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# Innovative and multifunctional bio-based resins for the durability of wood and wood-based composites.

Elsa Duret

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# THÈSE

UNIVERSITE DE PAU ET DES PAYS DE L'ADOUR  
École doctorale des Sciences Exactes et leurs Applications

Pour obtenir le grade de  
**Docteur de l'Université de Pau et des Pays de l'Adour**  
Avec le label doctorat européen  
Discipline : Chimie  
Spécialité : Chimie des Matériaux

Par

**Elsa DURET**

INNOVATIVE AND MULTIFUNCTIONAL BIO-BASED RESINS FOR THE  
DURABILITY OF WOOD AND WOOD-BASED COMPOSITES

Soutenue le 30 Novembre 2023

## MEMBRES DU JURY

### RAPPORTEURS

- Mme Maria GONZÁLEZ ALRIOLS
- Mme Anna SANDAK

Professeur associé - Université du Pays Basque, Donostia-San Sebastián  
Chef du département Matériaux d'InnoRenew CoE, Professeur associé -  
Université de Primorska, Izola

### EXAMINATEURS

- Mme Marie-France THÉVENON
- M. Jalel LABIDI

Directrice de recherche - CIRAD, Montpellier  
Professeur - Université du Pays Basque, Donostia-San Sebastián

### DIRECTEURS

- Mme Fatima CHARRIER-EL BOUHTOURY
- M. Eduardo ROBLES

Maître de Conférences, HDR - Université de Pau et des Pays de l'Adour  
Maître de Conférences - Université de Pau et des Pays de l'Adour



*« C'est avec la logique que nous prouvons et avec l'intuition que nous trouvons. »*

- Henri Poincaré

*« La nature est un professeur universel et sûr pour celui qui l'observe. »*

- Carlo Goldoni



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# Résumé

Le bois est un matériau de construction largement employé en raison de son caractère renouvelable, mais également de ses qualités mécaniques et structurelles. Cependant, il est vulnérable aux effets néfastes de divers facteurs environnementaux. Ainsi, l'exposition à l'eau, aux rayons UV, aux variations de température tout comme l'action des micro-organismes peuvent altérer ses qualités. Actuellement, les systèmes de protection existants sont efficaces, mais posent souvent des problèmes environnementaux, car la plupart d'entre eux sont élaborés à partir de matières issues de l'industrie pétrochimique. Aujourd'hui, la lutte contre le changement climatique et le respect de l'environnement sont des facteurs de plus en plus pris en compte. De nouvelles réglementations voient le jour encourageant le développement de produits de préservation du bois écoresponsables afin de remplacer les méthodes et produits actuels. Dans ce contexte, un produit de préservation qui serait non seulement biosourcé mais également polyfonctionnel serait un atout car, en plus de répondre aux exigences environnementales, il permettrait de limiter le nombre de produits et de traitements.

Dans le cadre de cette étude, une résine biosourcée a été développée en utilisant de la lignine, un sous-produit industriel issu de l'extraction de tanins, ainsi qu'un additif inorganique. Les produits employés étant locaux et biosourcés, ce travail s'inscrit dans un modèle d'économie circulaire dans le Sud-Ouest de la France. Le résidu industriel se compose principalement de subérine, permettant d'apporter un caractère hydrophobe à la résine. La lignine utilisée a été précipitée à partir de la liqueur noire puis a été silanisée. Ce type de modification chimique a permis une amélioration de la résistance thermique et une hydrophobicité de la lignine grâce à l'incorporation de groupes silanes et amines. Enfin, l'additif inorganique employé est un minéral argileux qui a permis de conférer à la résine une meilleure résistance thermique.

Les résines synthétisées, en faisant varier différents paramètres de réaction, ont été appliquées par immersion des échantillons de bois dans les solutions de résines. Les performances de ces échantillons ont par la suite été évaluées. Les résultats obtenus ont montré une importante hydrophobicité de la résine ainsi qu'une résistance au feu non négligeable. Cependant, une grande sensibilité de cette résine aux rayonnements UV a été observée. La résine développée dans ce travail en vue de protéger le bois nécessite des recherches plus approfondies afin d'obtenir une résine optimisée. Cependant, ce travail permet de fournir des bases solides quant au développement de cette résine multifonctionnelle.

# Abstract

Wood is a widely used building material, not only because of its renewable nature, but also because of its mechanical and structural qualities. However, it is vulnerable to the negative effects of various environmental factors, including exposure to water, UV radiation, temperature fluctuations, and the action of micro-organisms. Currently, protective systems are effective, but they often pose environmental problems, as most of them are produced from materials derived from the petrochemical industry. Today, the struggle against climate change and environmental concerns are increasingly considered. New regulations encourage the development of eco-responsible wood preservatives to replace current products and methods. In this context, a preservation product that would not only be biosourced but also polyfunctional would be an asset because, in addition to meeting environmental requirements, limiting the number of products and treatments is possible.

This study developed a biosourced resin using lignin, an industrial by-product from tannin extraction, and an inorganic additive. As the raw materials used are local and biosourced, this work fits into a circular economy model in the southwest of France. The industrial residue is mainly composed of suberin, which provides a hydrophobic character. The lignin was precipitated from black liquor using oxalic acid and chemically modified by silanization. This type of modification improved the thermal resistance and hydrophobicity of the lignin by incorporating silane and amine groups into its structure. Finally, the inorganic additive used is a clay mineral, which improved the thermal resistance of the resin.

The synthesized resins, with different reaction parameters, were applied by immersing the wood samples in the resin solutions. The performances of these samples were then evaluated. The results showed that the resins were highly hydrophobic and their fire resistance was not negligible. However, the resin was found to be highly sensitive to UV radiation.

The resin developed in this work protect wood requires further investigation to obtain an optimized resin. However, this work provides a strong foundation for the development of this multifunctional resin.

# Context

The environmental, mechanical, and structural properties of wood and wood-based panels enable them to occupy a major role in construction and interior design. However, these materials are sensitive to moisture and vulnerable to several degrading agents (fungi decay, UV radiation, and combustion, among others). Different approaches of protecting wooden structures have been developed over the years. These include treatment by impregnation, injection, deep immersion, or coating. The most convenient, economical, and effective wood protection methods are coatings or impregnation with preservatives. However, most of the chemical components contained in these products are either toxic to human health or harmful to the environment. Moreover, currently, no product on the market can protect wood against all the degradation mechanisms it can undergo. In this context, the need for a new generation of treatments is growing; consequently, it is necessary to find a biosourced treatment that provides complete protection for wood.

These observations motivated this study to develop hybrid organic-inorganic phenolic resins (lignin and tannins combined with nanoclays or nanosilicates), to protect wood and its derived composites. This work is based on positive results obtained with resins used as flame-retardant coatings for wood [1]. The use of local and biobased products enables a circular economy in the southwest of France.



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# Abbreviations Table

<b>AIL:</b> Acid-insoluble lignin	<b>M<sub>n</sub>:</b> Weight-average molar mass
<b>APTES:</b> 3-aminopropyltriethoxysilane	<b>M<sub>w</sub>:</b> Number-average molar mass
<b>ASL:</b> Acid-soluble lignin	<b>OMMT:</b> Organically Modified Montmorillonite
<b>ATR:</b> Attenuated Total Reflection	<b>POSS:</b> Polyhedral Oligomeric Silsesquioxanes
<b>BHT:</b> Butylated hydroxytoluene	<b>QAH:</b> Quantitative Acid Hydrolysis
<b>D:</b> Polydispersity index	<b>S unit:</b> Syringyl unit
<b>DMF:</b> N, N-Dimethylformamide	<b>SEC:</b> Size Exclusion Chromatography
<b>DMSO:</b> Dimethylsulfoxide	<b>TDS:</b> Total Dry Solid
<b>DPPH:</b> 2,2-Diphenyl-1-picrylhydrazyl	<b>TGA:</b> Thermogravimetric Analysis
<b>DSC:</b> Differential Scanning Calorimetry	<b>UV:</b> Ultraviolet
<b>DTG:</b> Derivative Thermogravimetric	<b>VOC:</b> Volatile Organic Compounds
<b>EtOH:</b> Ethanol	<b>VOS:</b> Volatile Organic Substances
<b>FTIR:</b> Fourier Transformed Infrared Spectroscopy	<b>WPG:</b> Weight Percent Gain
<b>G unit:</b> Guaiacyl unit	<u>Chemicals compounds:</u>
<b>H unit:</b> <i>p</i> -Hydroxyphenyl unit	<b>NaOH:</b> Sodium hydroxide
<b>HPLC:</b> High Performance Liquid Chromatography	<b>H<sub>2</sub>SO<sub>4</sub>:</b> Sulfuric acid
<b>MMT:</b> Montmorillonite	



# Chapter I - State of the art and objectives



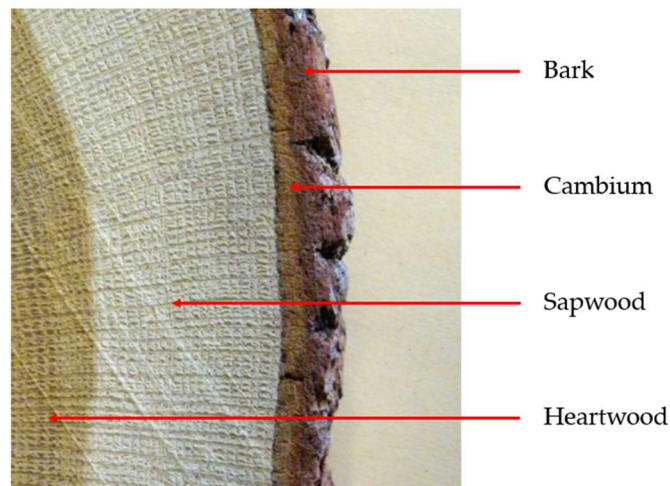


## I. 1. Wood and its weaknesses

Wood is composed of strong tissues that form the trunks, branches, and roots of trees. It is a heterogeneous and organized material that develops over many years. Its vegetal origin gives it a richness and variable characteristics that enable it to be used in construction, furniture, and as a finishing support.

### I. 1. 1. Anatomical wood structure

The trunk is composed of different layers, the main ones visible to the naked eye or with a magnifying glass. From the outside in, these are the bark, the phloem, the cambium, the sapwood, and the heartwood. These layers are shown in Figure I-1. The bark is the most exposed part of the wood, protecting it from external attack. The cambium is the area where new cells are formed. Those cells that grow towards the outside of the wood form the phloem, while those that grow towards the inside of the wood form the xylem, which in itself forms the sapwood and heartwood. The sapwood is part of the living tissue of the wood, its cells allowing the conduction of raw sap into the trunk. Over time, the sapwood cells die, forming the heartwood.



*Figure I-1 - Main structural elements of wood*

## I. 1. 2. Chemical composition of wood

As a living material, wood has a complex and heterogeneous chemical composition. It is mainly composed of the macromolecules of cellulose, hemicellulose, and lignin. The first two compounds are important for the structure and architecture of the material, while lignin acts as a binder. Lower molecular weight molecules such as extractives and ash are also present. The proportion of these constituents in the chemical composition of wood slightly varies according to the essence studied. The arrangement and proportion of these compounds are shown in Figure I-2.

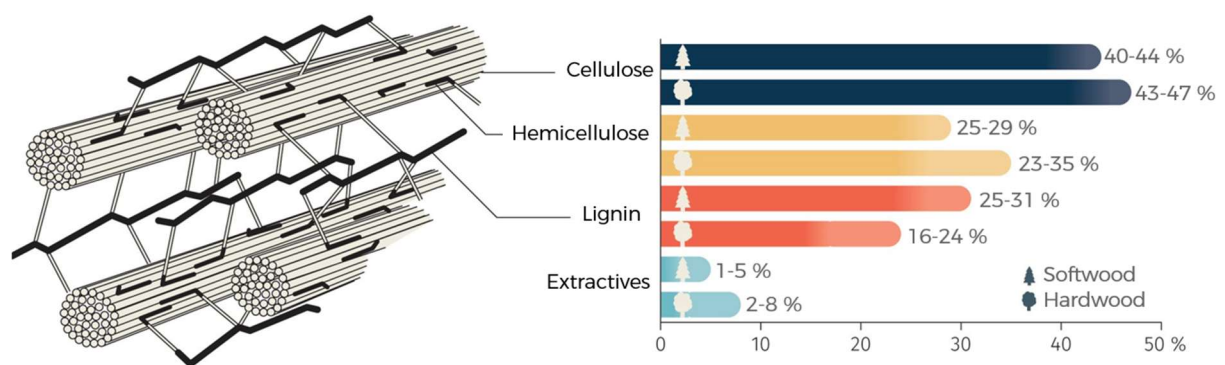


Figure I-2 - Chemical composition of wood (adapted from [2])

### I. 1. 2. 1. Cellulose

Cellulose is the main component of the wood. It is a long-chain biopolymer and represents the most abundant natural polymer. It is made up of  $\beta$ -D-glucopyranose units linked together by  $\beta$ -1,4 glucosidic bonds [3], forming a repeating unit known as cellobiose. Chemical structure of cellulose with its cellobiose unit is presented in Figure I-3. Cellulose chains are linked by inter and intramolecular bonds, creating microfibrils with both amorphous and crystalline areas [3], [4]. This structure gives wood rigidity and ensures excellent mechanical strength.

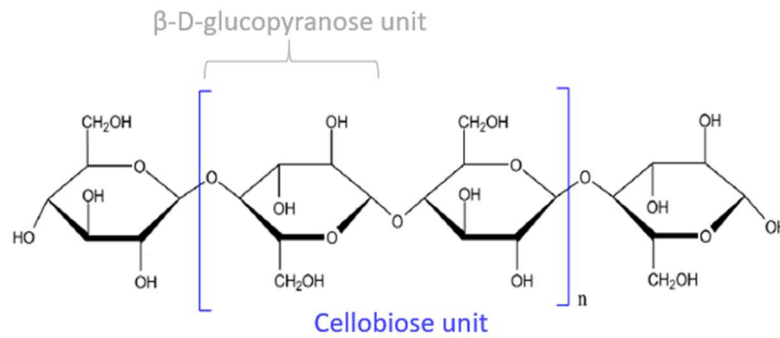


Figure I-3 - Chemical structure of cellulose

### I. 1. 2. 2. Hemicellulose

Hemicellulose is the second most abundant polymer in wood. Unlike cellulose, hemicellulose is composed of short, amorphous, and branched chains [5]–[7]. The polymer is mainly built up of pentoses (xylose and arabinose) and hexoses (glucose, mannose, galactose) [5], [7] linked by  $\beta$ -1,4 glycosidic bonds [6]. These units can also be substituted by other saccharides (rhamnose and fructose), uronic acids (galacturonic and glucuronic acids), or acetyl groups. Hemicellulose provides cohesion between cellulose fibers and compatibility between lignin and cellulose. Depending on the species studied, the composition of hemicelluloses varies. In hardwoods, the majority of hemicellulose chains are composed of xylose units, whereas in softwoods, a greater variety of saccharide residues can be observed.

### I. 1. 2. 3. Lignin

The third most important wood constituent is lignin and is the most abundant natural phenolic polymer. A complex, amorphous, and highly branched polymer formed by the association of three phenylpropanoid units: sinapyl alcohol (syringyl, S unit), coniferyl alcohol (guaiacyl, G unit), and *p*-coumaryl alcohol (*p*-hydroxyphenyl, H unit) [8]. These monomeric units are presented in Figure I-4.

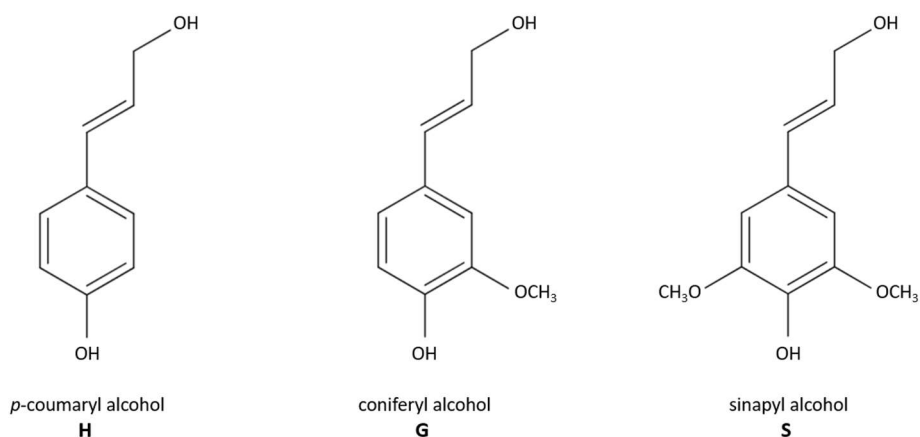


Figure I-4 - Molecular structure of the three phenylpropanoid units

The proportion of these monomers in lignin composition depends on the species studied [8]. Softwoods are essentially composed of G units, whereas the lignin structure of hardwoods is more complex, with a combination of G and S units. In both species, a small amount of H unit can be observed. However, this H unit is mainly found in non-woody species such as grasses. In this case, lignin is a blend of the three monomeric units. The monomers possess a great amount of polar functional groups and are randomly crosslinked, resulting in a three-dimensional amorphous structure. Depending on the position of the radical, several types of bonds can be generated ( $\beta$ -O-4,  $\alpha$ -O-4, 5-5...) but the main one is  $\beta$ -O-4, which represents between 45 and 60% of the bonds present in the structure [9], [10]. An example of the lignin structure for a softwood is shown in Figure I-5.

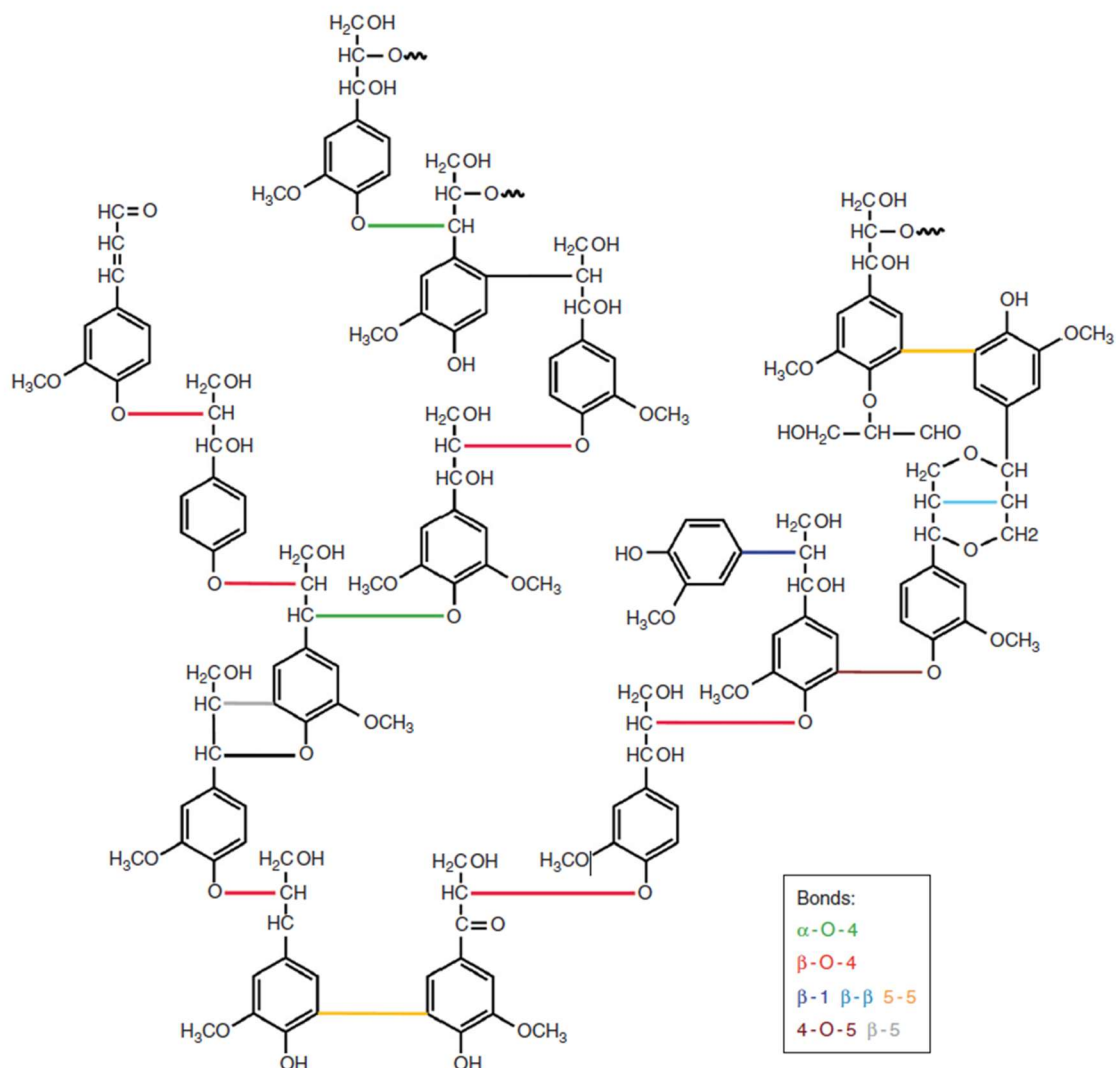


Figure I-5 - Softwood lignin structure [11]

#### I. 1. 2. 4. Extractives

Extractives are low molecular weight molecules that can be extracted from wood using solvents of different polarities. They do not contribute to the growth of the tree, but help to protect it from attack by pests. Extractives content varies according to species; however, differences can also be observed within the tree itself, i.e. the zone studied (bark, heartwood, or sapwood) and its height on the tree. The different types of extractives can be classified according to their chemical nature: polyphenols, terpenoids, fatty acids, minerals, among others [12].

### **I. 1. 3. Wood weaknesses and degradation agents**

Wood is a material with a number of attractive qualities: low density, high strength, ease of processing, thermal insulation, aesthetic properties, low cost, and low environmental impact. As a result, wood represents a major opportunity both ecologically and economically. For thousands of years, it has been used for interior and exterior construction, decoration, tools, furniture, and fuel. However, wood is also vulnerable to some degradation agents. For example, its hydrophobic properties make it sensitive to water and damp environments. It is also vulnerable to microorganisms, insects, fire, and climatic conditions such as UV or acid rain. These degradation agents lead to a reduction in original properties and consequent deterioration of the materials, which can result in a lack of safety for the occupants of wooden buildings, for example. Consequently, wood needs to be protected before being used in a wide range of applications.

#### **I. 1. 3. 1. Hygroscopy**

Wood is a highly hydrophilic material. Its affinity with water will influence its mechanical properties [13]. A good understanding of the interaction between water and wood is therefore necessary to understand the behavior of wood in any environment. Wood tends to absorb water molecules from the air. This absorption takes place through weak bonds between water and the hydroxyl sites of the macromolecules present in wood (mainly hemicellulose and amorphous cellulose). This interaction occurs up to a level of around 30% moisture content (depending on the species). Below this value, the term "bound water" is used. When wood absorbs water, the material swells [14]. The dimensions increase until the 30% level of humidity is reached. When this is exceeded, the fiber saturation point is reached; additional water molecules will no longer be bound, and are referred to as "free water". Once the fiber saturation point is exceeded, no dimensional variation is observed; the material is maintained at its maximum swelling. At this stage, an increase in humidity has no influence on sample dimensions, but it does have an influence on vulnerability to fungi and bacteria [13]. Indeed, a very humid environment in the presence of oxygen promotes the development of microorganisms. Moreover, when wood is not in a state of hygroscopic equilibrium, defects such as warping, cupping, or splitting can occur. These defects are due to the anisotropy of the material, involving the flow of water in different directions. Figure I-6 gives an example of the various degradations that can occur due to humidity and water.



Figure I-6 - Wood in damp conditions (left) and with drying damage after swelling (right)

### I. 1. 3. 2. Biological agents

Bacteria attack water-saturated wood, as explained above. However, compared with fungi, degradation is very slow. The rapid degradation of wood by fungi is important for the ecosystem, since it enables the renewal of forests and soils. However, this vulnerability is an issue for wood utilization. Wood fungi can be divided into two distinct categories: lignicolous fungi and lignivorous fungi.

Lignicolous fungi do not degrade structural wood compounds such as lignin or cellulose, but feed mainly on the reserve molecules present in the wood. Consequently, deterioration of the wood by these fungi does not lead to a reduction in the mechanical properties of wood. Most of the time, only the aesthetic side of the wood, such as color, is affected.

In contrast, lignivorous fungi possess all the enzymes needed to hydrolyze the structural components of wood. Several types of deterioration can be observed: brown or cubic rot, white or fibrous rot, and soft rot. Wood attacked by these different types of decay sees its mechanical properties reduced to the irreversible point of total loss.

Brown or cubic rot leads to cracking into small cubes and a brown discoloration of the wood as it is possible to observe in Figure I-7. These fungi are basidiomycetes such as *Serpula lacrymans* or *Coniophora puteana*. They degrade the hemicellulose and cellulose of wood, preferentially of coniferous trees [15]–[17]. Since brown rot fungi do not possess the enzymes needed to degrade lignin, direct oxidation of cellulose occurs [18]. This results in a higher degree of wood degradation when attacked by brown rot fungi than when attacked by white rot fungi [19].



White or fibrous rot fungi also damage cellulose, as they are also basidiomycetes. However, the enzymes found in this type of fungus also allow lignin to deteriorate. Both compounds (cellulose and lignin) may be degraded at the same time, or the fungi may selectively degrade lignin [15]. White rot fungi are mainly found on hardwoods [20]. Due to the production of ligninolytic extracellular oxidative enzymes (e.g., laccase), white rot fungi are the main degraders of lignin; however, they can also decompose polysaccharides. The with color of degraded wood is due to the remaining crystalline cellulose which is lighter in color compared to lignin. *Coriolus versicolor* fungus, for example, is part of this group.

Finally, soft rot is caused by ascomycete fungi. Higher humidity is required for these fungi to grow properly. They mainly attack cellulose and hemicellulose, reducing mechanical properties [21]. The result is black discoloration of the wood, with the formation of tiny cubes. Moreover, these fungi develop more rapidly in the presence of mineral salts.



Figure I-7 - Wood degraded by brown or cubic rot fungi (left) and soft rot fungi (right) [18]

### I. 1. 3. 3. Photodegradation

Ultraviolet radiation emits in the wavelength range from 100 to 400 nm. These ultraviolet (UV) rays are found in sunlight, although some are filtered by the ozone layer. Exposure of wood to UV radiation influences the aesthetics value of the wood, and more specifically its color. As previously mentioned, the three main compounds in wood are cellulose, hemicellulose, and lignin. All three have an absorption band in the UV-visible spectrum, but lignin has a stronger band than the others. Lignin is therefore the compound with the strongest influence on wood color. When lignin is irradiated with UV and visible light, bonds are cleaved, leading to the formation of radicals and thus a color change in the material [22]. However, this degradation

is only aesthetic, since the color change is only present on the surface [18] as it is possible to see in Figure I-8.



*Figure I-8 - Wood that has undergone color change due to UV irradiation [18]*

### **I. 1. 3. 4. Fire degradation**

As everyone knows, wood is also highly vulnerable to fire. In fact, one of its first uses by humans was as a fuel, despite its relatively low calorific value compared with hydrocarbons ( $20 \text{ MJ}\cdot\text{kg}^{-1}$  and  $50 \text{ MJ}\cdot\text{kg}^{-1}$ , respectively) [23]. This value depends on the species, but is always in the same range. Thermal degradation of wood and permanent reduction in strength and modulus elasticity can occur when the temperature exceeds  $65 \text{ }^\circ\text{C}$ . The extent of this reduction varies according to the moisture content, exposure period, temperature, chemical treatment, pH of the wood, heating medium, and species [24]. During the thermal degradation of wood, several pyrolysis stages occur [24]. First of all, the free water evaporates once the temperature of  $100 \text{ }^\circ\text{C}$  was reached. Above  $200 \text{ }^\circ\text{C}$ , the first chemical reactions take place with the decomposition of hemicellulose, followed by cellulose, and then lignin. Between  $300$  and  $500 \text{ }^\circ\text{C}$ , pyrolysis reactions increase with the production of volatile flammable gases due to the decomposition of cellulose [25]. At this stage, a char layer formation can also be observed. At temperatures above  $400 \text{ }^\circ\text{C}$ , the char is oxidized, reducing the thickness of the layer. Several factors can affect pyrolysis, such as humidity, wood species, oxygen concentration, density, and sample orientation relative to the incident flow [26]. A representation of a burned wood sample and a burning building are illustrated in Figure I-9.



*Figure I-9 - Wood residue after burning (left) and wooden house burning (right)*

In this section, we have seen that wood has excellent properties for use in a wide range of applications. Moreover, it is a natural and renewable resource, making it a suitable candidate as a raw material for construction, decoration, and other materials. Indeed, given the current environmental problems, the use of renewable raw materials not derived from the petrochemical industry is a major challenge. However, as we have seen, wood has weaknesses that do not allow it to be used in its original state. For this reason, wood needs to be protected to limit its rapid degradation.

## **I. 2. Wood protection methods**

Wood can be protected in two different ways. Chemical wood protection can be used, or the wood can be modified by chemically activating compounds already present in the wood.

### **I. 2. 1. Chemical wood protection**

This kind of wood preservative has a specific composition that protects the wood from various degradation agents. It is one of the best methods for protecting wood [27]. In addition to their protective properties, these preservatives also have an aesthetic aspect. Because of the compounds used in their formulation, they can be colored, totally opaque, semi-opaque, or slightly transparent. A totally opaque protection will be more effective against UV light than a semi-transparent one. This is because UV radiation is absorbed by the dark pigments present in the protection. On the contrary, if the protection is slightly transparent, UV radiation will penetrate and attack the lignin, causing wood discoloration as mentioned above. However, with opaque protection, the attractive warmth of the wood is lost. Moreover, if any further deterioration occurs, it is impossible to detect.

