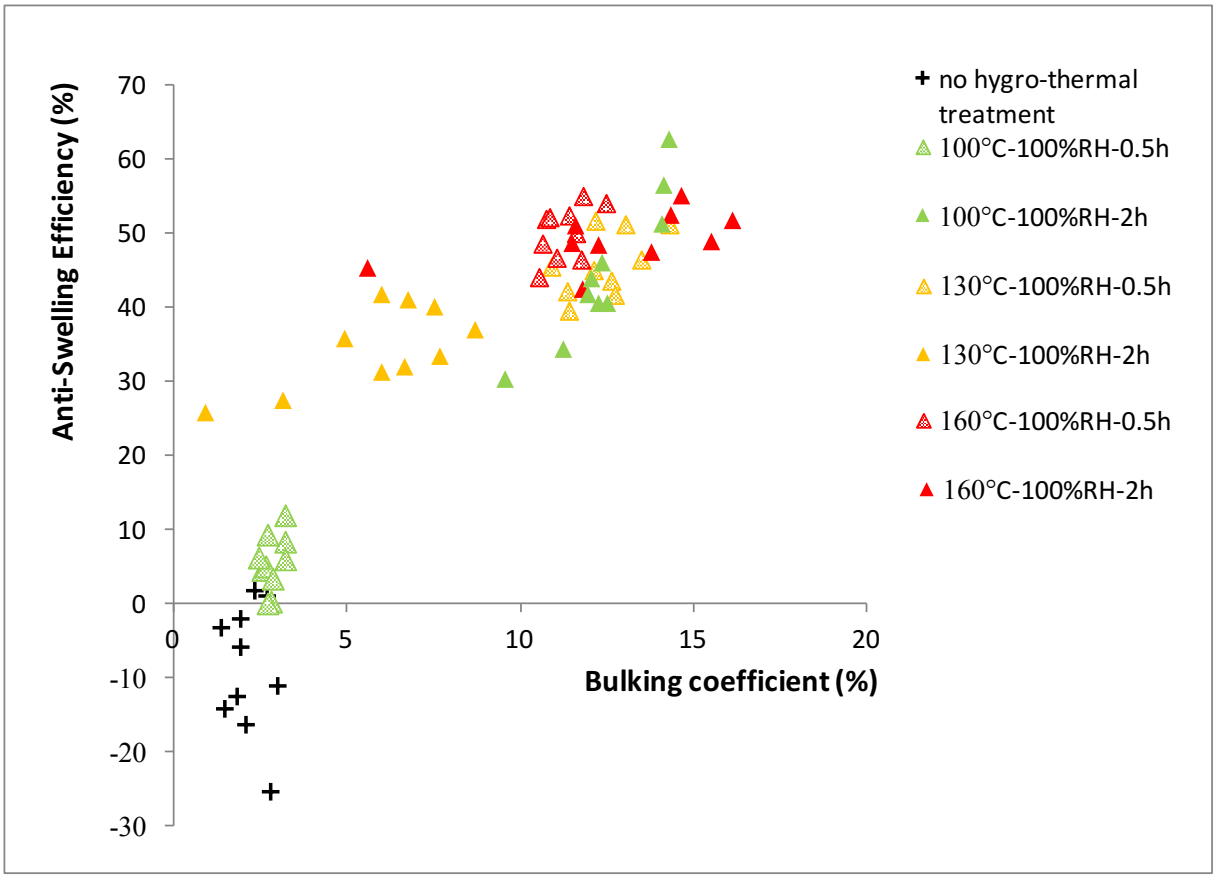


Figure 38 : Effect of temperature and duration of hygro-thermal treatment at 100% relative humidity on OBS diffusion and treatment anti-swelling efficiency.

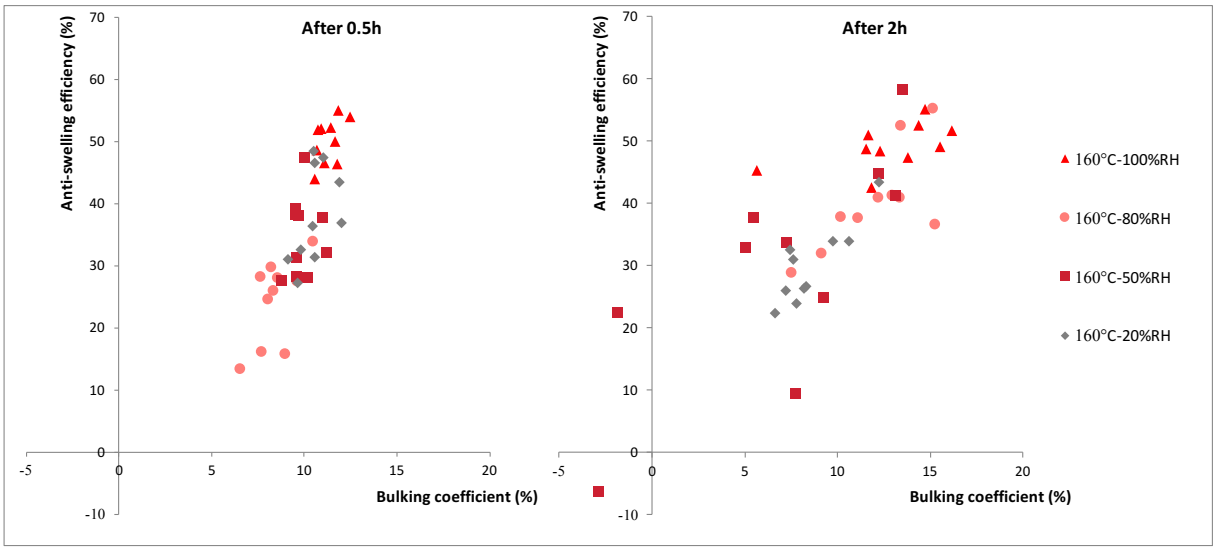


Figure 39 : Effect of relative humidity during hygro-thermal treatment (HTT) at 160°C on OBS diffusion and treatment anti-swelling efficiency for HTT of 0.5h and 2h.

Two options of HTT at 100%RH appear to be competing for effective diffusion of OBS and sufficient treatment ASE: high temperature (160°C) for short time (0.5h) or low temperature (100°C) for long time (2h).

However, wood exposure at high temperature in a pressurised reactor leads to substantial wood degradation (Figure 40) due to a combination of factors acting simultaneously (Altgen *et al*. 2016). Hemicelluloses are preferentially affected under moist conditions, with cleavage of acetyl groups resulting in the formation of acetic acid (Tjeerdsma *et al.* 2005). In humid conditions, deacetylation of hemicelluloses is catalysed by acids and temperature. By reducing the relative humidity and/or the duration of HTT, it is possible to decrease wood polymers degradation, but it is also resulting in a lower ASE. In the case of HTT at high temperature and high RH, ASE performance are most likely due to hemicelluloses degradation and not necessarily due to OBS impregnation.

Furthermore, treatments for which extended OBS hydrolysis was assumed showed the lowest persistence. HTT at 160°C-20%RH-2h resulted in an efficient diffusion with enhanced persistence of OBS in wood, most likely because oligomers were further polymerized but ASE is only about 40%. Performance of HTT at 100°C-100%RH-2h are promising. This HTT combined with a post-treatment at higher temperature (120-140°C) should be investigated further.

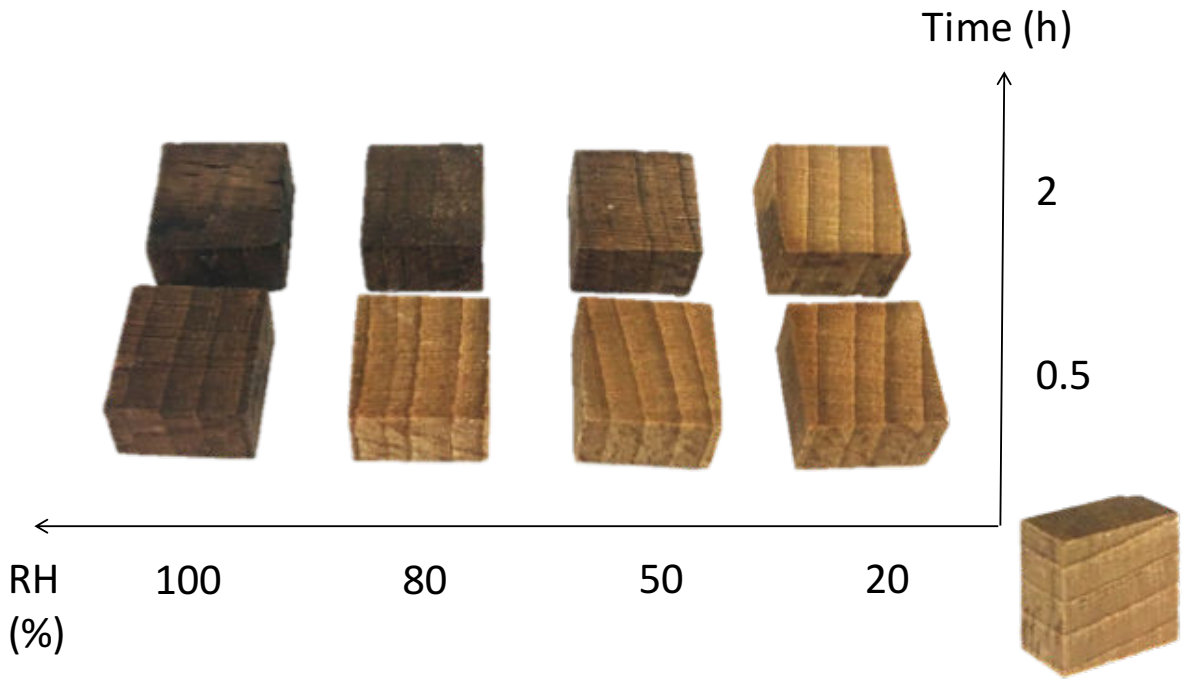


Figure 40 : Increased wood degradation with relative humidity and duration of hygro-thermal treatment at 160°C.

2. Wood-OBS interactions

Chemical modification of wood with bio-polyesters has recently been reported (Noël *et al.* 2015a, Grosse *et al.* 2017a). Poly(butylene succinate) oligomers treatment confer interesting properties to wood for outdoor applications. They are based on the impregnation of oligomers in oven-dried beech wood (*Fagus sylvatica L.*), followed by a curing step at 103°C (only drying) or 120°C (post-treatment (PT)). The dry curing conditions did not allow any penetration of OBS in wood cell walls, thus no gain in ASE was seen. Humid treatment conditions were observed to allow a partial diffusion of OBS in cell walls, most likely because of water acting as swelling agent. Hygro-thermal treatment (HTT) was carried out at several temperatures, relative humidities and durations, to find optimal conditions of OBS diffusion in the wood structure. Treatment conferred ASE of ca. 50%, with a good correlation to OBS diffusion. (Grosse *et al*. 2017b).

Dynamic mechanical thermal analysis (DMTA) under varying humidity was carried out for understanding OBS interactions with wood polymers. The results are presented in **Paper 8:** Dynamic Mechanical Thermal Analysis of Wood Modified with Bio-Polyesters (Grosse *et al.* 2018d, in: *proceedings of ECWM9*).

Figure 41 presents the relative storage modulus (Relative E') at 35%RH for untreated and treated samples. Relative E' of untreated beech (not impregnated) decreases after 35°C, mostly due to water absorption. The similar variation of Relative E' for impregnated and untreated wood shows they are few interactions between OBS and the cell walls polymers when no HTT was performed. If only a post-treatment was carried on (impregnated + PT), OBS do not diffuse in the cell walls but further polymerise in the lumens. The modified wood becomes stiffer at higher temperature. With HTT, OBS diffuse in the cell walls and act as a plasticiser.

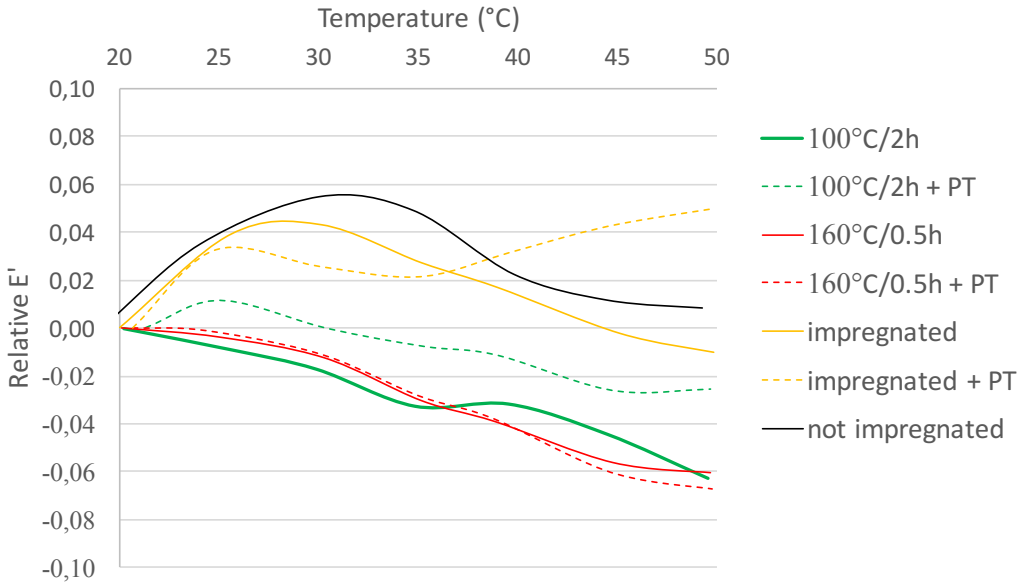


Figure 41 : Relative storage modulus of untreated and treated samples measured at 35%RH and 1Hz.

PAPERS

Paper 6: Wood modification with poly(butylene succinate) oligomers: influence of hygro-thermal treatment conditions

Wood modification with poly(butylene succinate) oligomers: influence of hygro-thermal treatment conditions

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Abstract

When exposed to moisture, wood undergoes swelling and is susceptible to fungal degradation. Chemical modification, with well-chosen environmentally friendly modifying agents, is one solution to this disadvantage. In this work, wood was impregnated with oligomers of butylene succinate (OBS), then hydrothermally treated in a pressurized reactor to induce partial swelling and subsequent diffusion of OBS in the wood structure. The effect of temperature, relative humidity (RH), pressure and time on factors explaining OBS diffusion, the extend of OBS hydrolysis, wood degradation and the resulting wood modification was investigated. This process technique for wood modification with OBS might lead to a more ductile material with enhanced dimensional stability and biological resistance.

Keywords: Wood; A. Biocomposite; B. Physical properties; D. Moisture

1. Introduction

Environmental concerns and the need of alternatives to fossil-based resources lead to the development of bio-based and biodegradable materials from renewable resources. Much attention has been paid to wood [1-3] and lignocellulolic materials on the one side, and biodegradable and/or bio-based polymers on the other side such as poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) [4, 5] due to the sustainable production of their monomers [6, 7]. Wood fibres are often used as reinforcement in polymer matrix for their mechanical properties [8-10] and wood-plastic composites are already widely commercialized [11, 12]. Appearance and organoleptic properties are part of a material selection process, which makes wood an appealing material. However, wood suffers from two limitations: hygroscopicity and limited biological resistance. Efficient treatments for wood preservation exist and several variants of modified wood are already commercialized (for

example Accoya® and Kebony®), but despite of a substantial improvement of wood dimensional stability and biological resistance, decreased mechanical properties result from treatment conditions [13-18]. Recently, the idea of using PLA or PBS to enhance wood properties gave promising results [19-23]. These treatments consist in a two-step process: bulk impregnation of oligomers in wood and subsequent *in-situ* polymerization performed by low temperature heat treatment (100-160°C). In the case of PLA oligomers (OLA), the treatment decreased wood ductility while increasing resistance. PBS is tougher [24] and more flexible than PLA (Tg = -32°C and 50°C respectively). Therefore, wood modification with PBS oligomers (OBS) is expected to lead to a more ductile material.

Former research [21-23] showed that dry heat treatment conditions did not allow any penetration of the oligomers in wood cell walls, thus any improvement of dimensional stability. The mechanical properties were not influenced either. However, the OBS lumen-filling led to a substantial decrease in wood hygroscopicity and a good retention of oligomers within the wood lumens was observed. Humid treatment conditions, resulting from wood water soaking after impregnation, were observed to allow a partial diffusion of OBS into the cell walls, most likely because of water acting as swelling agent inducing partial penetration of oligomers in the cell wall (Anti-swelling efficiency ASE of 60% to 70%). Development of hydrothermal treatment is necessary to OBS diffusion optimisation. The modification of wood properties relies on the interactions between OBS and the cell wall polymers, i.e. the amount and persistence of OBS within the wood cell walls. Despite of an impregnation yield (IY) of ca. 70%, wood swelling after impregnation (Si) was always lower than 2%. Thus, enhancement of OBS diffusion has been attempted through hydrothermal treatment (HT). Previous research [23] showed that at 100% RH in the reactor, two options appear to be competing for effective diffusion of OBS: high temperature (160°C) for short time (0.5h) or low temperature (100°C) for long time (2h). Despite of significant ASE increase, OBS fixation within wood was never improved using these HT conditions most likely because the high RH prevented OBS further polymerization *in situ*. This study reports the attempt of enhancing wood performance, with effective OBS diffusion in the wood cell walls because of moisture and extended OBS polymerization because of temperature.

2. Material and methods

2.1. Materials

Wood samples (15 x 15 x 10 mm^3, T x R x L) were cut from European beech (Fagus sylvatica L.) with an average density of 0.70 $g.cm^{-3}$. Dimethyl succinate (99%), butane-1,4-diol (98%) and titanium(IV) butoxide (97%) were sourced from Sigma-Aldrich (Switzerland).

2.1. Product preparation

Oligomeric polyesters were synthesised by their direct polymerization under vacuum, using a four-necked flask fitted with a magnetic stirrer and reflux condenser linked to an inline cold trap and vacuum pump. Thermometers were used to observe the polymerisation, condenser head and heater temperatures. Oligomers of Butylene Succinate (OBS) were synthesised by melt polymerization of dimethyl succinate and butane-1,4-diol. This was achieved by adding a 25% stoichiometric excess of butane-1,4-diol in the presence of titanium(IV) butoxide as esterification catalyst. The mixture was gradually heated under reduced pressure (0.015 MPa) in 3 steps: (1) a temperature increase at 3 $K.min^{-1}$ for 1h, (2) a 2h holding step at 200°C, (3) a 30-min holding step at 220°C. Oligomers temperature stabilised at 180°C during step 2 and reached 200°C at the end of step 3. Finally, OBS were poured into bottles, sealed and cooled. OBS solidify as a white block on cooling. The melt temperature of the resulting oligomeric material was rheologically measured at ca. 75°C.

2.2. Wood treatment

As described by Noël *et al.* [21], wood samples were immersed in liquid OBS at 90°C. Impregnation was achieved in a vacuum oven under reduced pressure (0.015 MPa) for 30 min, then atmospheric pressure over 30 min. Impregnated samples were wiped and stored in hermetic plastic bags with silica gel. Hydrothermal Treatment (HT) was carried out in a pressurized reactor. Parameters of all HT variants carried out are presented in Table 1: process peak temperature (T_{max}), maximal pressure (P_{max}), duration and relative humidity (RH).

Table 1: Summary of HT conditions

T (˚C)	RH (%)	P (MPa)	Duration (h)	WPG (%)
100	100	0.10	2	56.3 ±1.1
100	100	0.10	0.5	63.8 ±1.6
130	100	0.27	2	32.7 ±2.0
130	80	0.22	2	21.3 ±1.2
130	50	0.13	2	21.2 ±1.8
130	100	0.27	0.5	54.2 ±2.0
130	80	0.22	0.5	39.7 ±2.8
130	50	0.13	0.5	31.3 ±1.9
160	100	0.62	2	52.5 ±3.7
160	80	0.49	2	56.0 ±3.2
160	50	0.31	2	30.2 ±5.0
160	20	0.12	2	27.6 ±1.7
160	100	0.62	0.5	52.5 ±3.7
160	80	0.49	0.5	39.2 ±3.1
160	50	0.31	0.5	41.6 ±3.1
160	20	0.12	0.5	31.9 ±2.0

Vapour pressure was regulated by increasing temperature in the external water reservoir and releasing excess pressure to ensure constant process RH. A final post-treatment (PT) was carried out at 103°C for 48h to dry the treated samples. Swelling after impregnation (S_i), after HT (S_{HT}) and after PT (S_{PT}) were calculated as followed:

$$S_{i/HT/PT}\ (\%) = \frac{V_{i/HT/PT} - V_{u,d}}{V_{u,d}} \times 100 \qquad (1)$$

where V_i, V_{HT} and V_{PT} stand for the impregnated, HT and PT sample volume respectively and $V_{u,d}$ stands for the untreated samples dry weight before impregnation. Impregnation yield (IY), final weight polymer gain after complete treatment (WPG), weight uptake after HT and PT (WU_{HT} and WU_{PT} respectively) and mass loss due to PT (ML_{PT}) were calculated as followed:

$$IY\ (\%) = \frac{w_i - w_{u,d}}{w_{u,d}} \times 100 \qquad (2)$$

$$WPG\ (\%) = \frac{w_{PT} - w_{u,d}}{w_{u,d}} \times 100 \qquad (3)$$

$$WU_{HT}\ (\%) = \frac{w_{HT} - w_i}{w_i} \times 100 \qquad (4)$$

$$ML_{PT}\ (\%) = \frac{w_{HT} - w_{PT}}{w_{HT}} \times 100 \qquad (5)$$

where $w_{u,d}$ stands for untreated dry samples weight before impregnation and w_i, w_{HT} and w_{PT} stand for samples weight after impregnation, HT and PT respectively.

2.3. Methods

2.3.1. Gel Permeation Chromatography (GPC)

Accelerated solvent extractions were carried out on treated samples (ca. 2g, chipped samples) using a Dionex ASE 200 Accelerated Solvent Extractor. Two cycles were done with a 5-min heating step to 100°C followed by a 10-min static step at 100°C and 10MPa in 100% chloroform. After extraction, samples were oven-dried (103°C) to constant weight. Molecular weight (Mw) profiles of extracted oligomers were evaluated by gel permeation chromatography (GPC) using a Polymer Labs system and a mixed-C column (Polymer Labs). Elution was with chloroform solvent. All samples were dissolved in GPC solvent (40 mg/mL) and run on the GPC employing both refractive index (RI) and UV detectors. Molecular weight profiles were calculated according to polystyrene calibration standards.

2.3.2. Leaching

Treated samples were immersed in water at room constant temperature (23°C) for 504 hours, in separated boxes according to the treatment procedure undergone by the samples. The weight loss due to water leaching (WL_l) was calculated according to Eq. 6:

$$WL_l = \frac{w_{t,d} - w_{t,l,d}}{w_{t,d}} \times 100 \qquad (6)$$

where $w_{t,l,d}$ is the specimen weight after treatment, leaching and drying and $w_{t,d}$ is the specimen weight after treatment at dry state before leaching procedure.

3. Results and Discussion

3.1. Effect of hydrothermal treatment on wood components and OBS

Wood exposure at high temperature in a pressurised reactor leads to substantial wood degradation due to a combination of factors acting simultaneously [25]. Hemicelluloses are preferentially affected under moist conditions, with cleavage of their acetyl groups resulting in the formation of carbonic acids, mainly acetic acid [26]. In humid conditions, deacetylation of hemicelluloses is catalysed by acids and temperature. Because of the

high pressure needed to reach high process RH for temperatures above 100°C, the boiling points of wood compounds are increased and products of hemicelluloses degradation remain within the wood catalysing further degradation reactions. Also resulting from high process RH, the increase of wood EMC in the reactor leads to the softening and increased mobility of cell wall polymers. This lowers activation energy and facilitates chemical reactions. Thus, thermal degradation is possible even at low temperature. Altgen *et al.* [25] concluded that for beech, pressure in the reactor has a stronger influence on wood thermal degradation, estimated by wood mass loss, than the temperature applied. They evidenced an almost exponential mass loss increase with pressure, before saturation effect at high mass loss, most likely due to the limited amount of material within the wood to be degraded. In the case of OBS impregnated wood, additional factors should be taken in account to explain the influence of HT on wood modification.

High RH in the reactor might lead to degradation of OBS during HT (Figure 1), especially in combination with high temperature. Indeed, OBS is sensitive to hydrolysis, leading to random ester linkage cutting along the main chain, with resulting decrease of polymerization degree [27-29]. Furthermore, if the wood is saturated with moisture during HT, further polymerization could be prohibited [30]. Reducing RH during HT might allow efficient OBS diffusion in the cell walls while avoiding extended oligomers hydrolysis. In that case, enhancement of wood performance is expected because of interactions between wood cell wall polymers and OBS. Besides, further in situ polymerization is expected to lead to enhanced OBS persistence within the wood structure.

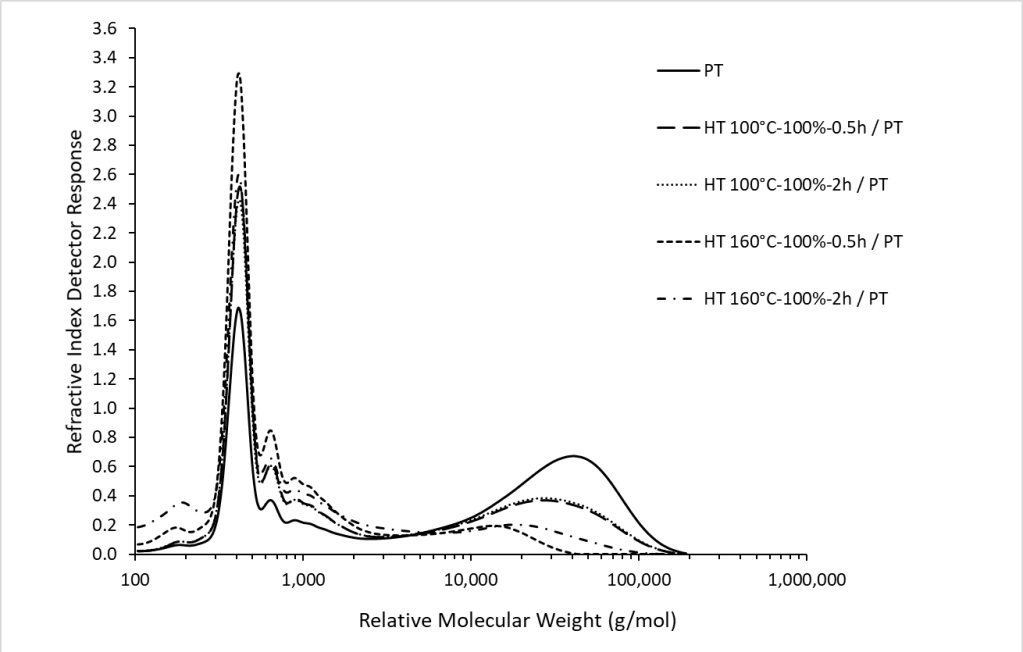


Figure 1: extracted OBS relative molecular weight distribution.

3.2. Products flow during treatment

Evaluated up to 160°C and 100% RH, the mass loss due to wood polymers degradation during hydrothermal treatment of unmodified wood was reported to be <4% except for treatment conditions above 130°C and 50% RH (<18% in that case) [25]. As stated by Altgen *et al*. [25], the direct relation between pressure and wood components degradation might indicate likely lower WPG at severe HT conditions in the case of OBS treated wood. However, such correlation was not observed (Table1).

3.2.1. OBS and wood polymers modifications

Because OBS remains in lumens after impregnation, impregnated wood treated in the reactor can be considered as a two independent components material at the beginning of the process, made of untreated wood on one hand and OBS on the other hand. Untreated beech wood equilibrium moisture content (EMC) during HT is mostly affected by RH in the reactor, but is decreased with higher temperature (15 to 20% at 100% RH, 5 to 10% at 80% RH, and below 5% at 50 and 20% RH, in the range of temperatures used in the reactor) [25]. Thus, HT should induce weight uptake of OBS impregnated samples because of water absorption.

On the contrary, HT seems to induce a preliminary weight loss shortly after the treatment starts followed by a further weight increase overcompensating the loss (Figure 2). This weight loss is most likely due to melted OBS leaching out from wood samples and not yet compensated with water absorption. After 2h, considering OBS might have additionally absorbed water during HT (not measurable with this set of data), there is a good correlation between the expected EMC and the weight loss distribution at 130°C. Nevertheless, a different result is observed for treatments at 160°C. Figure 2 shows that weight uptake during HT seems to be rather correlated to pressure in the reactor than temperature or process RH. Combination of high temperature and humidity most likely leads to OBS hydrolysis and to an increasing proportion of short oligomer chains. Pressure might prevent OBS and wood degradation products from leaching out.

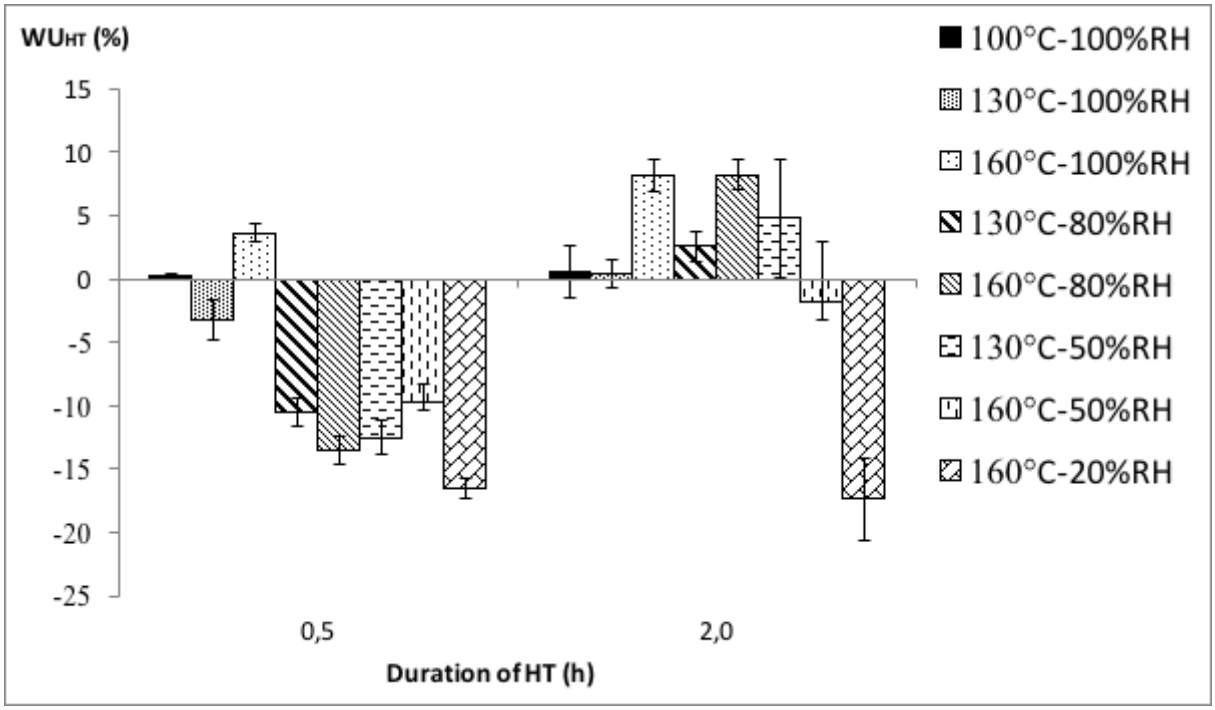


Figure 2: Weight Uptake after hydrothermal treatment (WU_{HT}) variations according to HT conditions.

Figure 3 shows that PT leads to further weight loss (ML_{PT}), most likely due to the evaporation of volatile compounds from OBS and/or wood degradation occurring during HT (ML_{PT} = ca. 4% for impregnated samples not subjected to prior HT). For HT at 100°C-100%RH, only small weight variations were observed during PT, which means that the water absorption during HT was very limited. Because non-impregnated wood EMC in these HT conditions is supposed to be higher than 20%, it can be concluded that OBS had a blocking effect regarding wood water absorption. For HT at 160°C-20%RH, the ML_{PT} decreased for long HT most likely because of OBS polymerization during HT, reducing the amount of volatile oligomers in wood. No increase of ML_{PT} was noticed after long HT at 160°C – 100%RH. Combination of high pressure reducing leaching and high temperature catalysing reactions, might allow degradation products to react with themselves or with the remaining cell wall components.

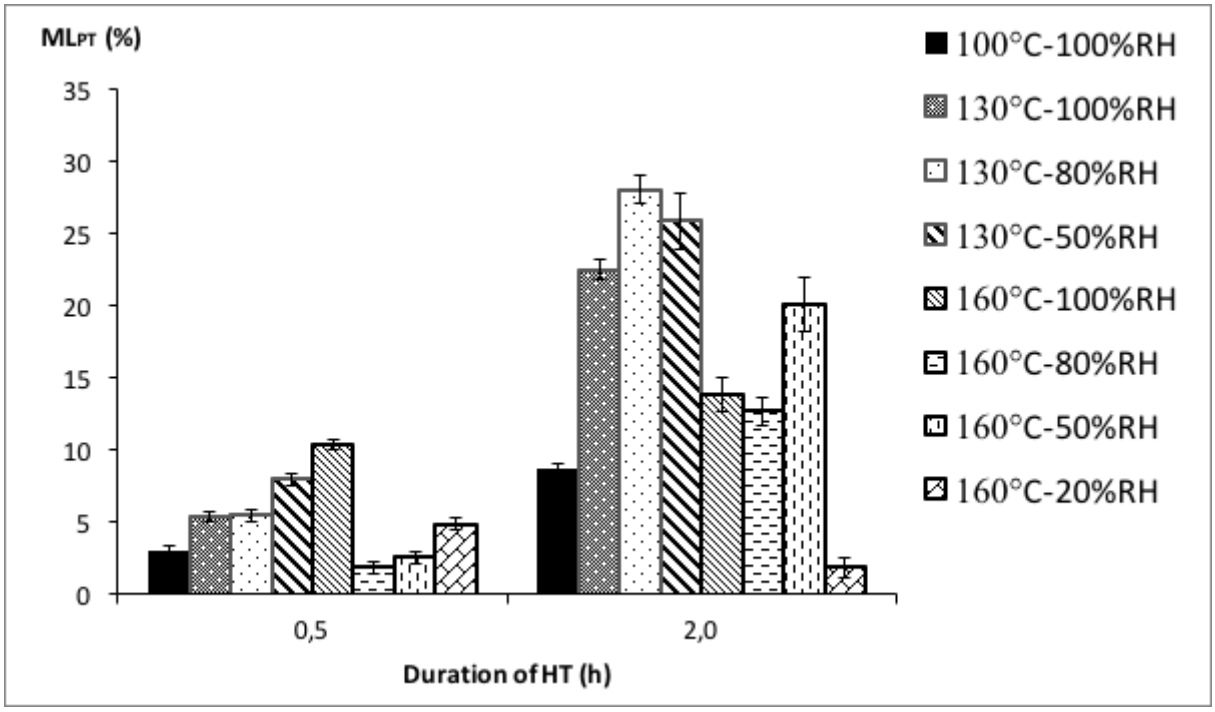


Figure 3: Mass loss due to post treatment (ML_{PT}) variations according to HT conditions. Origin point corresponds to ML_{PT} of samples impregnated and only PT.

3.2.2. Diffusion of generated products

Residual swelling after PT (S_{PT}) is representative from products diffusion in the cell walls. Figure 4 shows again correlation between S_{PT} and pressure in the chamber, rather than temperature or process RH. Altgen *et al.* [25] suggested that with high pressure, wood degradation products may remain within wood during hydrothermal treatment. The same conclusion could be drawn for hydrolyzed OBS chains. At higher pressure, chemicals have a higher boiling point. Therefore, combination of OBS hydrolysis producing smaller molecules able to penetrate the cell walls and high pressure reducing volatility of chemicals and saturating the cell walls with it, can explain the increase of S_{PT} only when the pressure is high enough. For long HT, a significant amount of volatile products diffused in the cell walls (Figure 5). Shrinkage during PT is correlated with ML_{PT}, meaning that mostly water or volatile molecules were created in the cell wall and not released during HT because of pressure or OBS blocking. Short HT allows substantial and persistent diffusion of non-volatile products in the cell walls. Furthermore, WPG and S_{PT} appeared to be correlated (Figure 6), except for the short HT at 100°C-100%RH. This might indicate that OBS hydrolysis is not necessary for efficient diffusion. Two options still appear to be competing for effective diffusion of OBS and limited wood degradation: long HT at 100°C-100%RH or short HT at 160°C-100%RH.