This type of protection includes resins, varnishes, oils, and woodstains. Most coating formulations are composed of the following components: a resin or binder, a solvent, additives, and pigments (optional). This is a global formulation, but not all preservatives contain these four compounds. In addition, it is necessary to optimize the formulation according to the type of wood species, the future application of the wood and the method of application.

#### **I. 2. 1. 1. Components of the wood protection**

##### Resin or binder

Resins are the main components of wood preservative formulations. They are carefully selected according to the properties they can bring to the resin, in addition to their film-forming properties. There are several types of resins, the main ones being alkyl, acrylic, epoxy, and polyurethane. Recently, mixtures of two resins have also been developed, such as alkyd-urethane resins.

Alkyd resins are the result of the reaction between drying or semi-drying oils, polyalcohols (glycerol, pentaerythritol), and polyacids (phthalic anhydride) [27]. They are among the most

widely used resins in preservative formulations for exterior elements, despite their lower durability outdoors than acrylic or polyurethane resins [28]. They tend to turn yellow when exposed to the weather. Their low cost explains their extensive use. Another weakness of alkyd resin is their curing. They cure through a process of oxidation, which takes time when the wood is exposed outdoors. The performance of the preservative is not fully active until the preservative has cured. This type of resin can have low molecular weight molecules, so with a low resin viscosity, penetration of the wood surface can be achieved. As a result, better cohesion between wood and resin takes place.

Acrylic resins are synthetic products that can be used in both aqueous and organic phases. These resins have high molecular weight molecules, so they cannot penetrate the wood surface as alkyd resins can, but these larger molecules enable them to acquire high film strength [28]. They also have good outdoor properties. Acrylic resins are particularly renowned for their high resistance to UV exposure, preventing yellowing as previously seen. Unlike alkyd resins, this type of resin cures rapidly.

Polyurethane resins are obtained by a condensation polymerization reaction between a polyol (R-OH) and an isocyanate (R-NCO) forming urethane or carbamate bonds ( $>NH-CO-O<$ ) [28]. These resins are mainly used as finishing coats. Like alkyd resins, polyurethane resins have low-molecular-weight molecules, enabling penetration of the resin into the cell walls of wood. Furthermore, they are also able to form chemical bonds with the hydroxyl groups of the wood, improving penetration and cohesion with the wood. These properties enable polyurethane resins to exhibit high chemical resistance and superior abrasion resistance [28].

### Solvent

The main function of solvents is to dissolve compounds to create a uniform coating by evaporation. They are also used to regulate resin viscosity. Indeed, a low viscosity is required for spray application, whereas for brush application, the resin needs to be more viscous. Solvents are chosen to optimize viscosity as well as to improve drying times. They can be either organic liquids or water. The organic solvents most commonly used in this type of application are acetone, toluene, butanol, xylene, ethanol, and ethyl acetate [27], [29]. Due to the evaporation of these solvents during the drying phase, volatile organic compounds (VOC) may be released. To limit the emission of these VOC and reduce the undesirable effects on both the environment and human health, the partial or total replacement of organic solvents by water was developed.

## Additives

Additives are incorporated into the formulation to provide new properties. Several classes of additives exist: light stabilizers, driers, biocides, antifoams, dispersants, and others. A small quantity can improve the required properties of the formulations.

## Pigments

The role of pigments is to provide color, opacity and, as explained above, UV protection to the preservative. They are frequently used in formulations for exterior protection. Pigments are mostly inorganic compounds. Iron oxide, for example, is used to stain wood brown, black, red, or yellow. Titanium dioxide ( $\text{TiO}_2$ ), by contrast, is used for light or white colors. In addition to its efficacy as a colorant, it also has excellent covering properties. The weak point of this pigment is its excessive price. A substitute for  $\text{TiO}_2$  is calcium carbonate ( $\text{CaCO}_3$ ), which is more affordable but less effective in terms of covering properties [27]. Pigments are also incorporated in the nanoparticle form. They do not affect the color of the final preservative, but provide UV protection and improve the scratch and wear resistance of coatings. This is the case, for example, of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) [30], [31].

### **I. 2. 1. 2. Application method**

The wood preservatives can be applied to wood samples in different manners. The method of application will influence the future properties of the wood. The next paragraph explains these different application methods.

#### By coating

The application of the product to the wood creates a protective film on the surface. The use of brushes to apply chemicals has a long history in human society [32]. This type of application protects the surface of the wood. The preservative penetrates the surface of the wood by capillary action. The product can be applied in several different ways: with a brush or a spray, for example. The depth of impregnation depends on the product, the quantity applied, the application method, and the wood species. Despite good wood protection with this type of product, renewal of protection is necessary after a few years [33].

#### By impregnation

Impregnating the wood in a protective solution can offer better protection than using a brush or spray. It also ensures that the product is applied homogeneously to the entire wood sample.

In this case too, penetration into the wood is capillary. Several impregnation methods are available: dipping, soaking, and impregnation (which combines vacuum and pressure or not) [34]. Dipping involves immersing the material in the protective solution for a few seconds. With this method, penetration depths from 25 to 75 mm can be achieved. This method is also known as dip-coating, the material can be dipped into the solution at a controlled or uncontrolled speed. It is possible to increase the quantity of solution impregnated, and therefore the depth of impregnation, by dipping the material several times into the solution. Soaking is performed in the same way as dipping, but the material is left in the solution for hours, days, or even weeks. With this method, the depth and quantity of impregnated product is greater. This process is currently used in a few sawmills. Finally, vacuum impregnation is the most widely used method at industrial scale. It requires special equipment, including vacuum pumps and large tanks that can be pressurized. The different stages of the impregnation cycle are shown in Figure I-10. This type of process enables the product to be impregnated deep down.

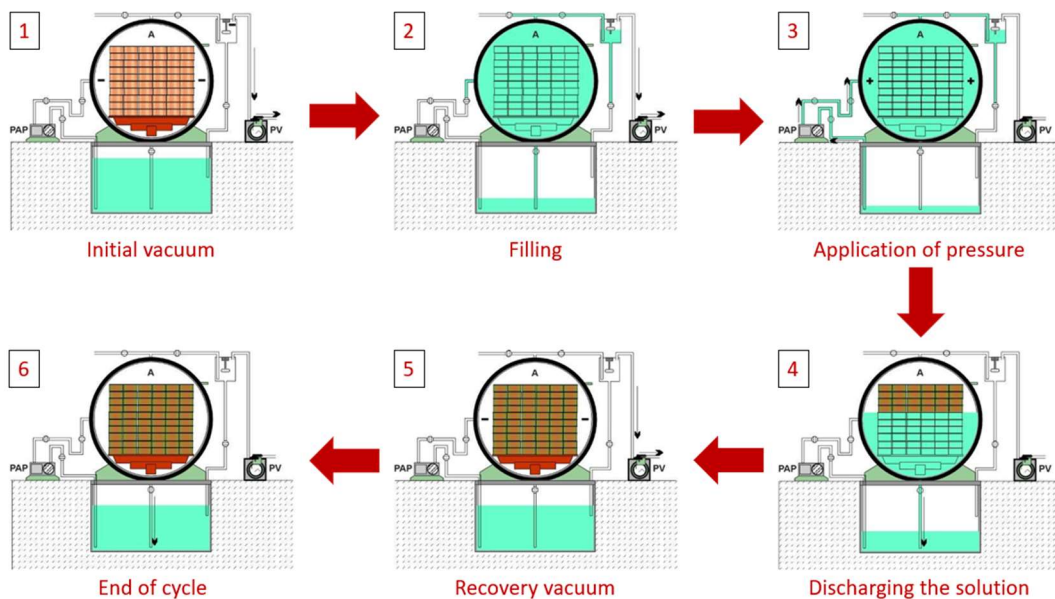


Figure I-10 - Steps of an impregnation cycle (Photo: [35])

## **I. 2. 2. Wood modification**

Over the years, research was carried out to limit wood degradation. Scientists observed that modifying wood molecules has an impact on the future properties of the wood material. The process was discovered only recently, in the 20th century [36], [37]. These compounds can be modified by both chemical and thermal treatment. Many of these modifications are primarily aimed at increasing resistance to biological decay. However, these treatments have been shown to improve dimensional stability and some mechanical properties, as well as reducing the hydrophilicity of the wood [37].

### **I. 2. 2. 1. Chemical modification**

The process of chemical modification occurs when a component present in the wood structure reacts with an external agent, leading to a covalent bond between them. As a reminder, the three main polymers composing wood are cellulose, hemicellulose, and lignin. The chemical structure of these compounds influences the chemical reactivity of wood. The main chemical groups present on the surface of wood are hydroxyl groups. This explains the high affinity of wood with water. However, these hydroxyl groups are not the only ones capable of interacting with external molecules. The aromatic rings present in the lignin structure are also a potential source of reaction. Other functional groups, such as carboxylic acids and carbonyls, can also react [38].

At present, modifications by acetylation and furfurylation are the most widely used on an industrial scale throughout the world. The main reasons for this are efficiency, cost, and simplicity of the modification process [39].

#### Acetylation

The acetylation reaction is shown in Figure I-11. This chemical modification was one of the most extensively studied, and was commercialized since the early 2000s [37]. Acetic anhydride reacts with the hydroxyl groups in the wood. The reagent (acetic anhydride) can be replaced by maleic anhydride or succinic anhydride. However, acetic anhydride is still the most widely used, providing the best modification. The reaction is mainly performed in a liquid medium, with or without the addition of a catalyst, and in a temperature range from 100 to 130 °C [38]. As can be seen from the reaction scheme, the products of this reaction are modified wood on the one hand, and acetic acid on the other. The latter is usually removed because of its unpleasant odor. Substituting acetyl groups for the hydroxyl groups provides a hydrophobic



character to the wood [40]. Another advantage of this modification is the non-toxicity of the process [41]. In addition to hydrophobicity, acetylation provides dimensional stability and biological resistance. Mechanical properties, meanwhile, remain unchanged, or change only slightly.

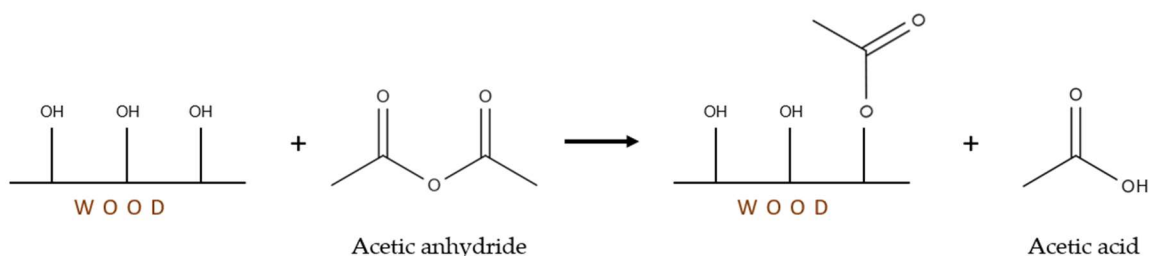


Figure I-11 - Schematic of the acetylation reaction

### Furfurylation

Furfuryl alcohol is produced from agricultural waste such as sugarcane or corn cobs. Wood is furfurylated by impregnation with furfuryl alcohol and initiators, followed by a heating phase for polymerization. This creates a highly cross-linked, viscous polymer. The resulting product is a dark brown with advantageous properties. This process has long been known and now commercialized [38]. Unlike acetylation, which only affects the primary and secondary cell walls, furfurylation enables deeper penetration of the product under certain conditions [42]. The exact process for modifying wood with furfuryl alcohol is not yet fully understood. Some researchers suggest that, in addition to reacting with itself, furfuryl alcohol may also react with the lignin present in cell walls [43], [44]. Wood modification with this type of process depends on the degree of retention of polymerized furfuryl alcohol in the wood. Depending on the level of modification, several properties can be improved, such as hardness, biological resistance, and dimensional stability. In addition, great UV resistance can also be achieved [45]. The mechanisms of polymerization and reaction with lignin of furfuryl alcohol are shown in Figure I-12.

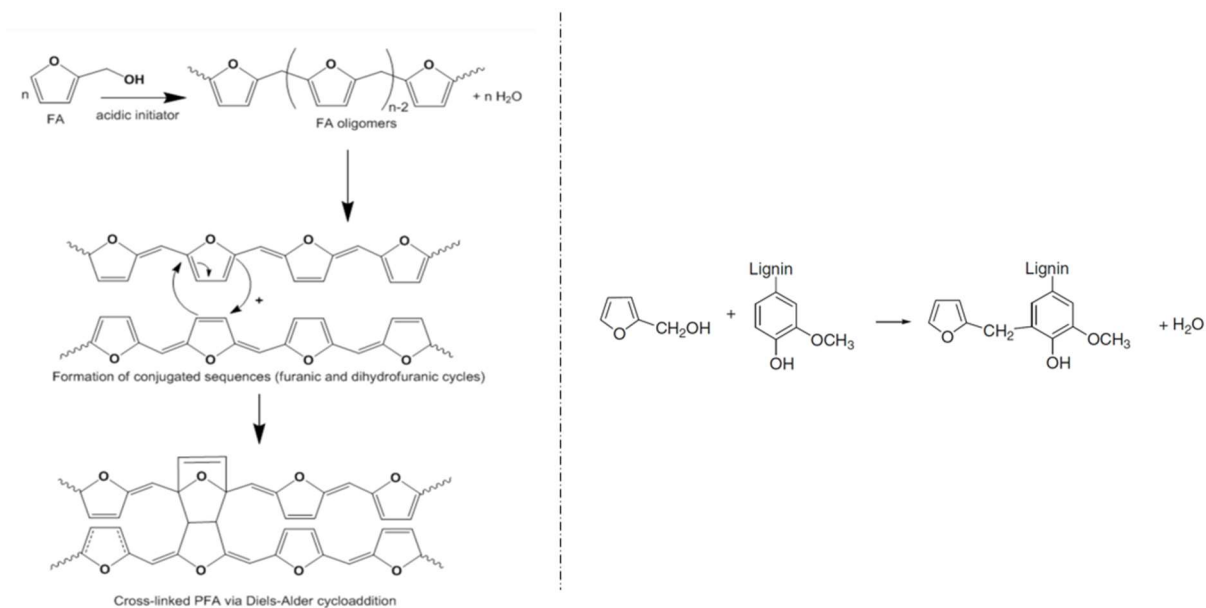


Figure I-12 - Schematic diagram of furfuryl alcohol polymerization (left) [37] and reaction of furfuryl alcohol with lignin (right) [43]

### Thermosetting resins

Thermosetting resin is a type of synthetic resin that polymerizes to produce a high-molecular-weight polymer whose macromolecular chains are cross-linked to form a three-dimensional network. These resins are first obtained by impregnating wood with monomers solubilized in a solvent. Then cross-linking takes place under the action of heat, pressure, or a curing agent. There are currently three types of thermosetting resins used in wood modification: phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde. Modifying wood with these resins provides dimensional stability, great heat resistance, and high strength [39]. One of the major problems with these resins is the emission of formaldehyde. Even if these emissions can be reduced by various methods, they remain unavoidable [37].

Phenol-formaldehyde resins are applied to wood as described above. They are the result of polycondensation between phenol and formaldehyde. Depending on the parameters applied, low-molecular-weight phenolic resins can be obtained. They are then easier to impregnate into the wood and penetrate the cell walls [46]. This type of resin is used for its low cost, simple production, good mechanical properties, dimensional stability, and weather resistance.

Urea formaldehyde resins are formed by the polycondensation of urea and formaldehyde. Among the three resins presented here, this is the most widely used industrially [47].

Modifying wood with a urea-formaldehyde resin will improve the stability of wood, durability and strength, while also being inexpensive.

Research on the use of melamine-formaldehyde resins has intensified in recent years, especially in Europe. Results shown that wood modified with this type of resin has good dimensional stability and resistance to fungi [48]. The main drawbacks of this type of resin are cost and the possibility of cracks appearing due to humidity during the process [41].

### **I. 2. 2. 2. Thermal modification**

Thermal modification of wood is a method that is becoming increasingly popular and is considered to be environmentally friendly. The procedure is carried out at temperatures between 160 and 240 °C [49], under dry or wet conditions and under air, vacuum, or inert atmosphere among others [50]. This temperature range is a compromise between the properties acquired and the attenuation of unwanted properties. Temperatures above 240 °C could excessively degrade the wood to the point of making it unusable.

During heat treatment, both the chemical and physical properties of wood are altered. Unwanted but sometimes unavoidable changes can occur at both anatomical and chemical levels. At the anatomical level, most changes are unintentional and lead to structural weakness. Indeed, internal and external cracks can appear as early stages as the heating process. This phenomenon increases with temperature, due to degradation of the cell walls [51]. On the chemical level, by contrast, modifications are usually intended to improve properties. Hemicellulose is the first compound to undergo degradation, with the breaking of  $\beta$ -1,4 bonds. In the case of cellulose, only the amorphous part degrades, leading to an increase in the crystallinity index [52]. Finally, lignin is the most thermally stable compound, starting to decompose at around 220 °C. Despite its greater stability, lignin nevertheless undergoes degradation. This results in the formation of low-molecular-weight compounds [49]. The extractives initially present in wood are degraded during the initial heating steps, but are replaced by new ones derived from the degradation of cell wall polymers.

After heat treatment, the wood becomes darker. This type of modification does not allow the lignin to be photostabilized; as a result, heat-treated wood will still be sensitive to UV degradation [49]. In terms of biological resistance, the degradation of cellulose and hemicellulose leads to the formation of new compounds which are more resistant to fungi. Still due to the degradation of cell wall polymers, modified wood shows a significantly

reduced degree of swelling [41]. One of the undesirable properties of this heat treatment is the reduction in the mass and consequently the density of the wood. This leads to a considerable reduction in hardness. Finally, researchers differ on the question of surface energy. Some report a reduction in surface energy, while others have observed no change at all, or even an improvement in some cases [27].

### I. 2. 3. Regulations

In the current context, limiting negative environmental and human impacts is an urgent priority. Some of the compounds described above are derived from the petrochemical industry. Their use can be dangerous for both humans and environment. Organic solvents, for example, generate VOC emissions.

Regulations have been established to minimize harmful effects. The content of VOC, volatile organic substances (VOS), heavy metals, and substances classified as hazardous to health and/or the environment is controlled. Directives have been introduced at national, European and even international level. At European level, the directive 1999/13/CE [53] concerns the reduction of VOC emissions due to the use of organic solvents, and the directive 2001/81/CE [54], which sets emission limits for certain atmospheric pollutants. At international level, the Göteborg protocol [55], regulates several atmospheric pollutants (sulfur dioxide, nitrogen oxides) responsible for acidification and eutrophication, as well as VOC emissions responsible for ozone accumulation in the lower atmosphere.

Labels exist to enable manufacturers to guarantee their products' compliance with regulations. Among these are the European Ecolabel and the French "NF environment" label.



Figure I-13 - Ecolabel EU (left) and NF environment (right) logos

## **I. 2. 4. Biobased components for the development of new wood preservatives**

As mentioned earlier, wood has weaknesses that restrict its use in its natural state. So far, the various methods of protecting wood, both chemical and thermal, were presented. With the exception of thermal modification, all processes involve the use of chemical compounds. However, today, the synthesis of these compounds is increasingly being called into question, particularly with the regulations implemented and mentioned above. First of all, petrochemical resources are in perpetual decline. Moreover, the manufacturing processes and even the use of these synthetic products generate considerable environmental pollution, adding to the climate emergency. Added to this major environmental issue is the fact that some products are dangerous to the human organism. Some of the compounds used to protect wood have been shown to be carcinogenic, mutagenic, and reprotoxic.

A major challenge has therefore emerged to find alternatives to these environmentally and humanly toxic compounds. Furthermore, we must not forget that wood is a natural and renewable resource, so it would be a shame to protect it with non-renewable synthetic chemical products. A great deal of research is being carried out to find biosourced, renewable, and affordable substitutes.

In this section, a presentation of the major substituents for each desired protection (resistance to water, microorganisms, UV, and fire) is done.

### **I. 2. 4. 1. Water and biological resistance**

Due to the high-water affinity of wood, hydrophobic protection is necessary for both indoor and outdoor use. This hygroscopicity can lead to the proliferation of microorganisms within the wood structure. In fact, these microorganisms grow under specific environmental conditions: a temperature between 15 and 45 °C, the presence of oxygen, and a humidity level above 20% [56]. Because of this humidity requirement, sensitivity to fungi is closely linked to the hydrophobicity of the wood. Hydrophobic protection will therefore limit the propagation of fungi, which can lead to a reduction in both aesthetic and mechanical properties.

The hydrophilicity of wood can be reduced by using hydrophobic compounds of animal or vegetable origin. For example, linseed oil and tung oil have demonstrated good performance against wood degradation by fungi [57]. However, the development of this technique is

limited by the quantity of oil required for effective protection and by the problem of oil exudation that can occur because there is no bond between the oil and the wood cell walls [58], [59]. Waxes are also used as hydrophobic coatings for wood. Beeswax contains a wide variety of compounds, including long-chain alkanes, acids, and polyesters, which enable the wood to become hydrophobic [60]. Natural resins and phenolic extracts are also part of the natural components that can improve the hydrophobic and fungal properties of wood. These resins and extracts can be derived from animal or plant sources [61]. Tannins, for example, are phenolic species rich in antifungal properties that have demonstrated very good resistance to fungi [56]. Finally, biopolymers such as chitin, chitosan, and starch also represent an alternative for wood protection coatings. In fact, chitin and chitosan are currently used in the cosmetics and food industries for their antifungal properties [62].

#### **I. 2. 4. 2. Weather resistance**

To prevent photodegradation of the wood, light stabilizers are used. These include UV absorbers and radical scavengers. A natural alternative to photostabilizers is the use of phenolic extracts present in the wood. These extracts, particularly tannins, have been demonstrated to have better antioxidant activity than some synthetic antioxidants. This property is explained by the large number of radical scavengers in their structure. These compounds capture the radicals created during the first stage of lignin degradation by UV light. This reaction between the two radicals stops the degradation before it can become visible [63]. However, this ability to reduce degradation thanks to their radical scavengers depends on the wood species used; not all essences protect against photodegradation [64]. Another compound used to reduce photodegradation is wax. It was mentioned in the previous paragraph as a compound that makes wood hydrophobic. Waxes have also been demonstrated to slow down the photodegradation of wood [65].

#### **I. 2. 4. 3. Fire resistance**

The substances used to protect wood will reduce the amount of heat released, delay flame propagation, and limit the production of smoke and volatile substances. Compounds based on inorganic salts are used as flame retardants. These salts can include hydroxides, sulfates, carbonates, and phosphates. They provide wood with good thermal stability and reduce smoke and toxic gases. The disadvantage of these salts is their high solubility in water. When wood treated with these salts is leached, the salts penetrate into the cell walls of the wood,

making it more hygroscopic [66]. Boron is also a compound used as a flame retardant. In addition to being non-toxic, inexpensive, and easy to use, it offers high thermal and biological resistance. Their deep penetration into the wood provides long-term protection [67]. There are also silicone-based compounds. These enable the formation of a highly stabilized silica layer that protects wood against fire. This class includes silicones, silicates, organosilanes, and silesquioxanes [68].

The compounds presented here represent an alternative to the use of synthetic compounds for wood protection. In addition to being natural and renewable, they are easily available and cost-effective. Some of them can even be recovered from industrial waste. The main problem with using these materials is their heterogeneity, due to their natural character. Indeed, the precise chemical composition of this type of compound depends on a wide range of parameters, including the source of origin (type of biomass, animal, synthesis). In addition, these compounds may have weaknesses compared with toxic synthetic protections, such as poor penetration into wood cell walls or easy leaching. However, they can be combined with other biobased materials to provide a complete protection. As a result, these natural compounds provide a valuable alternative to toxic products.

### I. 3. Thesis objectives and methodology

Given the current environmental context, the development of biobased products to replace petrochemicals is a major challenge. There is thus a need to develop biosourced components that are non-toxic for humans and for the environment. At present, the existing wood preservatives are synthesized from petrochemical raw materials. Research has already been carried out to replace existing toxic compounds, but needs to be further developed before commercialization and large-scale use. Moreover, at present there is no multifunctional biobased preservative to protect wood against all agents of degradation, including water, photodegradation, fungi, and fire.

The objective of this thesis is to develop multifunctional phenolic resin for the protection of wood and wood composites. This new resin will be developed using mainly co-products from the local wood and paper industries, in line with the circular economy in South-West of France and the Landes department in particular. The use of this type of product reduces the amount of waste produced by companies, while providing a way to valorize it.

Maritime pine (*Pinus Pinaster*) is the most widespread species in the Landes department. Consequently, the chemical derivatives of this species will be the most widely used in the development of these resins.

The first chapter will be dedicated to the presentation of the wood material with its structural components and its weaknesses regarding to degradation factors. The state of the art of existing protections to overcome these degradations will be also presented.

The second chapter will describe the characterization of resin previously developed by a PhD student, Dr. Pedro de Hoyos Martinez [69]. He has synthesized a biosourced resin that protects wood from fire. The resin will be characterized to determine its performance. The results obtained led to a research phase aimed at improving properties to make the resin multifunctional. These modifications and the characterization of these new resins applied to wood will be presented in this chapter.

The third chapter of this thesis will be devoted to new raw materials used in the development of a multifunctional resin. A characterization of the two main raw materials used will be presented as well as their modification.



Finally, the fourth and last chapter of this thesis will be devoted to the synthesis of new resin formulations. A study of the application method and synthesis parameters was carried out. The performance provided by the resin to the wood was then determined by a series of characterizations. All these experiments conducted will be presented in this chapter.

Chapter II -  
Performance study and  
modification of a  
biosourced resin

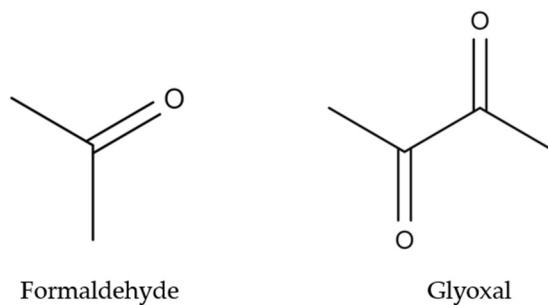


A biosourced phenolic resin was developed previously at this laboratory during a previous project by Pedro Luis de Hoyos Martinez in 2018 [69]. Its main property was to protect wood against fire. The formulation was based on a phenol-formaldehyde resin. This type of resin is widely used in the current industry for various applications such as composites, additives for paints or coatings, binders, or even in the automotive industry. However, as mentioned above, the two main components of this resin: phenol and formaldehyde, are considered as toxic for the environment and for humans. Moreover, they are also derived from non-renewable sources. Consequently, it is essential to replace these two compounds with natural and environmentally-friendly materials.

A considerable amount of research has already been carried out to solve this issue. In many of these studies, lignin and tannins appear to be suitable substitutes for phenol. Tannins, for example, are already used on the market as adhesives in resin synthesis [70]. The major problem with their use is the high added value they currently present on the market. In fact, they are already widely used in the pharmaceutical and food industries, thanks to their high antioxidant activity [71]. Regarding lignin, studies on the replacement of phenol by this phenolic polymer have also been carried out [72], [73]. However, the development of this concept is less mature than in the case of tannins, due to the complex structure of lignin, which limits its reactivity with other compounds.

Because of the two main disadvantages discussed above, studies to combine tannins and lignin have been conducted in recent years [74]–[76]. In this way, the use of tannins can be limited and the valorization of lignin developed.

According to the literature, several compounds can also be used to replace formaldehyde in the resin such as propionaldehyde, glutaraldehyde, or glyoxal. Nevertheless, with these two first compounds there are still a problem of toxicity, solubility, or volatility, which makes glyoxal the most suitable compound for replacing formaldehyde [77], [78]. The glyoxal is a non-toxic dialdehyde, it is non-volatile, and can partially or totally replace the formaldehyde due to its very similar structure (Figure II-1). Moreover, it can be obtained from natural resources like a by-product of biological processes or by the oxidation of lipids [79].



*Figure II-1 -Chemical structure of formaldehyde (left) and glyoxal (right)*

Consequently, the two phenolic compounds lignin and tannins were used to synthesize this resin. Inorganic particles were also added to improve the fire resistance of the resin. The first part of this chapter will be devoted to a presentation of the raw materials used in the synthesis. Then, the chemical modification of lignin will be presented, followed by resin synthesis and its characterization. Finally, the modifications made to improve the resin will be described followed by evaluation of resin performances.

## II. 1. Raw materials used

### II. 1. 1. Lignin

Lignin is the most abundant phenolic polymer and one of the major constituents of wood after cellulose and hemicellulose. Its characteristics are described in the first chapter (I. 1. 2.), its aromatic structure allows it to be used as a new chemical raw material.

Lignin can be extracted from cellulose and hemicellulose by a number of different treatments. The method of extraction has an influence on the final lignin structure, its purity, and properties. Extraction method can be divided into two groups: sulfur process and sulfur-free process. For first process two kinds of lignin can be obtained, namely Kraft and lignosulfonates lignins whereas for the sulfur-free process these are organosolv and soda lignins [80].

The Kraft process is the most use in industry and represents around 85% of the worldwide production of lignin [81]. However, the organosolv process is often used for its high-purity and sulfur-free lignin production. It also offers many other advantages, such as the possible use of green solvents, reduced water consumption, and poor water solubility. For all these reasons, the process chosen for resin synthesis is the organosolv process.

Lignin was extract from maritime pine (*Pinus Pinaster*) wood residues. The lignin used was extracted by a third person, but this extraction was performed using an ethanol solution (70%) and a ratio liquid/solid of 6/1. The reaction was conducted in a reactor during 90 min at 200 °C. The solid part was removed to the liquid part by filtration. Then, the lignin was precipitated by adding acidified water to the liquid. The solution was left overnight to promote the precipitation of lignin. After that, the lignin was filtered and dried at 50 °C for a minimum of 2 days.

### II. 1. 2. Tannins

Tannins are among the phenolic compounds that constitute wood. They are the second most important natural source of phenolic compounds after lignin [82]. Its structure is mainly dependent on the species studied and the environment of the wood. Tannins are not vital to the development of the tree, but they play a role in protecting it from insects [83].