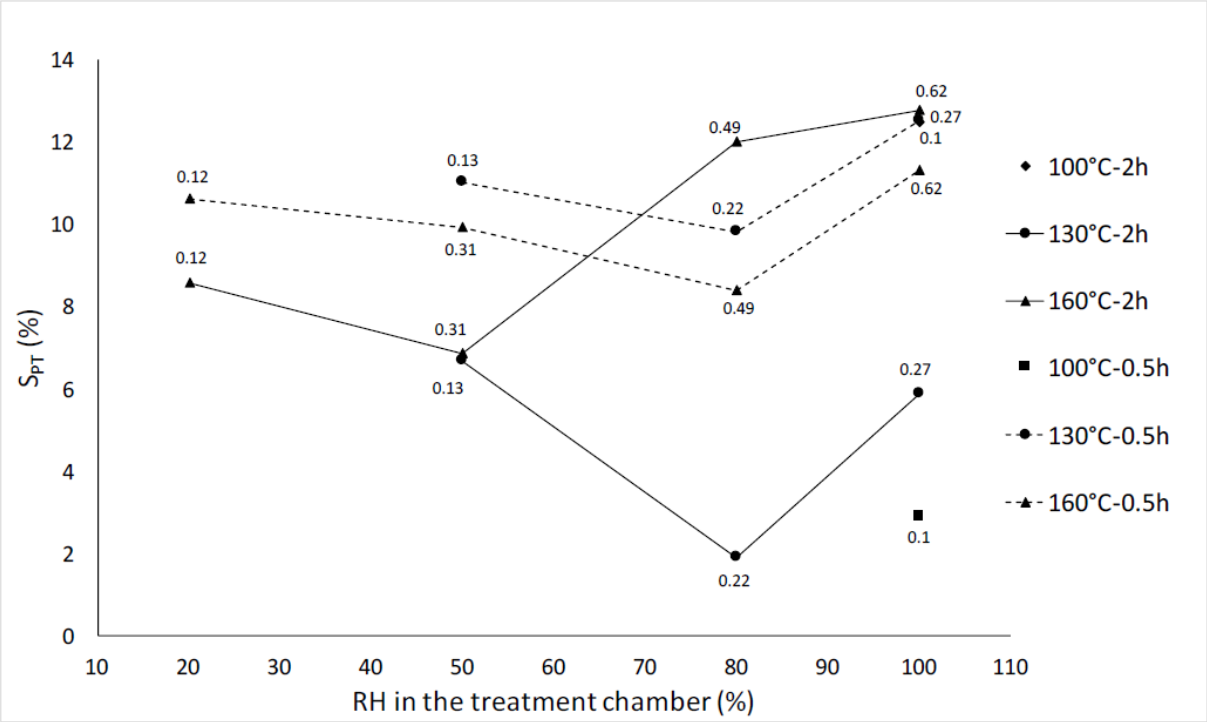


Figure 4: Final dry swelling after post-treatment (S_{PT}) according to hydrothermal-treatment conditions (pressures are indicated in MPa above the data points).

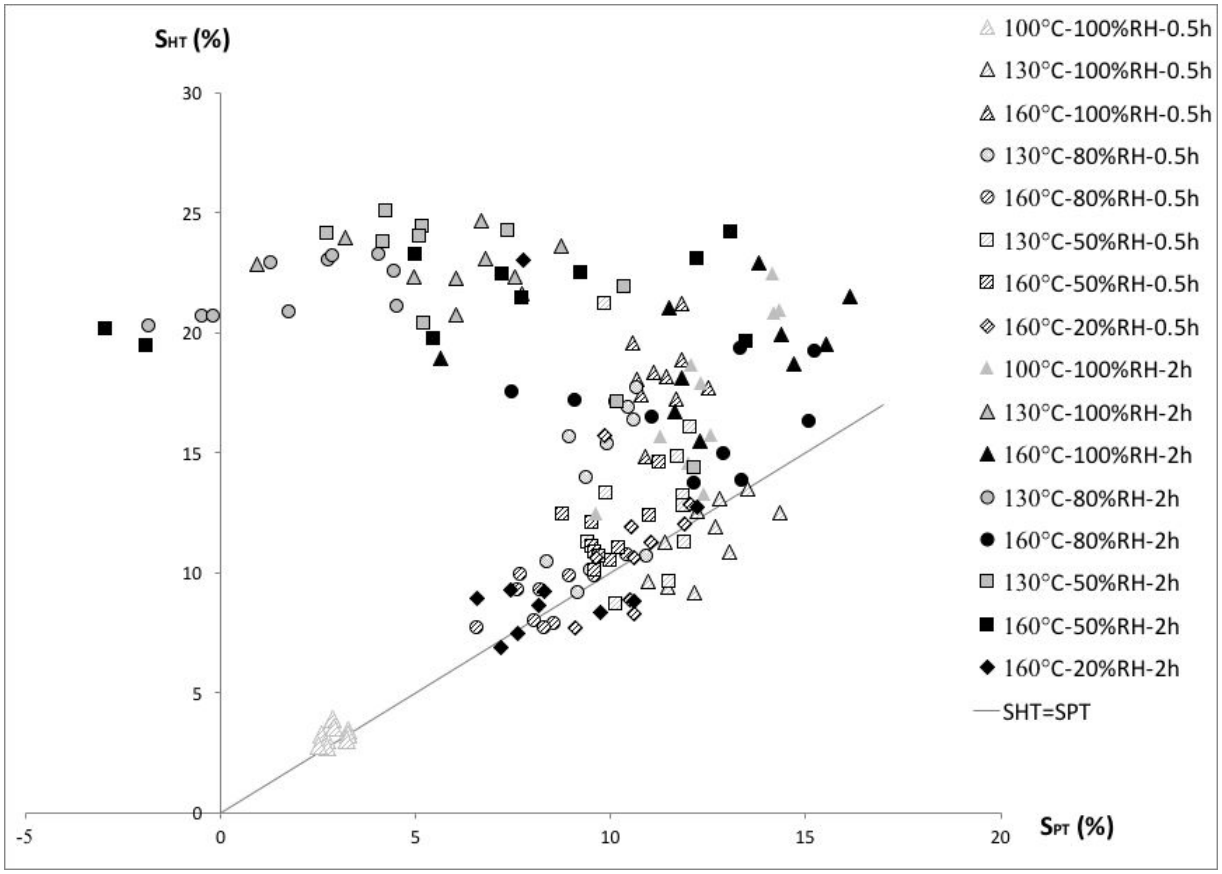


Figure 5: Relationship between swelling after HT (S_{HT}) and after PT (S_{PT}) according to HT conditions.

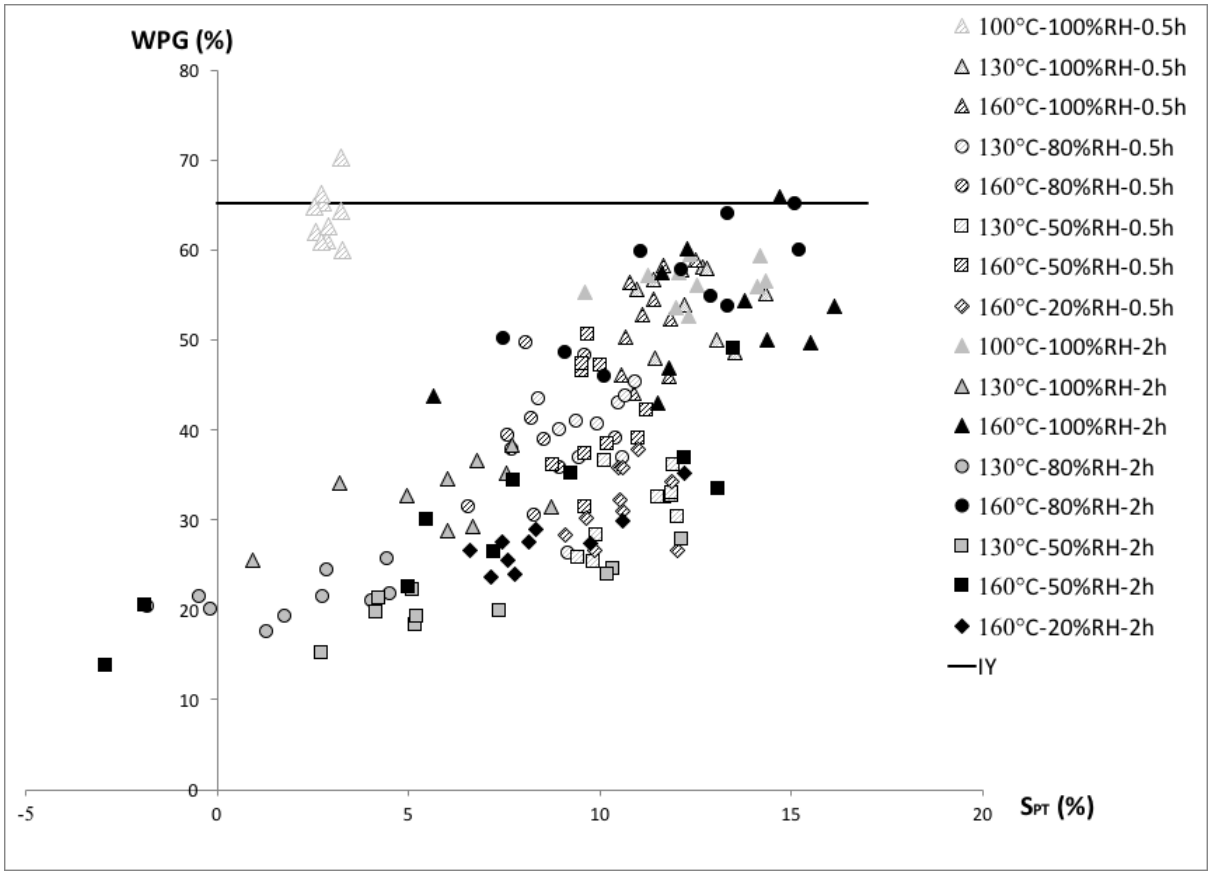


Figure 6: WPG and S_{PT} variations according to HT conditions.

3.3. OBS persistence within wood

For comparison, samples impregnated with OBS and not submitted to HT, showed a WL_l of 5.3 ±0.1%. At 100°C, short HT did not influence OBS persistence nor diffusion, but long HT allowed a significant increase of OBS diffusion for the same resistance to water leaching (Figure 7). At high temperatures, WL_l appeared correlated with S_{PT}. Treatments for which extended OBS hydrolysis was assumed showed the highest WL_l. HT at 160°C-20%RH-2h resulted in an efficient diffusion with enhanced persistence of OBS in wood, most likely because oligomers were further polymerized. Performance of HT at 100°C-100%RH-2h combined with PT at higher temperature should be investigated further.

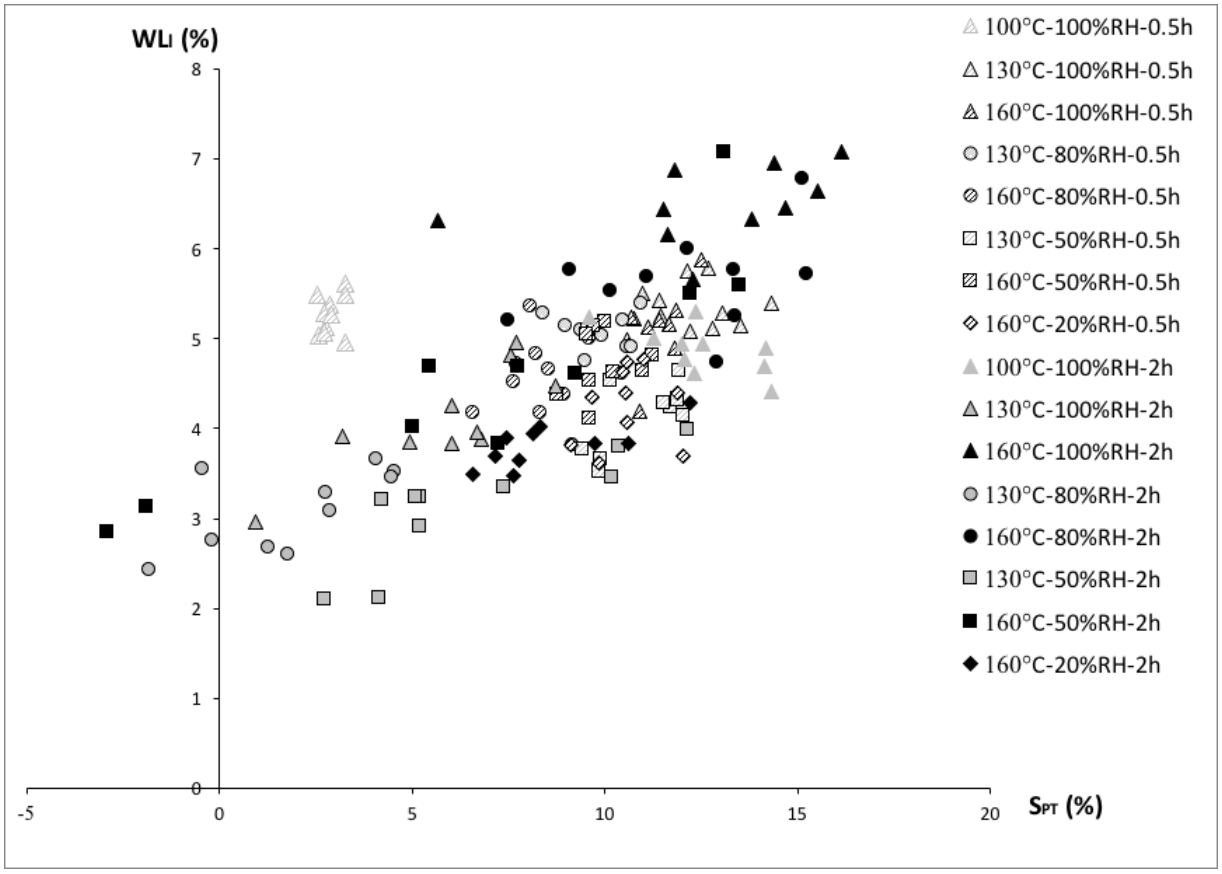


Figure 7: Evolution of OBS persistence (WL_l) according to diffusion (S_{PT}) and HT conditions.

4. Conclusion

There was a high impregnation yield of OBS in wood under soft impregnation conditions. An effective diffusion of oligomers can be achieved through hydrothermal treatment. The impact of temperature, pressure and RH during the process on wood and OBS degradation, and wood degradation products, oligomers and water diffusion have been studied. Final WPG and swelling appeared to result from several factors that act simultaneously. At high temperature, OBS and wood degradation were increased by high RH. The pressure necessary to have high RH at high temperature prevents material leaching and evaporation and allows diffusion of small molecules created during HT. However, decreased treatment persistence in wood results from OBS hydrolysis. None of the HT conditions evaluated in this study allowed to substantially improve simultaneously OBS diffusion and fixation. Three options appear to be competing for effective HT: low temperature at high process RH for 2h, high temperature at high process RH for 0.5h or high temperature at low RH for 2h.

It is likely that each combination of HT parameters lead to different modified wood properties. Therefore, evaluation of modified wood performance (repeated anti-swelling efficiency cycles, hygroscopicity, mechanical properties, biological resistance) is currently carried out to fulfill this study.

Acknowledgments

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Paper 7 : Influence of hygro-thermal treatment temperature and duration on dimensional stabilisation of wood modified with poly(butylene succinate)

IRG/WP 17-40813

THE INTERNATIONAL RESEARCH GROUP ON WOOD PROTECTION

Section 4 Processes and properties

Influence of hygro-thermal treatment temperature and duration on dimensional stabilisation of wood modified with poly(butylene succinate)

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Influence of hygro-thermal treatment temperature and duration on dimensional stabilisation of wood modified with poly(butylene succinate)

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ABSTRACT

To improve wood properties, especially dimensional stability, a treatment based on poly(butylene succinate) oligomers (OBS) was experimented. After impregnation in wood, a further hygro-thermal treatment (HTT) was carried out in a pressurized reactor at 100% relative humidity (RH) at differing temperatures for differing durations. The aim of HTT is to induce partial swelling of wood cell walls so that the OBS can diffuse into the structure. A final thermal post-treatment (PT) was carried out to dry the treated samples and attempt the oligomers fixation in wood. Due to OBS sensitivity to water, especially at high temperatures, the oligomers hydrolysis in the process is possible. This article relates the products flow in wood structure under varying HTT conditions, as well as the influence of OBS diffusion in wood on the treatment anti-swelling efficiency (ASE*). After HTT, there is an effective diffusion of the oligomers into wood cell walls. This was evidenced by the residual wood swelling after complete treatment (HTT and PT). Wood dimensional stabilisation correlates with the amount of OBS into the wood cell walls. Dimensional stability was improved by all treatments, but seemed to reach a maximum value of ca. 50%. HTT temperature played an essential role into treatment efficiency. Temperature as high as 130°C led to the highest ASE* obtained in this experiment set, not improved by longer HTT. However, longer HTT allowed to reach the same efficiency at 100°C. For higher temperature, the leaching rate increases significantly, up to 20%.

Keywords: wood, chemical modification, PBS, hygro-thermal treatment, swelling.

1. INTRODUCTION

Despite having many interesting properties and being widely used for construction and industry since ages, wood suffers, however, from two limitations: its hygroscopicity and limited durability. Thanks to nowadays awareness of environment protection duty, the use and development of natural, biodegradable and carbon sink materials, like wood, overcoming the two drawbacks mentioned above, has become a main concern in the wood sector over many decades. During this time, many methods for wood modification have been developed. Wood chemical constitution determines most of its properties. Thus, wood modification methods often seek to make changes at this level. They can be classified in four main types: chemical modification, thermal modification, surface modification and impregnation modification (Hill 2006). Performant modified wood are already commercialised (for example Accoya or Kebony) and are

based on diverse technics. Accoya modified wood results from wood acetylation. The process is based on an active chemical treatment which consists of the esterification of wood hydroxyls groups with acetic anhydride. Other similar treatments have been made with other anhydrides or aldehydes or methylation reactions (Rowell 2005). Kebony modified wood stem from wood furfurylation which consists of wood impregnation with monomeric furfuryl alcohol followed by polymerisation within the wood structure (Lande et al. 2004).

Recently, a hybrid method has been developed by Noël et al. (2015a, 2015b, 2015c) and Vitkeviciute (2016) using poly(butylene succinate) oligomers (OBS). The treatment consists in a two-step process: impregnation of OBS in wood and subsequent in-situ polymerization performed by low temperature heat treatment. OBS easily diffused into the wood (70% of polymers weight uptake) and decreased its hygroscopicity, but were found to provide only limited dimensional stabilisation. They appeared only partially retained within the wood structure on water leaching, with 20% of polymer loss. The treatment did not influence the mechanical properties of the treated wood (Noël et al. 2015a). Later, Noël et al. (2016) investigated the influence of water and humidity on the OBS treatment under several aspects and following different treatment methods. They evidenced the role of water in OBS diffusion into the wood structure. OBS effective diffusion into wood cell walls improved wood dimensional stability but not the product persistence into the wood. This article reports the systematic characterization of wood treated with OBS under varying conditions of hygro-thermal treatment (temperature and duration).

2. MATERIALS AND METHODS

2.1. Materials

Wood samples (15 x 15 x 10 mm^3 T x R x L and 15 x 5 x 25 mm^3 TR x RT x L) were cut from beech (*Fagus sylvatica L.*, 700 ± 0.01 $kg.m^{-3}$) and oven-dried to constant weight prior to impregnation. Dimethyl succinate (99%), 1,4-butanediol (98%) and titanium(IV) butoxide (97%) were sourced from Sigma-Aldrich (Switzerland).