Tannins can be divided into 2 categories: condensed and hydrolysable tannins. A more recent and minor class of tannins has come into consideration: complex tannins.

Condensed tannins represent over 90% of the total world production of commercial tannins [84]. They are constituted by a flavonoid unit, represented in Figure II-2. Each flavonoid is composed of two phenolic rings having different reactivities. Depending on the presence or absence of the hydroxyl group in positions 5 and 5', four configurations of the flavonoid unit are possible. The bonds between each unit depend on the wood species, but in most cases are C-C bonds, more specifically C4-C8 or C4-C6 [85].

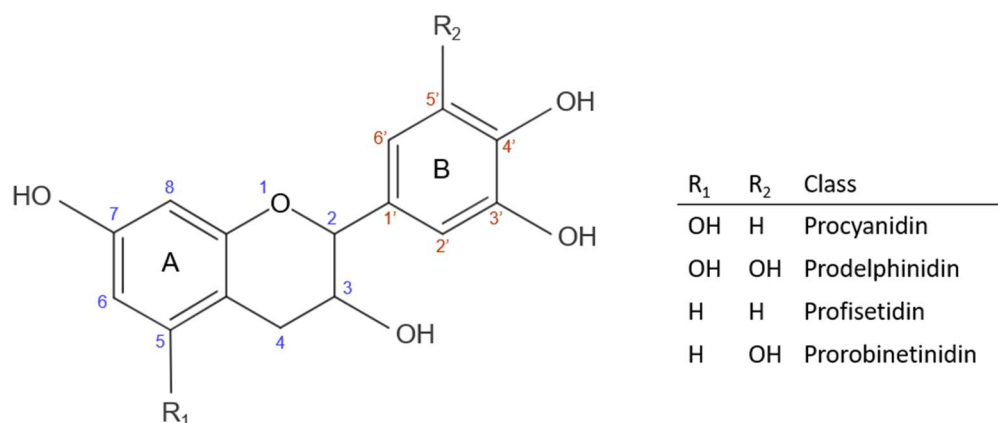


Figure II-2 - Structure of monoflavonoid

Hydrolysable tannins are composed of polyphenolic acids and their derivatives, esterified with a polyol [86]. They can be divided into two categories: gallotanins and ellagitanins. Gallotanins are the simplest class of tannins, composed of gallic acid chains and polyol residues. As the ester bond between gallic acids is weak, they are easily hydrolyzed. During hydrolysis, gallotanins release gallic acid and its polyol derivatives. The second category, ellagitanins, are formed from gallotanins containing an intermolecular C-C bond between two galloyl units. An example of hydrolysable tannins is given in Figure II-3.

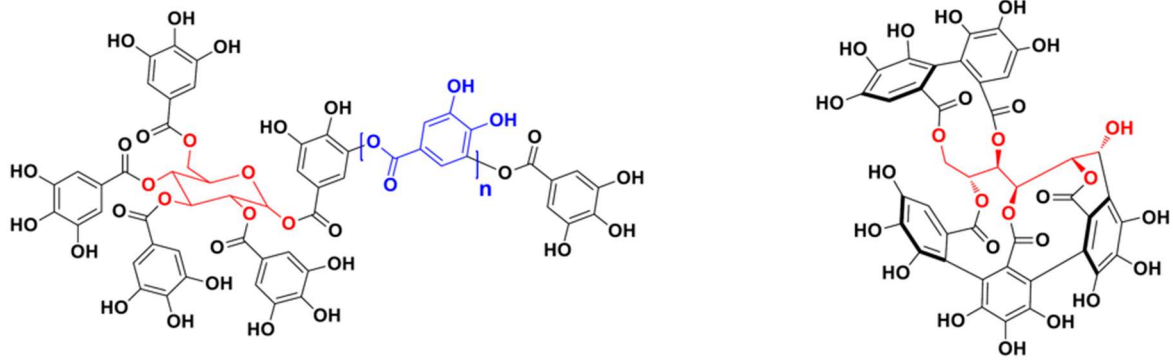


Figure II-3 - Characteristic structure of gallotanins with gallic acid in blue and the polyol residue in red (left) and of a wood ellagitannin: castalagin with the polyol residue in red (right) [87]

Finally, complex tannins are composed of an ellagitannin or gallotanins unit and a flavonoid linked by a glucosidic linkage. The most famous of these tannins is acutissimin A, shown in Figure II-4.

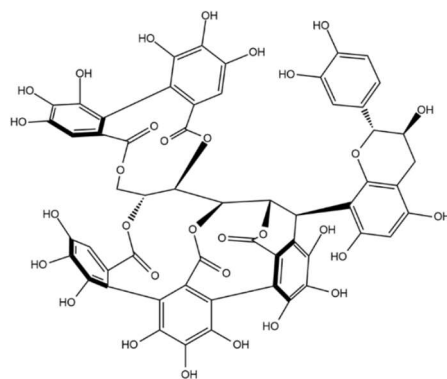


Figure II-4 - Chemical structure of a complex tannin: acutissimin A

The tannins used in resin synthesis are mimosa (*Acacia mearnsii*) tannins. They are renowned for their good reactivity with other compounds and are among the main tannins available industrially.



## II. 1. 3. Inorganics compounds

The last major component of the biobased phenolic resin is an inorganic compound. Indeed, despite the effectiveness of lignin as a matrix for biobased materials, some weaknesses are present depending on the desired use. Weaknesses in thermal and mechanical properties can be observed. To overcome this, the development of a hybrid material, i.e. combining lignin and an inorganic compound, appears to be a solution [88]. This type of material offers a multitude of advantages, since it combines the properties of an organic material with those of an inorganic one. Currently, these hybrid materials are mainly synthesized using nanoclays or nanosilicates. The dispersion of nanoclay within the polymer matrix was shown to stop the diffusion of volatile compounds during thermal degradation, thus improving the thermal properties of the material [89]. One of the most widely used nanoclays is montmorillonite (MMT), a member of the smectite group. These are 2:1 charged layered silicates consisting of two tetrahedral silica sheets  $[\text{SiO}_4]^{4-}$  with a central octahedral sheet  $[\text{AlO}_3(\text{OH})_3]^{6-}$  [69], [90]. The advantages of this material are its low price and easy intercalation between the polymer matrix. Among nanosilicates we find polyhedral oligomeric silsesquioxanes (POSS), which has received a great deal of attention in recent years. This compound is a silica cage with organic functional groups attached to the corner of the structure.

During resin synthesis, only the first compound (MMT) was tested. Its chemical structure is shown in Figure II-5. It is important to note that the montmorillonite used in this section is purified and then modified with a quaternary ammonium salt (dimethylbenzylhydrogenation of tallow ammonium). In the following, this compound will be referred to as organically modified montmorillonite (OMMT). Studies demonstrated that this compound provides the desired fire resistance [91]–[93]. Indeed, they showed that the addition of OMMT reduced mass loss, charring index and rate of spread. They also revealed a reduction in smoke production and heat release. All these parameters point to the positive effect of adding nanoclays, and OMMT in particular. Moreover, this compound derived from a natural clay does not present any toxicity or volatility hazards during its use, as confirmed by the safety data sheet for the organically modified montmorillonite (CAS No. 1318-93-0). This naturally derived compound could therefore provide the desired fire resistance properties while being a bio-sourced resin.

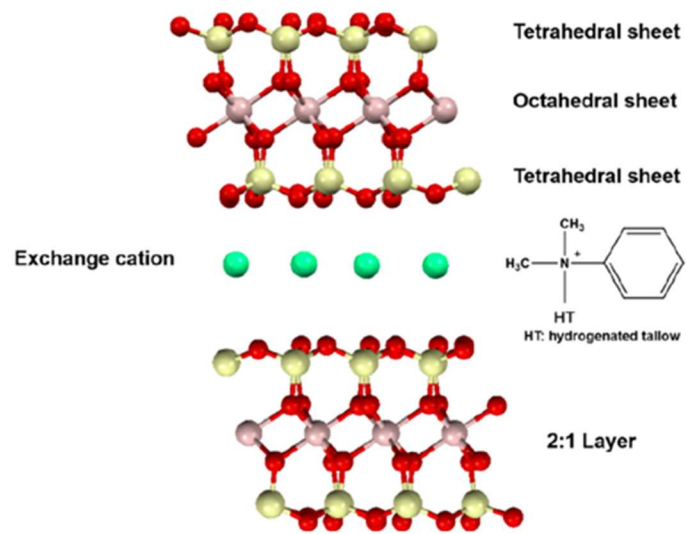


Figure II-5 - Structure of the modified montmorillonite (OMMT) [1]

## II. 2. Modification of lignin with glyoxal

Lignin extracted from biomass can be incorporated into a matrix to improve or provide new properties to the material. However, usually the lignin is functionalized to make it more reactive and to use for the development of a lots of chemical products. Indeed, the hindered phenolic structure of lignin allows it to be used as antioxidant, UV-stabilizer, and flame retardancy too [80].

Lignin appears to be a suitable candidate for controlled chemical modifications due to the functional groups already present within its structure. Functionalization possibilities derive mainly from the reactivity of the aromatic rings of the G and S units, as well as aliphatic hydroxyl groups [94]. On aromatic groups, hydroxymethylation, amination, or nitration can be performed. In the case of hydroxyl groups, esterification, acetylation, silylation, etherification, or phenolation may be carried out.

In this chapter, hydroxymethylation was selected, which leads to the introduction of the hydroxymethyl groups in the structure thanks to the reaction of the formaldehyde with the lignin in alkaline medium. However, for the same conditions as explained at the beginning of this chapter, it is necessary to replace formaldehyde by a non-toxic compound with the same performance. Glyoxal was mentioned as a suitable compound to replace formaldehyde in resin development. It also appears to be a good candidate for lignin modification [78]. Like with the formaldehyde, the glyoxalation of the lignin leads to incorporate in lignin molecules some hydroxymethyl units (-CH<sub>2</sub>OH).

During glyoxalation, the main reaction is the addition of the glyoxal molecule to the free ortho position (C5) of the lignin molecule. However, side reactions can also occur, such as the reaction between two glyoxal molecules, or the addition of glyoxal to the aliphatic chain rather than the aromatic ring. All the reaction mechanisms are shown in Figure II-6.

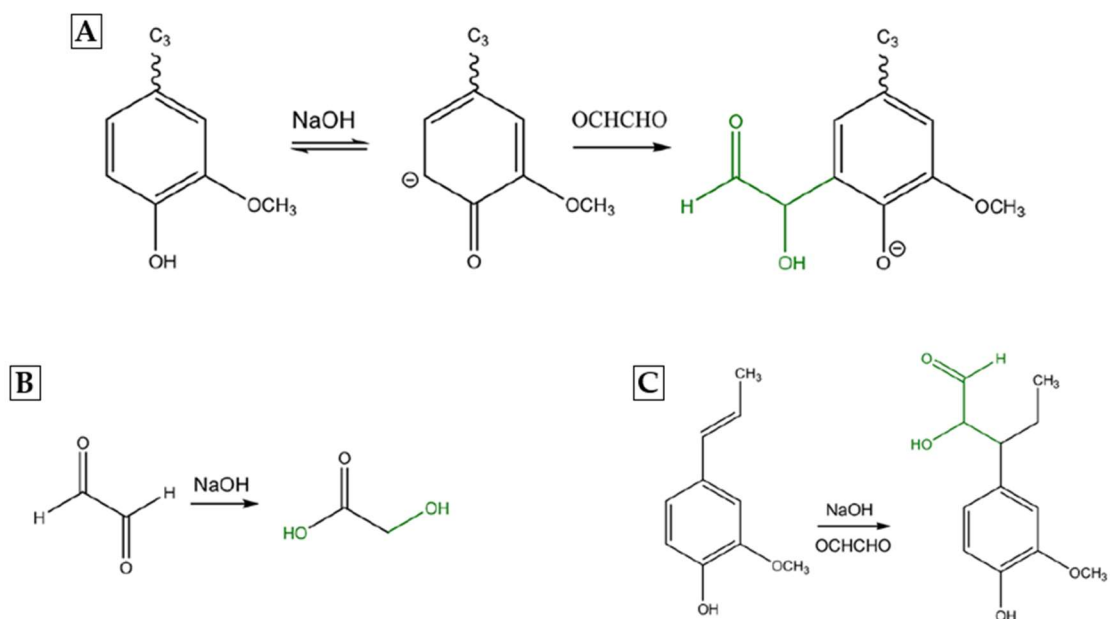


Figure II-6 - Main reaction mechanism of lignin glyoxalation (A), side reaction mechanisms (B and C) [78]

## II. 2. 1. Experimental procedure

### II. 2. 1. 1. Raw materials and reagents

The lignin used in this chapter was the organosolv lignin mentioned in part II. 1. 1, of this chapter. Extraction was carried out according to the protocol mentioned, and a rapid characterization was also carried out by a third person. As a reminder, this lignin was extracted from maritime pine (*Pinus Pinaster*). It had a percentage of 94.60% of acid insoluble lignin, 2.17% of acid soluble lignin, and 3.16% of sugar content. Lignin modification was carried out using glyoxal (40% in aqueous solution) purchased from Acros Organics and sodium hydroxide (NaOH) from Sigma Aldrich.

### II. 2. 1. 2. Protocol of glyoxalation of lignin

The entire reaction was performed in a reactor with constant mechanical stirring at 450 rpm (Figure II-7). First, 20.0 g of organosolv lignin was dissolved in 32.4 g of water. To enable the solubilization of lignin, a 30% sodium hydroxide solution (w/w) was added until a pH of between 12 and 12.5 was reached. Once the correct pH was achieved and the solution was completely homogenized, 11.8 g of glyoxal was slowly added to the reaction mixture, before

heating at 58 °C for 8 h. At the end of the reaction, a small quantity of the final solution was removed and placed in an oven at 50 °C for a minimum of 48 h for future analysis.



Figure II-7 - Reactor for lignin glyoxalation

### II. 2. 1. 3. Characterizations performed

Fourier Transformed Infrared Spectroscopy analysis (FTIR) and thermogravimetric analysis (TGA) were carried out to determine if the modification was successful. The experimental conditions for these analyses are described in Appendix 1. 1.

## II. 2. 2. Results and discussion

### II. 2. 2. 1. Fourier transform infrared spectroscopy analysis (FTIR)

FTIR spectroscopy was used to characterize the chemical functions of lignin. Through this analysis, it is possible to observe the evolution of the chemical groups in the material and thus follow the modification. The FTIR spectra of raw organosolv lignin (OL) and glyoxalated lignin (OL\_G) are shown in Figure II-8. The spectra were normalized using the band at 1510  $\text{cm}^{-1}$  corresponding to the aromatic rings of lignin. Indeed, according to the reaction mechanism shown in Figure II-6, the aromatic rings remain unchanged during the glyoxalation reaction.

In these spectra, an initial broad band around  $3350\text{ cm}^{-1}$  corresponds to phenolic and aliphatic hydroxyl groups (-OH). After modification, this band broadened towards lower wavenumbers, indicating an increase in the number of these hydroxyl groups. The bands at  $2935$  and  $2848\text{ cm}^{-1}$  correspond to symmetrical and asymmetrical -C-H stretching of the methyl and methylene groups in the side chains. The absorbance corresponding to carbonyl groups (-C=O) is located at  $1700\text{ cm}^{-1}$ , and a decrease in this band can be observed after glyoxalation of lignin. At  $1590\text{ cm}^{-1}$ , a band corresponding to C=C bonds of the aromatic rings is present in both spectra, with a higher intensity for OL\_G. Another study observed similar phenomena for the band at  $1700$  and  $1590\text{ cm}^{-1}$  [1]. A slight increase in the absorbance of the bands at  $1364$  and  $1325\text{ cm}^{-1}$  can be observed after glyoxalation. These bands, corresponding to phenolic hydroxyl groups [95], support the assumption of an increase in hydroxyl groups mentioned above. However, the most characteristic bands of the modification are located between  $1140$  and  $1030\text{ cm}^{-1}$ . They correspond to the -C-O stretching of the secondary alcohol and the -C-O stretching and deformation of the primary alcohol.

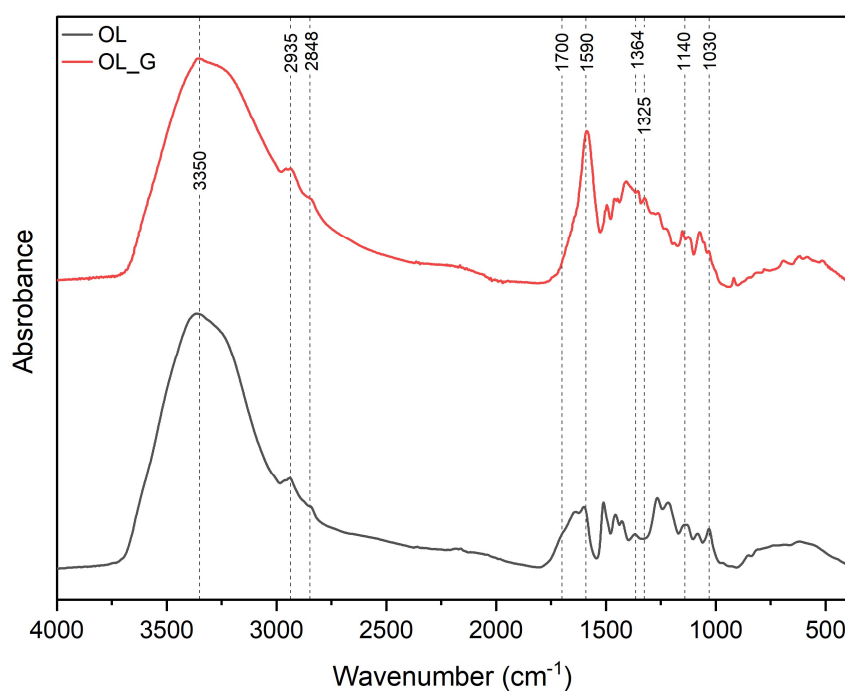


Figure II-8 - FTIR spectra of organosolv lignin (OL) and glyoxalated organosolv lignin (OL\_G)

## II. 2. 2. 2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis shows the thermal resistance of lignin before and after modification. The curves corresponding to this analysis (TGA) and the derivatives of the curves (DTG) for a better visualization are presented in Figure II-9.

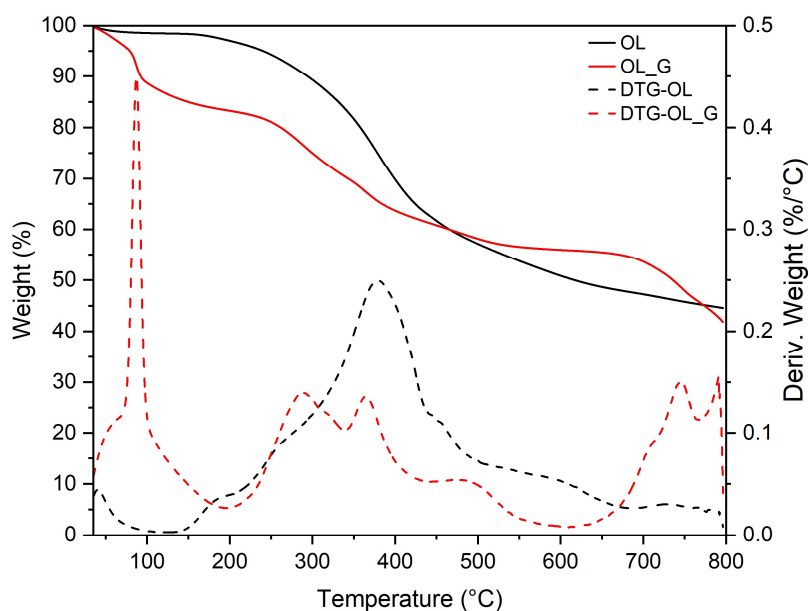


Figure II-9 - TGA (solid line) and DTG (dash line) curves for OL and OL\_G

The major observation that can be made after a quick visualization of the curves is a faster degradation of lignin when it was chemically modified with glyoxal. On the DTG curve, two main thermal decomposition phases for OL can be observed, whereas there are four for OL\_G. The first appears at approximately the same time in both cases, around 50 °C, and may be associated with evaporation of moisture and volatiles. At this stage, OL\_G has already undergone a major loss of mass, while the mass loss of OL is very minor. This degradation of OL\_G can be explained by the presence of unreacted glyoxal or glyoxal which reacts with itself to form dimers or trimers. After 180 °C, another loss of mass occurred for OL, with a progressive evolution up to 375 °C. This can be attributed to the degradation of the lignocellulosic material. For OL\_G, the second mass loss occurred between 200 and 340 °C and corresponds to the formation of low-molecular-weight polymers resulting from the reaction between lignin and glyoxal. These low-molecular-weight polymers are the result of condensation reactions between lignin molecules [96]. The third and fourth mass losses for OL\_G are between 340 and 415 °C and between 450 and 650 °C respectively, and can be

attributed to the decomposition of lignin-glyoxal polymers with higher molar masses. At 800 °C, the residual mass for OL is 44.6% and 41.8% for OL\_G.

### **II. 2. 3. Conclusion**

The modification of lignin by glyoxal was presented in this part. FTIR analysis highlighted chemical differences before and after glyoxalation, particularly with the increase in hydroxyl groups. TGA analysis demonstrated a lower thermal resistance of glyoxalated lignin.

The differences observed between unmodified and modified lignin confirmed the successful modification. Moreover, the addition of hydroxyl groups within the structure confers a better reactivity to the lignin. Nevertheless, the reduced thermal resistance may appear to be a weakness, but as mentioned in section II. 1. 3., the addition of inorganic particles during resin synthesis will improve this property.



## **II. 3. Synthesis of resin and application on wood samples**

### **II. 3. 1. Experimental procedure**

#### **II. 3. 1. 1. Raw material and reagents**

Lignin and tannins were the main raw materials used in resin synthesis. The lignin used was the maritime pine organosolv lignin previously modified with glyoxal: OL\_G. The tannins used were the mimosa tannins (TM) mentioned above, supplied by TANAC Inc (Brazil).

The reagents used in this section were acetone purchased from Fischer Scientific and sodium hydroxide bought from Sigma Aldrich. Hexamethylenetetramine (hexamine) was obtained from Acros Organics and the organically modified montmorillonite (OMMT) was kindly provided by Laviosa Advance Mineral Solutions.

#### **II. 3. 1. 2. Synthesis protocol**

The resin was synthesized in three main stages. The first involved the modification of lignin with glyoxal and nanoparticles. The second consisted in making a solution of tannins and hexamine. The latter was used as a hardening agent during the reaction; as it was more stable at a basic pH, the pH was increased prior to its addition. Finally, the two solutions obtained in the first two steps were mixed to synthesize the final resin. These two stages are described in details in the following paragraphs.

In the first step, 1 g of OL\_G was chemically modified with glyoxal according to the protocol explained in part II. 2. At the end of this reaction, 0.05 g (5%, w/w, with respect to the amount of lignin) of OMMT was added to the reaction medium. This mixture was then stirred at 550 rpm, at a temperature of 40 °C overnight.

The second step was carried out by dissolving 1 g of TM in a 70% (w/w) aqueous acetone solution to produce a 45% (w/w) tannin solution. After homogenization of the solution, the pH was increased with a 30% (w/w) NaOH solution to reach a value between 10 and 10.5. Then, 0.05 g (5%, w/w, relative to the amount of tannins) of hexamine was added to this mixture.

Finally, the lignin and tannin solutions were mixed and the whole mixture was agitated at 550 rpm at room temperature for 45-60 min. The resin synthesized was named RP.

The reaction that occurs between lignin and tannins according to Pizzi [97] is illustrated in Figure II-10.

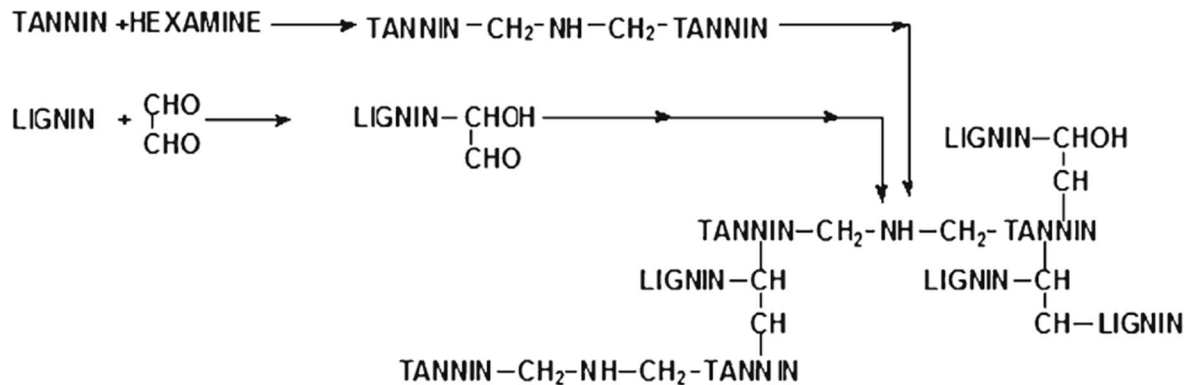


Figure II-10 - Suggested reaction mechanism between tannins and lignin in resin formulations [97]

### II. 3. 1. 3. Application of resin to wood samples

The species chosen for resin application was sapwood of *Pinus pinaster*. The surfaces of the wood samples were first sanded to open the pores and facilitate resin penetration into the wood. The resins were applied to the wood samples using a brush, trying to spread the resin uniformly over the entire sample. To ensure effective curing and drying, the resin-coated wood samples were placed in an oven at 60 °C for 15 h. A higher temperature would have caused degradation of some compounds present in the wood, which could have affected the final performance of the resin.

### II. 3. 1. 4. Characterizations performed

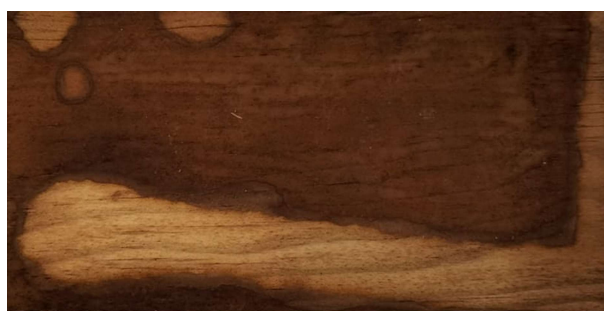
Resin performance on wood samples was assessed first, by testing the water resistance of the coatings. The protocol described in Appendix 2. 4. 1 was followed.

An aliquot of the synthesized resin was dried in an aluminum dish at 50 °C before being analyzed by TGA according to the protocol mentioned in Appendix 1. 2. 1.

## II. 3. 2. Results and discussion

### II. 3. 2. 1. Assessment of water resistance

A picture of the wood obtained after assessing the water resistance of the resin is shown in Figure II-11. As can be seen from the image, the path of the water is clearly visible. According to the protocol, drops of water are applied to the wood sample for 10 minutes. As soon as the first drops were applied, the resin was leached out. This result indicates that on contact with water, the resin became soluble and detached from the wood surface. The liquid recovered in the collection bottle was brown, corresponding to a mixture of resin and water. This leaching may be due to the high solubility of resin in water. Indeed, OH groups present on the surface of lignin that did not react with tannins can influence the degree of resin solubility. This water sensitivity can also be due to a poor interaction between the molecules on the wood surface and the resin. As a result, during contact with water, the resin had more affinity with the water than with the wood. Finally, this leaching can also be due to a poor cross-linking. The OH groups of glyoxalated lignin reacted with the tannin molecules via intermediate methylene groups. The low water resistance may then be due to a rupture of this bond between lignin and tannins, or to poor cross-linking. As this bond between the two components is a chemical bond (strong bond), the second hypothesis is the most plausible. However, the conclusion of these results is clear: resin did not provide any water resistance to wood.



*Figure II-11 - Wood sample (RP) after the water resistance test*

### II. 3. 2. 2. Thermogravimetric analyses (TGA)

The TGA and DTG curves for RP, OL\_G, and TM are presented in Figure II-12. A first mass loss between 80 and 100 °C was mainly attributed to evaporation of resin moisture. A further

loss of mass was observed between 250 and 300 °C, followed by a second between 350 and 400 °C. These degradations are due to the presence of tannins and lignin respectively, the two main resin compounds. Indeed, the DTG curves for TM indicate a loss of mass around 250 °C. Regarding the mass loss between 350 and 400 °C, this is due to the presence of both lignin and tannins; this peak is visible for both DTG curves (TM and OL\_G). The values obtained for tannins and lignin are in line with the degradation temperatures observed in the literature [93]. At 800 °C, the total mass loss of RP was 51.7%, compared with 58.2% and 64.6% for OL\_G and TM, respectively. As a result, an improvement in thermal resistance was observed for resin synthesis. This improvement may be due to the presence of inorganic particles (OMMT) added to the resin. The aim of this addition was precisely to provide thermal resistance to the resin and thus limit the vulnerability of the wood to fire. Despite this improvement in thermal resistance, fire resistance tests were nevertheless required to confirm the usefulness of this inorganic additive.