2.2. Synthesis of the PBS oligomers (OBS)

Oligomeric polyesters were synthesised by their direct polymerisation under vacuum, using a four-necked flask fitted with a magnetic stirrer and reflux condenser linked to an inline cold trap and vacuum pump. Thermometers were used to observe the polymerisation, condenser head and heater temperatures. Oligoesters (OBS) were synthesised by melt polymerisation of dimethyl succinate and 1,4-butanediol. This was achieved by adding a 25% stoichiometric excess of 1,4-butanediol in the presence of titanium(IV) butoxide as esterification catalyst. A mixture of dimethylester, 1,4-butanediol, and catalyst was poured into the flask under a nitrogen purge. The mixture was gradually heated to 180°C over 130 minutes under reduced pressure (150 mbar). At the end of the reaction, oligomers were poured into bottles, sealed and cooled. OBS esters solidify as a white block on cooling. The melt temperature of the resulting oligomeric OBS material was rheologically measured at ca. 75°C.

2.3. Wood treatment

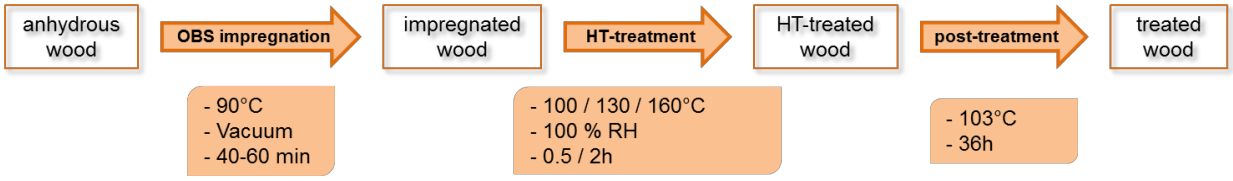


Figure 1: description of the whole treatment process (HT=hygro-thermal)

As described by Noël *et al*. (2015b), wood samples were immersed in liquid oligomers (OBS) at 90°C. Containers were then placed in a vacuum oven under reduced pressure (150 mbar) for 20 to 30 min, then atmospheric pressure over 20 to 30 min. Impregnated samples were then wiped and stored in hermetic plastic bags with silica gel. The following hygro-thermal treatment (HTT) was carried out in a pressurized reactor at 100% relative humidity (RH) and different temperatures for different durations (Figure 1). A final thermal post-treatment (PT) was carried out to dry the treated samples and was expected to partially fix the oligomers in wood. Table 1 summarises the treatment conditions.

Sample weight was measured anhydrous before impregnation, then after impregnation and after hygro-thermal treatment. Impregnation yield (IY) and weight percentage gain (WPG) have been calculated according to Eq.1 and Eq.2

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

$$WPG\ (\%) = \frac{w_{t,d} - w_{u,d}}{w_{u,d}} \times 100 \quad (2)$$

where w_i stands for the impregnated sample weight, $w_{t,d}$ for the sample weight after complete treatment (impregnated and cured), and $w_{u,d}$ the oven dried sample weight before treatment (untreated anhydrous).

Weight variation after hygro-thermal treatment was also measured and weight uptake (WU) was calculated according to Eq.3:

$$WU\ (\%) = \frac{w_{t,w} - w_{u,d}}{w_{u,d}} \times 100 \quad (3)$$

where $w_{t,w}$ stands for the wet sample weight after autoclave treatment.

Volumetric variation was measured at each treatment step. Volumetric variation after impregnation (ΔV_i), after hygro-thermal treatment ($\Delta V_{t,w}$) and after thermal post-treatment ($\Delta V_{t,d}$) have been calculated according to Eq. 4, Eq.5 and Eq.6:

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

$$\Delta V_{HTT}\ (\%) = \frac{V_{HTT} - V_{u,d}}{V_{u,d}} \times 100 \quad (5)$$

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

where V_i stands for the impregnated sample volume, V_{HTT} for the sample volume after hygro-thermal treatment (impregnated, treated), V_{PT} for the sample volume after PT, and $V_{u,d}$ the oven dried sample volume before treatment (untreated anhydrous).

Table 1 : description of wood treatment conditions

Impregnation		Treatment	Hygro-thermal treatment				Thermal post-treatment	
Product	Temperature [°C]	n°	P [bar]	RH [%]	Temperature [°C]	Duration [h]	Temperature [°C]	Duration [h]
OBS	90	T0	-	-	-	-	103	36
		T1	1.01	100	100	0.5		
		T2	2.70		130			
		T3	6.18		160			
		T4	1.01		100	2		
		T5	2.70		130			
		T6	6.18		160			

2.4. Anti-swelling efficiency (ASE)

ASE was measured following the method described by Noël *et al*. (2015a). Treated samples (15 x 15 x 10 mm^3, T x R x L) were placed at ca. 100% RH at constant temperature (23°C). Samples dimensions were measured before exposure (dry state) and after weight stabilisation. Regular weight measurements were made in order to determine the equilibrium moisture content (EMC) of samples with time. The swelling of the reference samples (S_R) was calculated according to Eq.6:

$$S_r\,(\%) = \frac{V_{r,100\%} - V_{r,d}}{V_{r,d}} \times 100 \quad (6)$$

where $V_{r,100\%}$ stands for the untreated reference sample volume after stabilisation at 100% RH, $V_{r,d}$ for the oven dried untreated reference sample volume. For the impregnated wood, the ASE* calculation was based on the corrected swelling calculation of treated samples (S_t^*) as defined in Eq.7 and Eq.8 according to Thybring (2013):

$$S_t^*\,(\%) = \frac{V_{t,100\%} - V_{t,d}}{V_{u,d}} \times 100 \quad (7)$$

$$ASE^*(\%) = \frac{S_r - S_t^*}{S_r} \times 100 \quad (8)$$

where $V_{t,100\%}$ stands for the treated sample volume after stabilisation at 100% RH, $V_{t,d}$ for the treated dry sample volume before stabilization at 100% RH, $V_{u,d}$ the oven dried sample volume before treatment.

2.5. Leaching

Treated samples (15 x 15 x 10 mm^3, T x R x L) were immersed in water at room constant temperature (23°C) for 504 hours, in separated boxes according to the treatment procedure undergone by the samples. LR was calculated according to Eq.9

$$LR\,(\%) = \frac{w_{t,d} - w_{t.l,d}}{w_{t,d} - w_{u,d}} \times 100 \quad (9)$$

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

3. RESULTS AND DISCUSSION

3.1 Treatment description - Products flow in wood structure

In all cases, despite of a mean impregnation yield of 67.4%, only ca. 1% volumetric increase is observed after impregnation, showing that OBS do not penetrate the cell walls at this stage of the process.

The aim of the hygro-thermal treatment (HTT) is to induce partial swelling of wood cell walls so that the OBS can diffuse into the structure. Due to OBS relative sensitivity to water at those high temperatures, there is a risk of oligomers hydrolysis in the process (Kanemura *et al*. 2012). Besides, the high pressure needed to get to 100% RH at high temperature could certainly influence the oligomers flow into wood structure. Thus, the resulting weight uptake (WU) and volumetric variation (ΔV_{HTT}) must be due to a combination of phenomena happening during HTT. The WU is not necessarily only due to water uptake, because a partial weight loss due to oligomers hydrolysis and/or OBS extraction might occur simultaneously. Likewise, wood ΔV_{HTT} is not necessarily due only the water penetration into the cell walls. Partial oligomers diffusion is also possible. The kinetics of oligomers hydrolysis and diffusion into the cell walls is most likely depending on the treatment conditions, especially temperature (Freyermouth 2014). For that reason, each variant describes a precise progression state of the combined phenomena. Post-treatment (PT) at 103°C for 36h was expected to remove the residual water absorbed during HTT. The weight loss induced by PT is most likely due to water evaporation only as the weight loss of samples T0 during PT is limited. The total weight loss resulting from the whole treatment process, in comparison to the impregnated samples weight, confirms partial OBS hydrolysis and extraction from wood, because further polycondensation would be prohibited by water saturated reaction medium (Garin 2012). The final volumetric increase (ΔV_{PT}) is possibly due only to OBS diffusion and persistence into wood structure.

As observed on Figure 2 and Figure 3, during HTT, impregnated samples do not always absorb the same amount of water. That does not depend on HTT duration either.

At 100°C HTT (T1 and T4), there is no significant difference between IY and WU. The amount of hydrolysed oligomers extracted from wood might be equivalent to the amount of impregnated water. The whole treatment leads to simultaneous weight loss (higher if longer) and persistent volumetric increase (higher if longer). This indicates the effective diffusion of oligomers into wood cell walls.

At 130°C HTT (T2 and T5), the whole treatment leads to simultaneous weight loss (higher if longer) and persistent volumetric increase (higher if shorter). There is an effective diffusion of the oligomers into wood cell walls. T2 is the only treatment where the oligomers weight lost during HTT is higher than the amount of water impregnated. The highest final weight loss of samples is observed through T5. Besides, T5 is the only long HTT leading to final volumetric decrease in comparison to short HTT. It seems that the oligomers degradation is substantially stronger at 130°C.

At 160°C, long HTT (T6) is equally efficient as 100°C long HTT, in terms of final WPG and persistent volumetric increase. Besides, short HTT leads to the same efficacy. This is evidenced in Figure 4: temperature must be as high as 130°C to ensure a significant diffusion of oligomers into the cell walls after short HTT. Long HTT leads to the similar efficacy at 100°C and 160°C. However, there is a detrimental effect of a long HTT at 130°C, most likely due to stronger hydrolysis of oligomers and/or wood degradation.

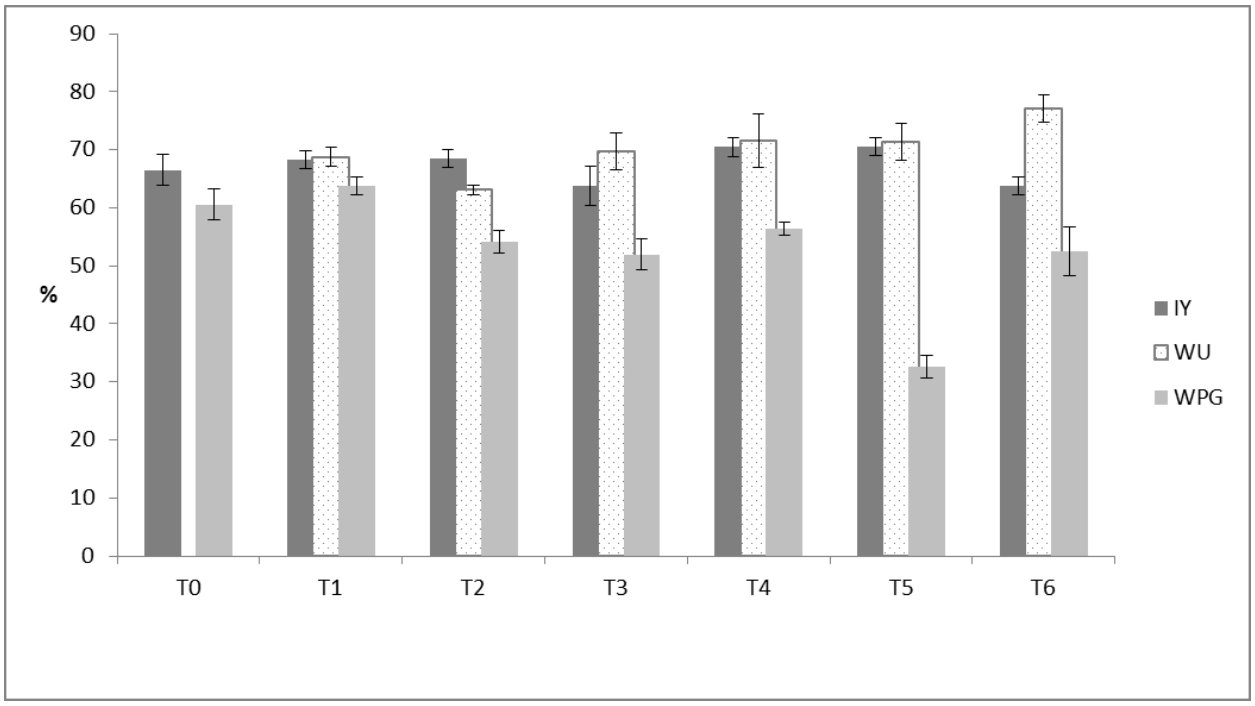


Figure 2: Weight variations calculated on untreated anhydrous weight after each step of the process: IY (%) after impregnation, WU (%) after HTT and WPG (%) after PT.

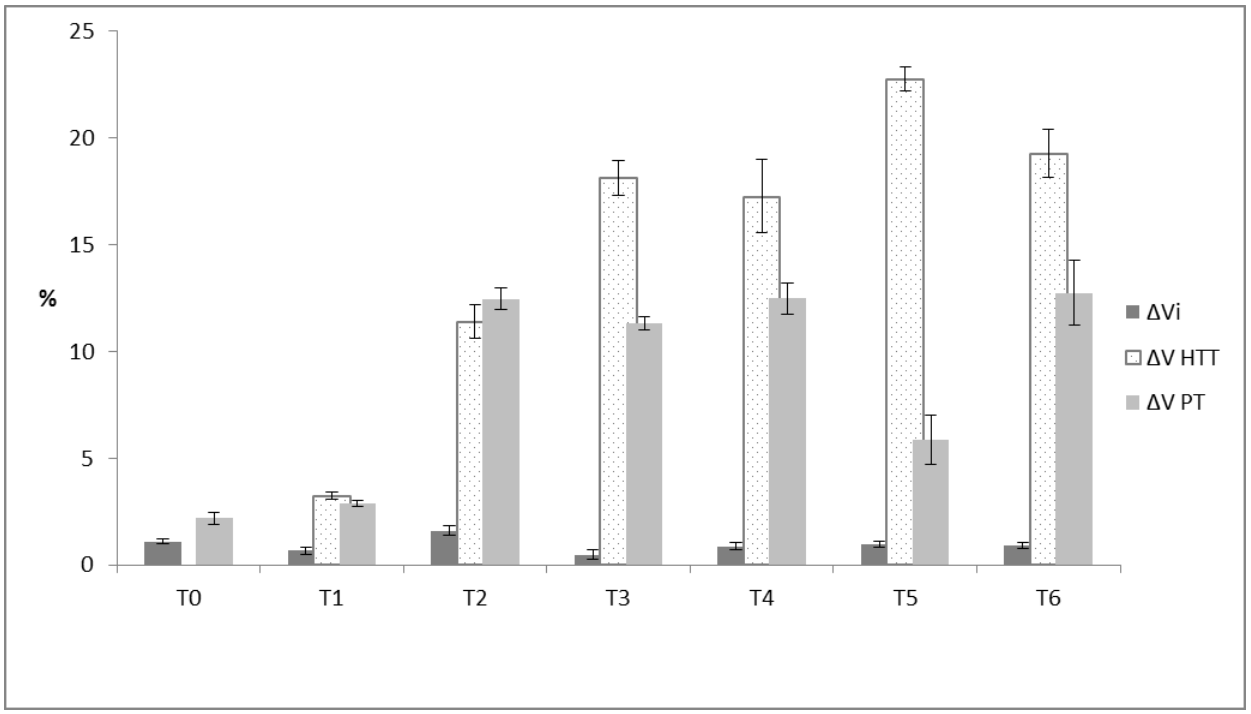


Figure 3: Volumetric variations calculated on untreated anhydrous volume after each step of the process: ΔV_i (%) after impregnation, ΔV_{HTT} (%) after HTT and ΔV_{PT} (%) after PT.

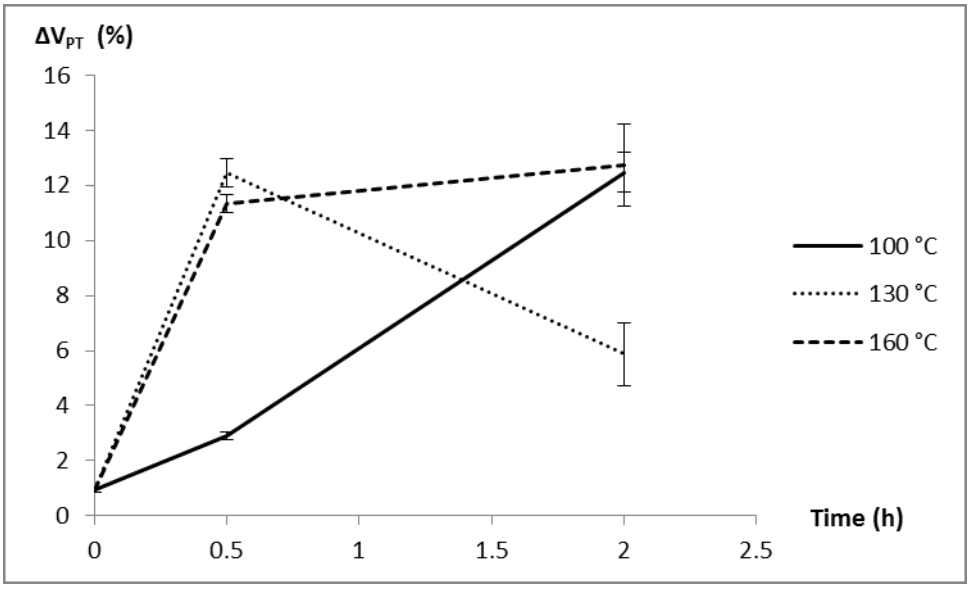


Figure 4: Evolution of final persistent swelling (ΔV_{PT}) in time, according to temperature

3.2 Performance

HTT temperature and duration are determining factors in wood dimensional stabilisation and product persistence in wood, according to ASE* and LR results.

3.2.1 Dimensional stability

Samples T0, not submitted to HTT, showed only limited diffusion of oligomers in the cell walls (ΔV_{PT} = 2.2 ± 0.3 %), logically leading to no dimensional stabilisation (ASE* = -8.7 ± 4.3 %). As seen in Figure 5a, HTT temperature plays an essential role into treatment efficiency. Temperature as high as 130°C leads to the highest ASE* obtained in this experiment set (ca. 49%). This value is not improved with longer HTT. However, longer HTT allows reaching the same efficiency at 100°C. While a long HTT at 160°C does not decrease the ASE*, there is a detrimental effect of time at 130°C, well correlated to the shrinkage observed in Figure 4 under these conditions. Longer HTT were not considered in this work, because HTT duration at 100°C was proven to be not ameliorative if longer than 2h (Noël et al., 2016).

This observation opens the discussion on the most effective HTT to carry out for eventual up-scaling: low temperature for long time, or short time at high temperature. The question of wood components degradation might be decisive. Further analyses are being carried out on that matter.

3.2.2 Persistence of treatment in wood

For comparison, samples T0, not submitted to HTT, showed a significant LR of 14.3 ± 0.4%. As seen in Figure 5b, 100°C HTT does not impact the LR substantially, while an increase in HTT temperature and duration is detrimental.

Short treatment at 130 or 160°C, or long treatment at 100°C, are again the best option for further development.