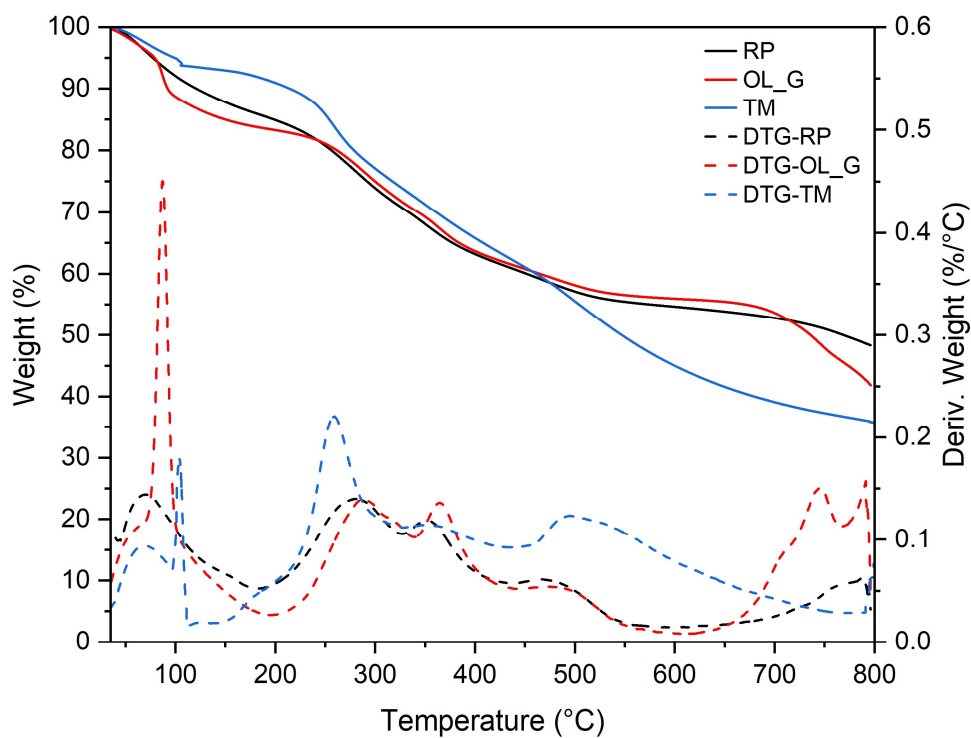


Figure II-12 - TGA (solid line) and DTG (dash line) curves of RP, OL\_G, and TM

### **II. 3. 3. Conclusion**

This section was dedicated to the identical reproduction of the previously developed resin to determine its characteristics. The TGA showed that the resin had better thermal resistance than tannins and glyoxalated lignin, notably due to the presence of the inorganic part (OMMT). However, the first water resistance test showed that the resin was completely dissolved on contact with water. Consequently, this coating provides no protection against water. Water sensitivity is the most important parameter in the development of wood preservatives. As a reminder, protection against water also improves the wood protection against fungi. For this reason, no further tests were carried out.

In the rest of this chapter, modifications done to this protocol to improve the water resistance of the resin will be described.

## **II. 4. Modifications to improve resin properties**

Firstly, with the aim of maintaining a circular economy in the southwest of France, the use of maritime pine tannins to replace mimosa tannins was considered. Indeed, maritime pine is one of the main species cultivated in the Landes department. However, tannins from maritime pine are widely used in the food and, above all, pharmaceutical industries. They present a great antioxidant and anti-inflammatory properties, and are marketed all over the world under the name Pycnogenol [98], [99]. Therefore, before replacing mimosa tannins with maritime pine tannins, a tannin-free formulation was developed to determine its influence on the resin.

Due to the poor resistance of the resin to water, various options have been considered to solve this major issue.

The addition of a hydrophobic compound to provide water resistance to the resin was first studied. As a hydrophobic compound, there is rosin; it comes from pine trees and some other plants. Due to its hydrophobic nature and affinity for wood, rosin is a suitable compound to provide water resistance to a material [100]. Another well-known family of hydrophobic compounds is wax. As mentioned in the introduction, wax is used for hydrophobic coatings [60] and can also be used to protect wood against photodegradation. [65].

Another solution was to add glyoxal. As noticed above, glyoxal replaced the formaldehyde in the modification of lignin, but also replaced the formaldehyde in the synthesis of the phenol-formaldehyde resin. In the protocol described in the previous section, glyoxal was only added during lignin modification. A supplementary addition of glyoxal was therefore added in an attempt to multiply and reinforce the reaction between lignin and glyoxal.

In this section, resins were synthesized based on the initial formulation with the above-mentioned modifications. When hydrophobic compounds were added, a surfactant was used to ensure a great dissolution of these compounds in the resin.

### **II. 4. 1. Experimental procedure**

#### **II. 4. 1. 1. Raw material and reagents**

The same raw materials and reagents mentioned in paragraph II. 3. 1. 1 were used again here. Rosin was supplied by Holiste and was extracted by BioGemme® process. Beeswax was

purchased from Sigma Aldrich and the surfactant used, Tween 80, was obtained from Fisher Scientific.

## II. 4. 1. 2. Synthesis protocol

The same protocol as above (II. 3. 1. 2) was used, with a few modifications, except for the RP resin, which is the same as previously formulated.

For the resin without tannins (RM 01), the same protocol was followed excluding the addition of tannins. Hexamine was added directly to the lignin solution after reducing the pH of the lignin solution to 10-10.5.

Concerning the others, the first step, involving resin modification with glyoxal and the addition of organic nanoparticles, remained unchanged. New components were added to this solution: beeswax, rosin, or glyoxal.

Then, after addition of the hydrophobic compounds, the solution was stirred at 550 rpm at 80 °C for 1 h. For wax, surfactant (Tween 80) was added before heating. In the case of glyoxal addition, stirring at 550 rpm at 58 °C for 2 h was carried out after this adding.

Finally, the pH was reduced using a 30% NaOH solution in both cases. Hexamine was then incorporated and stirred at 550 rpm at room temperature for 45-60 min.

Table II-1 summarizes the compounds and masses of the formulations synthesized.

Table II-1 - Compounds and masses of synthesized formulations

Resin	Mass of compounds (g)							
	Lignin	Glyoxal	OMMT	TM	Rosin	Beeswax	Tween 80	Hexamine
<i>RP</i>	1	0.59	0.05	1	-	-	-	0.05
<i>RM 01</i>	1	0.59	0.05	-	-	-	-	0.05
<i>RM 02</i>	1	0.59	0.05	-	0.05	-	-	0.05
<i>RM 03</i>	1	0.59	0.05	-	-	0.05	0.12	0.05
<i>RM 04</i>	1	0.59 + 1	0.05	-	-	-	-	0.05
<i>RM 05</i>	1	0.59 + 2	0.05	-	-	-	-	0.05
<i>RM 06</i>	1	0.59 + 1	0.05	-	-	0.05	0.12	0.05

In this way, RM 01 provided an indication of the influence of tannins (TM) on resin properties. RM 02 and RM 03 highlighted the potential effect of hydrophobic compounds on water resistance. RM 04 and RM 05 showed if the addition of glyoxal also improved water resistance. Finally, the last resin formulation (RM 06) was a combination of glyoxal and beeswax addition.

### **II. 4. 1. 3. Application of resin to wood samples**

In this case, the wood samples were also sapwood of maritime pine. Resin application and drying was carried out in the same way as described in section II. 3. 1. 3.

### **II. 4. 1. 4. Characterizations performed**

The main aim of this part was to improve the hydrophobic properties of the resins, so the water resistance test was carried out. The protocol was described in Appendix 2. 4. 1.

Then, a thermogravimetric analysis (TGA) was carried out according to the protocol in Appendix 1. 2. 1, to see the influence of the modifications on thermal resistance.

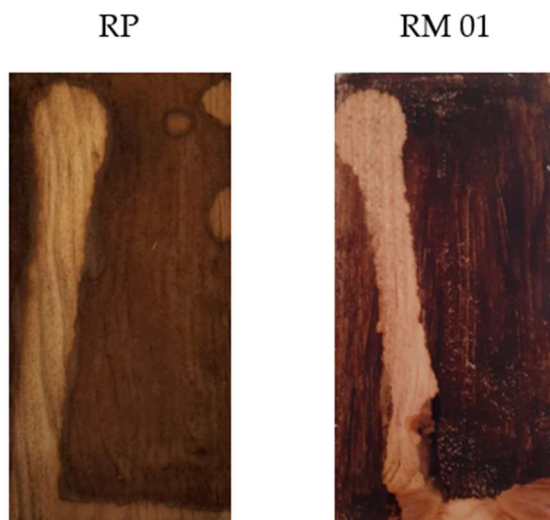
## **II. 4. 2. Results and discussion**

### **II. 4. 2. 1. Influence of tannins**

#### Water resistance tests

Figure II-13 illustrates the wood samples after the water resistance test. In both cases (formulation with and without tannins), it is possible to observe a deterioration of the resin when water drops were applied to the wood samples. This sensitivity to water was probably due to the reasons explained in the previous section. However, even if this difference was not large, it is possible to see a very slight improvement in the resin when tannins were present. Indeed, the mark observed is lighter for RM 01 than for RP. The presence of tannins in resins to improve resistance to water or weathering was already proven by studies [85], [101]. However, despite a slight difference, it is still not possible to conclude that tannins had a impact on the water resistance of resins.





*Figure II-13 - Resin-coated wood samples (with and without tannins) after water resistance test*

### Thermogravimetric analysis (TGA)

The TGA and DTG curves for RP, RM 01, and TM are presented in Figure II-14. At the beginning of the increase in temperature, between 50 and 100 °C, a higher mass loss is observed for RM 01. This corresponds to the moisture present in the samples. At 250 °C, a loss of mass is visible for RP. This same mass loss was shifted to higher temperatures for RM 01. This shift was due to the presence of TM in the resin. Indeed, an important mass loss at 250 °C can be observed on the TGA and DTG curves for TM. Then, after 300 °C, the TGA curves cross, indicating a higher mass loss for RP. After 700 °C, the curves cross again, resulting in a slightly higher total mass loss for RM 01 (54.8 and 51.7%, respectively for RM 01 and RP). However, even if slight differences can be observed on the TGA and DTG curves of the two formulations, they remain very similar. Thus, tannins have no real impact on the thermal resistance of the resin.

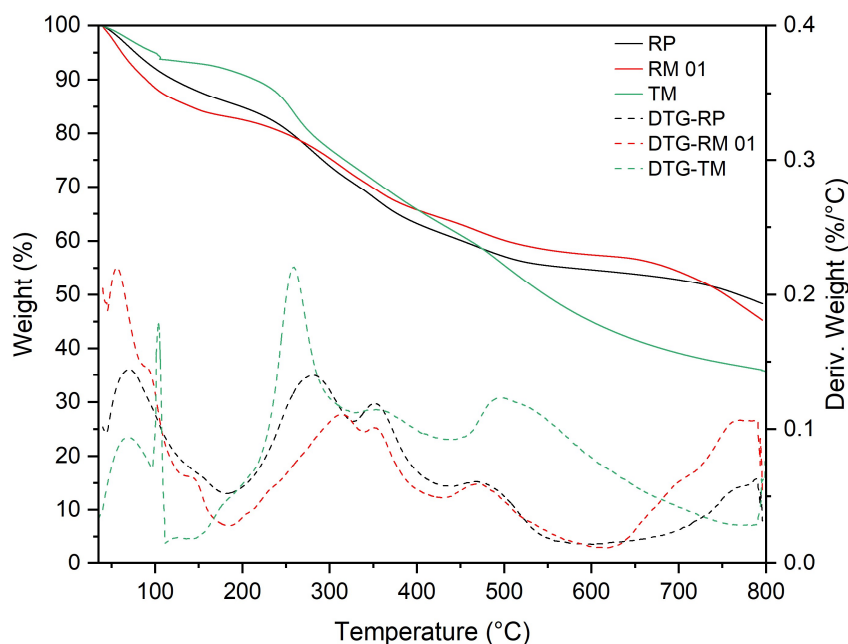
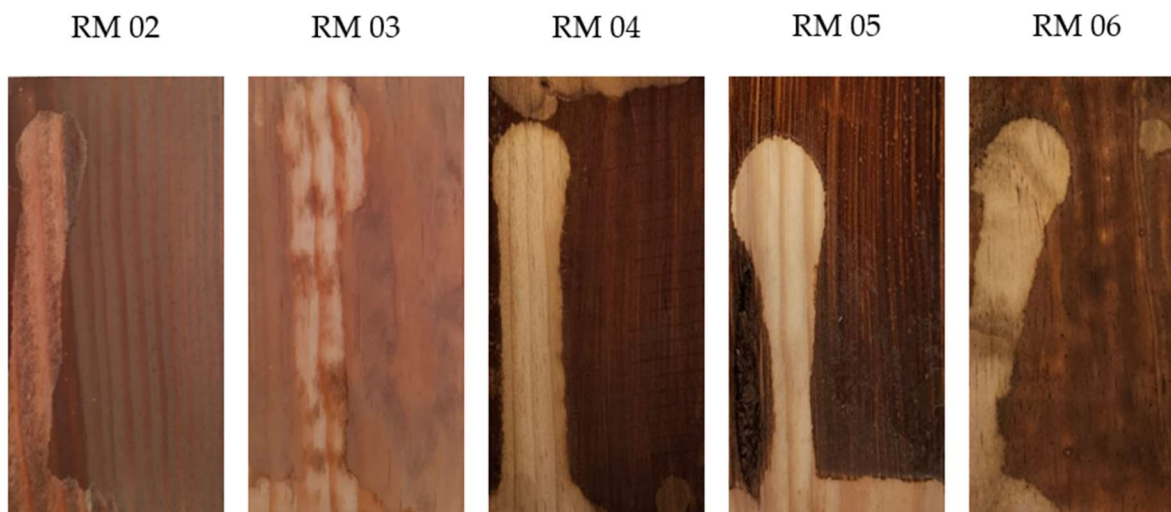


Figure II-14 - TGA (solid line) and DTG (dash line) curves of RP, RM 01, and TM

This brief test showed that tannins were not essential for resin synthesis. Water resistance tests showed no great difference, as did TGA. Consequently, in the formulations that were subsequently synthesized, the tannins were completely removed.

#### II. 4. 2. 2. Influence of additional compounds

The results of the water resistance tests for formulations RM02 to RM06 are shown in Figure II-15. In this section too, the water run-off on the wood samples resulted in leaching of the resin. This phenomenon was visible for all the formulations studied. However, a slight improvement was noted for RM 02 and RM 03, corresponding to formulations containing rosin and beeswax, respectively. The addition of hydrophobic compounds slightly modified the sensitivity of the resin to water, without making the resin hydrophobic. The problem of this sensitivity to water was therefore probably due to a poor interaction between the resin and the wood, or to a poor cross-linking of the resin. On the other hand, the addition of glyoxal during resin synthesis did not improve water resistance either (RM 04, 05, and 06). As a result, the addition of these new compounds did not improve the interaction between the wood surface and the resin, or the hydrophobicity of the resin.



*Figure II-15 - Resin-coated wood samples (containing additional compounds) after water resistance test*

### **II. 4. 3. Conclusion**

In this section, solutions for modifying the resin formulation and giving it a hydrophobic character were developed. Firstly, the influence of tannins was investigated. The results showed that these compounds have no real influence on the future properties of the resin. This type of phenolic compound can easily be replaced by lignin, itself a phenolic compound. Furthermore, as already mentioned, maritime pine tannins have a high value-added. For this reason, tannins were excluded from the formulation.

The second alternative proposed to reduce water sensitivity was to add compounds with hydrophobic properties and/or to add glyoxal. The compounds involved were rosin and beeswax. Water resistance tests were carried out on these resins applied to wood samples. The results showed that these additional compounds did not improve surface hydrophobicity, and neither did the addition of glyoxal. Although it is possible to see a slight difference in the water resistance of resins containing hydrophobic compounds, this resistance is not sufficient to allow the wood to be completely protected from water. The quantity of hydrophobic compounds added is low (5% related to the quantity of lignin), but an increase in the quantity of this compound can lead to a reduction in the fire resistance of these resins. Indeed, these compounds are also known to be fire-sensitive.

As a result, new alternatives need to be found to provide real protection for wood against water and thus prevent its degradation.

## **II. 5. Urea-formaldehyde resin type**

Another type of resin widely used in the industry is urea-formaldehyde resin. This kind of resin has several advantages over its competitors. It has a low cost, a low drying temperature, and also exhibits great thermal properties and resistance to microorganisms. However, like phenol-formaldehyde-based resin, it has the drawback of VOC emissions due to the formaldehyde.

Research was therefore carried out to replace formaldehyde in this type of resin [102]–[104]. As with phenol-formaldehyde resins, glyoxal appeared to be a good candidate for this purpose. In addition, the introduction of lignin, particularly glyoxalated lignin, has enabled the development of wood adhesives with the relevant properties [104], [105]. Several research groups have developed urea-lignin-glyoxal resins as a replacement for urea-formaldehyde resins. However, a number of studies have highlighted the reduction in mechanical strength of glyoxal-based resins [95], [106]. As a result, additives are crucial for improving properties. One study, for example, showed that the incorporation of nanoclays modified the physico-chemical properties of resins, in particular by reducing water absorption and improving mechanical properties [107].

This section will describe the formulation of a urea-formaldehyde resin for wood protection.

### **II. 5. 1. Experimental procedure**

#### **II. 5. 1. 1. Raw material and reagents**

The main raw material used in this part was the organosolv lignin glyoxalated in part II-2.

The reagents used were urea and glyoxal (40% in water) purchased from Acros Organics. NaOH and formic acid were obtained from Sigma Aldrich and organically modified montmorillonite (OMMT) was kindly provided by Laviosa Advance Mineral Solutions.

#### **II. 5. 1. 2. Synthesis protocol**

##### Initial formulation (RU 01):

The protocol used for the synthesis of the urea-formaldehyde type resin was inspired by the protocol described by Younesi-Kordkheili and co-workers [97] with a few modifications. Firstly, 17 g of glyoxal were introduced into a round bottom flask. The pH was adjusted to a

range between 7.5 and 8.5 with a 40% NaOH solution. A first fraction of urea (6.46 g) was added to this solution and the flask was heated for 30 min at 40 °C. The temperature was then slowly increased to 90 °C and the solution was stirred (450 rpm) at this temperature for 90 min. The pH was then decreased to 5-5.5 by adding formic acid. After this, stirring at 450 rpm for 60 min at 75 °C was performed. The pH was then neutralized with a 40% NaOH solution before adding 1 g of the glyoxalated lignin (OL\_G) to the mixture before stirring (450 rpm) at 90 °C for a further 90 min. After this reaction time, the solution was distilled using a vacuum pump and bath at 60 °C for 60 min. Finally, the second part of the urea (3.54 g) was added.

### Modified formulations:

At the end of the resin synthesis (RU 01) described above, urea particles were observed. Consequently, modifications to the protocol were carried out. They are listed in Table II-2.

*Table II-2 - Compounds and their masses for urea-formaldehyde resin types*

Resin	Mass of compounds (g)				Comments
	Glyoxal	Urea	OL_G	OMMT	
<b>RU 01</b>	17	13 (8.4 + 4.6)	1	-	Initial formulation but presence of urea particles at the end of synthesis
<b>RU 02</b>	17	13	1	-	Same protocol as RU 01, but urea was added in a single step: after neutralization of the glyoxal solution
<b>RU 03</b>	17	10	1	0.05	Same protocol as RU 01, but urea was inserted in a single step and the inorganic part (OMMT) was added to the glyoxalated lignin solution before it was added to the resin.

### **II. 5. 1. 3. Application of resin to wood samples**

As for the other formulations, the resins were applied to samples of maritime pine. Resin application and drying were also carried out in the same way as for previous formulations.

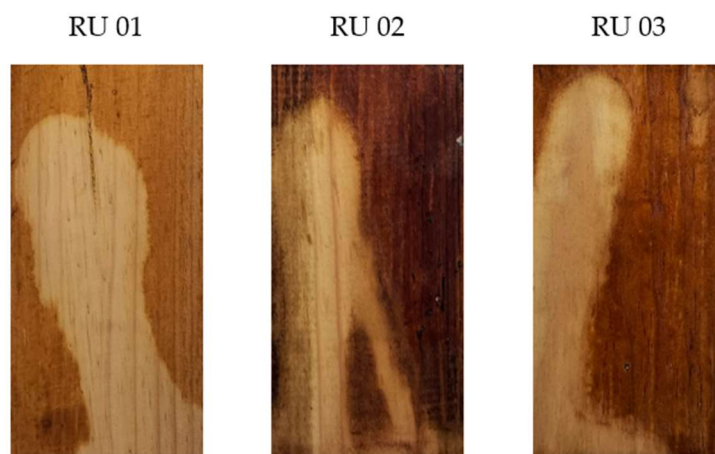
#### II. 5. 1. 4. Characterizations performed

Resins were first characterized using the water resistance test described in Appendix 2. 4. 1. Fire resistance tests were also carried out on these formulations. The protocol and equipment used are described in Appendix 2. 4. 2.

### II. 5. 2. Results and discussion

#### II. 5. 2. 1. Water resistance

Pictures of wood samples coated with resins are presented in Figure II-16. In this case too, a rapid observation reveals the high sensitivity of the resins to water. After 10 minutes of water flowing over the surface, no resin was yet attached to the wood samples. This may be due to a poor reaction between urea, glyoxal, and lignin or, as in the previous sections, to poor interaction between wood and resin. The literature, which reports great properties for this type of resin, used it as adhesive. Consequently, this study showed that coating with this type of resin does not provide the same properties. These results are not in agreement with the work reported by Younesi-Kordkheili [107], who reports that the addition of 1-3% nanoclays reduces water absorption while improving mechanical properties.



*Figure II-16 - Resin-coated wood samples (RU 01, 02, and 03) after water resistance test*

#### II. 5. 2. 2. Fire resistance

When performing a fire test according to the ASTM D635, it is possible to determine the burning rate of the sample by dividing the distance burned by the burning time. According to

the standard, the timer should be started when the flame exceeds the previously drawn line (here indicated by the red arrows in Figure II-17). A combustion rate of 12 mm/min was then measured for the "Control" sample. However, for samples RU 01, 02, and 03, as the flame did not cross the line, the burning rate could not be measured. Consequently, only a photo analysis could be carried out to compare the results obtained. These photos are presented in Figure II-17.

Observation of these photos reveals that urea-formaldehyde type resins showed a fire resistance compared with the Control. RU 01 burned slightly more than the other two formulations, but this difference was very minor. It should also be noted that RU 03, containing the flame retardant (OMMT), did not necessarily provide a better fire resistance than the others. One study showed that urea-formaldehyde-lignin resins provided positive thermal properties. This result was due to an important interaction between urea and lignin, reinforcing the structure and consequently the thermal stability of the resin [108]. The relevant thermal properties obtained in this study may therefore be due to the same phenomenon. Consequently, the use of this type of resin does not require the addition of inorganic parts to improve thermal resistance.

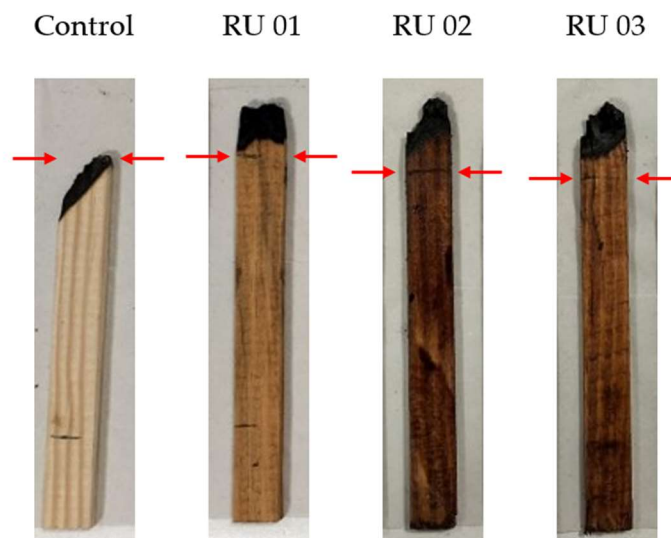


Figure II-17 - Control and resin-coated (RU 01, 02, and 03) samples after fire test

### **II. 5. 3. Conclusion**

In this section, the development of a urea-formaldehyde resin was studied. Formulations were carried out, as well as fire and water resistance tests. The results showed that the fire resistance of the wood samples was positive, even without the addition of the flame retardant. This result may be due to the high degree of interaction between lignin and urea, making thermal degradation more difficult and thus providing better fire resistance. On the other hand, water resistance tests did not provide satisfactory results. The resin was still as sensitive to water as the phenol-formaldehyde type resins developed previously.



## II. 6. Chapter conclusion

This chapter was devoted to the formulation of the resin developed by a previous PhD student. He synthesized a phenol-formaldehyde resin to provide fire protection for wood. Because of the environmental and human health effects of phenol and formaldehyde, these compounds were replaced. Phenol was replaced by lignin and tannins, two natural phenolic polymers. As lignin is not very reactive, it was chemically modified with glyoxal. Formaldehyde was replaced by glyoxal because of its structural similarity and its biobased and non-toxic properties.

Water resistance tests were carried out on this resin and the results indicated a high level of water sensitivity. Modifications were then applied to the initial formulation.

First of all, the presence of tannins in the formulation was reconsidered, since they were already widely valorized on the market. After checking the impact of their elimination on resin properties, they were removed from the formulation. In addition, to improve the water resistance of the resins, hydrophobic compounds such as rosin and beeswax were added in small quantities. The results obtained once again demonstrated the high sensitivity of the resin.

Another alternative to this water-sensitivity problem was to develop a urea-formaldehyde resin, rather than a phenol-formaldehyde resin. Studies have shown that this type of resin can reduce water absorption by wood. In this case too, glyoxalated lignin was used and formaldehyde replaced by glyoxal. The urea-lignin-glyoxal formulations developed provided satisfactory results in terms of the thermal resistance of resin-coated wood, but their sensitivity to water remained unchanged. Indeed, in this case too, water applied to the wood caused a complete leaching.

The modifications and alternatives proposed to the previously developed resin did not allow the synthesis of a resin able to protect wood not only against fire, but also against other degradation agents, especially water.

Consequently, further research was required to find a new resin formulation offering the desired properties for wood. The following chapter will present all the research and synthesis carried out.

Chapter III -  
Raw materials and lignin  
modification for a new  
resin synthesis



One of the main challenges of this thesis is the use of local and biobased products to adopt a circular economy approach in the southwest of France. The circular economy model is a sustainability concept that aims to develop more sustainable products while limiting consumption, resource wastage, and waste production. For this reason, and because of the unsatisfactory results obtained in the previous chapter, each component of the initial resin was modified.

First, concerning tannins, their presence has already been discussed in the previous chapter. Indeed, it was highlighted that maritime pine tannins are highly valued, mainly in the cosmetics and nutraceutical industries. As a result, tannins were removed from the resin formulation. However, when tannins are extracted, industries end up with a waste product at the end of the process. This product is currently not valorized, whereas it could be used to improve the properties of some biobased materials. A characterization of this material was therefore carried out to find a recovery route and the properties it could bring to the resin.

Then, the lignin used was an organosolv lignin chosen for its high purity and the possible use of green solvents in the extraction protocol. However, this type of lignin is also known for its low extraction yield compared with other processes, especially with softwoods [109]. Consequently, considering all this information and with a perspective of valorization of industrial waste or by-products, the Kraft process seems to be a valuable option for lignin extraction. Indeed, this process provides a high extraction yield and the lignin is extracted from an industrial by-product. The Kraft process is used in the paper and pulp industries, and consists in separating the cellulose from the biomass, producing a by-product: the black liquor containing lignin molecules. Until now, black liquor was used by the industry itself as a source of energy, due to its high calorific value [110]. More than 50 million tons of lignins are extracted every year, but only 5% are used for applications other than energy [111]. However, an estimate predicts an annual lignin production of 225 million tons by 2030, due to the increase in biofuel production [112]. A cost-effective recovery of this by-product is therefore essential for the paper and pulp industries.

The most common lignin modification used in the first part of this work is hydroxymethylation, which involves grafting hydroxyl (OH) groups onto the lignin structure. This modification was carried out with glyoxal as a replacement for toxic formaldehyde. However, the addition of OH groups to the lignin structure can lead to undesired hydrophilicity for this application. Consequently, a new type of modification needs to be investigated. Among existing modifications, silanization was chosen. This reaction involves

grafting silane groups onto the hydroxyl sites of lignin. Indeed, lignin silanization is known to increase the hydrophobicity and thermal resistance of lignin [113].

In this chapter, new formulations were synthesized to bring all the desired properties to the wood. To achieve this, several parameters were modified, and a presentation and characterization of each of the components will be described. Firstly, the characterization of industrially extracted tannin residues will be reported, before presenting the synthesis of new formulations and the properties they provide to the wood. Then, precipitation and characterization of maritime pine kraft lignin will be presented, followed by its modification by the silanization process.

### **III. 1. Characterization of residues from tannins extraction**

Tannins are an important component of lignocellulosic biomass. A description of the structure of tannins is given in section II. 1. 2. The properties of tannins depend on species, tree origin, and age [114]. Thanks to their antifungal and antioxidant properties, they are used in the pharmaceutical and medical fields [84], [115], or as antifungal agents [71] and textile dyes [116]. Moreover, due to their phenolic nature, they can react with aldehydes such as formaldehyde to form highly cross-linked networks [117]. As a result, they are used in the production of adhesives [118]–[121], foams [122]–[124], and resins [93], [125]. Maritime pine tannins, for example, are used for their strong antioxidant activity, and are marketed all over the world under the name Pycnogenol [98]. This product is a nutritional supplement and phytochemical medicine for various diseases. Alternatively, tannins extracted from oak are mainly used in oenology, thanks to their excellent antioxidant activity [126]. They complement the effects of tannins from grape skins and seeds, which provide color stability and aroma protection during wine aging [127], [128].

The extraction of tannins is a process that is being used more and more at industrial level, resulting in large waste production. In the current context, waste management is a crucial issue for companies. Therefore, recovering the by-products of tannin extraction appears to be an effective alternative for reducing the quantity of waste while providing an added value. These by-products, derived from natural resources, could be used to replace synthetic compounds and improve properties in the development of new materials.

In this section, two residues were characterized. The first residue was a by-product obtained after the extraction of maritime pine tannins. Characterization of this residue will enable the determination of the properties that it can bring to a material, and its possible use in resins. A second by-product from the extraction of oak tannins was also characterized. The characterization of these two residues will allow to observe the differences in composition according to the extraction process, but also according to the species (softwood or hardwood).