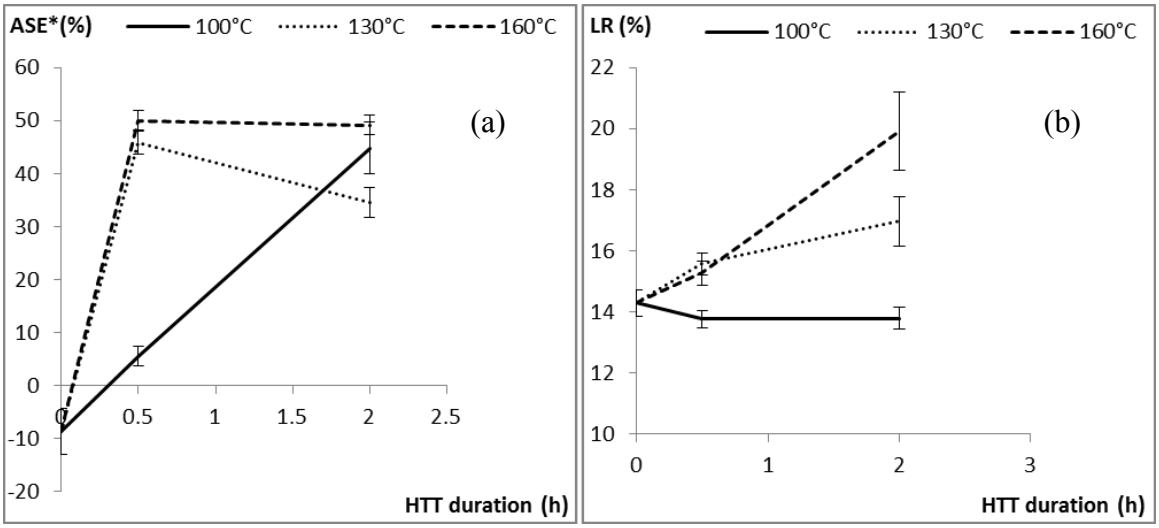


Figure 5: Evolution of ASE* (a) and LR (b) in time according to temperature

3.2.3 Correlation with cell wall bulking

Wood dimensional stabilisation logically correlates with the amount of OBS into the wood cell walls. This is demonstrated in Figure 6. The better diffusion (higher ΔV_{PT}), the higher is ASE*. But this relation is not linear, most likely because dimensional stabilisation does not result only from the treatment diffusion into the cell wall. For example, T0 and T1, leading to similar ΔV_{PT}, do not induce similar ASE*. The quality of oligomers diffused (degree of polymerisation, depending on the hydrolysis extent), as well as the diffusion depth into the cell wall might be involved.

As seen in Figure 7a, there is no clear correlation in between the product persistence into wood and ΔV_{PT}. However, the higher the HTT temperature, the higher is the LR (Figure 7b). This observation might indicate that the temperature induce oligomer chains mobility, most likely by partial hydrolysis due to the combination with humidity, leading to good diffusion into wood structure, but easy leaching. Whereas a lower temperature combined to humidity provoke wood cell walls swelling and diffusion of oligomer chains into the structure with limited hydrolysis. In the latter case, there is a better persistence in wood after drying by physical fixation of the chains.

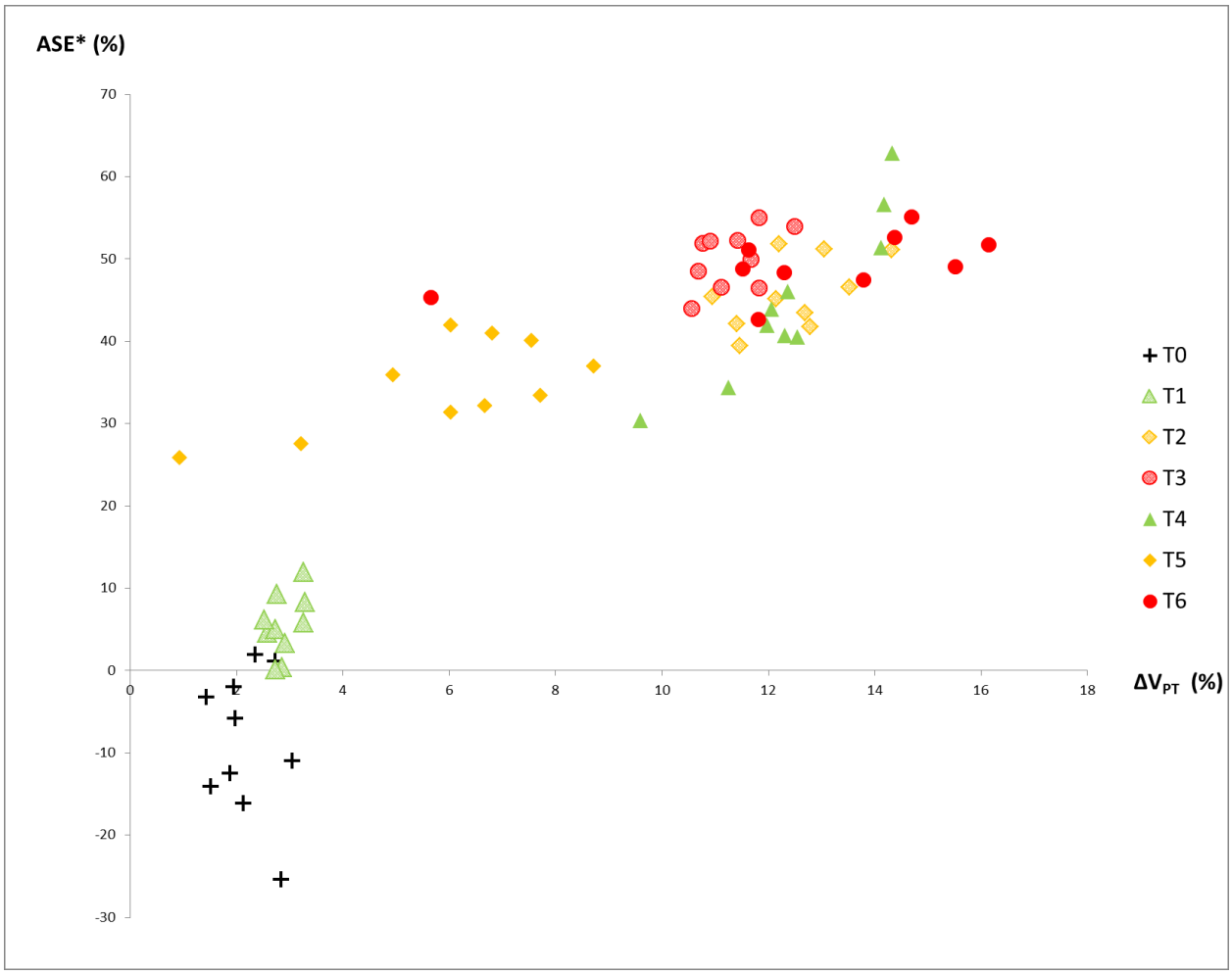


Figure 6: Evolution of ASE* according to volumetric variation after PT (ΔV_{PT})

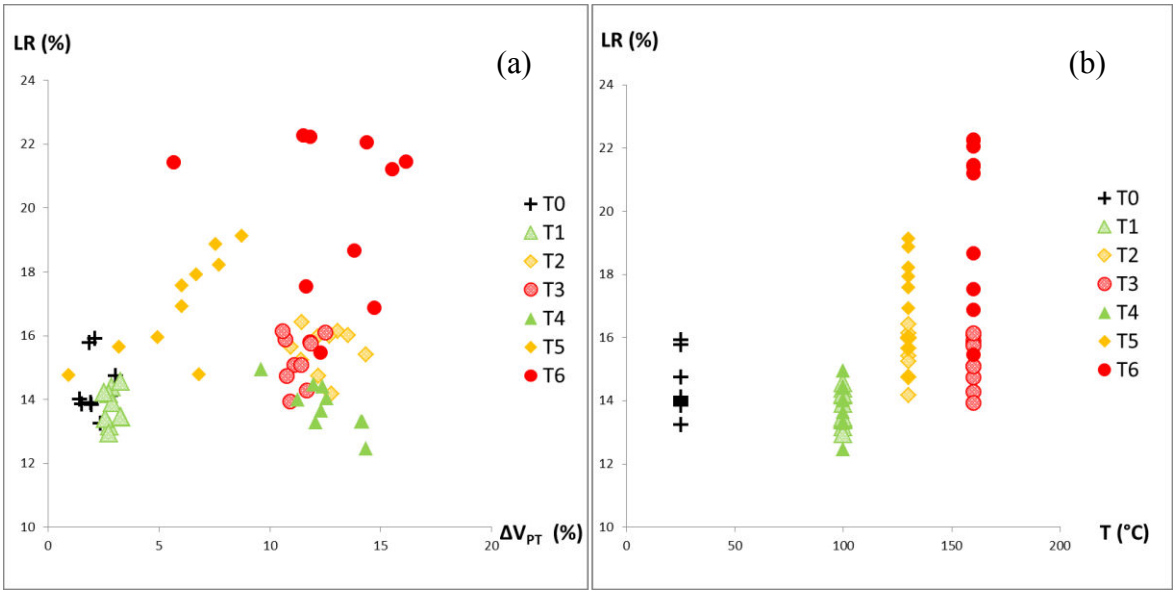


Figure 7: Evolution of LR according to swelling after PT (ΔV_{PT}) (a) and curing temperature (b)

4. CONCLUSION

There was a high impregnation yield of OBS treatment into wood structure under soft impregnation conditions. An effective diffusion of the oligomers into wood cell walls during HTT was noticed. Wood dimensional stabilisation correlated well with the amount of OBS into the wood cell walls. Temperature rising generally allowed a more effective diffusion of OBS into wood structure, with however an upper limit of ca. 50% ASE*. It is highly possible that OBS hydrolysed during HTT (Freyermouth 2014, Garin 2012, Kanemura *et al* 2012), which might have made the oligomers diffusion in wood possible. The length decrease of oligomer chains, in combination with cell walls swelling induced by water vapour, were most likely responsible of the OBS diffusion into the structure. Temperature increase catalysed hydrolysis (Freyermouth 2014, Garin 2012, Kanemura *et al* 2012). That might explain the higher wood swelling with higher temperature of short HTT. However, in all cases, increasing HTT temperature was detrimental to product persistence into wood, despite of good ASE* values.

For better understanding of the phenomena observed, further analyses are being carried out on the parameters combination of treatment. Two options appear to be competing for effective HTT: low temperature for long time, or short time at high temperature. For up-scaling consideration, the question of wood components degradation due to treatment conditions might be decisive. The influence of PT is also being investigated by varying the post-treatment conditions in order to attempt an eventual further in-situ polymerization, or at least partial fixation. Besides, hot solvent extraction of treated wood will allow the measurement of molecular mass distribution of the extracted oligomers, proving or refuting the oligomers hydrolysis and/or in-situ polymerization. Furthermore, HTT carried out at varying relative humidity was achieved. Those results will be reported in the near future.

5. ACKNOWLEDGEMENT

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Paper 8: Dynamic Mechanical Thermal Analysis of Wood Modified with Bio-Polyesters

Dynamic Mechanical Thermal Analysis of Wood Modified with Bio-Polyesters

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Keywords: beech, bio-polyester, hydrothermal treatment, impregnation, lactic acid, polybutylene succinate, wood modification

ABSTRACT

Chemical modification of wood with bio-polyesters, namely polylactic acid (PLA) and polybutylene succinate (PBS), has recently been reported (Noël *et al.* 2015, Grosse *et al.* 2017a). Both oligomeric treatments (OBS and OLA) confer interesting properties to wood for outdoor applications. They are based on the impregnation of oligomers in oven-dried beech wood (*Fagus sylvatica* L.), followed by a curing step at 100 or 120°C for OBS or 160°C for OLA. Unlike treatment with OLA, the dry curing conditions did not allow any penetration of OBS in wood cell walls, thus no gain in anti-swelling efficiency (ASE) was seen. Humid treatment conditions were observed to allow a partial diffusion of OBS in cell walls, most likely because of water acting as swelling agent. Hydro-thermal treatment (HTT) was carried out at several temperatures, relative humidities and durations, to find optimal conditions of OBS diffusion in the wood structure. Treatment conferred ASE of 60% to 70%, with a good correlation to OBS diffusion. (Grosse *et al*. 2017b). In this study, dynamic mechanical thermal analysis (DMTA) under varying humidity was carried on for understanding OBS/OLA interactions with wood polymers. First, temperature scans were performed from -150°C to 150°C at a heating rate of 5 °C/min and for a frequency of 1, 10 and 100 Hz. Glass transitions of wood components and oligomers appeared in the tan δ response of the modified wood. In a second set of experiments the relative humidity in the chamber was set at 35% and the temperature changes were manually performed when the conditions in the chamber were stable. Wood impregnated with OBS but not hydrothermally-treated has the same behaviour as untreated wood, indicating few interactions between the polymer and the cell walls. This is well correlated with the low diffusion of OBS into wood structure. In the case of hydrothermally-treated samples the same global behaviour can be observed. In the case of OLA treated wood, the stiffness of the material decreases more rapidly with the temperature, in comparison with the OBS treated wood. Oligomers of lactic acid, more hydrophilic and smaller than the PBS ones, are more likely diffusing then interacting with the cell walls polymers.

INTRODUCTION

As a renewable material, wood has many advantageous properties such as workability, mechanical strength, sustainability and pleasant aesthetic features. However, wood is sensitive to its environment, especially regarding moisture. Due to its chemical composition, the dimensional stability against humidity and biological resistance of wood are limited. Chemical modification of wood with polybutylene succinate (PBS) has been reported to confer interesting properties to wood for outdoor applications (Noël *et al.* 2015a, 2015b, Vitkeviciute *et al.* 2014). This treatment was based on the hot impregnation (90°C) of PBS in oven-dried beech wood (*Fagus sylvatica* L.), followed by a curing step at 100/120°C for 6h/96h. The dry treatment conditions did not allow any penetration of the oligomers in wood cell walls, thus any anti-swelling efficiency (ASE). The mechanical properties were not influenced either. However, the PBS lumen-filling led to a substantial decrease in wood hygroscopicity. Moreover, a good retention of oligomers into the wood lumens was observed, with ca. 80% retention rate of the impregnated polymers in wood during water leaching. Humid treatment conditions were observed to allow a partial diffusion of the oligomers into the cell walls, most likely because of water acting as swelling agent inducing partial penetration of oligomers in the cell wall. Humid treatment conferred anti-swelling efficiency (ASE) of 60% to 70%, with a good correlation to PBS diffusion. This phenomenon is not yet fully understood. For that reason, the dynamic mechanical thermal analysis (DMTA) under varying humidity is expected to help the understanding. Hydro-thermal treatment (HTT) was carried out at several temperatures, relative humidity and duration, in order to find optimal conditions of PBS diffusion into the wood structure. Most effective HTT to carry out for eventual up-scaling is to be determined: low temperature for long time, or short time at high temperature. The question of wood components degradation might be decisive. DMTA under varying humidity is expected to help the selection of the best option through analyse of the influence of treatment parameters (temperature, relative humidity and duration) on wood/oligomers interactions.

EXPERIMENTAL

Samples preparation

Samples were prepared as described by Noël *et al*. (2015b). Oven-dried wood samples were immersed in liquid oligomers, OBS, OLA L and OLA S respectively, at 90°C, 60°C and 20°C respectively. Containers were then placed in a vacuum oven under reduced pressure (150 mbar) for 20 to 30 min, then atmospheric pressure over 20 to 30 min. Impregnated samples were then wiped.

Weight uptake (WUi) and swelling (Si) after impregnation have been calculated as follows:

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

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

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.

For the OBS-treated samples, the following HTT was carried out in a pressurized reactor at 100% relative humidity (RH) and different temperatures for different durations. For all samples, a final thermal post-treatment (PT) was carried out to dry the treated samples and was expected to partially cure and fix the oligomers in wood. Table 1 summarises the treatments conditions.

Weight uptake (WUt) and swelling (St) after treatment were calculated as follows:

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

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

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. All samples were then stabilised at 35% RH.

Table 1: description of treatments conditions

Sample	Impregnation product	Hygro-thermal treatment			Post treatment	
		Temperature [°C]	RH [%]	Duration [h]	Temperature [°C]	Duration [h]
PBS A	PBS	100	100	2	103	72
PBS B					120	72
PBS C		130	100	0.5	103	72
PBS D					120	72
PBS E		160	100	0.5	103	72
PBS F					120	72
PBS G		-	-	-	103	72
PBS H		-	-	-	120	72
OLA S	Short OLA	-	-	-	160	48
OLA L	Long OLA	-	-	-	160	48
REF	None	-	-	-	-	-

Dynamic mechanical analysis

First, the dynamic mechanical thermal analysis (DMTA) has been carried out on a Triton TTDMA. Temperature scans were performed from -150°C to 150°C at a heating rate of 5 °C/min and for a frequency of 1, 10 and 100 Hz.

A second DMA analysis has been then carried out using a humidity generator connected to the Triton TTDMA, to allow a temperature ramp while controlling the RH in the chamber. Samples of dimensions 50×10×4mm (L×RT×TR) were used in both sets of experiments. RH was set at 35% and the temperature changes were manually performed when the conditions in the chamber were stable. Once the temperature and RH were stable, the average of five values of the stabilised storage modulus was calculated. Only relative storage modulus values and tan delta for 1Hz are reported.

RESULTS AND DISCUSSION

Dynamic mechanical thermal analysis (DMTA)

Table 2 summarises samples weight and volumetric variations during treatment. After impregnation, both polymers mostly remain in the cell lumens according to the low S_i. With heating, there is a product migration into the wood structure. S_t is most likely due to product diffusion in the cell walls. For PBS, diffusion is more effective with HTT than with only PT and for OLA, a PT carried out at 160°C is sufficient.

Table 2: Samples weight variations (WUi and WUt) and volumetric variations (Si and St) after impregnation and after treatment (only the data of the one sample used for DMTA are presented).