## III. 1. 1. Experimental procedure

### III. 1. 1. 1. Raw material

The two by-products obtained after extraction of tannins from maritime pine (PR) and oak (OR) were kindly provided by two companies: Biolandes and Biossent respectively. Maritime pine (*Pinus pinaster*) tannins were extracted from bark. First, the company performed a solvent extraction before removing the bark and concentrating the liquid part. PR corresponds to the solid part recovered during filtration of this concentrate. The residue was supplied as a red-brown solid and ground to a powder with a mortar and pestle. The oak residue was extracted from oak heartwood chips (*Quercus robur* and *Quercus petraea* Liebl.). During the tannin recovery process, the residual fraction precipitated to the bottom of the tank, forming a highly viscous paste. This paste was received as is and dried at 50 °C to remove moisture, before being ground with a mortar and pestle to obtain a powder. Figure III-1 illustrates the visual appearance of the by-products received.

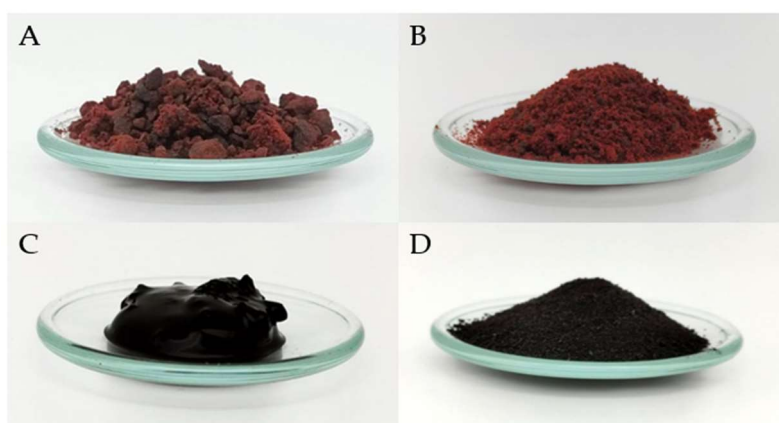


Figure III-1 - Pine residue (PR) as received (A) and after grinding (B). Oak residue (OR) as received (C) and after grinding (D)

### III. 1. 1. 2. Chemical characterization

Firstly, the chemical structure of the by-products was studied using FTIR spectroscopy, the acquisition parameters are provided in the Appendix 1. 1. 1. Then, the chemical composition was studied by determining total phenols, condensed and hydrolysable tannins, extractives, and ash content. The reactivity of tannins was then assessed by determining the Stiasny

number. Residual suberin content and antioxidant activity were also measured. All the protocols used for this chemical characterization are described in Appendix 2. 4.

### III. 1. 1. 3. Thermal characterization

The thermal properties of the residues were assessed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The equipment and analysis parameters are described in Appendix 1. 2.

## III. 1. 2. Results and discussion

### III. 1. 2. 1. Chemical characterization

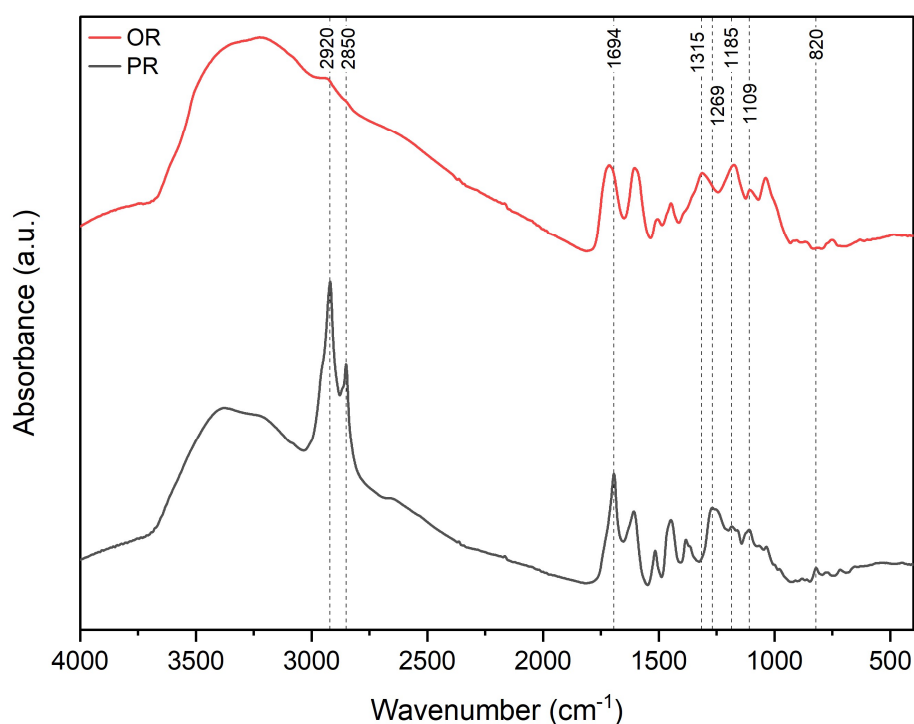


Figure III-2 - FTIR spectra of pine (PR) and oak (OR) residues

Figure III-2 presents the FTIR spectra of the two by-products PR and OR. At first glance, it is clearly possible to observe differences between PR and OR. Two bands at 2920 and 2850  $\text{cm}^{-1}$  are present in both residues, but with a lower intensity for OR. This difference may indicate a smaller number of aromatic methoxyl, methyl, and methylene groups within the structure.



Both compounds also show a band at  $1694\text{ cm}^{-1}$ , corresponding to the possible presence of resin acids providing carboxyl functions. This band is stronger in PR. Another absorption band can be observed at  $1315\text{ cm}^{-1}$  for OR and not for PR. It may be associated to the  $\text{CH}_2$  vibrations of cellulose [129], suggesting a lower amount or even an absence of cellulose in PR. Another study shown that this absorption band was more important for hardwoods than for softwoods [130]. Secondly, the spectrum of PR presents an absorption band at  $1269\text{ cm}^{-1}$ , which is absent in OR. This band corresponds to the presence of guaiacyl nuclei. Considering that softwood lignin contains around 80% guaiacyl nuclei, compared with 40% for hardwood lignin, the absence of this band for OR can be explained by the difference in species. Vibration of the C-O-C bond can be seen in the band at  $1185\text{ cm}^{-1}$  for PR and  $1174\text{ cm}^{-1}$  for OR. A shift towards the lower wavenumbers is also noted for the bands at  $1109\text{ cm}^{-1}$  and  $1105\text{ cm}^{-1}$  for PR and OR respectively. A stronger intensity of these bands can be observed for OR, indicating a higher amount of hemicellulose and cellulose in OR. This shift towards higher wavenumbers was also recorded by another study in the case of softwoods [130]. Table III-1 shows all the wavenumbers and band assignments of the PR and OR spectra.

Table III-1 - FTIR bands and related band assignments

PR	OR	Assignments	References
Band position (cm <sup>-1</sup> )			
3385	3225	OH stretch vibrations of the aliphatic and phenol structures	[98], [131]
2920	2938	CH stretch vibrations of aromatic CH <sub>2</sub> , CH <sub>3</sub> et O-CH <sub>3</sub>	[98], [132]
2850	2840		
1694	1713	C=O vibrations of COOH	[133]
		Hydrolysable tannins	[134]
1607	1604	C=O conjugated to aromatic rings	[135]
1516	1504	C=C of aromatic skeleton	[136]
1447	1446	CH deformations	[98], [134]
1383		C = O, C-H, C-O-C, C-O deformations or stretching	[136], [137]
		deformations of aliphatic -CH of CH <sub>3</sub> groups and OH stretch vibrations of phenolic (common to lignin)	[98]
	1312	CH <sub>2</sub> vibrations of the cellulose	[129]
1269		C = C, C-O stretching or bending	[130], [136]
1185	1174	C = O, C-H, C-O-C, C-O deformations or stretching	[136]
1109	1106		
1036	1037	C-O stretch vibrations	[98]
820		CH of guaiacyl units	[133]

Table III-2 contains all the values obtained during the chemical characterization of the two by-products.

Concerning total phenolic content, a relatively higher amount was observed for OR (624.5 mg GAE/g dry residue for OR compared with 154.5 mg GAE/g of dry residue for PR). In a previous study, higher total phenolic content values were obtained for oak than for pine [138]. In addition, results of the equivalent range were reported by other studies. For example, values between 460 and 675 mg GAE/g of bark extract (extracted with water/ethanol) were measured by Ferreira-Santos and colleagues [134]. Chupin and co-authors [98], on the other

hand, obtained lower values for total phenolic content when analyzing maritime pine extract (between 22 and 62 mg GAE/g of bark). The differences in values observed from one study to another may be due to several factors, such as age or species type. Indeed, one study showed that the quantity of total phenols was also related to the altitude of the tree and its exposure to the sun [139].

The values obtained for the determination of condensed tannins were relatively similar between the two by-products: 116.8 and 112.8 mg EC/g of dry residue for PR and OR respectively. The data obtained are surprising, considering that bark usually contains a higher quantity of condensed tannins than heartwood [140], particularly for conifer bark [141]. However, it should be kept in mind that the residues analyzed in this section were obtained after tannin extraction. Therefore, the previous extraction could be the reason for a similar amount of condensed tannins for PR and OR. On the other hand, it seems important to mention that condensed tannins have better properties and are therefore more widely used than hydrolysable tannins in various fields and applications [142].

Compared to condensed tannins, a lower amount of hydrolysable tannins was observed for PR (25.1 mg TAE/ g of dry residue for PR versus 41.0 mg TAE/ g of dry residue for OR). Another study [143] obtained similar values (26.3 mg TA/g of dry extract) in a hot-water extraction of softwood bark. Furthermore, Bianco and Savolainen reported in their article a difference in hydrolysable tannin composition between hardwood and softwood [144].

The determination of the Stiasny number provides an indication of the reactivity of tannins with aldehydes, including formaldehyde. This data can then be used to predict the ability of the compounds studied to produce phenol-formaldehyde-type resins. In the case of the by-products studied in this section, stiasny numbers of 36.9% and 16.7% were obtained for PR and OR respectively. The required value to admit a correct reactivity of the compound with the aldehyde, and thus produce adequate products, is 65% [145]. This value was not reached in the present study, indicating a low reactivity of by-products towards aldehydes. However, this result could appear quite logical in this case, since the residues were obtained after extraction of the tannins. By assumption, they contained less reactive phenols than the original raw material. The measured stiasny index was therefore in line with the measured tannin content.

The quantity of extractives was determined using a toluene/ethanol (2/1, v/v) solvent mixture. The results obtained indicated a greater quantity of extractives for PR than for OR (50.2% and

13.9% respectively). Studies on *Pinus Pinaster* and *Picea abies* bark found values between 16 and 25% [114], [117]. For hardwoods, and in particular the *Quercus* group, an extractives content between 5 and 6% was obtained [146]. However, the values mentioned in these studies correspond to studies carried out on bark or heartwood directly. The process that the residues were subjected previously probably influenced the final quantity of extractives. Nevertheless, the large difference observed between PR and OR can be explained by the difference in origin. Indeed, it was shown that a greater quantity of extractives is present in the bark than in the heartwood [147], [148].

The level of suberin was also determined during the characterization of these by-products. The results showed a considerably higher amount for PR than OR (50.1 and 3.2% respectively). This major difference was due to the origin of the residues: OR comes from the heartwood, while PR comes from the bark. Indeed, suberin is mainly found in the bark of trees to create a barrier against external aggression, hence a larger amount of suberin in PR [149], [150].

Antioxidant activity was assessed and IC<sub>50</sub> values were calculated for each residue. The value obtained for PR was very close to the value obtained for the commercial antioxidant: BHT (7.37 and 8.03 µg/mL respectively). As a result, PR presented a satisfying antioxidant activity, almost equivalent to BHT. Remarkable antioxidant activity was also reported in an article studying *Picea abies*, where an IC<sub>50</sub> value of 6.3 µg/mL was calculated [114]. In the present study, an even lower value was obtained with OR, which presented an IC<sub>50</sub> value of 2.29 µg/mL, meaning a better radical-scavenging activity than PR and even better than BHT (commercial antioxidant). This antioxidant activity was related to the chemical structure of the compounds. Indeed, one study shown that antioxidant activity is directly proportional to the amount of total phenolic content, and inversely proportional to molecular weight [151]. This assumption can be confirmed here, as OR presents a low molecular weight but a high quantity of total phenolic content.

The mass molecular weight ( $M_w$ ), number molecular weight ( $M_n$ ), and polydispersity ( $\mathcal{D}$ ) were determined. The results showed a relatively low molecular weight, indicating that the polyphenolic chains were degraded during the tannin extraction process. This would also explain the high polydispersity obtained. However, it is possible to observe a higher molar mass for PR than for OR. This result is in line with a study showing that softwood polyphenols have a higher molar mass than hardwoods [152].

Finally, the determination of ash content showed a higher quantity for PR than for OR (2.36 and 0.02% respectively). A study of maritime pine bark reported an ash content of 0.8% [117]. However, a higher ash content is mainly measured in heartwood and sapwood samples, with a lower value in bark samples [114], [153]. The treatment undergone by the compounds during tannin extraction can explain the values obtained in this study.

Table III-2 - Composition of pine (PR) and oak (OR) residues

	Pine residue (PR)	Oak residue (OR)
<i>TPC (mg GAE/g of dry residue)</i>	154.5 ± 4.3	624.5 ± 18.3
<i>Condensed tannins (mg CE/g of dry residue)</i>	116.8 ± 6.9	112.8 ± 9.6
<i>Hydrolysable tannins (mg TAE/g of dry residue)</i>	25.1 ± 1.7	41.0 ± 2.1
<i>Stiasny number (%)</i>	36.9 ± 5.8	16.7 ± 0.7
<i>Ash (%)</i>	0.02 ± 0.02	2.36 ± 0.05
<i>Extractives (%)</i>	50.2 ± 11.8	13.9 ± 4.6
<i>Suberin (%)</i>	50.1 ± 2.8	3.2 ± 0.5
<i>M<sub>w</sub> (g/mol)</i>	3226	1287
<i>M<sub>n</sub> (g/mol)</i>	559	385
<i>Đ</i>	5.77	3.34
<i>IC<sub>50</sub> (μg/mL) (BHT: 8.03 ± 0.13 μg/mL)</i>	7.37 ± 0.01	2.29 ± 0.05

### III. 1. 2. 2. Thermal characterization

The TGA and DTG curves of the two by-products studied are shown in Figure III-3. Around 100 °C, a first mass loss is visible and is associated with water evaporation. This loss is about 8.5% for PR and 5.6% for OR. A second loss of mass is visible from 200 °C for both residues, with a maximum inflection of the DTG curve at 260 °C for PR and 305 °C for OR. This large loss of mass from 260 °C for PR can be due to the presence of suberin. Indeed, other studies associate mass loss between 200 and 300 °C with the presence of suberin [154], [155].

Degradation at lower temperatures for PR can also be explained by the fact that this residue comes from the bark. Similar results were observed by Neiva and colleagues [114], who found that higher extractives content reduced thermal stability, since extractives are easily degraded. In this study, a greater quantity of extractives was observed for PR, which may explain its lower thermal resistance. Between 400 and 550 °C, a third mass loss is observed for OR, and may correspond to lignin decomposition [156]. Overall, the TGA results obtained for these residues demonstrated a better thermal resistance for OR (81.8% mass loss for PR compared with 59.5% for OR at 800 °C). Studies shown that mass loss is generally greater for hardwoods than for softwoods, with a large mass loss below 270 °C [156], [157]. In this study, the difference in origin (bark and heartwood) could explain the inverse phenomenon obtained. Another possible explanation is the high presence of suberin in PR. Indeed, one study showed a mass loss of over 80% of suberin at 470 °C [154].

The DSC thermograms of PR and OR are presented in Figure III-3. For PR, a first endothermic peak can be observed at 10 °C and a second, more notable peak at 40 °C. These two peaks are related to the large amount of suberin present in this compound. Studies analyzing suberin reported similar peaks at 40 °C or 50 °C [154], [158]. The small amount of suberin in OR explained the absence of peaks. Then, at 100 °C, another phase change is visible for both compounds, corresponding to the evaporation of water despite an initial heating cycle until 105 °C to remove it. The curve associated to OR then shows a visible peak around 150 °C, which could be associated with the start of hemicellulose degradation. The fact that this degradation is not visible in PR curve is consistent with the results obtained by FTIR indicating an absence or a small amount of hemicellulose and cellulose in PR.

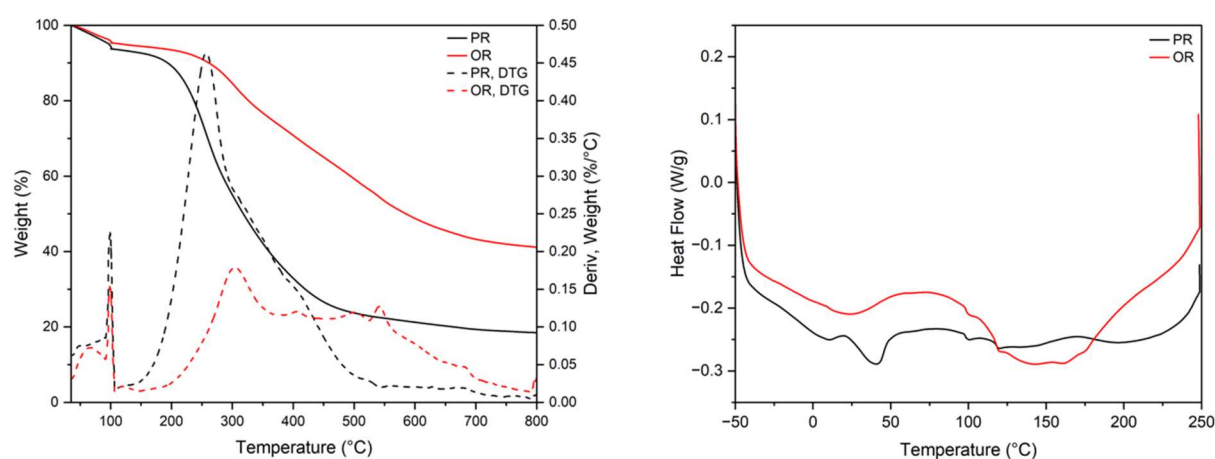


Figure III-3 - TGA, DTG (left), and DSC (right) curves of pine (PR) and oak (OR) residue

### III. 1. 3. Conclusion

In this section, a complete chemical and thermal characterization was carried out on two by-products obtained by companies during tannin extraction. The first residue (PR), derived from *Pinus Pinaster* bark, exhibited a large amount of suberin, providing a hydrophobic character. In addition, this compound also displayed antioxidant activity comparable to antioxidant currently available on the market. Such properties allow this by-product to be used in a variety of applications, as an additive in the development of hydrophobic coatings or wood adhesives. The high content of extractives and the antioxidant activity of this residue also suggest its use in cosmetics and pharmaceuticals. The results obtained for the second by-product (OR), derived from oak heartwood (*Quercus robur* and *Quercus petraea* Liebl.), showed the presence of a large number of phenolic groups, as well as antioxidant activity superior to commercial antioxidant. Moreover, analysis of this compound also demonstrated a thermal stability. As a result, this compound could be used as a raw material in the development of bioactive compounds or biosourced materials.

## III. 2. Lignin obtention and purification

The valorization of black liquor produced by the paper and pulp industries has become a major issue, considering the significant amounts of these by-products expected in the future. Extracting lignin from this industrial by-product seems to be one of the best ways to valorize it. Indeed, lignin is one of the rare polymers with aromatic chains, and presents properties such as thermal stability, a carbon-rich composition, and high biodegradability [159]. The extraction and valorization of lignin could therefore become an important process in the development of new sustainable chemical products.

Precipitation and ultrafiltration are the two main methods for extracting lignin from black liquor [160]. Precipitation is achieved by reducing pH with the addition of acid or carbon dioxide (CO<sub>2</sub>). The addition of CO<sub>2</sub> is mainly used in the innovative LignoBoost process, which produces high-purity lignin. In this process, the pH of the black liquor is first reduced by CO<sub>2</sub> to a pH of 8-9. A second pH reduction is then carried out with the addition of sulfuric acid [161]. The main precipitation processes, LignoBoost and others, mainly use sulfuric acid to lower the pH of the black liquor. However, given current environmental conditions, the use of this strong acid is being challenged. In addition to presenting environmental and human health risks, precipitating lignin with this acid can lead to the release of toxic gases such as hydrogen sulfide (H<sub>2</sub>S) and/or sulfur dioxide (SO<sub>2</sub>) [162]. Consequently, new, greener, and less hazardous alternatives need to be investigated. Research shown that precipitating lignin with organic acids can produce lignin with a lower percentage of impurities and at a lower cost [162]. The use of this type of acid therefore appears to be a suitable alternative. A study by Da Silva and colleagues [163] presented the characteristics of lignins precipitated with citric, acetic, and lactic acid from a hardwood industrial black liquor. The different types of lignin obtained in this work showed a better antioxidant activity than commercial antioxidants, as well as better purity than lignin precipitated with sulfuric acid. In addition, another study [164] precipitated lignin with acetic, citric, and oxalic acids. Better purity was also demonstrated in this study, but in low yield. Although these studies have provided an alternative to lignin precipitation, this line of research requires further investigation.

This chapter is devoted to the characterization of a softwood black liquor, followed by lignin precipitation using various organic acids: acetic, citric, lactic, malic, and oxalic. The precipitated lignins were then thoroughly characterized. This work is based on the work of Da Silva and co-authors [163] mentioned above, exploring new acids and new characterization



techniques. The main objective of this research is to produce high-quality lignin by valorizing industrial by-products while respecting the context of sustainable chemistry.

### **III. 2. 1. Experimental procedure**

#### **III. 2. 1. 1. Raw material and reagents**

The industrial black liquor (BL) used in this study was obtained by the kraft process on maritime pine (*Pinus pinaster*) and was kindly donated by Gascogne Papier, France.

The reagents employed in this part were sulfuric acid 96%, oxalic acid 99%, malic acid 99%, and citric acid 99% obtained from Thermoscientific. Lactic acid was purchased from Honeywell while acetic acid was bought from Fischer Scientific. Finally, hydrochloric acid 37% was obtained from Acros Organics.

#### **III. 2. 1. 2. Black liquor characterization**

Firstly, the black liquor was subjected to a complete characterization. For this, density, total solids content (TDS), FTIR, ash content, and TGA were carried out. In addition, to determine the percentage of acid-insoluble lignin, acid-soluble lignin, and carbohydrates, the black liquor was also subjected to quantitative acid hydrolysis (QAH).

All the above-mentioned characterizations are presented in Appendix 2. 1.

#### **III. 2. 1. 3. Lignin precipitation using organic acids**

The precipitation of lignin was performed using five different organic acids: acetic, citric, lactic, malic, and oxalic. Sulfuric and hydrochloric acids, widely used in industrial lignin production, were also used for comparison. The acids were added to the BL until the pH reached and was stable at 2. Solid acids (citric, malic, and oxalic) were poured directly into the BL using a spatula, while liquid acids (acetic, lactic, sulfuric, and hydrochloric) were added using a burette. The pH was controlled throughout the reaction using a pH meter maintained in the solution. The schematic experiment is illustrated in Figure III-4. The total amount of each acid added to achieved a pH 2 was noted for acid quantity comparison. The sample were then vacuum filtrated and washed with distilled water until neutralization. The precipitated lignin was oven dried at 50 °C until a constant weight, noted for yield determination. The

lignin from acetic, citric, lactic, malic, oxalic, sulfuric, and hydrochloric acids were identified by the following codes AL, CL, LL, ML, OL, SL, and HL, respectively.

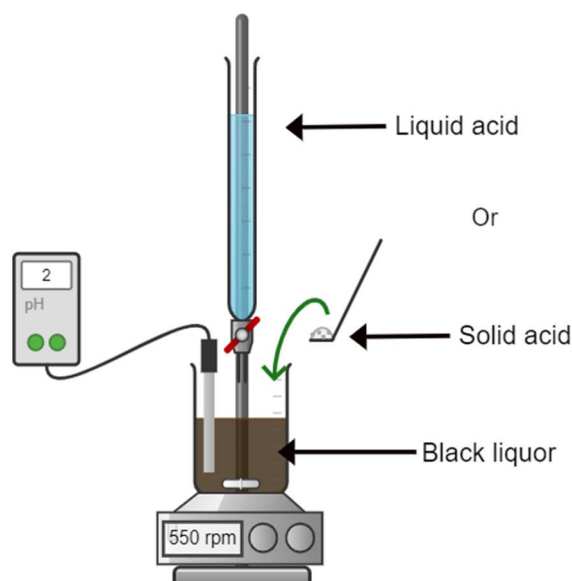


Figure III-4 - Schematic representation of the system

### III. 2. 1. 4. Lignin characterization

The lignins recovered were evaluated in terms of yield, followed by characterization using various techniques to assess the quality of the lignin obtained by the different acids.

#### Chemical characterization

Chemical characterizations were first carried out using FTIR, determining total phenol content, or average molar masses using steric exclusion chromatography (SEC). Antioxidant activity was also assessed, as well as ash content. Finally, as for BL, quantification of acid-soluble lignin content, acid-insoluble lignin content, and carbohydrates content were calculated using QAH.

All the protocols and equipment used for these characterizations are presented in Appendix 2. 2.

#### Thermal characterization

For thermal characterization, TGA and DSC were performed. As for the other characterizations, the equipment and analysis conditions are described in Appendix 1. 2.

## III. 2. 2. Results and discussion

### III. 2. 2. 1. Black liquor characteristics

The characteristics of black liquor depend on the process employed by the paper industry and the species of wood used. Table III-3 presents the data obtained from the characterization of this black liquor. First, the density of the BL was around 1.14 with a pH between 12.0 and 13.5. QAH demonstrated that BL was composed of  $27.3 \pm 0.36\%$  of acid-insoluble lignin (AIL) that could be precipitated by lowering the pH. This value will be used as a reference to calculate the precipitation yield.

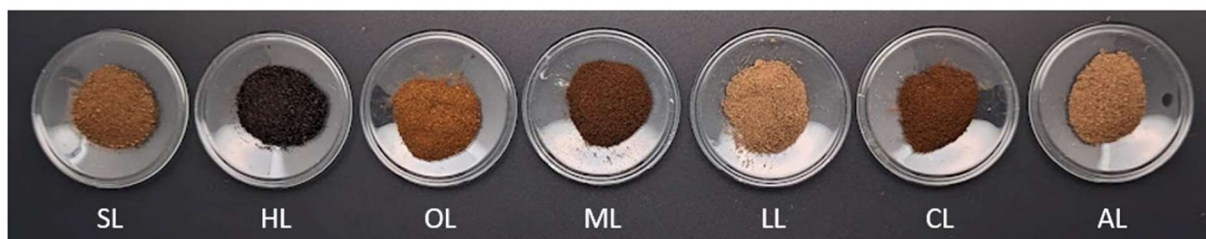
Table III-3- Characteristics of black liquor

<i>Density</i>	$1.14 \pm 0.00$
<i>pH</i>	$12.77 \pm 0.46$
<i>Total dry solid (%)</i>	$21.89 \pm 0.06$
<i>Acid soluble lignin (%)</i>	$6.66 \pm 0.04$
<i>Acid insoluble lignin (%)</i>	$27.31 \pm 0.36$
<i>Carbohydrates (%)</i>	$10.97 \pm 0.13$
<i>Ash (%)</i>	$47.16 \pm 0.85$
<i>Volatiles (%)</i>	$27.13 \pm 0.31$
<i>Fixed carbon (%)</i>	$21.71 \pm 1.47$

### III. 2. 2. 2. Lignin characteristics

The reaction time to reach a pH of  $2.0 \pm 0.2$  varied according to the acids used, typically between one and two hours.

Filtration was also observed to be influenced by the type of acid used. Filtration was longer with lactic acid and citric acid, while it was faster with oxalic acid. A similar observation was made by Da Silva and collaborators in their work [163]. In addition, depending on the acid used, color differences were observed between the lignins obtained. These differences can be seen in Figure III-5.



*Figure III-5 - Lignins precipitated with different acids leading to different colors*

After filtration and neutralization, it was possible to calculate the yield of precipitated lignin, which is presented in Figure III-6 together with the amount of acid used for each precipitated lignin. Like mentioned before, the yield was calculated in relation to the amount of AIL obtained during BL characterization. Using the same conditions, similar yields were obtained whether lignin was precipitated with organic or inorganic acids. However, the amount of acid needed to reach pH 2 was different. Indeed, a larger quantity was required in the case of organic acids. Oxalic acid, for its part, required a smaller quantity of acid and provided a high yield. Acetic acid, on the contrary, involved the largest quantity of acid, while the yield obtained was lower. It can be assumed that these differences were related to the strength of the acid. Acids with a low pKa are generally classed as strong, so a smaller amount of acid is needed to lower the pH. The strength of acids according to pKa is as follows: hydrochloric, sulfuric, oxalic, citric, malic, lactic, and acetic acids. The amounts of acid used in this study correspond to this order, with the exception of sulfuric acid and hydrochloric acid, which were reversed. According to two other studies [165], [166], the yield is related to the type of acid used: monoprotic, diprotic, or triprotic. A higher yield is obtained when the acid has more protons to release. For example, a triprotic acid with 3 protons will lead to a higher yield than a monoprotic acid with only one proton. In the present study, this hypothesis was not entirely respected, as precipitation with citric acid (triprotic) did not provide a better yield than precipitation with oxalic acid (diprotic) or hydrochloric acid (monoprotic). Another study [164] precipitated lignin with oxalic, acetic, citric, and sulfuric acids, and obtained a higher yield with citric acid. They obtained a value of 10.91 g/100 mL of black liquor, compared with 7.45 g/100 mL in the present study.

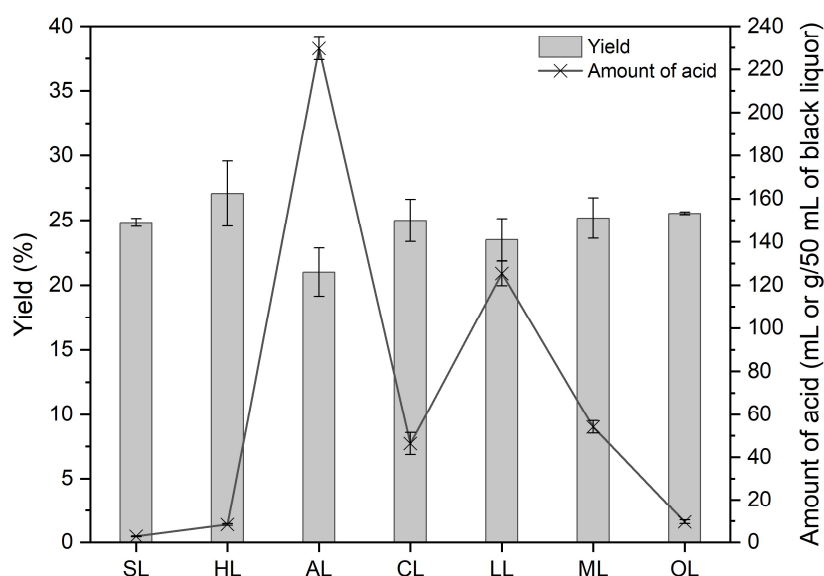


Figure III-6 - Lignin precipitation yields and amount of acid used

### Chemical characteristics

FTIR spectra of precipitated lignins and black liquor were recorded and are shown in Figure III-7. This technique allows the determination of the main functional groups and thus contributes to the identification of the complex structure that is lignin. The band between 3700 and 3000  $\text{cm}^{-1}$  is associated to the stretch vibrations of aliphatic, phenolic, and aromatic hydroxyl groups [167]. A difference of intensity in this band indicates a different hydroxyl group content in the lignins, but can also be explained by a different moisture content. Even if the conditioning of the lignins was the same, moisture absorption can differ according to the structure of the lignin. Then, all samples show bands around 2940 and 2840  $\text{cm}^{-1}$  related to symmetrical and asymmetrical C-H stretching of the methyl and methylene groups, respectively. In the case of black liquor, this is more a shoulder than a band at 2840  $\text{cm}^{-1}$ , and the same phenomenon is observed in lignins precipitated with inorganic acids (SL and HL). Da Silva and colleagues [163] observed the same phenomenon. The band associated to C=O stretching of non-conjugated carboxylic acids is present at 1715  $\text{cm}^{-1}$  in the spectra of precipitated lignins, but not in the BL spectrum. The vibration of the C=C bond of the aromatic skeleton is visible through the bands present at 1600 and 1510  $\text{cm}^{-1}$  [135], [166]. A shift of these two bands towards lower wavelengths is visible for the black liquor. Then, between 1460 and 1400  $\text{cm}^{-1}$ , two other small bands appear and may correspond to the C-H deformation in  $-\text{CH}_3$

and  $\text{-CH}_2$ , while the absorbance band at  $1365\text{ cm}^{-1}$  can be assigned to the C-H bond of the  $\text{-CH}_3$  groups of the syringyl unit. This band is slightly more pronounced for lignins precipitated with organic acids. Two new bands at  $1268$  and  $1210\text{ cm}^{-1}$  are assigned to C=O, C-O bonds, and aliphatic hydroxyl groups respectively [79]. The bands between  $1150$  and  $1060\text{ cm}^{-1}$  correspond to the stretching of C-O bonds. Finally, a band at  $1030\text{ cm}^{-1}$  can be observed in all samples except BL and SL and is attributed to the deformation of C-H bonds in syringyl rings [167].

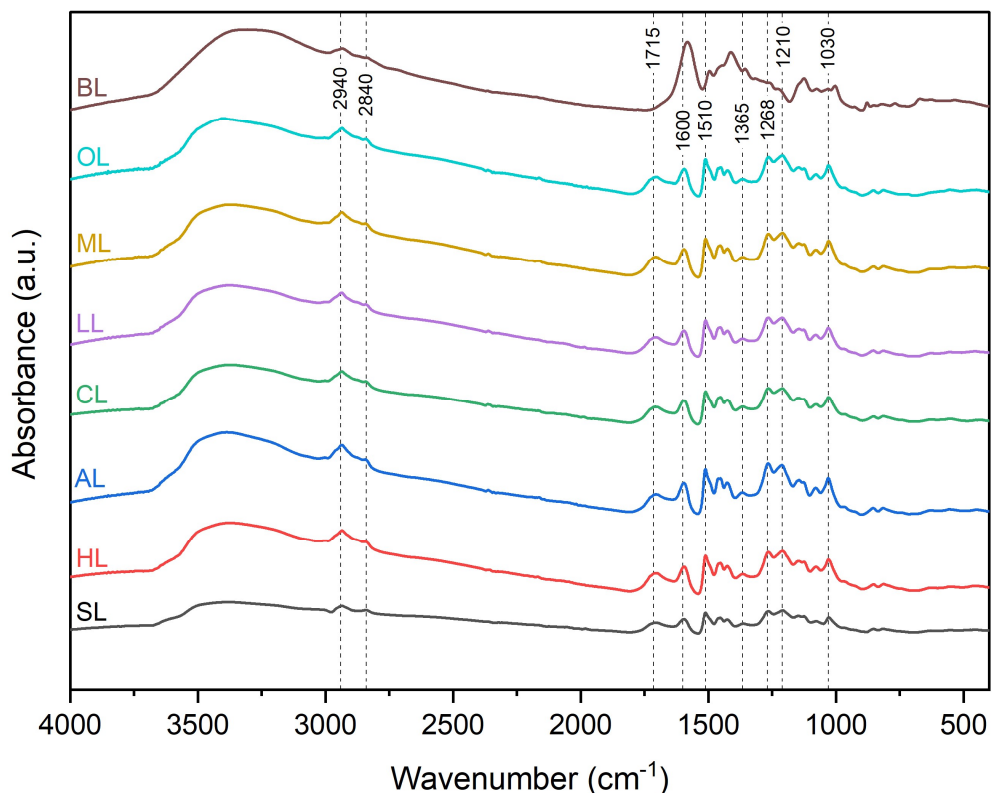


Figure III-7 - FTIR spectra of lignins and black liquor from  $4000$  to  $400\text{ cm}^{-1}$

The results of the determination of total phenolic content and the number of moles of hydroxyl per gram of precipitated lignin are presented in Table III-4. Although the values obtained were not really widely different, it is nevertheless possible to observe a greater quantity of total phenols for lignins precipitated with organic acids. This result indicates a greater number of hydroxyl sites within their structure and, consequently, a greater reactivity of the lignin. In their work, Da Silva and co-authors [163] suggested that the use of a strong acid during precipitation resulted in a lower content of total phenols. The results obtained in this study do not verify this hypothesis.

The antioxidant activity of lignins was studied and the calculated IC<sub>50</sub> values are reported in Table III-4. Similar values can be observed between lignins precipitated with organic acids and those precipitated with inorganic acids; the values varying between 27.35 and 36.82 µg/mL. As explained in the protocol, the IC<sub>50</sub> values of two commercial antioxidants (BHT and Trolox) were also determined. The values measured were 7.76 ± 0.12 and 5.78 ± 0.04 µg/mL for BHT and Trolox, respectively. It should be remembered that a low IC<sub>50</sub> value means that only a small amount of compound is required to exhibit effective antioxidant activity. Consequently, the results obtained show that the lignins precipitated in this work exhibit lower antioxidant activity than commercial antioxidants. Moreover, among the values calculated, SL was the lignin with the highest IC<sub>50</sub> value (36.82 ± 1.17 µg/mL). As a result, precipitation with organic acids slightly led to an improvement of this parameter. According to some studies [151], [168], the antioxidant activity of lignin is proportional to the quantity of methoxyl and phenolic hydroxyl groups present in the structure and inversely proportional to the quantity of aliphatic hydroxyl groups, polydispersity, and their molecular weight. In the case studied here, this trend cannot be observed. Furthermore, the IC<sub>50</sub> values calculated were not similar to those presented by Da Silva and colleagues [163] for the same acids. These variations could be explained by differences in the type of black liquor used or the reaction time. In their work, they used hardwood black liquor, and precipitation occurred over 24 h, compared with 1 to 2 h in this study.

Steric exclusion chromatography (SEC) was used to determine the average molar mass and polydispersity of each precipitated lignin. The results are listed in Table III-4. M<sub>n</sub> varied between 2042 and 3148 g/mol while M<sub>w</sub> varied between 14024 and 17358 g/mol. The process used (kraft) by the paper industry is the main reason for these low molecular weight values. Indeed, during the cooking stage of the Kraft process, β-aryl bonds are cleaved, resulting in low molecular weights [169]. However, the values obtained remain within the range reported in the literature. Indeed, overall, the number-average molar mass (M<sub>n</sub>) of kraft lignins is between 1000 and 3000 g/mol [80]. The strength of the acid is also a phenomenon that must be considered when analyzing molecular weights. A strong acid will allow the cleavage of a greater number of bonds, leading to lower molecular weights. This phenomenon can be observed for some of the lignins precipitated in this work. SL obtained after precipitation with sulfuric acid (strong acid) had lower M<sub>w</sub> and M<sub>n</sub> values than AL precipitated with acetic acid (weak acid). It can also be observed that the values obtained in this study were higher than those reported by Da Silva and co-authors [163]. This difference can be explained by the type

of species studied. Hardwoods are composed of guaiacyl (G) and syringyl (S) units, while softwoods are mainly composed of G units [80]. Since G units can create non-cleavable C-C bonds during the Kraft process, higher molecular weights can be observed for softwoods [170], [171]. A high polydispersity was observed for precipitated lignins, from 5.51 to 6.87, indicating a wide molecular weight range.

Quantitative acid hydrolysis was carried out to assess lignin purity. Values of acid-soluble lignin (ASL), acid-insoluble lignin (AIL), and carbohydrates are listed in Table III-4. SL had the lowest AIL value (77.66%, compared with over 85% for the other precipitated lignins). In terms of carbohydrates content, the lowest values were observed for SL and CL. However, considering that the values for all lignins were between 3.04 and 3.76%, the difference was not considerable. Consequently, it can be stated that the purity of precipitated lignins with organic acids was comparable or even better than lignin precipitated with sulfuric acid. Among the organic acids, LL had the lowest purity (86.25% of lignin) and OL the highest (93.7% of lignin). Yasuda et collaborators [172] explained that ASL was composed of low-molecular-weight degradation products and hydrophilic derivatives of lignin. Furthermore, it was mentioned above that the use of a weak acid leads to high-molecular-weight molecules. Consequently, the lower ASL values for LL, AL, and ML can be explained by the strength of the acid used. Lactic, acetic, and malic acids are considered as weak acids, leading to higher molecular weights.

The levels of ash, volatiles, and fixed carbon were determined; these parameters have an impact on lignin purity. A low ash content results in a higher lignin purity. The results obtained are listed in Table III-4. The first observation concerns the large difference in ash content between SL and the lignins precipitated with organic acids (3.28% for SL versus less than 0.50% for the others). This difference in ash content may be due to the possible presence of sulfur and the salt formation during precipitation with sulfuric acid. Precipitation with organic acids resulted in ash content comparable to lignins obtained by the LignoBoost process. Indeed, a study [161] showed that this process produced high-purity lignins with an ash content between 0.3 and 1.2%. A high fixed carbon content was measured (over 47%), enabling the lignins obtained to have suitable characteristics for use as precursors for carbon-based products [163].



Table III-4 - Results of lignins characterization

	SL	HL	AL	CL	LL	ML	OL
<b><i>g of lignin obtained/100 mL of black liquor</i></b>	7.41 ± 0.09	8.07 ± 0.75	6.26 ± 0.56	7.45 ± 0.32	7.01 ± 0.49	7.62 ± 0.39	7.62 ± 0.03
<b><i>Total phenolic content (µg GAE/g dry lignin)</i></b>	285.01 ± 25.40	333.40 ± 12.33	298.38 ± 7.74	336.34 ± 1.30	348.39 ± 8.77	331.84 ± 10.17	331.84 ± 32.51
<b><i>OH content (mmol OH/g dry lignin)</i></b>	0.67 ± 0.06	0.78 ± 0.03	0.70 ± 0.02	0.79 ± 0.00	0.82 ± 0.02	0.78 ± 0.02	0.73 ± 0.08
<b><i>IC<sub>50</sub> (µg/mL)</i></b>	36.82 ± 1.17	28.72 ± 0.32	27.35 ± 0.24	29.95 ± 0.34	31.93 ± 0.35	32.65 ± 0.09	32.50 ± 0.91
<b><i>AIL (%)</i></b>	77.66 ± 7.63	90.87 ± 0.61	89.76 ± 0.40	90.35 ± 1.01	85.20 ± 5.24	92.00 ± 0.99	92.43 ± 0.20
<b><i>ASL (%)</i></b>	1.68 ± 0.06	1.63 ± 0.04	0.65 ± 0.09	1.77 ± 0.33	1.05 ± 0.13	1.11 ± 0.17	1.27 ± 0.05
<b><i>Carbohydrates (%)</i></b>	3.25 ± 0.13	3.58 ± 0.02	3.76 ± 0.11	3.04 ± 0.02	3.37 ± 0.25	3.53 ± 0.13	3.38 ± 0.09
<b><i>M<sub>n</sub> (g/mol)</i></b>	2042	2781	3012	2667	2875	3148	2770
<b><i>M<sub>w</sub> (g/mol)</i></b>	14024	15415	17130	16025	16160	17358	15620
<b><i>Đ</i></b>	6.87	5.54	5.69	6.01	5.62	5.51	5.64
<b><i>Ash (%)</i></b>	3.28 ± 0.07	0.31 ± 0.04	0.17 ± 0.02	0.32 ± 0.02	0.10 ± 0.02	0.49 ± 0.02	0.45 ± 0.03
<b><i>Volatiles (%)</i></b>	44.83 ± 1.20	45.56 ± 1.27	45.13 ± 0.27	48.16 ± 0.73	40.49 ± 2.86	52.14 ± 2.55	46.02 ± 0.91
<b><i>Fixed carbon (%)</i></b>	51.53 ± 1.35	52.71 ± 1.51	54.08 ± 0.64	51.07 ± 0.38	54.95 ± 2.3	52.14 ± 2.55	47.60 ± 0.87
<b><i>Ash determined by TGA (%)</i></b>	2.07	4.01	1.09	0.77	3.73	1.36	0.97

### Thermal characteristics

Thermogravimetric analysis (TGA) under nitrogen was carried out to assess the thermal resistance of precipitated lignins. The TGA and DTG curves obtained are shown in Figure III-8. An initial loss of mass can be observed from 50 °C, with a peak at 100 °C, corresponding to moisture evaporation. This loss is more notable for SL. A second mass loss is visible between 150 and 185 °C and is probably due to the dehydration of OH benzyl groups and the presence of fatty acids. Then, another peak is observable on the DTG curves at around 250 °C and is associated with the fragmentation of the  $\beta$ -aryl and  $\alpha$ -aryl inter-unit bonds. This mass loss is almost invisible to AL. At 395 °C, the main mass loss occurs and corresponds to the cleavage of methyl-aryl-ether bonds. In ascending order, the mass loss of the various precipitated lignins is as follows: LL, CL, OL, SL, HL, ML, and AL. It continues until 500 °C, with a weight reduction of around 48% for all samples. When the temperature exceeded 500 °C, decomposition and condensation reactions of the aromatic rings occurred. The final residual weight was between 38 and 43%.

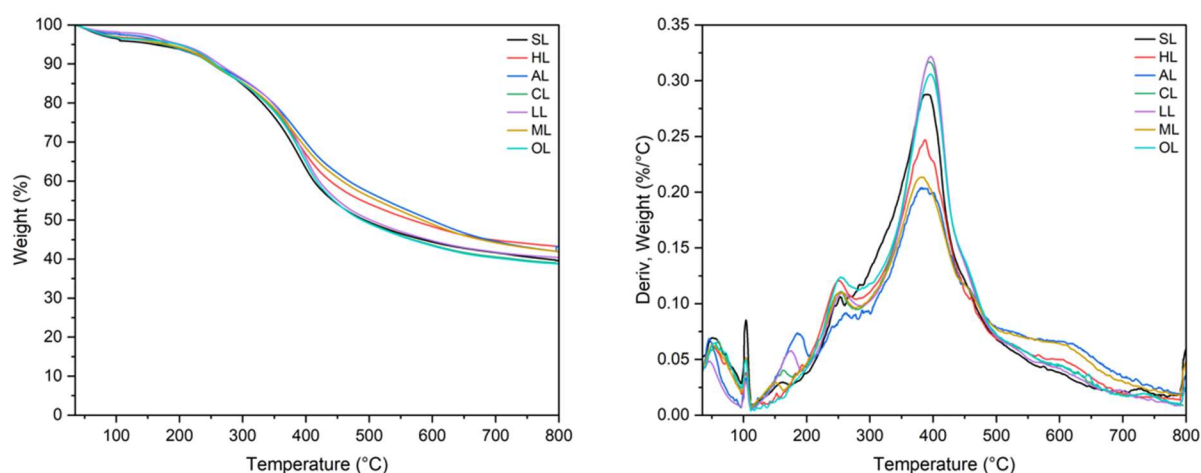


Figure III-8 - TGA (left) and DTG (right) curves of precipitated lignins

### III. 2. 3. Conclusion

This part of chapter III presented the precipitation of lignin from maritime pine black liquor. To limit the use of the toxic sulfuric acid ( $\text{H}_2\text{SO}_4$ ) mainly used during the precipitation phase,  $\text{H}_2\text{SO}_4$  was replaced by organic acids (acetic, citric, lactic, malic, and oxalic). The various lignins obtained were subjected to chemical and thermal characterization to compare the overall

properties and structural characteristics of a lignin precipitated with an inorganic or organic acid. The results showed that the use of organic acids generally produced lignin of higher purity and with higher yield than when  $\text{H}_2\text{SO}_4$  was used. Furthermore, a correlation between acid strength and molecular weight was observed, with a decrease in molecular weight when using strong acids such as  $\text{H}_2\text{SO}_4$ . Lignins precipitated with organic acids also exhibited a greater number of hydroxyl groups, favoring their reactivity towards other compounds. Therefore, the use of organic acids for lignin precipitation appears to be a suitable alternative to reduce the use of  $\text{H}_2\text{SO}_4$ .

### **III. 3. Modification with silane**

To improve the properties of the lignin precipitated in the previous section, lignin was silanized. This involves the addition of silane groups to the hydroxyl groups (OH) of lignin. This modification enhances the mechanical properties, thermal and chemical stability, and hydrophobicity of lignin [173], [174]. In addition, a number of studies have shown that silane can act as a crosslinker, promoting interfacial adhesion between polymers and inorganic fillers or solids [174]–[176]. For example, Devadasu and colleagues [177] developed a single-layer coating with better properties than a two-layer coating. The film created was relatively thick so it did not run and enhanced surface protection properties. Another study by Heo and co-workers [178] demonstrated an improvement in the thermal stability of lignins modified with different amino-silanes.

In this section, a presentation of an initial lignin modification was carried out using a protocol already published in the literature will be presented. This first modification provided an opportunity to observe the performance that this kind of modification could bring to the lignin. It should be noted that this first modification was carried out during a two-week stay at the InnoRenew CoE laboratory in Slovenia. As a result, the lignin and silane used were chosen due to the availability of the host laboratory. Trichlorododecylsilane was used for this modification. A second modification was then studied and developed with a more environmentally friendly solvent. This modification will be also presented in this section. This second modification was developed in the laboratory of Biorefinery Processes BioRP research group at the University of the Basque Country in Spain during a three-month stay. The silane used in this case was the 3-aminopropyltriethoxysilane (APTES).

#### **III. 3. 1. Lignin and residue silanization with trichlorododecylsilane**

##### **III. 3. 1. 1. Experimental procedure**

###### Raw material and reagent

The lignin used in this section was an industrial kraft softwood lignin (*Picea abies*). Lignin modification was carried out using trichlorododecylsilane obtained from Sigma Aldrich and toluene purchased from Fischer Scientific.

## Protocol

The modification of kraft lignin (KL) with silane was based on the protocol written by Torun and co-authors, with some modifications [179]. First, 2 g of kraft lignin were solubilized in 40 mL of toluene. The mixture was placed under stirring for 1 night to ensure a proper solubilization of the lignin. Then, 1 g of trichlorododecylsilane was slowly added to the solution. The mixture was stirred at 450 rpm for 3 h before being centrifuged for 15 min at 3000 rpm to remove unreacted silane molecules. The sediment corresponding to the modified lignin was recovered and dried at 50 °C in an oven for 24 h.

Given that the maritime pine (PR) residue contains polyphenols according to the characterization carried out previously, the modification with trichlorododecylsilane was also conducted on this residue. The same protocol was followed as for lignin.

LKm and PRm correspond respectively to KL and PR modified with trichlorododecylsilane.

## Characterizations performed

FTIR analyses were carried out to verify the success of the modification. Parameters used to perform this analysis are presented in Appendix 1. 1. 1.

### **III. 3. 1. 2. Results and discussion**

Only bands varying from one sample to another are presented in the following. Assignments of the other bands are listed in parts III. 2 and III. 1 for lignin and pine residue (PR), respectively.

The spectra of kraft lignin (KL) and of the extraction residue (PR) are shown in Figure III-9. In the case of lignin, it is possible to see an increase or apparition of bands at 2923 and 2850  $\text{cm}^{-1}$  corresponding to the vibration of the  $\text{CH}_3$  groups introduced into the lignin structure during silanization [179]. Then, an increase in the bands between 1200 and 950  $\text{cm}^{-1}$  is visible for LKm and PRm. These different bands correspond to the formation of Si-O-Si and C-O bonds during the modification process [173], [178], [180]. A weak band at 732  $\text{cm}^{-1}$  is also observed for both compounds and can be associated to the Si-C bond [173], [178]. Finally, the bands at 815 and 692  $\text{cm}^{-1}$  are accentuated after PR modification. These bands correspond to the Si-O-C and Si-O-Si bonds respectively, indicating a chemical interaction between lignin and silane [173], [178], [181], [182].

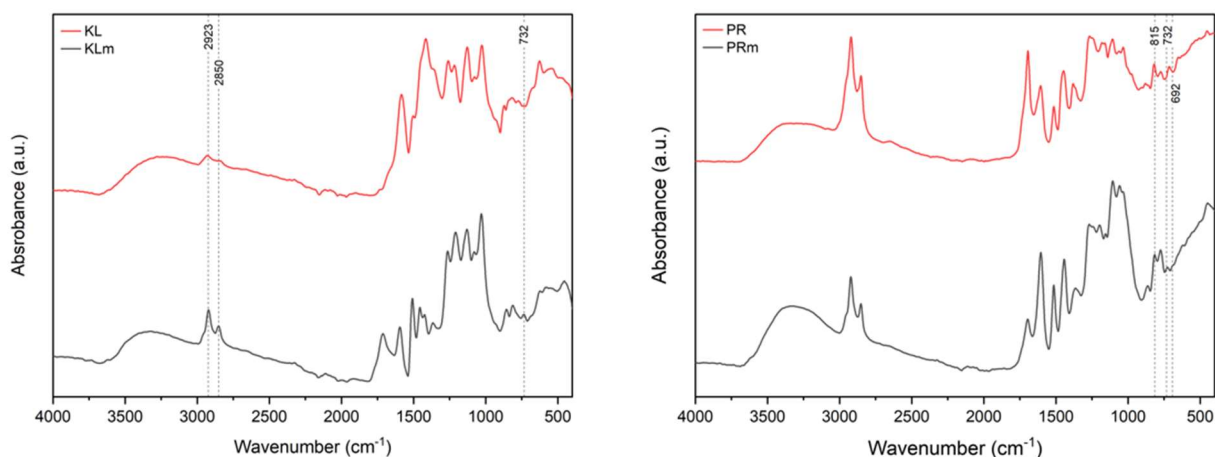


Figure III-9 - FTIR spectra of kraft lignin (KL) before and after modification (KLM) (left), and maritime pine residue (PR) before and after modification (PRm) (right)

All these observations suggest that these compounds were successfully modified with trichlorododecylsilane. Indeed, the formation or enhancement of bands such as CH<sub>3</sub> groups, Si-O-Si bonds, and Si-O-C bonds indicate the incorporation of silane molecules into the lignin structure.

Although spectral differences were observed in this study, further characterization would be required to confirm this modification. However, the aim was to carry out an initial modification of the lignin to assess the properties it could bring to the lignin and, consequently, to the final material. A modification of the protocol used here to make it more environmentally friendly was carried out with further characterization.

### III. 3. 2 Lignin silanization with 3-aminopropyltriethoxysilane (APTES)

The silanization process is usually carried out by mixing silane in toluene [173], [178], [179]. However, toluene is a compound that can be mutagenic, carcinogenic, and reprotoxic. To maintain a respectful approach to the environment and human health, the need to replace this solvent with a greener one was highlighted. Studies [174], [176] successfully modified lignin using ethanol as a solvent, either combined with water or alone. This solvent is necessary for silane hydrolysis. Indeed, silane needs to be hydrolyzed before reacting with the hydroxyl sites on lignin. As silanol is not stable, self-condensation reactions can occur. The mechanisms of hydrolysis and self-condensation are shown in Figure III-10. Silane hydrolysis can be carried out in an acidic [183], basic [184], or neutral [185] environment to catalyze the reaction.

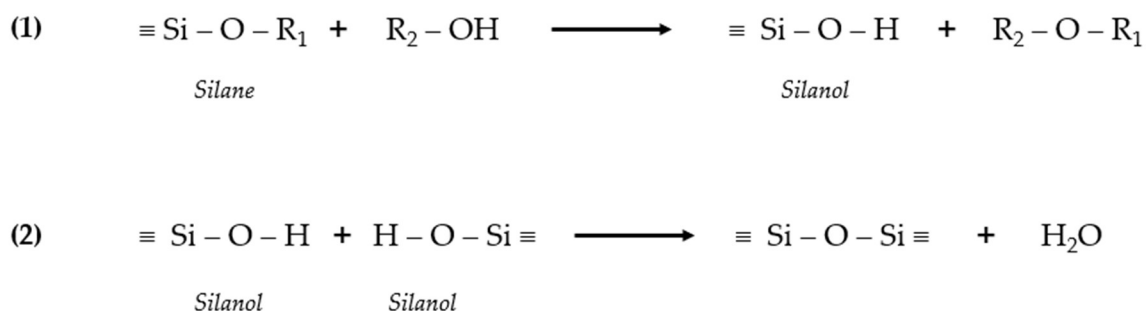


Figure III-10 - Mechanism of silane hydrolysis (1) and silanol self-condensation (2)

In this section, 3-aminopropyltriethoxysilane (APTES) was selected as silane firstly because studies successfully modified lignin with this silane. Moreover, thanks to its structure presented in Figure III-11, chemical modification using this compound enables lignin to be silanized and aminated in one step.

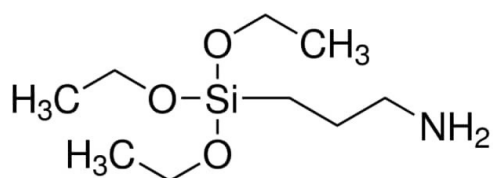


Figure III-11 - 3-aminopropyltriethoxysilane (APTES) molecule

The first part of this section will be dedicated to the study of silane hydrolysis in different ethanol/water ratios as solvent. Then, the various lignin modifications carried out will be presented.

Finally, characterization techniques used to determine the modification or non-modification of these lignins will be presented.

### III. 3. 2. 1. Silane hydrolysis

#### Experimental procedure

##### Raw material and reagents

The reagents used in this section were ethanol purchased from Fischer Scientific, 3-aminopropyltriethoxysilane (APTES), acetic acid, and sodium hydroxide obtained from Sigma Aldrich.

### Hydrolysis protocol

Silane hydrolysis was carried out using solutions with different ethanol/water ratios. As previously mentioned, this reaction may require the use of a catalyst. Therefore, an acid or basic catalyst was added to solutions to study the influence. The acid and base catalysts used were acetic acid and sodium hydroxide (NaOH) respectively. All the characteristics of the solutions prepared to study acid hydrolysis are listed in Table III-5.

For sample preparation, 25  $\mu\text{L}$  or 75  $\mu\text{L}$  of acetic acid or NaOH (1 M) solution respectively was added to the solvent. Then, 5% (v/v) of APTES by volume of solvent was added.

### Characterization of silane hydrolysis

The solutions prepared in this section were analyzed by FTIR after 15 min, 2 h, 5 h, and 24 h to follow the reaction. Analysis acquisition parameters are detailed in Appendix 1. 1. 1.