	WUi [%]	WUt [%]	Si [%]	St [%]
PBS B	86.9	77.5	0.5	15.1
PBS D	88.7	80.2	1.8	13.7
PBS F	82.4	66.1	2.6	12.8
PBS H	79.1	75.1	1.8	7.6
OLA S	62.7	29.9	0.4	12.1
OLA L	81.8	51.1	-0.5	16.3

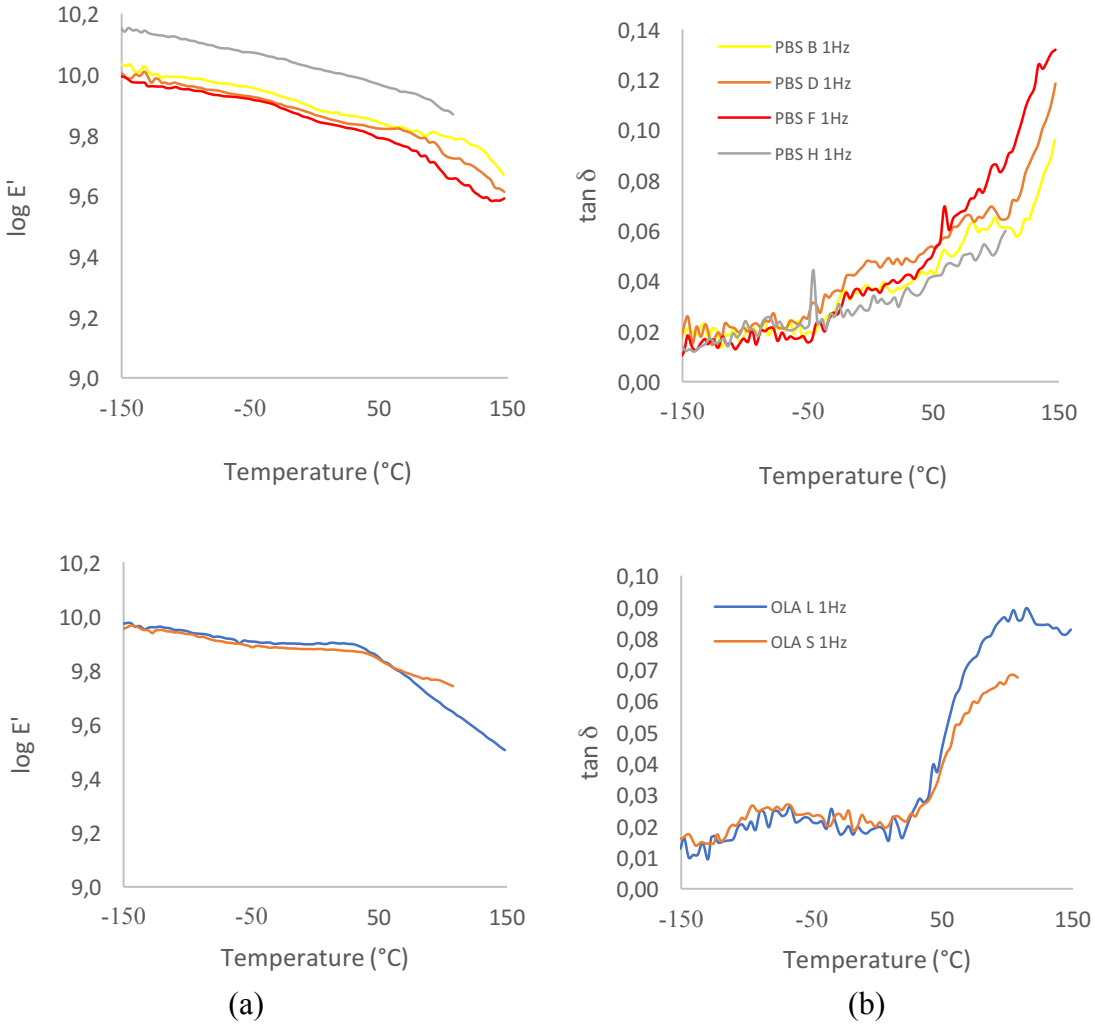


Figure 1: Effect of polymers on the dynamic mechanical response (a) log E' and (b) tan δ for a frequency of 1Hz.

Wood DMTA has been widely studied. The tan δ response of untreated wood usually shows a low temperature transition (β) at between -90 and -110 °C, and a broad transition (α1) centred around 80 to 100°C with a shoulder (α2) between 10 and 60°C (Kelley *et al*. 1987). Glass transition temperature (T_g) of PBS and PLA respectively is around -45 to -50 °C and around 40 to 60°C respectively. As oligomers present in the modified wood are smaller than industrial polymers, those transitions might appear in the lower range of temperature in the tan δ response of the modified wood (Figure 1).

For PBS treated wood, the tan δ response is very similar to untreated wood. However, the β transition is not clear and α1 transition might have been shifted to slightly higher temperature, showing a reduced amount of small molecules in wood structure and reduced mobility of cell walls components. A transition around -50 °C appears in the tan δ response of PBS H but not in the others. It might just be a measurement error or it can be the T_g of PBS from the lumens as it is the only variant not submitted to hydrothermal treatment. For OLA treated wood, the β transition is visible around -80 °C and α1 is broader than for untreated wood. α1 transition is most likely due to both wood and OLA as the PLA T_g is around 40 to 60 °C.

Effect of PBS on the dynamic mechanical response at 35% RH

Table 3 summarise samples weight and volumetric variation during treatment. First, one sample for each variant was run on the DMA after stabilisation in a desiccator at 35% RH. At this RH, treated samples were very dry as they all had an EMC below 2%. Figure 2 and Figure 3 show the relative storage modulus (E') and tan δ response for this first batch of samples. The reference sample (REF) relative E' is slightly increasing (about 5%) with the temperature from 20 to 30 °C and is then decreasing back to its original value at 20°C. Wood impregnated with PBS but not hydrothermo-treated (PBS G) has the same behaviour indicating few interactions between the polymer and the cell walls. This is well correlated with the low diffusion of PBS into wood structure (S_t = 3.1%). Impregnation followed by heat treatment at 120°C allows to double the wood swelling after treatment (PBS H). Relative E' is increasing with the temperature but seems to stabilise instead of decrease. In the case of samples impregnated with PBS and then treated with hydrothermal treatment and post-treatment (PBS A, B, E, and F), the same behaviour can be observed. Relative E' is decreasing with temperature. However, some variants ran a second time, with another sample, showed opposite behaviour, like PBS A (Figure 4). Information provided is not fully understood yet, but reproducibility of the experiment is uncertain. Thus, several replicates are currently on going to validate the results and understand the reasons of such variability.

Table 3: Samples weight variations (WUi and WUt) and volumetric variations (Si and St) after impregnation and after treatment (only the data of the one sample used for DMTA are presented).

	WUi [%]	WUt [%]	Si [%]	St [%]
PBS A3	80.7	74.6	-0.4	14.9
PBS A2	90.5	84.6	0.1	15.8
PBS B	85.8	78.6	1.2	15.4
PBS E	86.8	72.2	2.4	13.9
PBS F	86.2	69.1	4.4	13.1
PBS G	77.9	75.8	0.3	3.1
PBS H	80.1	76.6	1.0	7.4
REF	-	-	-	-

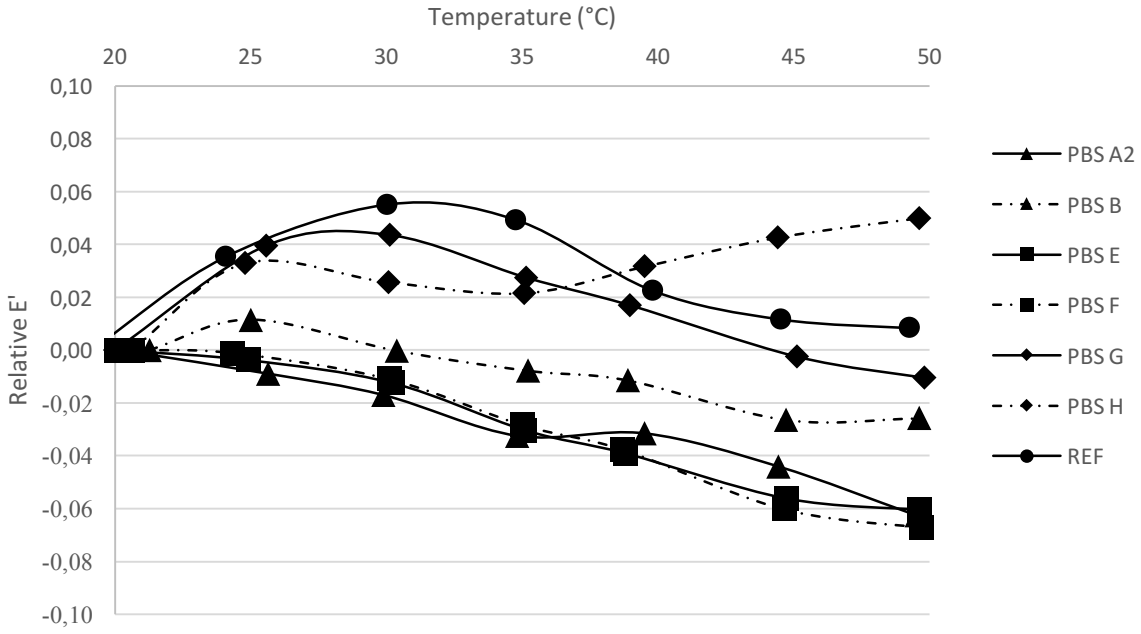


Figure 2: Effect of PBS on the dynamic mechanical response regarding relative E' for a frequency of 1Hz.

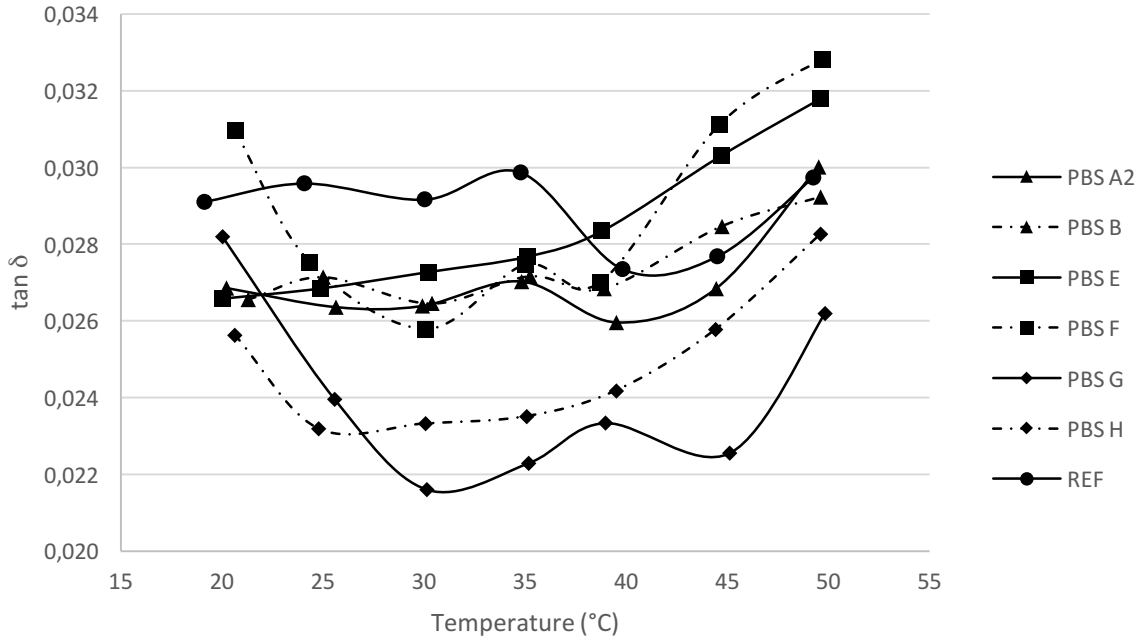


Figure 3: Effect of PBS on the dynamic mechanical response regarding tan δ for a frequency of 1Hz.

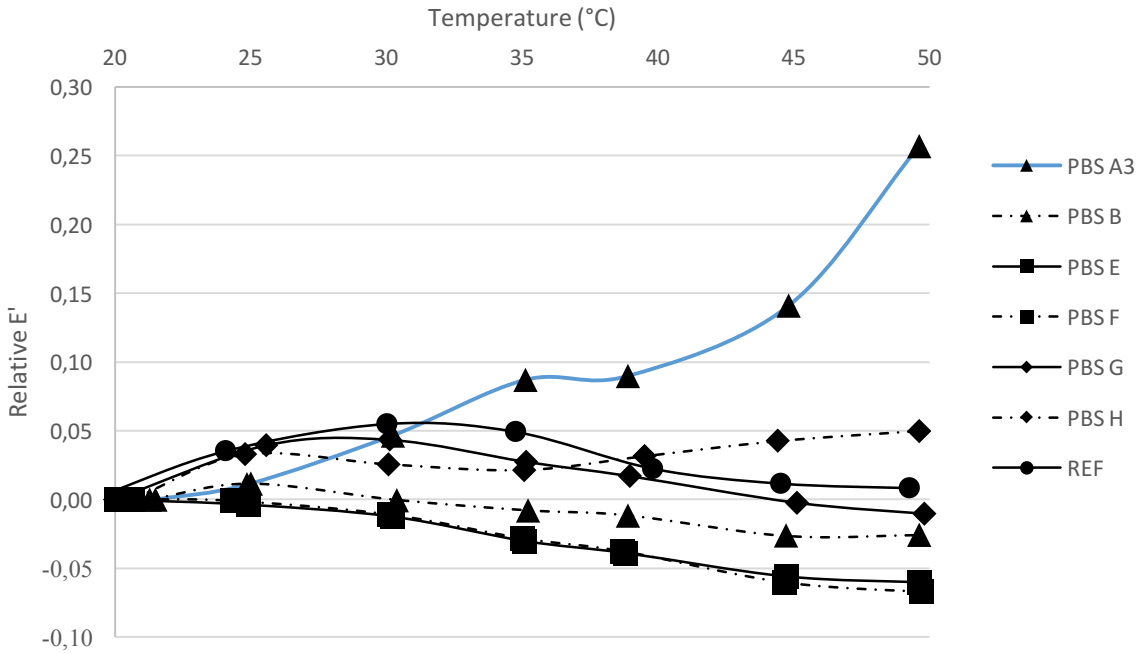


Figure 4: Effect of PBS on the dynamic mechanical response regarding relative E' for a frequency of 1Hz.

Effect of OLA on the dynamic mechanical response at 35% RH

In the case of OLA treated wood, the stiffness of the material decreases more rapidly with the temperature in comparison with the PBS treated wood. Oligomers of lactic acid, more hydrophilic and smaller than the PBS ones, are more likely diffusing then interacting with the cell walls polymers.

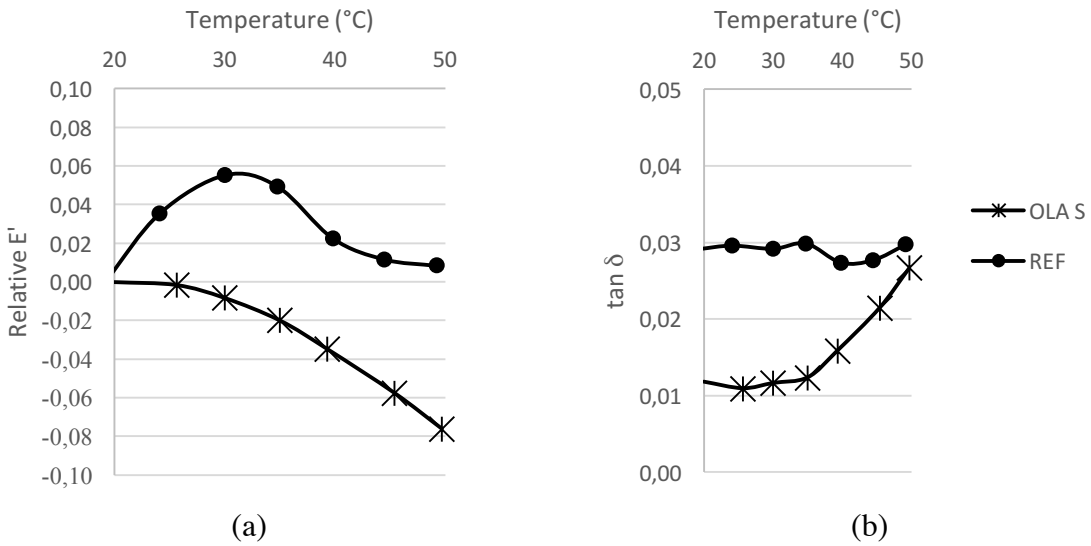


Figure 5: Effect of OLA on the dynamic mechanical response regarding (a) relative E' and (b) tan δ for a frequency of 1Hz.

CONCLUSIONS

As conclusion, the DMA provided interesting pre-results and revealed to be a possible way to investigate the influence of hydrothermal treatment and post-treatment conditions on the mechanical properties, as well as on the interaction of wood with the polymer. However, more experiments are still on going to reinforce the analyse and the results.

ACKNOWLEDGEMENTS

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PART C: Processability

For LA, OLA and OBS selected treatments, further testing was carried out to evaluate the potential of such treatments for further development of industrial scale applications. In the case of wood modified with lactic acid, process up-scaling feasibility was also studied.

The results are presented in **Paper 9**: Biopolyesters for wood modification: technical validation towards implementation (Noël *et al*. 2018, in: *proceedings of ECWM9*).

Paper 9: Biopolyesters for wood modification: technical validation towards implementation

Biopolyesters for wood modification: technical validation towards implementation

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Keywords: bio-polymers, in-situ polymerization, lactic acid, polybutylene succinate, thermal treatment, wood modification

ABSTRACT

Wood modification with bio-polyesters has been reported in terms of treatments synthesis, interaction between wood polymers and bio-polyesters, evaluation of the durability, leaching resistance and dimensional stability of treated wood. These investigations led to the selection of two variants. In view of industrial implementation, this article reports the mechanical characterization and process ability evaluation of wood modified accordingly.

INTRODUCTION

The original idea behind this research was to create a durable and sustainable new material, by association of bio-resources (namely wood and biopolymers). Unlike wood plastic composites combining wood fibres as reinforcement into a polymer matrix, the approach developed here was to impregnate the solid wood matrix with bio-based polymer(s) as reinforcement for performance improvement. The polymer choice inclined towards bio-polyesters as poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(butylene succinate) (PBS) and poly(butylene adipate) (PBA) because of their bio-based character and their expected chemical affinity with wood. Inspired by standard procedures intensively described in wood modification literature, the developed method consisted in a 2-step treatment: impregnation of polymers precursors in wood under vacuum followed by heat treatment to initiate in-situ polymerization and potentially chemical grafting on wood. The impregnation step revealed to be easily carried out leading to significant weight uptake of precursors. The *in situ* polymerization was proven by gel permeation chromatography of extracted polymers. The final material consisted in slightly darkened modified wood with excellent biological resistance and dimensional stability (Noël 2010, 2015). Beech wood was the main species considered in this work, because being readily available in Europe and in need of performance increase to promote its use. The high volumetric variation coefficient and poor durability constitute the main limitations of this species, which is on the other hand easily impregnable. Some tests were also carried out on pine sapwood, fir and douglas fir. According to bio-polymers, many variants were considered over the years with varying objectives. For rheology and

reactivity adjustment, PGA and PBA were evaluated as crude polymers for treatment, and as co-polymers. The following systems of oligomers were examined: PLA, PGA, and copolymers thereof (with varying ratios of monomers), PBS, PBA, and co-polymers thereof (with varying ratios of monomers) (Noël 2015, Vitkeviciute 2015, Noël *et al.* 2014, 2015). For compatibilization between wood and PLA, maleic anhydride was added to the treatment system (Grosse *et al.* 2016). To catalyse PLA treatments, additionally to thorough screening of usual catalyst of PLA polymerization (Noël 2010), citric and tartaric acids were also appraised separately. As polyacids, their addition into the mixture was expected to create ramifications in the oligomer chains. To increase durability, hydrolysable chestnut tannins were included in PLA mixtures (Grosse *et al.* 2016). Out of those combinations, best results were obtained with PLA and PBS, with which the process was developed and characterized further. Precursors were constituted of lactic acid monomers or short oligomers produced by polycondensation (OLA), and of PBS oligomers obtained by catalyzed pre-polymerization (OBS) of butan-1,4-diol and dimethylsuccinate. Viscous liquid, OLA diffused into wood under vacuum at room temperature, while OBS must be heated over melting temperature to penetrate wood structure. The treatment conditions revealed to be more influent than any additives mentioned above. For that reason, many optimization trials were carried out to define the most efficient parameters combination: treatment temperature, duration and relative humidity (Noël *et al.* 2016, Grosse *et al.* 2017, 2018). Besides, once most important properties validated, the implementation feasibility was investigated: efficiency of treatment wood at 12% and 30% equilibrium moisture content (EMC), impregnation of real scale wooden objects, elaboration of thermal treatment judicious cycle, … This article reports the global characterization of the most promising treatments elaborated within the framework of several R+D projects and exposes the first attempts of implementation in collaboration with the companies Corbat Holding SA (Glovelier (JU), Switzerland) and Jungbunzlauer AG (Headquarters in Basel, Switzerland).