Table III-5 - Solutions prepared to study silane hydrolysis

Solutions	Catalyst		Ethanol/Water ratio
	Acid	Basic	
<i>EW10-A</i>	X		100/0
<i>EW10-N</i>			
<i>EW10-B</i>		X	
<i>EW82-A</i>	X		80/20
<i>EW82-N</i>			
<i>EW82-B</i>		X	
<i>EW55-A</i>	X		50/50
<i>EW55-N</i>			
<i>EW55-B</i>		X	
<i>EW28-A</i>	X		20/80
<i>EW28-N</i>			
<i>EW28-B</i>		X	
<i>EW01-A</i>	X		0/100
<i>EW01-N</i>			
<i>EW01-B</i>		X	



## Results and discussion

All FTIR spectra of APTES hydrolysis solutions are shown in Figure III-13. In this figure, only the bands varying from one solution to another are shown, i.e. in the wavenumber range between 1120 and 840  $\text{cm}^{-1}$ . During the reaction, an increase in three bands characteristic of silane hydrolysis can be seen for solutions EW55, EW28, and EW01, with a clearer increase for EW01. These bands are located around 1087, 1047, and 880  $\text{cm}^{-1}$ . Those around 1087 and 1045  $\text{cm}^{-1}$  are associated with the vibration of the C-C-O skeleton of ethanol [186], but also with the vibration of Si-O-C and Si-O-Si bonds [184]. These bands are overlapping, creating broad bands. The increase in the band corresponding to the C-C-O skeleton indicates the formation of ethanol molecules over time due to the hydrolysis reaction (see Figure III-10 (1)). The creation of Si-O-Si bonds also indicates hydrolysis of the APTES molecule, followed directly by self-condensation (see Figure III-10 (2)). Regarding the influence of acidic or basic catalysts, it can be observed that the increase in bands and thus silane hydrolysis occurs whether the medium was acidic (A), basic (B), or neutral (N). The increase in these bands is more and more notable when the quantity of water relative to the quantity of ethanol increases, indicating a better hydrolysis of the silanes in the presence of a large quantity of water

The spectrum presented in Figure III-12 shows the entire FTIR spectrum (4000-400  $\text{cm}^{-1}$ ) for the EW01-N formulation. Only the spectrum of this solution is presented here since no spectral differences other than those presented above were observed. It can be seen from the reaction mechanism shown in Figure III-10 (1) that during silane hydrolysis, OH groups were formed. An increase in the number of hydroxyl groups and therefore in the corresponding band around 3300  $\text{cm}^{-1}$  should be visible. However, no increase in this band was apparent in any of the formulations presented. This may be due to direct self-condensation of APTES molecules after hydrolysis. Since no other compounds were present in the medium, the hydrolyzed molecules react with each other. The non-change in the band at 3300  $\text{cm}^{-1}$  can also be explained by the large number of hydroxyl groups present in the solution: water, ethanol, and silane. A minor difference in the number of silane groups was therefore not perceptible.

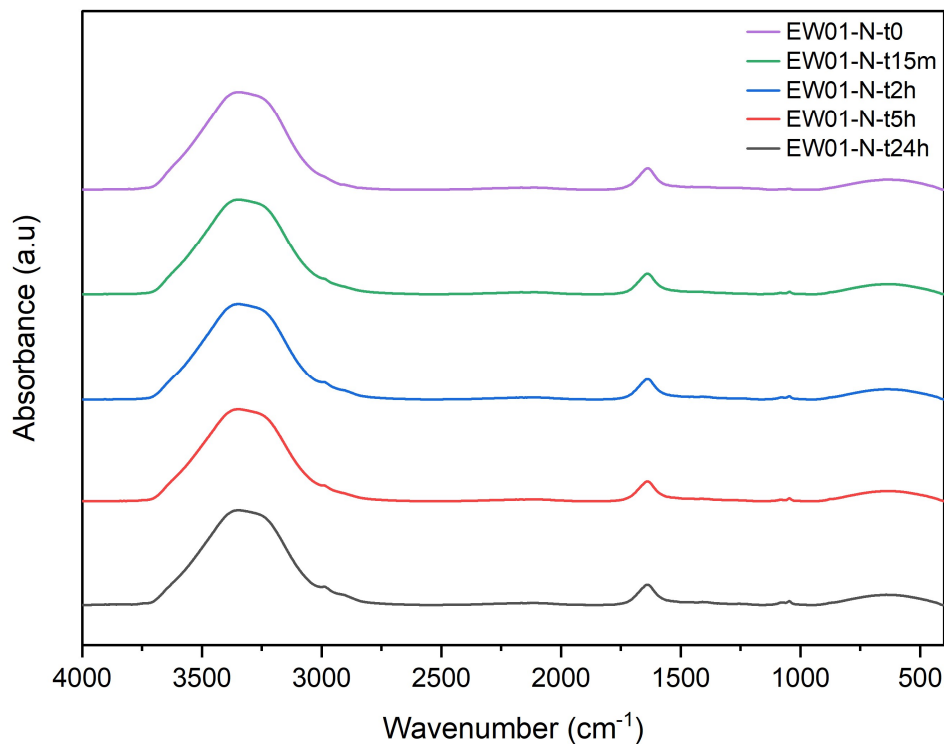


Figure III-12 - FTIR spectrum of EW01-N solution from 4000 to 400  $\text{cm}^{-1}$

Water as the solvent for APTES hydrolysis appeared to be the most appropriate choice, based on previous spectral observations. However, a small amount of organic solvent was required to improve lignin solubility, and mainly because organic solvents generally have a better influence on alkoxy silane hydrolysis [184]. For this reason, an ethanol/water ratio of 10/90 was chosen as the solvent for lignin modification with APTES. Secondly, no difference in hydrolysis was observed on the FTIR spectra concerning solvent pH. Consequently, the choice of not adding a catalyst was adopted. Although, according to the literature, hydrolysis reactions with silanes are generally slow, an exception was noted when using 3-aminopropyltriethoxysilane (APTES) [185].

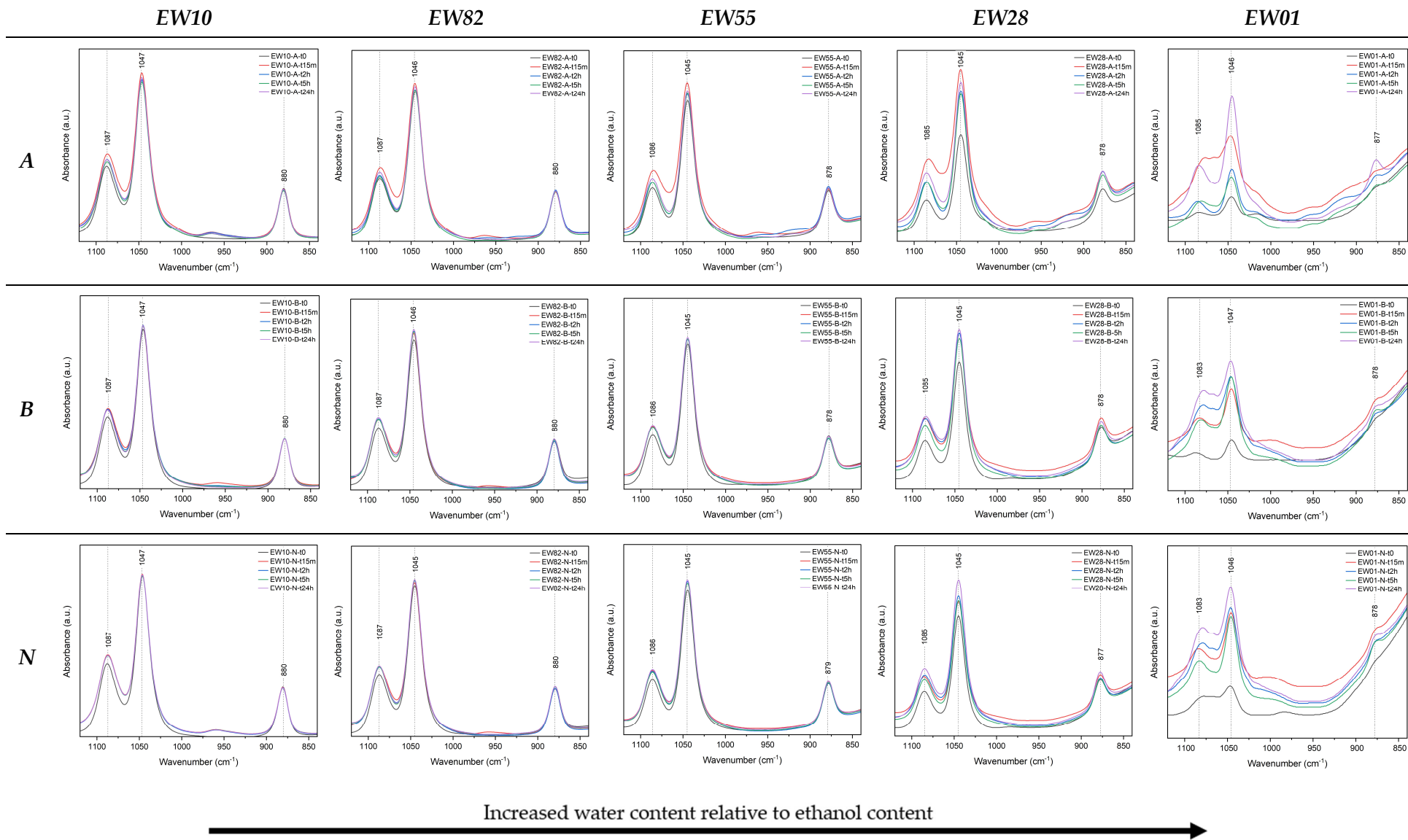


Figure III-13 - FTIR spectra of silane hydrolysis over time with acid catalyst (A), with basic catalyst (B), or without catalyst (N) for the different EtOH/Water ratio

### III. 3. 2. 2. Silanization of lignin

#### Experimental procedure

##### Raw material and reagents

The lignin used for the modification was the lignin precipitated in the previous section with oxalic acid. This acid was chosen because it combines all the important factors: high purity, a high OH number for correct reactivity, low acid content to reduce pH, and a rapid process (precipitation and filtration).

Regarding reagents, the ethanol and 3-aminopropyltriethoxysilane (APTES) mentioned in the previous section (III. 3. 2. 1.) are used in this one.

##### Modification protocol

The reaction mechanism of lignin modification with APTES is presented in Figure III-14.

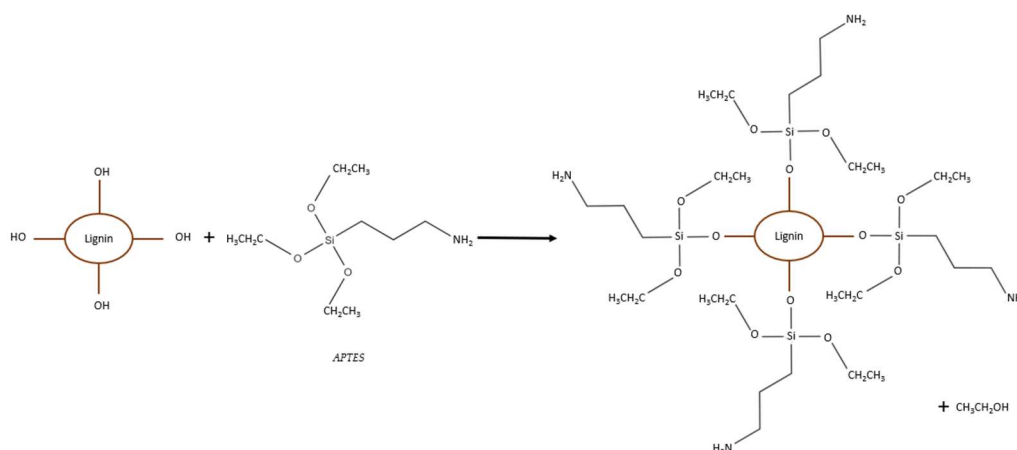


Figure III-14 - Reaction mechanism of lignin silanization with APTES

First, 1 g of lignin was added to 40 mL of ethanol/water solvent (10/90) and stirred until a homogeneous solution was obtained. Then, 0.5, 1, or 2 mL of APTES, depending on the formulation synthesized, were added to the previous solution. The silane was added dropwise to minimize self-condensation reactions and promote reactions with lignin hydroxyl sites. The solution was then stirred for different reaction times and at different temperatures, depending on the formulation. At the end of the reaction time, the solution was vacuum-filtered through a 0.45  $\mu\text{m}$  nylon membrane. The solid lignin recovered was then washed with a large quantity of ethanol/water solvent (10/90). Water was needed to remove unreacted silane molecules, and

ethanol to remove silane molecules which, once hydrolyzed, were not water-soluble. The washed lignin was then dried in an oven at 50 °C for a minimum of 48 h.

The parameters of the different formulations synthesized are presented in Table III-6. The minimum amount of silane required was found experimentally. Initial tests were based on stoichiometric equilibrium, i.e. 1 mol silane to 1 mol OH lignin. This ratio was chosen to ensure more effective interaction of the silane molecules with the lignin hydroxyl sites than with themselves. However, the FTIR analyses carried out did not show the presence of silane within the lignin structure. Therefore, the incorporation of silane in excess was tested and led to a modification of the lignin verified by FTIR. The two amounts of silane tested in this section were intended to verify the effect of a smaller amount of silane on lignin modification, while still leaving it in excess. The different temperatures studied were room temperature ( $T_{amb}$ ), 40 °C, and 70 °C. In the literature, the majority of lignin modifications by silane occurred at a temperature of 70 °C [173], [187]. However, to maintain the aim of developing an environmentally-friendly material, an attempt was made to reduce the reaction temperature. The same was done with the reaction time, several times were tested to see if lignin modification occurred in less than 24 h as indicated in the literature.

#### Characterization of silane hydrolysis

Changes in lignin according to different parameters were monitored by FTIR. An analysis of the thermal resistance of modified lignins was also carried out by TGA. In addition, the molecular weights of the modified lignins were determined by steric exclusion chromatography (SEC). This method enabled the determination of the weight-average molar mass ( $M_w$ ), number-average molecular mass ( $M_n$ ), and polydispersity index ( $\mathcal{D} = M_w/M_n$ ) of lignins. An increase in molecular weight should be observed as new chemical groups have bonded to the lignin structure.

All the above-mentioned acquisition parameters are described in Appendices 1. 1, 1. 2, and 1. 3.

Table III-6 - Parameters of the formulations used to study lignin silanization

Modified lignins	Reaction time	Reaction temperature	Amount of APTES per 1 g of lignin
<i>LS-5m</i>	5 min	T.amb	2 mL
<i>LS-15m</i>	15 min	T.amb	2 mL
<i>LS-30m</i>	30 min	T.amb	2 mL
<i>LS-1h</i>	1 h	T.amb	2 mL
<i>LS-2h</i>	2 h	T.amb	2 mL
<i>LS-6h</i>	6 h	T.amb	2 mL
<i>LS-8h</i>	8 h	T.amb	2 mL
<i>LS-24h</i>	24 h	T.amb	2 mL
<i>LS-40°C</i>	1 h	40 °C	2 mL
<i>LS-70°C</i>	1 h	70 °C	2 mL
<i>LS-1mL</i>	1 h	T.amb	1 mL
<i>LS-0.5mL</i>	1 h	T.amb	0.5 mL

## Results and discussion



Figure III-15 - Photos of lignin before and after modification

The first observation was the change in color of the lignin after the modification, which can be seen in Figure III-15. This change was a first indication of the success of the modification.

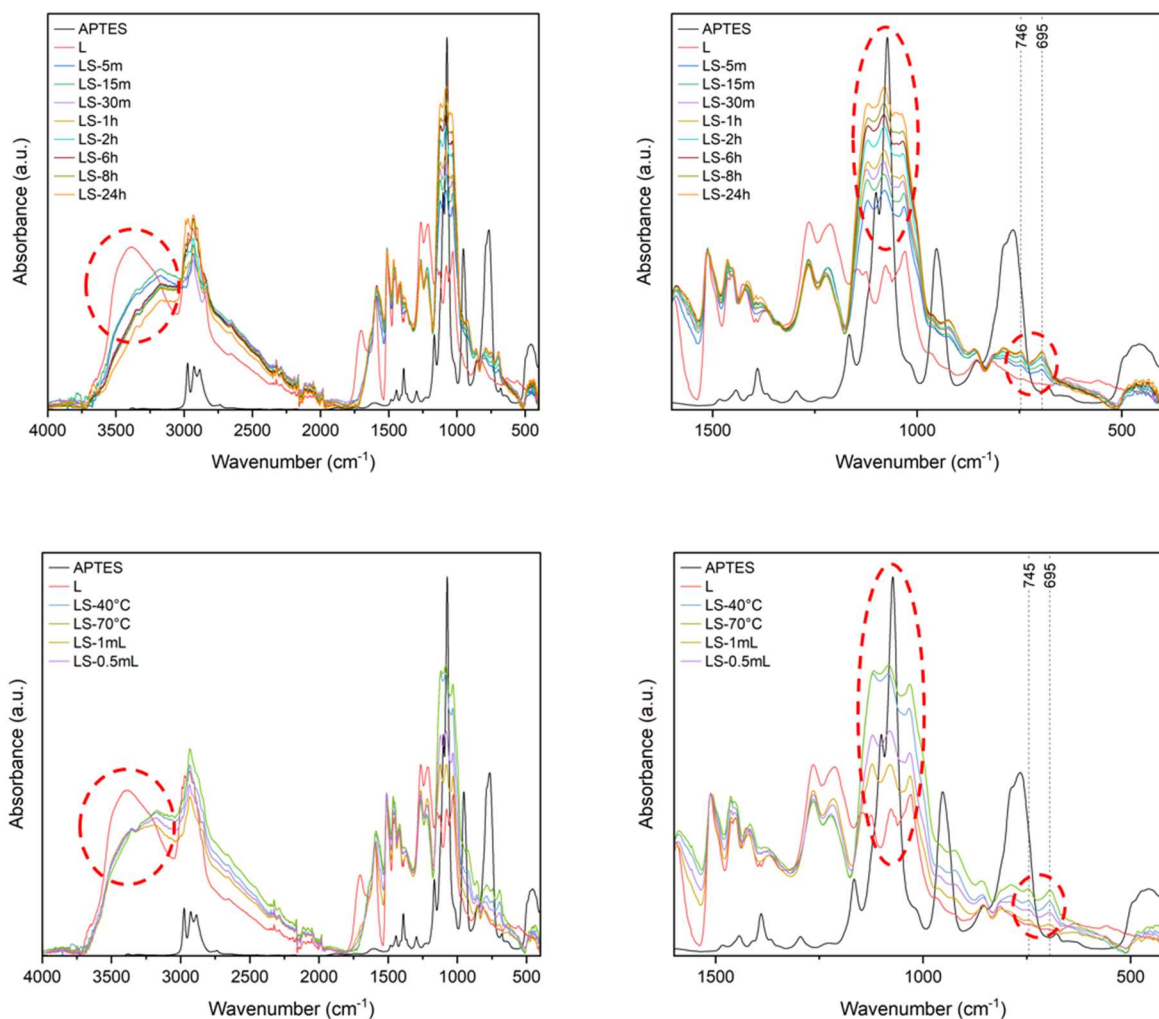


Figure III-16 - FTIR spectra of modified lignins with variations in time, temperature and silane quantity. Wavenumber range of spectra: 4000-400  $\text{cm}^{-1}$  (left) and 1600-400  $\text{cm}^{-1}$  (right)

The FTIR spectra of the various lignins obtained are shown in Figure III-16. Spectra were separated into two graphs for a better visibility. It is important to note that the FTIR spectra presented in this section were normalized from the band at 1510  $\text{cm}^{-1}$ , corresponding to the vibration of the aromatic rings. Regarding spectral analysis, a decrease in the OH band at 3390  $\text{cm}^{-1}$  can first be noted for all modified lignins. The spectra then show an increase in the intensity of the bands between 1200 and 950  $\text{cm}^{-1}$ , corresponding to the formation of Si-O-Si and C-O [173]. Finally, new bands can be observed at 745 and 693  $\text{cm}^{-1}$ , which may be associated with the formation of Si-C and Si-O-Si bonds, respectively [173], [176], [178]. These results indicated that the silanization of lignin was successfully carried out. The OH groups of the lignin reacted with the silane, resulting in a decrease in the number of OH groups and the

creation of new Si-O-Si and C-O bonds. In terms of variation in parameters, when reaction time is increased, the bands between 1200 and 950, at 737, and 693  $\text{cm}^{-1}$  increase, while the broad OH band at 3390  $\text{cm}^{-1}$  decreases. The same phenomenon can be observed with increasing temperature or silane quantity.

To confirm the success of silanization, the lignins obtained were analyzed by steric exclusion chromatography (SEC) to observe the evolution of molecular weights. After checking the success of lignin silanization for all reaction times by FTIR spectroscopy, the number of samples was reduced to limit the amount of analysis. Consequently, the following modified lignins were removed for the subsequent analyses: LS-5m, LS-30m, LS-2h, LS-6h, and LS-8h. Table III-7 shows the results obtained

Table III-7 - SEC analysis results for lignins silanized with different parameters

Lignins	Before lignin modification	$M_n$ after modification	$M_w$ after modification	$\bar{D}$ after modification
<i>LS-15m</i>		2181	18606	8.53
<i>LS-1h</i>		1457	3986	2.74
<i>LS-24h</i>	$M_n = 2770$	804	1248	1.55
<i>LS-40°C</i>	$M_w = 15620$	1870	6106	3.27
<i>LS-70°C</i>	$\bar{D} = 5.64$	1776	10108	5.69
<i>LS-1mL</i>		2535	24532	9.68
<i>LS-0.5mL</i>		2911	30535	10.43

An increase in molecular weight is visible only for LS-15m, LS-1mL, and LS-0.5mL. However, during sample preparation for SEC analysis, lignins were solubilized in dimethylformamide (DMF) according to the protocol. However, poor solubilization of lignins was observed, as shown in Figure III-17. This poor solubilization was particularly pronounced for lignins LS-24h, LS-40°C, and LS-70°C. In Table III-7, these lignins displayed low  $M_w$  values compared with the values obtained before the modification. This may be explained by the solubilization step: DMF may have solubilized only the smallest lignin molecules, so only the smallest molecules were analyzed by SEC. As a result, it might be thought that poor solubility in DMF



indicates greater modification. Regarding polydispersity, when the molecular weights were increased for LS-15m, LS-1mL, and LS-0.5mL, a large increase in polydispersity could be observed. Values between 8.53 and 10.43 were measured. This phenomenon can be explained by secondary reactions on the lignin skeleton, such as condensation or cross-linking during amine silanization [173].

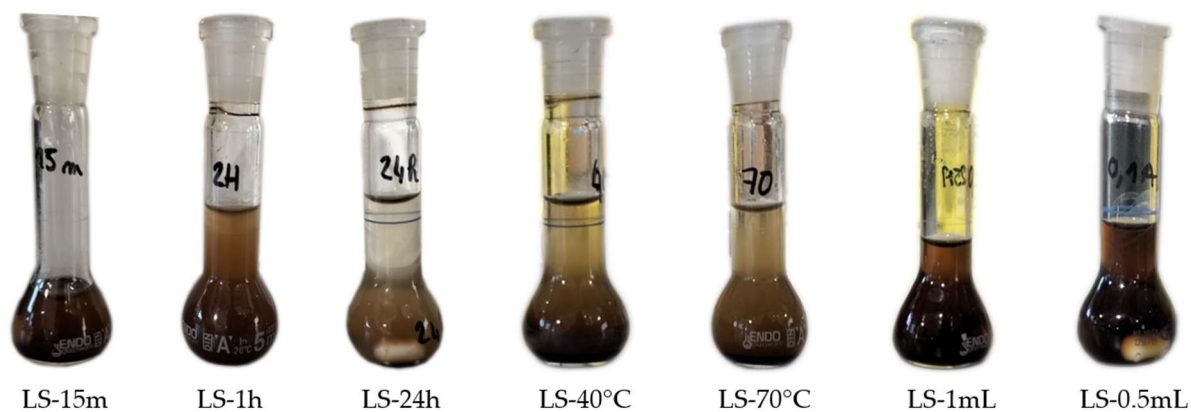


Figure III-17 - Dissolution of modified lignins in DMF for SEC analysis

The TGA and DTG curves are shown in Figure III-18. First of all, the curves for modified lignins show the same shape as the curves before modification. A first degradation below 120 °C took place due to moisture evaporation. Then, above 200 °C, a further loss of mass occurred, probably due to the presence of APTES molecules physically absorbed by the lignin [188]. Indeed, despite washing with ethanol and water, it is very difficult to remove all residues. After 300 °C, the mass loss is due to the decomposition of APTES molecules chemically bound to lignin, with a maximum degradation temperature between 400 and 450 °C. It is possible to observe that this decomposition temperature increases when the lignin was modified, indicating a better thermal resistance after silanization. This increase in degradation temperature also indicates a successful reaction of the silane on the lignin molecules [178]. A similar observation was also noted in other studies [173], [174], [188]. In addition, the residual mass at the end of the heating stage (800 °C) was higher for modified lignins, due to the incorporation of silicon atoms during modification. Concerning the different formulations studied, it can be observed that an increase in reaction time resulted in better thermal resistance. This property was also improved by increasing the silane content. Regarding temperature, it can be observed that a reaction at 40 or 70 °C provided the same resistance. Finally, with the exception of the LS-15m, LS-1mL, and LS-0.5mL formulations, all

modified lignins showed comparable thermal resistance and mass loss at 800 °C. These three modifications correspond to the ones soluble in DMF in the previous section and consequently to the ones with a low modification according to the conclusions made.

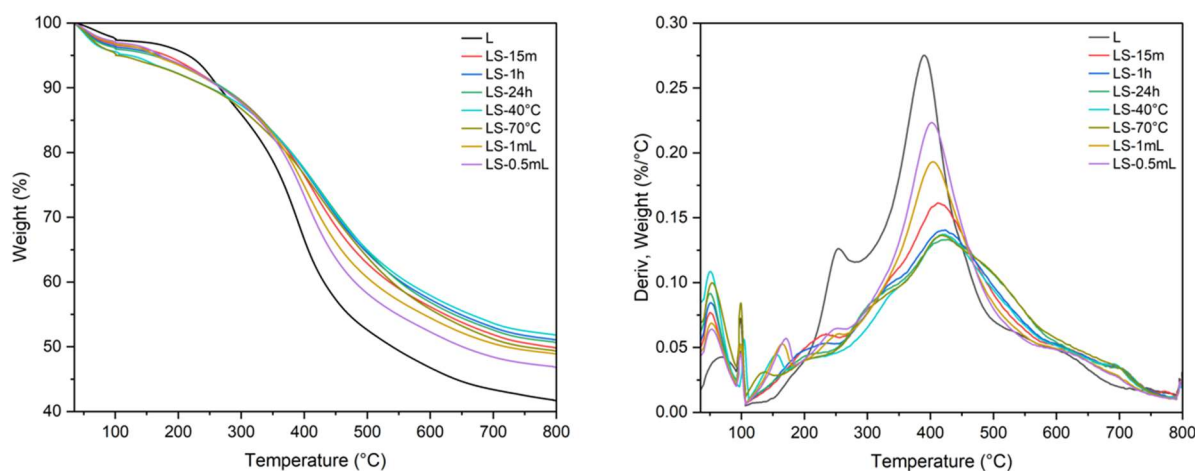


Figure III-18 - TGA (left) and DTG (right) curves for modified lignins

### III. 3. 3. Conclusion

The first part of this section presented the modification of an industrial kraft lignin with a silane in the presence of toluene as solvent. After verification of silanization by a chemical reaction between lignin and silane, an improvement of this protocol was necessary to provide a more environmentally-friendly protocol.

The second part was dedicated to the development of a method for the modification of lignin with a silane. To replace the toxic solvent usually used (toluene), a mixture of ethanol/water (10/90) was used. FTIR, SEC, and TGA analyses demonstrated the successful modification of lignin with an amino-silane: APTES. Thermal analysis showed an improvement in thermal resistance after the modification. Concerning the protocol, the various lignin modification tests demonstrated that a longer heating time, a higher lignin quantity, and a higher temperature resulted in a better lignin modification rate. However, heating for 24 h at 70 °C is energy-intensive. Therefore, for the remainder of the work, modification will be carried out with 2 mL of APTES per 1 g of lignin, with 24 h stirring at room temperature. The advantage of room temperature is the above-mentioned energy limitation, as well as an easier protocol.

### III. 4. Chapter conclusion

In this chapter, a presentation and characterization of the raw materials used in the resin synthesis were carried out. Firstly, two extraction residues were characterized, one from maritime pine (PR) and the other from oak (OR). The results obtained demonstrated a large amount of suberin in PR and an important thermal resistance for OR. Furthermore, both showed remarkable antioxidant activity. In the context of this work, the residue of maritime pine (PR) was the most interesting to maintain a circular economy approach in the southwest of France. Moreover, due to its properties, the incorporation of this compound into a protective impregnating solution for wood could provide protection against water and prevent the development of micro-organisms. In addition, this residue, composed of around 50% suberin, could have an influence on the desired fire-retardant property. Indeed, according to Trovagunta and Hubbe [189], suberin can form a carbonized residue during combustion, creating a protective layer. Moreover, in this study, they also highlight the potential benefits of combining suberin with lignin for the development of flame-retardant biosourced materials.

Then, lignin precipitation with organic acids was carried out and the lignin obtained showed high purity and favorable characteristics to be used in the development of materials. Among the acids studied, oxalic acid was chosen. The results obtained for this acid showed a good compromise between high yield, a non-excessive quantity of acid used, and properties suitable for product development.

The lignin was then silanized. A first modification using trichlorododecylsilane and an industrial kraft lignin provided a lignin chemically bonded with a silane. To make this protocol more environmentally friendly, a protocol was developed using precipitated lignin, another silane (APTES), and ethanol as solvent. Characterization of the modified lignin showed an improvement in thermal stability. Several modification protocols were tested; taking into consideration the results obtained and the conditions of modification, the final choice was a modification time of 24 h at room temperature.

As a result, the incorporation of this by-product with the modified lignin into the formulation of a wood preservative resin was studied and will be presented in the following chapter.

Chapter IV -  
Synthesis of resins and  
study of their  
performance on wood



In this chapter, the resins synthesized using various protocols and the raw materials described in the previous chapter will be presented. The formulations carried out were then characterized and applied to wood. These wood samples were subjected to different tests to determine the degree of protection of the resin-impregnated wood. All the results obtained will be presented in the following sections.

The first part of this chapter will present the continuation of the work carried out in Slovenia. Lignin modified with a silane according to the first protocol described was used for resin synthesis. In these first resin formulations, the residue from maritime pine extraction was also used. Application to wood and characterization of these resins provided an opportunity to verify the viability of silanization of lignin and the use of the residue for the development of wood preservatives.

The second part of this chapter will be devoted to the presentation of resins developed this time using the extraction residue combined with lignin precipitated and then modified with the protocol developed during the three-months stay in Spain. A more detailed characterization was done for the modified lignin to check the modification. In addition, various parameters were used to optimize this protocol. All the results obtained for the characterization and optimization sections will be reported here.

Finally, a third part will present the application of these resins to wood samples, followed by characterization to determine the performance of the impregnated wood. Tests for water, fire, fungus, and UV radiation resistance were performed.