EXPERIMENTAL

Wood treatment

LA treatment consisted in a commercial lactic acid water solution (88%). OLA-treatments consisted in oligomers of lactic acid obtained by limited polycondensation, with wide molecular mass distribution and degree of polymerization of 5 - 10. OBS-treatments consisted in oligomers of PBS obtained by polymerization of butan-1,4-diol and dimethyl succinate (catalyzed with titanium (IV) butoxide), with wide range of molecular mass distribution and degree of polymerization of 15 – 25 (full procedures in Noël *et al.* 2014). Wood samples (beech, fir, douglas fir and pine) were treated either at 0%, 12% or 30% EMC. Depending on treatment, the impregnation was carried out under vacuum (0.015MPa) at room temperature (LA/OLA-based treatments) or 70-90°C (OBS-based treatments). After ca. 2h of impregnation (30min-alternation of vacuum and soaking), samples were either set on aluminium foil for thermal treatment in ventilated oven (LA/OLA-based treatments), or subjected to wet cycle in autoclave (100°C/100% relative humidity (RH) for 2h) beforehand (OBS-based treatments) (full procedures in Noël *et al.* 2014). Thermal treatment temperature and duration differed and are defined thereafter.

Mechanical evaluation

Bending modulus (MOE) was measured according to EN 408 (2010). The 4-point bending test was done on oriented samples (150 x 7 x 12 mm^3, L x R x T for all dimensions in the text). The largest deflection was measured at the samples mid-length by a deflection

sensor (accuracy 0.02 mm). The MOE was calculated with Eqn. 1 between $0.1F_{max}$ and $0.4F_{max}$ (maximal force):

$$MOE = \frac{3al^2-4a^3}{2bh^3\left(2\frac{w_2-w_1}{F_2-F_1}-\frac{6a}{5Gbh}\right)} \quad \text{(MPa)} \qquad (1)$$

with a = spacing between one support and the closest load application point (mm); l = spacing between supports (mm); b = sample width (mm); h = sample height (mm); $F_2 - F_1$ = force increase on the regression line (N); $w_2 - w_1$ = deflection increase corresponding to ($F_2 - F_1$) (mm) and G = shearing modulus, defined as ∞ when not known (MPa).

Compression resistance was measured according to NF B51-007 (1985). The test was achieved on oriented samples (60 x 20 x 20 mm^3, L x R x T). Prior to testing, samples were stabilized at 12% EMC. Axial compression strength was calculated with Eqn. 2:

$$C_H = \frac{P}{ab} \text{ (MPa)} \qquad (2)$$

with P = maximal force (N) and ab = sample section (mm^2).

A comparative approach of wood shearing strength of treated and untreated wood was carried out by applying tensile force on samples prepared according to the EN 302-1 (2013), normally dedicated to adhesive evaluation. Samples were not glued. Two grooves were cut on each side of solid samples (110 x 12 x 24 mm^3), deep to the same wood plan, defining the area submitted to shearing force. Shear strength was calculated with Eqn. 3:

$$f_v = \frac{F_{max}}{A} \text{ (MPa)} \qquad (3)$$

with Fmax = breaking force (N) and A = glued surface (mm^2).

Process ability

Cutting tools wear

For each treatment variant, a new blade was used to produce 3.4 km of wood chips (samples dimensions: 600 x 50 x 40 mm^3). Blades were used on one half of their length; the other half constituted the reference. Wood samples were milled in length as shown in Figure 1. Blade's wear was measured with scanning electron microscope (SEM), positioned as shown in Figure 2. Micrographs were taken after generation of 0.5, 1.6 and 3.4 km. Each micrograph was scaled and exhibited measurements of the edge recession.

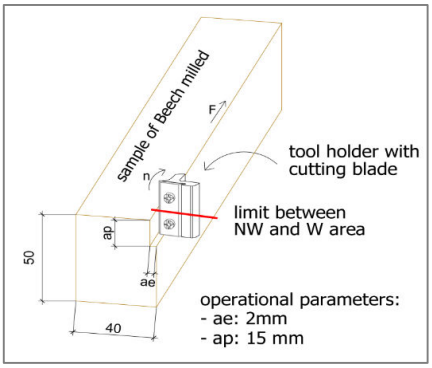


Figure 1: Description of milling parameters. W : worn, NW : non worn sections (Ruberu Q.)

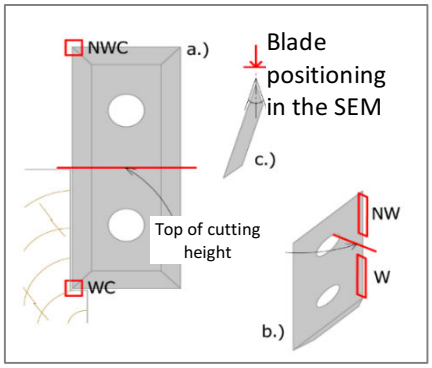


Figure 2: Description of milling parameters. WC : worn, NWC : non worn corners (Ruberu Q.)

Gluing

The longitudinal tensile shear strength was evaluated according to the procedure described in the standard EN 302-1 (2013). The test was carried out on oriented samples

(110 x {2 x 6 + glue line} x 24 mm^3). Samples gluing was achieved with one-component polyurethane resin Collano RP 2710 (200 $g.m^{-2}$ on one side), under 0.8 MPa for 5h. After gluing, samples were stored for one week at 20°C/65%RH. Shear strength was calculated with Eqn 3.

Coating

Wood samples were planed, sanded and stabilized at 20°C/65% RH before spray gun application of a 2-layer acrylate coating (Aquaprotect, Feyco Treffert) for a total wet thickness of 100 $g.m^{-2}$ each. Coated samples were stored at 20°C/65% RH until weight stabilization before conducting pull-off adhesion test (EN ISO 4624 (2016)). Adhesion strength was calculated with Eqn. 4. The nature of failure was always observed and described.

$$\sigma = \frac{F}{A} \text{(MPa)} \quad (4)$$

with F = breaking force (N) and A = the dolly area (mm^2).

RESULTS AND DISCUSSION

Optimization of treatments and treatment conditions

LA/OLA based treatments

The addition of catalysts into lactic acid monomers and oligomers before *in situ* polymerization was never beneficial, leading to strong degradation of the material (observed with 0.6% of sulfuric acid, or 5% of tin octoate a.o., Noël 2010) or no significant effect on wood physical properties (citric and tartaric acid). For compatibilization, maleic anhydride (MA) conferred resistance to water leaching similar at high and low treatment temperature, but this improvement was not substantial enough to compensate the non-renewable nor non-environmentally friendliness of MA (Grosse *et al.* 2016). The addition of hydrolysable chestnut tannins (TH) lead to biological resistance similar at high and low treatment temperature, but this improvement was not substantial enough to compensate the increase in wood hygroscopicity resulting from TH addition, even with tannins acetylated prior to *in situ* polymerization (Grosse *et al.* 2016). The pre-polymerization of LA was expected to promote the extent of *in situ* polymerization, and to pre-evaporate the water contained in the commercial aqueous solution. However, LA aqueous solution without any prior preparation conferred similar final performance. The resulting decisive parameters for performance improvement with LA treatment (dimensional stability, fixation in wood and durability) were the treatment temperature (threshold at 160°C) and duration (threshold not defined yet), even though this selection is only valid for anhydrous, small dimension samples.

OBS based treatments

The OBS oligomers were made of longer chains, unable to diffuse into wood cell wall during thermal treatment. However, it was observed that carrying out wet thermal treatment induced cell wall swelling by water vapour leading to polymers partial diffusion in wood ultra-structure. That procedure appeared to be the most efficient procedure for dimensional stabilization of wood. It resulted that the decisive parameters for performance improvement (dimensional stability, fixation in wood and durability) were defined after impregnation as a first wet step at 100°C/100% RH for 2h, followed by drying at 120°C for 48h, even though this selection is only valid for anhydrous, small dimension samples. OBS oligomers did not show any significant further *in situ*

polymerization even at high temperature (160°C). For that reason, the attention focused on good diffusion and fixation in the cell wall (Noël 2015, Noël *et al.* 2016, Grosse *et al.* 2017).

Mechanical performance

Given that the mechanical characterization was carried out on small no defect samples, a complete evaluation on bigger dimensions is still under investigation. However, the data below allowed the pre-evaluation of the up-scaling potentiality.

Two distinct mechanical behaviours were revealed depending on the bio-polymer constituted into wood and its interaction with the lignocellulosic matrix.

As thermal treatment makes LA or OLA diffuse into the cell wall and polymerize *in situ*, leaving lumens free, mechanical resistance and material elasticity were impacted. While bending and compression resistance increased because of polymer reinforcing action in wood, the elasticity decreased slightly resulting in stiffer material (Figures 3, 4, 5). Treatment acidity combined with high temperature leads to simultaneous weakening of wood internal cohesion, measured by shearing strength significant decrease (Figure 6). Final application of LA/OLA-treated wood must be wisely designed.

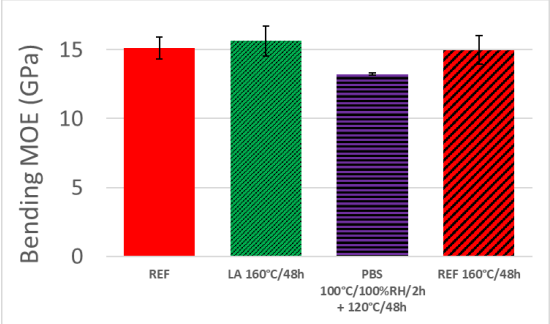


Figure 3: MOE of treated wood in comparison to references

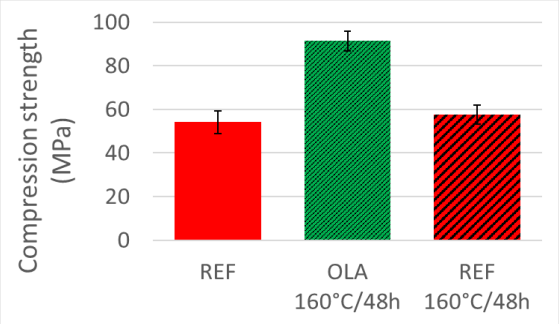


Figure 4: compression strength of treated wood in comparison to references

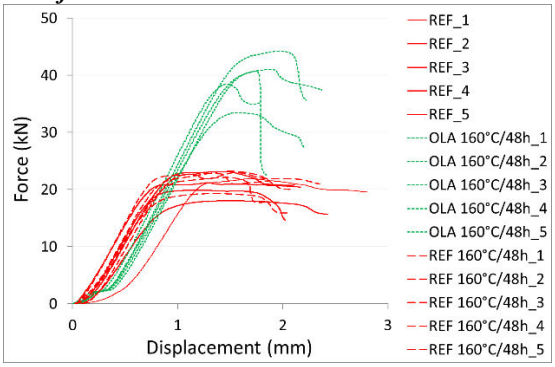


Figure 5: force/displacement curve of samples subjected to axial compression force

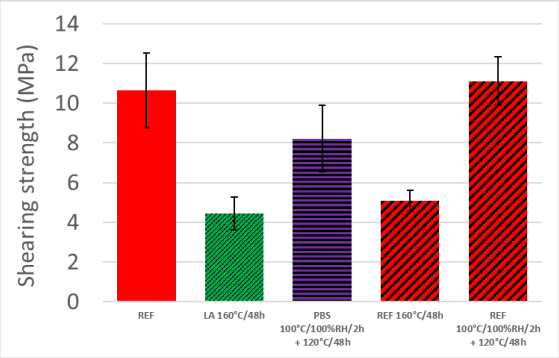


Figure 6: shearing strength of treated wood in comparison to references

Although not reported here, it was observed that thermal treatment of LA/OLA treated wood could be achieved at either 140°C or 160°C without any significant effect on final mechanical properties. The addition of TH did not show any significant impact either. Co-polymerization of LA and GA did not lead to any significant difference either. With only partial diffusion into the cell wall and filling of pores mostly, OBS treatment did not show significant influence on mechanical properties. The impact on wood internal cohesion was also limited, with slight shearing strength decrease observed (Figures 3, 4, 6). Together with very good durability and dimensional stability, OBS treatment gave better promises, mechanically wise, than LA/OLA treatments. Mechanical properties of treated wood (either LA/OLA or OBS) seem to be of interest for selected applications,

especially in comparison to thermally treated wood, known to lose mechanical resistance during the process (Esteves and Pereira 2009). Thermally treated under relatively soft conditions in comparison to most industrial procedures (160°C/48h/0%RH), thermo-treated references produced in the lab (REF 160°C/48h) showed no loss of strength in bending nor in compression in comparison to the untreated controls. However, the impact on fibres cohesion was significant.

Process ability

Cutting tools wear

Wood treatments increased wood density and material acidity significantly. *In situ* polymers might also lead to higher cutting tools fouling. Quantification of the influence of treatment on cutting tool wear was therefore necessary before implementation attempt.

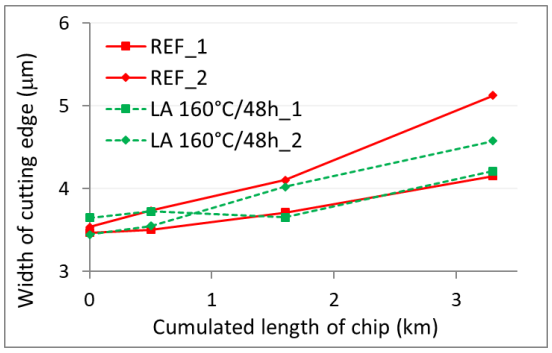


Figure 7: Growth of edge with cumulated length of chip created.

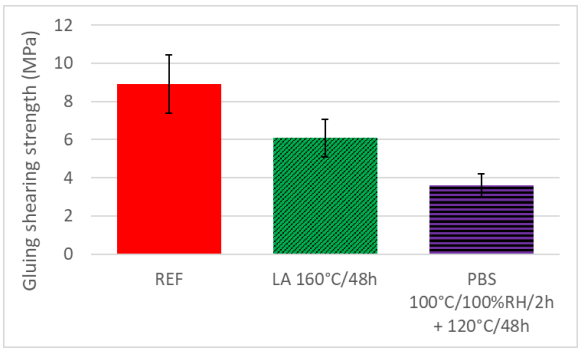


Figure 8: Gluing shearing strength of wood reference and wood treated (LA – PBS)

It was shown that the LA led to similar pattern to controls (Figure 7). There was no significant increase in cutting tools wear observed (variations due to measurement accuracy). The test must however be done with OBS treated samples, that might demonstrate bigger influence, not necessarily on tools wear but rather on tools clogging.

Gluing

Figure 8 reports the substantial influence of treatments on gluing resistance with usual polyurethane adhesive for structural applications. The acidity of LA treatment and the lumen filling with OBS polymers were the likely explanations of the significant decrease in gluing performance. More investigation must be carried out on this matter to determine the definitive feasibility of gluing: wood preparation, type of adhesive,… However, because dimensional stability of wood was increased by treatment, the lesser stress applied on wood assemblies in use should be taken into consideration.

Coating

The nature of failure of reference samples (heated or not) corresponds mainly to adhesive failure between substrate and first coat. The influence of temperature was indicated by higher proportion of cohesive failure in the substrate (REF 160°C/48h) linked to lower adhesive strength. Nature of failure of LA treated samples corresponds mainly to cohesive failure of substrate with similar decrease in adhesive strength as observed on heated references (REF 160°C/48h). This would mean a slightly better adhesion (nature of failure) coupled with impact on material resistance (adhesive strength). Nature of failure of OBS treated samples was 100% adhesive failure between substrate and first coat with significantly lower adhesive strength than other samples. This shows a clear

incompatibility between coating and OBS oligomers on samples surface. Not reported here, the inclusion of TH had no substantial effect on coating adhesion properties, nor the pre-polymerization of LA before treatment (Figure 9).

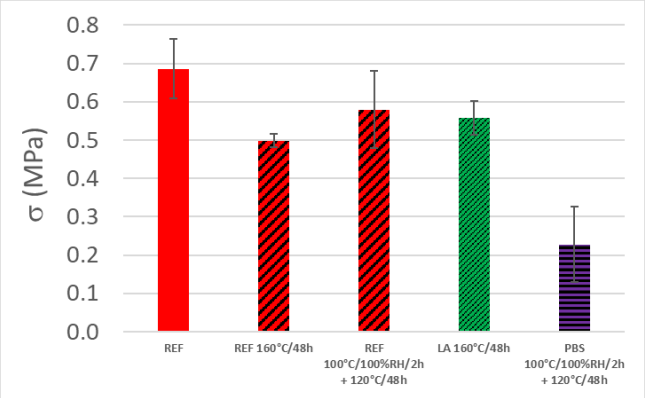


Figure 9: Adhesion strength of coating

Implementation

The industrial implementation of LA and OBS implies that treatment must be possible on wet wood (EMC higher than fiber saturation point for some applications) and good diffusion in real scale products must be feasible. Besides, treatment conditions must be in accordance with productivity concerns. Despite the product acidity, LA formulation storage and impregnation seem to be feasible. The raw material is readily available and aqueous solutions diffuse properly in wood. However, conducting thermal treatment at 160°C on wet wood is hardly possible without causing deleterious defects on wood pieces due to stress relaxation. Unfortunately, water and high temperature are logically preventing polycondensation of LA *in situ* (Grosse *et al.* 2018). First real scale investigations were carried out for railway sleepers treatment in industrial wood thermo-treatment facilities (Corbat Holding SA, Switzerland). A 48h thermal treatment cycle was carried out starting with 12h ramp to reach 180°C / 20% RH followed by 36h maintaining these conditions. The cracks on raw pieces were drastically enlarged by the treatment process. The current work carried out consists in defining a suitable thermal treatment cycle with wise combination of temperature and relative humidity, leading to no wood performance decrease. In the OBS case, handling treatment of wet wood might be beneficial to polymer diffusion. Impregnation at 70-90°C is feasible as well. The most limiting parameter is raw material supply. Heat initiated reaction of butan-1,4-diol and dimethylsuccinate, non-miscible liquids, directly in wood, was never attempted but seems hardly feasible. There is a necessary pre-polymerization step that would have significant impact on economic viability due to investment/sub-contracting cost. This kind of treatment appears to be non-economically viable for the time being for usual applications in wood construction sector.

CONCLUSIONS

LA/OLA and OBS treatments have shown many promising effects on wood, especially in terms of durability and dimensional stability (weight loss according to EN113, exposure to *Coriolus versicolor* and *Coniophora puteana* < 3% and anti-swelling efficiency (ASE) > 65% for LA/OLA; weight loss according to accelerated screening test, exposure to *Coriolus versicolor* ≈ 2%, 3.7% according to EN113 and ASE ≈ 60% for OBS). Leaching values due to exposure to water were also very acceptable (< 2% according to NF X 41-568 (2014) for OLA). Besides, durability tests revealed the absence of mould attack, and OBS treated wood kept very attractive appearance and homogeneous colour change after 24 months of exposure. Further investigation via hyperspectral imaging of weathered samples revealed a different ageing pattern of OBS-treated samples in comparison to references and OLA modified wood.

Most chemical modification processes lead to wood structure weakening because of the influence of treatment on wood ultra-structure. LA/OLA treatments impacted wood fibers

connection, while OBS treatments made gluing particularly challenging. If specific attention must be given to a wise application design, the general performance of LA/OLA and OBS treatments seems competitive with current commercial technologies. Their implementation would widen the bio-modified wood offer on the market.

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General conclusion

This research target was to promote the use of wood as technological material by limiting its main drawbacks: sensitivity to water and moisture and biological degradation. Especially, some indigenous species are abundant, while not performing well enough to guarantee efficient consumption, as European Beech, and were chosen for this project. The product of this research was the development of bio-based material from wood and bio-polyesters, with suitable properties to be used as a building material for outdoor applications. This work was undertaken in the framework of two R+D projects: BioCoPol (WoodWisdom Net+ JC4 funding) and BioThermoWood (funded through the Swiss national body of COST in the frame of COST Action FP1303). The importance of possible industrial implementation had always been kept in mind, as well as the effort to limit as much as possible the impact of treatments on the environment.

The work focused on wood chemical modification to reach a wide range of properties. Chemical modification implies structural changes of wood, leading to high dimensional stability, significant reduction of the equilibrium moisture content, and high resistance against bio-degradation agents. The challenge was to develop only bio-based treatments for wood modification, and to focus on the environmental impact by trying to keep the energy consumption during treatment as low as possible, and to avoid any emission and any leaching during treatment or use.

The results obtained were numerous, miscellaneous but conclusive. Several variants were very promising, conferring excellent dimensional stability and durability with no detrimental impact on the mechanical properties.

Lactic acid oligomers (OLA) were considered for wood modification based on bulk impregnation followed by *in situ* polymerisation. Lactic acid treatment consists in the impregnation of lactic acid oligomers into anhydrous wood structure by brief vacuum step followed by long thermal treatment to induce *in situ* polymerisation. The parameters combination (temperature, duration) of the thermal treatment plays a crucial part in the overall treatment efficiency. Evaluation of the performance of OLA treatment under certain temperature and duration conditions revealed a threshold temperature of 160°C to treatment efficiency. The potential of several additives was investigated to reduce the curing temperature of OLA. Maleic anhydride was considered to evaluate grafting possibilities of the oligomers on wood, tannins in order to improve the durability, or citric and tartaric acid to catalyse the polycondensation.

Performance of the best variants was comparable to Accoya®. Bending and compression tests were carried out and showed that treated wood had become a stronger and more brittle material, with higher density and weight. That would be ideal for applications as long-range beams and would allow a cross-section decrease for similar properties.

After a year of natural exposure, no mould attack had been noticed at all. The cracks amount and physical degradation, as well as the colour change decreased significantly in comparison to unmodified wood. Considering the leaching rate, several methods were employed and showed that the treatment conditions were the dominating parameters. Increasing treatment temperature led to drastically decreasing long-term leaching rate.

The following aspects, related to practical implementation, have been studied additionally:

- wood initial moisture content for impregnation (up to 30%)
- impregnation with lactic acid not pre-polymerised to avoid one production step
- dilution of OLA in water because vacuum impregnation of wet wood might lead to partial water/sap extraction from wood and its accumulation in the treatment product at different concentration (up to 75%)

For all variants, the anti-swelling efficiency (ASE) slightly decreased (50-60% instead of 70% for the controls with oligomers and dry wood) and might be improved by adjusting the treatment conditions. Only the one variant where oligomers have been diluted into 75% of water showed a drastically decreased ASE of 35%. Performance of treatments based on lactic acid not pre-polymerised were promising as well if the curing temperature was as high as 160°C.

The pure lactic acid oligomers gave promising results: ASE of ca. 70%, low EMC (decreased by 43%) and high durability (class 1 / EN350 and EN113). The treatment conditions, especially the temperature, were proven to be very influent on the modified wood performance, with a positive impact of an increase in temperature.

Oligomers of poly(butylene succinate) (OBS) were considered for wood modification as lumen filling impregnation followed by *in situ* polymerisation. Wood was impregnated with OBS, then hydrothermally treated in a pressurized reactor to create similar conditions as most industrial heat treatment processes where steam ensures heat conduction. This induced partial swelling and subsequent diffusion of product in the wood structure. The effect of temperature, relative humidity (RH), pressure and time on the OBS diffusion, the extend of OBS hydrolysis, the wood degradation and the resulting wood modification was investigated. The wood was modified at different temperatures (100-160°C), durations (0.5-2h) and maximum water vapour pressure (0.10-0.62 MPa). Wood weight and volumetric variations as well as extracted OBS molecular weight were analysed. At high temperature, OBS and wood polymers degradation was promoted by high process RH. The pressure necessary to reach high RH at high temperature prevented excessive material leaching. Therefore, combination of OBS hydrolysis producing smaller molecules and high pressure reducing volatility of chemicals explains the OBS diffusion in wood cell wall. However, decreased treatment persistence in wood resulted from OBS hydrolysis. This process technique for wood modification with OBS lead to a material with enhanced dimensional stability and biological resistance. Potential applications of this treatment were investigated with evaluation of the modified wood mechanical properties, and gluing and coating adhesion.

To ensure the up-scaling ability of treatments, the treatment process was always considered as a limiting parameter. This could be guaranteed by the global concept of impregnating and curing, which is a classic process for chemically modified wood. For the treatments developed, the impregnation was easily carried out. Simple vacuum cycles allowed sufficient diffusion of treatments in wood structure, even for volumes up to 100 x 100 x 600 mm^3. The main limitation is the necessity of using stainless steel for all parts of the industrial equipment, because of treatments acidity.

Thermal treatment represents a challenge for up-scaling because of the high temperature needed to reach the desired performance. Pre-tests on real scale treated railway sleepers were carried out in an industrial thermal treatment chamber (Corbat Holding SA, Glovelier (JU), Switzerland). Real size beech wood railway sleepers (0.13 x 0.26 x 2 m^3) were impregnated with lactic acid. Some pieces will be evaluated in terms of product diffusion, extent of curing and durability, while others will be long-term exposed in ground contact with regular observations.

Two partial market evaluations have been carried out and showed that the lactic acid- and the polyesters-based treatments would potentially be price competitive for applications as high-end wood for outdoors, comparable to Accoya® or Kebony®, even though a R+D project is still running on that matter. EcoViaLactique (funded through the Swiss national office for the environment) is dedicated to the evaluation of the viability of launching LA treatment on the Swiss market.

Wood modification with bio-polyesters appears as a potential new alternative for biocidal treatments replacement. Research need however to continue for a better understanding of mechanisms of wood protection through those treatments, as well as a complete LCA analysis including potentiality of cascade use considering selected applications.

Conclusion

Le but de ces recherches était de promouvoir l'utilisation du bois, en tant que matériau pour la construction, en limitant deux de ces inconvénients majeurs : sa sensibilité à l'eau et à l'humidité et sa résistance biologique limitée. En particulier une essence locale, le hêtre européen, abondement disponible, souffre de ces désavantages et n'est actuellement pas consommé de façon optimale. C'est pourquoi ces recherches ont été focalisées sur cet essence. Ces travaux ont conduit au développement d'un nouveau matériau innovant, totalement bio-sourcé, à base de bois et de bio-polyester, aux propriétés prometteuses permettant d'envisager l'utilisation du bois modifié en construction extérieure.

Deux projets européens ont permis d'encadrer ces recherches : BioCoPol (financement WoodWisdom Net+ JC4) et BioThermoWood (financé par l'antenne Suisse du COST à travers l'Action FP1303 (Performance of bio-based building materials)). La possibilité d'une implémentation industrielle des procédés de traitement développés était de première importance, de même que la limitation de leurs empreintes sur l'environnement.

Plusieurs niveaux de modification chimique du bois ont été envisagés afin d'atteindre une large gamme de produits possibles en fonction de leurs propriétés. La modification chimique implique des changements structurels au sein de la structure du bois. Elle a généralement pour but d'améliorer la stabilité dimensionnelle du matériau, de diminuer l'hygroscopie et réduire l'humidité d'équilibre, et d'améliorer la résistance aux agents pathogènes. Le défi était de développer un traitement totalement bio-sourcé, sans biocides, permettant d'améliorer ces différentes propriétés du bois, avec pour objectif de limiter le plus possible l'impact environnemental du procédé. Ainsi, la réduction des coût énergétiques et des co-produits émis, pendant le procédé et pendant l'usage du produit, ont toujours été considérés.

Les résultats obtenus sont nombreux, variés et concluants. Plusieurs variantes se sont révélées très prometteuses, conférant au bois une excellente stabilité dimensionnelle et une bonne résistance biologique sans nuire aux propriétés mécaniques du matériau.

Les oligomères d'acide lactique (OLA) ont été utilisés pour la modification du bois par imprégnation et remplissage des parois cellulaires. Le traitement se déroule en deux étapes. D'abord du bois sec est imprégné d'OLA, puis un traitement thermique permet leur polymérisation *in situ*. Les paramètres du traitement thermique (température et durée) ont un rôle clé dans l'amélioration des performances du bois modifié. L'étude de l'influence de ces paramètres sur les propriétés du matériau a révélé une température seuil à l'efficacité du traitement de 160°C. Plusieurs additifs pouvant servir à réduire ce seuil ont été testés. Le greffage des OLA aux polymères du bois par l'intermédiaire de l'anhydride maléique, l'amélioration de la résistance biologique au moyen de tannins, et l'amélioration de la polymérisation à plus basse température à l'aide d'acide citrique ou tartrique, ont été considérés dans cette étude.

Les performances de la meilleure variante sont comparables à celles du bois acétylé Accoya®. Les tests de flexion et de compression ont montré que le bois modifié était un matériau plus rigide qu'à l'origine, avec cependant une résistance augmentée, de même que sa densité et sa masse. Ce type de matériau conviendrait pour des applications où l'on voudrait pouvoir réduire les sections des poutres en construction.

Après une année d'exposition au vieillissement naturel, aucune attaque de moisissure n'a été observée. La dégradation physique, le nombre de fissures et les changements de couleur, ont significativement été réduits en comparaison au bois non modifié. Plusieurs méthodes ont été utilisées pour évaluer la persistance des OLA dans le bois. La température du traitement thermique est le paramètre influençant le plus sur la fixation du produit qui augmente avec la température.

En considération d'une implémentation industrielle, les aspects suivants ont également été étudiés :

- L'humidité initiale du bois au moment de l'imprégnation (jusqu'à 30%) : limiter le séchage du bois constituerait une réduction des coûts.
- L'imprégnation d'acide lactique non pré-polymérisé : éviter une étape de synthèse permettrait de diminuer les coûts également et faciliterait le procédé.
- La dilution des OLA dans l'eau (jusqu'à 75%) : lorsque le bois humide est imprégné, le risque de dilution des OLA par migration de l'eau ou de la sève contenue dans le bois est possible.

Pour toutes les variantes ci-dessus, l'efficacité anti-gonflement (ASE) du traitement a diminué (50-60% au lieu de 70% pour le traitement OLA réalisé sur du bois sec), mais cela pourrait être compensé en adaptant les paramètres du traitement thermique. Seule la dilution des OLA jusqu'à 75% dans l'eau a conduit à une perte réelle des performances (ASE = 35%).

Le traitement à l'acide lactique non pré-polymérisé suivi d'un traitement thermique à 160°C s'est révélé très prometteur : l'ASE est élevée (70%), l'humidité d'équilibre du bois est diminuée de 43% et la résistance biologique est élevée (classe 1/EN350 et EN113).

Les oligomères de butylène succinate (OBS) ont été utilisés pour la modification du bois par imprégnation et remplissage des lumens. Du bois sec a été imprégné d'OBS, puis traité thermiquement sous pression de vapeur, dans un réacteur reproduisant des conditions similaires à la plupart des chambres de traitement thermique industrielles où la vapeur d'eau est utilisée comme moyen de convection de la chaleur. Le procédé induit un gonflement partiel des parois cellulaires à l'aide de la vapeur d'eau, ce qui permet une certaine diffusion de produit dans la structure du bois. L'effet de la température, de l'humidité relative (HR), de la pression et de la durée du traitement sur la diffusion et l'hydrolyse des OBS, la dégradation du bois, et les propriétés du bois modifié a été évalué. Le bois a été traité à différentes conditions de températures (100-160°C) et pression de vapeur (0.10-0.62 MPa) à différentes durées (0.5-2h).

Les variations de masse et de volume du bois et les oligomères extraits après traitement ont été analysés. A haute température, les OBS et les polymères du bois subissent des dégradations importantes, encore accentuées par la forte HR du milieu. La pression nécessaire pour atteindre de telles HR à haute température empêche un lessivage excessif des OBS. Ainsi, l'hydrolyse des OBS produisant de plus petites molécules capables de diffuser dans les parois, combinée à la haute pression réduisant leur lessivage, permettrait une diffusion efficace de produit de traitement dans les parois cellulaires. Cependant, l'hydrolyse des OBS diminue la persistance du traitement dans le bois.

Ce procédé de traitement conduit à un matériau ayant une meilleure stabilité dimensionnelle et une meilleure résistance biologique. Les potentielles applications de ce matériau ont été évaluées après caractérisation des propriétés mécaniques, de l'adhésion des revêtements de surface et de la capacité de collage du bois traité.

L'implémentation industrielle de ces traitements devant être possible, le procédé lui-même a toujours été considéré comme un paramètre limitant ses propres conditions. L'imprégnation et le traitement thermique du bois étant des technologies connues et maîtrisées, la possibilité d'un passage à une plus grande échelle est assurée.

Dans le cas du traitement OLA, l'imprégnation était toujours facile. Un vide simple permettait une diffusion du produit homogène et à cœur, pour des échantillons allant jusqu'à 100 x 100 x 600 mm^3. L'acidité des OLA constitue la principale limitation au procédé car l'utilisation d'équipements industriels en acier inoxydable est nécessaire.

Le traitement thermique est un second défi du passage à grande échelle car la température nécessaire à la polymérisation des OLA est élevée. Des pré-essais sur des traverses de chemin de fer ont été réalisés dans une enceinte de traitement thermique industrielle (Corbat Holding SA, Glovelier (JU), Suisse). Des traverses de chemin de fer, aux dimensions réelles (0.13 x 0.26 x 2 m^3), ont été imprégnées d'acide lactique. Certaines ont servies à l'évaluation de la diffusion du produit, et d'autres vont être exposées au vieillissement naturel au contact du sol.

Deux évaluations partielles du marché ont été menées. Les traitements du bois à base de bio-polyesters, et en particulier d'acide lactique, pourraient être compétitifs pour des applications à haute valeur ajoutée, comparable à Accoya® ou Kebony®. Un projet de recherche et développement est encore en cours. EcoViaLactique (financé par l'Office National Suisse de l'Environnement) est dédié à l'évaluation de la viabilité économique du traitement à l'acide lactique pour le marché Suisse.

La modification du bois avec des bio-polyesters apparaît comme une nouvelle alternative aux traitements biocides. Les recherches doivent encore être poursuivies afin de mieux comprendre les mécanismes de protection du bois impliqués dans ces traitements. Une analyse du cycle de vie, incluant le recyclage en cascade du matériau, permettrait une évaluation complète de l'impact environnemental des produits.

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Abstract

Wood thermo-chemical modification process consists of permanent enhancement of wood properties in the core of the material. By decreasing wood equilibrium moisture content below the limit of fungi development, one could in addition reduce the dimensional variations due to humidity. A better dimensional stability of wood would be beneficial to durability of assemblies and surface coatings, further improving the performance of the material. Hydroxyl groups from wood polymers are responsible for the material hydrophilicity. The thermochemical modifications considered in this work mainly consist in limiting the access to these groups and / or reducing their number, by impregnation of bio-based monomers / oligomers (oligomers of lactic acid (OLA) or oligomers of butylene succinate (OBS)) followed by their *in situ* polymerisation by heat treatment. The hygroscopic behaviour of the material, the persistence of oligomers in the wood and the biological resistance of the treated wood are the criteria for the selection of treatments. The selected treatments lead to materials with enhanced dimensional stability and biological resistance. The potential applications of these materials have been evaluated after characterisation of mechanical properties, adhesion of the surface coatings and bonding capacity of the treated wood.

Key words : wood, polymers, bio-resources, chemical modification, dimensional stability, durability.

Résumé

La modification thermo-chimique est un procédé qui consiste à modifier la matière à cœur, avec pour objectif d'améliorer les propriétés du bois, en particulier la résistance fongique. Pour ce faire, conférer au bois un équilibre hygroscopique inférieur à la limite basse de développement des champignons est une approche qui permet en sus de limiter les variations dimensionnelles dues à l'humidité de l'air. Limiter les variations dimensionnelles augmente logiquement la durabilité des assemblages et des revêtements de surface, ce qui améliore encore les performances du matériau. Les constituants du bois possèdent des groupements hydroxyles qui rendent le matériau hydrophile. Les modifications thermochimiques envisagées dans ces travaux de recherche consistent principalement à limiter l'accès à ces groupements et/ou à réduire leur nombre, par imprégnation de monomères/oligomères bio-sourcés (oligomères d'acide lactique (OLA) ou de poly(butylène succinate) (OBS)) suivie de leur polymérisation *in situ* par traitement thermique. Le comportement hygroscopique du matériau, la persistance des oligomères dans le bois et la résistance biologique du bois traité sont les critères de sélection des traitements. Les traitements retenus conduisent à des matériaux ayant une meilleure stabilité dimensionnelle et une meilleure résistance biologique. Les potentielles applications de ces matériaux ont été évaluées après caractérisation des propriétés mécaniques, de l'adhésion des revêtements de surface et de la capacité de collage du bois traité.

Mots-clé : bois, polymères, bio-ressources, modification chimique, stabilité dimensionnelle, durabilité.