## **IV. 1. First resins synthesized using lignin modified by trichlorododecylsilane**

In this section, the synthesis of resins was performed using lignin silanized in section III. 3. 1 and the maritime pine residue (PR) described in the previous chapter. Furthermore, the usefulness of adding an inorganic component to improve fire resistance was investigated. For this purpose, an inorganic additive currently used in industry was added to the formulation. To produce a resin as biobased as possible, formulations using montmorillonite instead of this commercial additive were also synthesized.

In this section, the wood was treated with plasma prior to be impregnated with the resin. This treatment is one of the methods used to modify wood [41]. Plasma treatment modifies the surface of the wood without altering its physical aspect or bulk chemical characteristics. This modification can reduce the hydrophilicity of the wood and improve the adhesion of a preservative to the wood surface [190], [191].

All the formulations presented in this chapter were characterized to determine the protection provided to wood against water and fire.

### **IV. 1. 1. Resin synthesis protocol and application to the wood**

#### **IV. 1. 1. 1. Experimental procedure**

##### Raw materials and reagents

The raw materials used in this section were the modified or unmodified lignin with trichlorododecylsilane (KL and KLm, respectively) and the modified or unmodified residue with the same silane (PR and PRm, respectively).

Ethanol was purchased from Fischer Scientific. The commercial ammonium phosphate additive (Exolit AP 423) was kindly supplied by Clariant and montmorillonite was purchased from Sigma Aldrich. They will be referred to in the following as AP and MMT respectively.

##### Protocol of resin synthesis

The resin was synthesized by first solubilizing 1 g of KLm or KL with 1 g of PRm or PR in an ethanol/water mixture (70/30). The solution was stirred at 450 rpm at room temperature until

a homogeneous solution was obtained. Then, 0.25 g of inorganic additive (AP or MMT) was added, and the solution was stirred again at 450 rpm for a further 15 minutes.

Different formulations were synthesized, varying the parameters to check the influence of each components. The different formulations synthesized are presented in Table IV-1.

*Table IV-1 - Different resins synthesized by varying parameters*

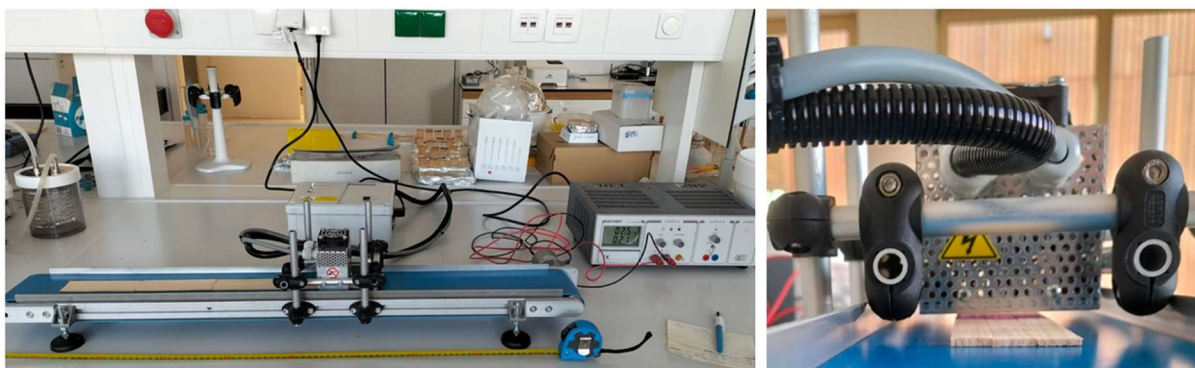
<b>Resins</b>	<b>KL</b>	<b>PR</b>	<b>KLm</b>	<b>PRm</b>	<b>AP</b>	<b>MMT</b>	<b>Ratio LK/PR</b>
<i>LP1</i>			X	X	X		50/50
<i>LP2</i>		X	X		X		50/50
<i>LP3</i>			X	X		X	50/50
<i>LP4</i>			X	X	X		70/30
<i>LP5</i>			X	X	X		30/70
<i>LP6</i>		X	X				50/50
<i>LP7</i>	X	X			X		50/50
<i>LP8</i>	X	X				X	50/50

#### **IV. 1. 1. 2. Wood modification before resin application**

Plasma modification of the wood was carried out using an atmospheric plasma diffuse coplanar surface barrier discharge (DCSBD). Samples were exposed under ambient conditions to a micro discharge at a distance of 1 mm from the surface, with a passing velocity of 2 s/mm.

To assess the influence of this plasma treatment on the hydrophobic character of the wood, a comparison of properties as a function of the number of passes under the plasma was carried out. For this purpose, 0, 1, or 2 passes were made.





*Figure IV-1 - Equipment used for plasma treatment*

### **IV. 1. 1. 3. Resin application on wood samples**

The synthesized resins were applied to wood samples (sapwood) of maritime pine and beech to assess the efficiency of the protection on a softwood and on a hardwood.

The samples were dip-coated; they were dipped into the resin three times. The immersion times were 10 minutes, with 3 minutes drying at room temperature between each dip. This type of application ensures that all samples were coated with a similar quantity of resin, and that surface impregnation was uniform along the entire length of the sample.

### **IV. 1. 1. 4. Characterizations performed**

To determine the influence of resins on wood protection, fire resistance and surface hydrophobicity tests were carried out. Surface hydrophobicity tests were carried out by measuring contact angle. Fire resistance tests were performed using a horizontal/vertical flammability tester in accordance with the ASTM D635. The presentation of the equipment and conditions of use are presented in Appendices 1. 4. 1 and 2. 4. 2, respectively.

### **IV. 1. 2. Results and discussion**

The results obtained by measuring the contact angles of the samples without plasma treatment are shown in Figure IV-2. The first observation is that the contact angle was approximately four times higher when the wood sample was impregnated with resin. Although contact angles did not vary greatly between the different resins, it can be observed that resins with the double modification (K<sub>Lm</sub> + P<sub>Rm</sub>) showed overall better results (resins LP1, LP3, LP4, and LP5). Slightly lower contact angle values were observed for resins containing only one

modified compound. Finally, resins composed of unmodified KL and PR (LP7 and LP8) displayed a lower contact angle. Furthermore, these last synthesized resins (LP8) presented a decrease in contact angle over time, indicating a low water resistance of this resin. This decrease, also observable with the naked eye, was also observed for LP1 on a few measurements, resulting in a large standard deviation for this resin. The problem may be due to a defect in the wood sample.

The results obtained indicated that silane modification improved water resistance. Similar results were obtained in previous studies [179], [192]. These works highlighted the fact that modifying a material with trichlorododecylsilane can improve the hydrophobicity of the surface, creating superhydrophobic coatings in some cases.

For impregnated wood species (pine and beech), no major differences were observed in the contact angle analysis. Indeed, results were quite similar and no trend was noted. These results suggest that, whatever the wood species studied, similar impregnation and interaction between wood and resin occurred.

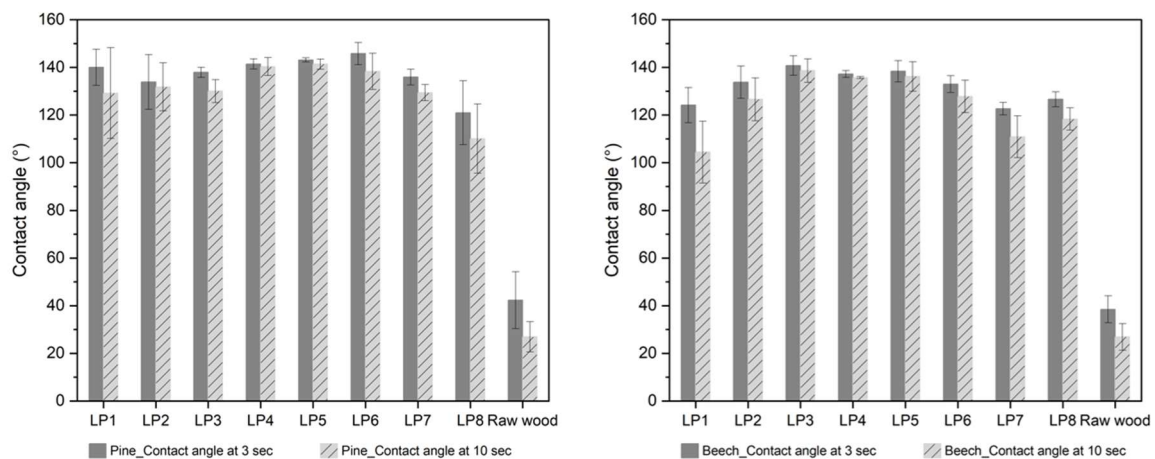


Figure IV-2 - Contact angle results for resin-coated samples without a plasma pretreatment for pine samples (left) and beech samples (right)

Figure IV-3 shows the contact angle results for plasma-treated samples. It can be observed that plasma treatment performed before impregnation provided a better contact angle overall. For LP1, two plasma treatments (P2) instead of zero (P0) or just one (P1) led to a better contact angle value. This was not the case for the raw wood, but the standard deviations calculated for P2 samples were important. However, the improvement in contact angle resulting from the plasma treatment was visible, but not substantial. Indeed, an increase of around 5.6 ° was

measured between samples without treatment (P0) and samples treated twice (P2) for formulations LP1, LP2, and LP3. The results obtained seem to show that plasma treatment did not improve water resistance, but improved surface reactivity. This improved interaction between the wood surface and the resin resulted in greater resistance to possible degradations such as water. Studies have also demonstrated that plasma treatment led to a decrease in contact angle but also an increase in surface reactivity [193], [194].

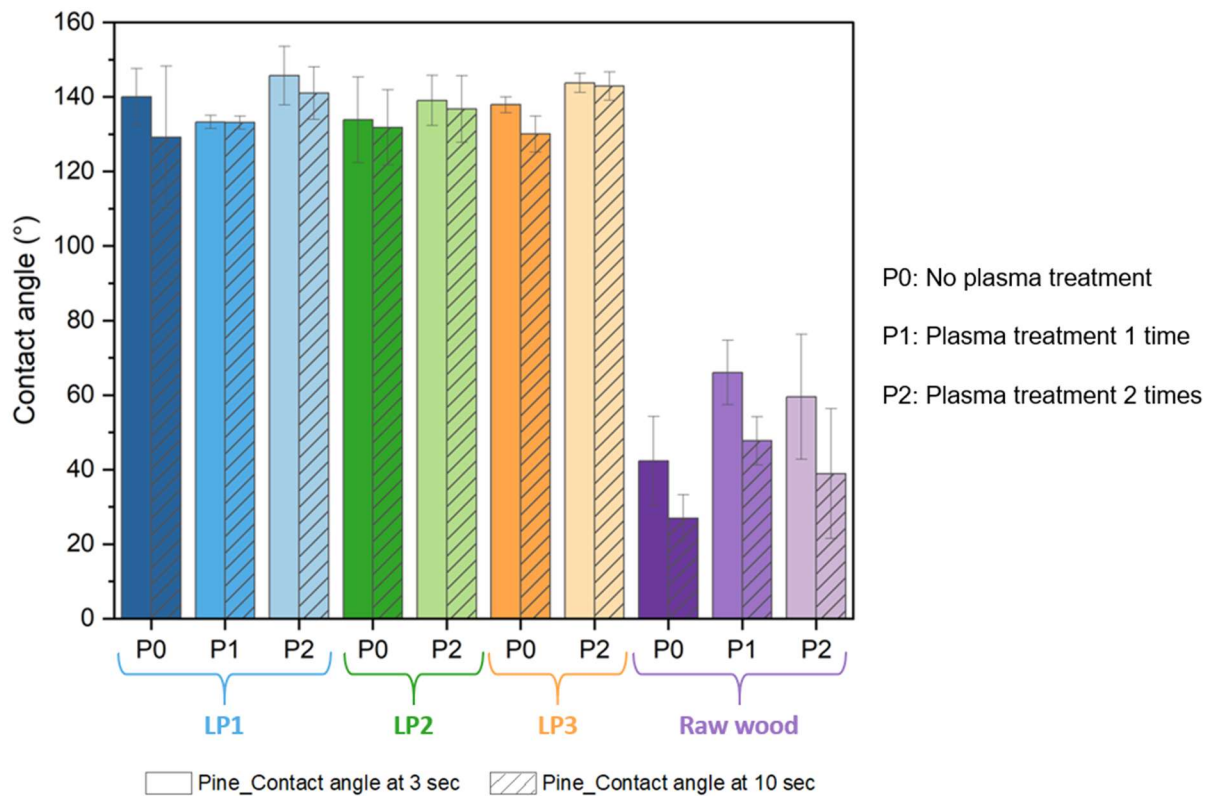


Figure IV-3 - Contact angle results for resin-coated samples with a plasma pretreatment

The results of fire resistance tests are listed in Figure IV-4. Only the formulations used to compare the type of inorganic additive used are presented.

The fire tests highlighted the effectiveness of the inorganic additive; indeed, the samples with the highest burned length and burning rate were LP6 (without additive) and the control group (raw wood). LP3 and LP8 for beech wood presented better fire-retardant properties than LP1 and LP7 respectively. A similar trend was observed for maritime pine LP3, compared with LP1. These observations indicated that the commercial additive was more effective than the biosourced additive. The values measured were similar between the two-wood species, except that the values for beech were higher for LP6 and for the raw wood. This result was surprising

since maritime pine, as a softwood, contains a greater quantity of lignin and resin, which increases its sensitivity to fire [93]. Although the inorganic additive was more effective. It is nevertheless possible to conclude that the use of MMT (inorganic additive of biological origin) resulted in a clear improvement in fire resistance. The use of this type of material could provide effective fire protection at low cost and with bio-based materials.

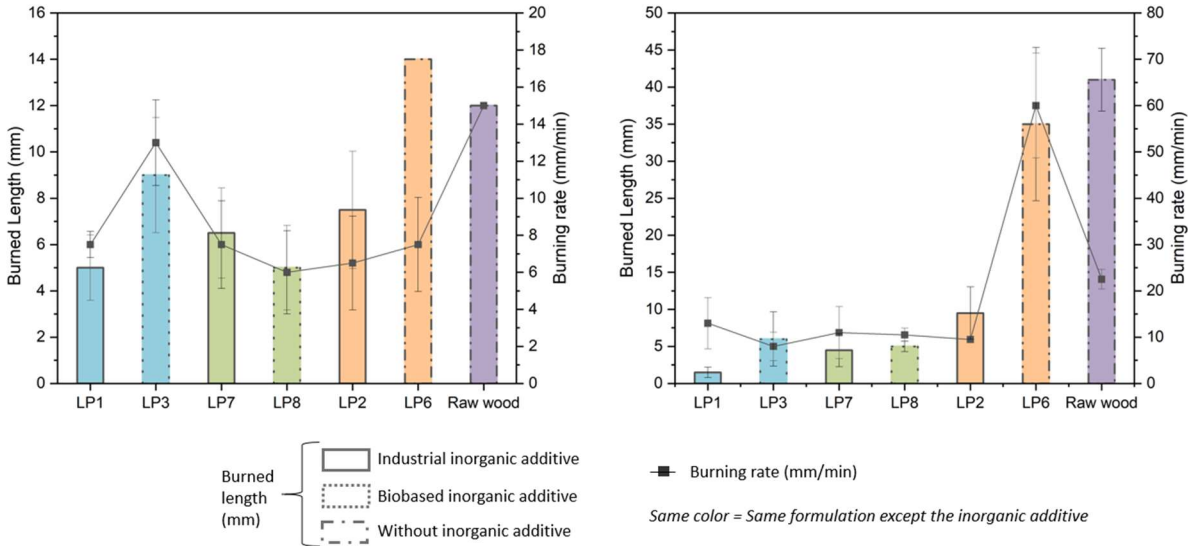


Figure IV-4 - Results of fire resistance tests on maritime pine (right) and beech (left)

### IV. 1. 3. Conclusion

This study demonstrated the benefits of chemical modification of the lignin and/or residue in terms of surface hydrophobicity. Indeed, high contact angle values were obtained when both lignin and residue were modified. This study also confirmed the importance of adding an inorganic additive to improve fire resistance. Despite the better efficacy of the commercial additive, positive results were nevertheless obtained when using the biobased additive. Its use in a resin formulation should not be excluded. With regard to plasma pre-treatment, measurements of contact angles indicated the effectiveness of this treatment. However, this improvement in hydrophobicity was small. Consequently, this treatment was discarded for the future. A very suitable contact angle was obtained for samples not subjected to this plasma treatment step.

This section demonstrated the viability of using silanization as a lignin modification combined with the extraction residue (PR). However, as the silanization protocol was not very

environmentally friendly, the replacement of toluene by ethanol was necessary. This protocol was described in the part III. 3.

## **IV. 2. Resins synthesized using lignin modified by 3-aminopropyltriethoxysilane (APTES)**

Thanks to the positive results obtained in the previous section, new resins containing the extraction residue and silanized lignin were synthesized. In this part, the lignin used was lignin precipitated and then modified according to the protocol developed in Spain using 3-aminopropyltriethoxysilane (APTES) and ethanol as solvent. In this section, the inorganic additives were the same as before, i.e. the commercial additive (Exolit AP 423) and montmorillonite.

Several formulations were developed, varying parameters such as reaction time, temperature, lignin/residue ratio, and inorganic additive quantity. All these formulations and the corresponding characterizations will be presented in the following section.

### **IV. 2. 1. Experimental procedure**

#### **IV. 2. 1. 1. Raw material and reagents**

The raw materials used in this section were lignin precipitated with oxalic acid, which was then modified with silane (LOm) according to the protocol described in section III. 3. Then the second main raw material was the maritime pine (PR) extraction residue characterized in part III. 1.

To these resins, commercial and biobased reagents such as montmorillonite (MMT) or ammonium phosphate (AP) were used as inorganic additives. MMT was purchased from Sigma Aldrich and AP was kindly provided by Clariant. Ethanol (EtOH) was supplied by Fischer Scientific.

#### **IV. 2. 1. 2. Synthesis protocol**

Resin formulation was carried out as follows: 0.5 g of LOM and 0.5 g of PR were mixed in 30 mL of an ethanol/water solution (70/30). After 30 min of stirring at room temperature at 450 rpm, 0.05 g of ammonium phosphate (AP) were added to the solution before continuing

stirring for a total of 24 h. This resin was the initial formulation (BL0). Other formulations were synthesized by varying various parameters such as the reaction time, the temperature, the ratio Lom/PR, or the inorganic part. All the synthesized resins are listed in Table IV-2.

Table IV-2 - Different resins synthesized according to their parameters

Resins	Reaction time	Reaction temperature	Ratio LOM/PR	Inorganic part
<i>BL0</i>	24 h	T.amb	50/50	0.05 g AP
<i>BL_1h</i>	1 h	T.amb	50/50	0.05 g AP
<i>BL_40°C</i>	24 h	40 °C	50/50	0.05 g AP
<i>BL_70°C</i>	24 h	70 °C	50/50	0.05 g AP
<i>BL_r1</i>	24 h	T.amb	20/80	0.05 g AP
<i>BL_r2</i>	24 h	T.amb	80/20	0.05 g AP
<i>BL_AP10%</i>	24 h	T.amb	50/50	0.10 g AP
<i>BL_M5%</i>	24 h	T.amb	50/50	0.05 g MMT
<i>BL_M10%</i>	24 h	T.amb	50/50	0.10 g MMT
<i>BL_0%</i>	24 h	T.amb	50/50	0

#### IV. 2. 1. 2. Characterizations performed

The resins were characterized chemically and thermally by FTIR and TGA. Acquisition parameters used are given in Appendices 1. 1. 1 and 1. 2. 1, respectively.

#### IV. 2. 2. Results and discussion

The FTIR results are shown in Figure IV-5. Spectrum A shows the spectra of the BL0 resin with the components (PR, LOM, and AP). It can be seen that the spectrum of the resin was clearly influenced by the presence of the major compounds (PR and LOM). The band characteristic of methyl and methylene groups [98], [132] present in the PR spectrum at 2920 cm<sup>-1</sup> is also present in the resin spectrum. The same phenomenon is observed with the band at 1695 cm<sup>-1</sup>, characteristic of the C=O bond of COOH groups and hydrolysable tannins [133], [134], and the band at 1610 cm<sup>-1</sup> corresponding to conjugated C=O groups [135]. Then, a band at 1240 cm<sup>-1</sup>

can be observed in the resin spectrum, which may come from the PR, which presents an absorbance at the same wavenumber corresponding to C=C bonds [130]. This band can also indicate the presence of AP, which has a strong absorption at  $1240\text{ cm}^{-1}$ . The resin spectrum also exhibits bands between  $1200$  and  $900\text{ cm}^{-1}$  which may be associated with the presence of LOM and their characteristic bands associated to Si-O-Si and C-O bonds [173]. Finally, the presence of the inorganic additive AP can be observed through the absorption at  $545\text{ cm}^{-1}$ , which is assigned to the Si-O-Al bond of this compound [195]. Spectra B and C represent the formulations of the resins with variation in temperature and variation of the LOM/PR ratio. Regarding the reaction temperature, it is possible to observe an increase in most of the bands when the temperature increases up to  $40$  or  $70\text{ }^{\circ}\text{C}$ . Then, in graph C, the spectrum of BL\_r1 resin, which corresponds to a higher percentage of PR, displays an increase in the bands at  $2920$ ,  $1695$ , and  $1610\text{ cm}^{-1}$ , which are characteristic PR bands. By contrast, the spectrum of resin BL\_r2 shows an increase in the absorbance bands between  $1200$  and  $900\text{ cm}^{-1}$  characteristic of LOM. Spectra of formulations with a variation in inorganic portion or reaction time were recorded but are not presented in Figure IV-6. Their spectra are very similar to the BL0 spectrum, with no notable changes observed. The addition of the inorganic part is too small to observe any spectral difference.

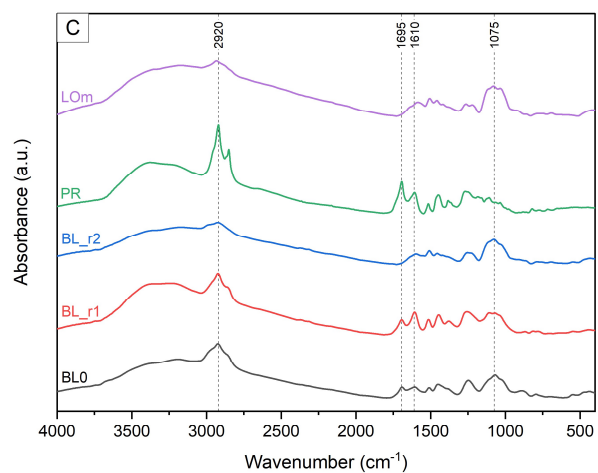
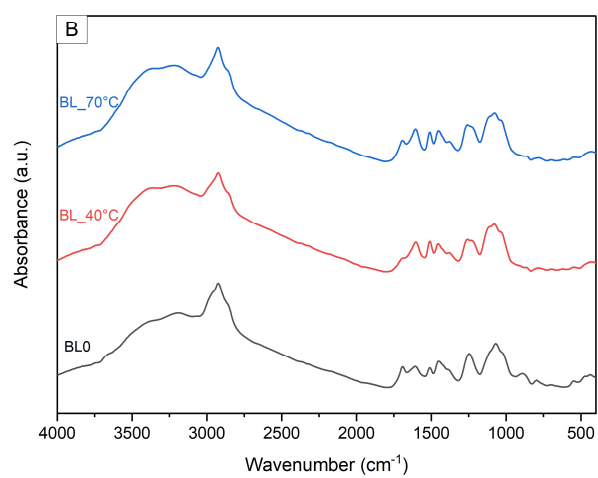
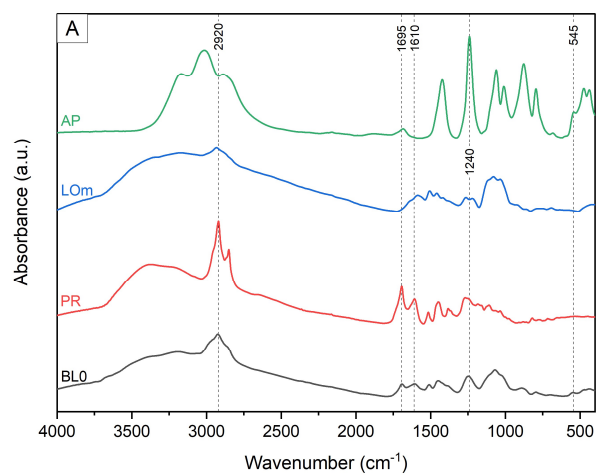


Figure IV-5 - FTIR spectra of synthesized resins and their compounds. A: BL0, PR, LOm, and AP. B: BL0, BL<sub>40°C</sub>, and BL<sub>70°C</sub>. C: BL0, BL<sub>r1</sub>, BL<sub>r2</sub>, PR, and LOm



The results of the thermogravimetric analysis are reported in Figure IV-6. In the first TGA spectrum (A), it is possible to observe a slight decrease in the thermal resistance of the resin after a reaction time of just one hour. Then, a similar slight decrease in thermal resistance is observed when the temperature was increased (B). A modification of the LOM/PR ratio demonstrated an increase in thermal resistance for BL\_r2 and an important decrease for BL\_r1 (C). Thus, the presence of LOM in higher quantities than PR results in good thermal properties of the resin. This thermal resistance is certainly due to the silanization carried out previously. Finally, with regard to the additives added (AP and MMT) and in different proportions (5 and 10%), very minor spectral differences can be observed (D). Indeed, all formulations have the same thermal degradation curve. However, it is possible and relevant to note that the BL\_0% formulation, which has no inorganic additives, exhibits a decrease in thermal resistance, demonstrating the benefits of this inorganic additive.

Most of the DTG spectra present three main degradation stages. Up to around 110 °C, a first loss of mass occurred due to evaporation of the moisture present in the sample. This was followed by a second major mass loss at around 240 °C. This second loss is due to the suberin present in PR, for which thermogravimetric analysis has been carried out and is presented in Part III. 1. This also explains the higher mass loss in the BL\_r1 formulation. Finally, the third mass loss at around 400 °C is probably due to the presence of LOM and more specifically to APTES molecules chemically bound to lignin. This same mass loss was observed in the thermogravimetric analysis of modified lignin in Part III. 3. 2.

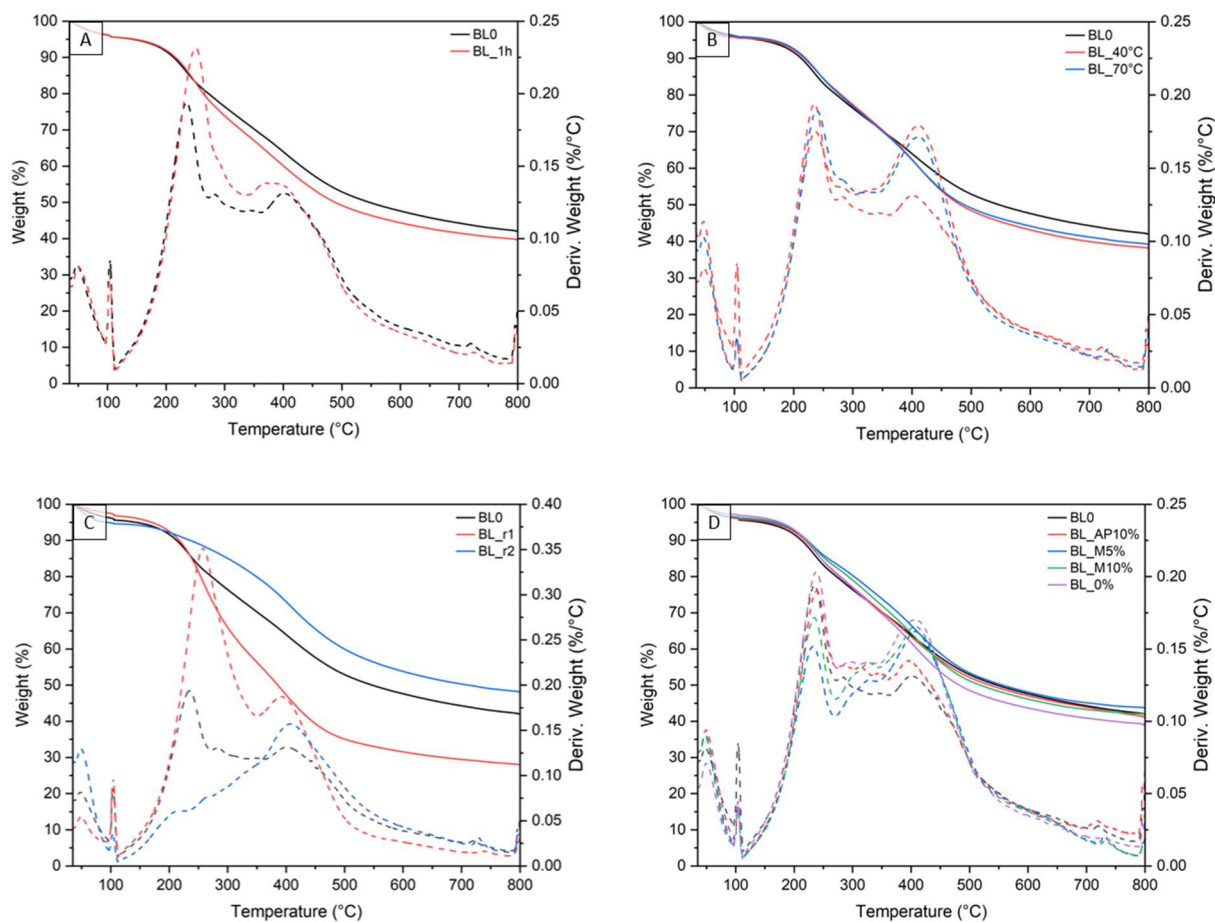


Figure IV-6 - TGA and DTG curves of different formulations according to variation of reaction time (A), temperature (B), LOM/PR ratio (C), and inorganic additive (D)

## IV. 2. 3. Conclusion

In this section, a biobased resin was synthesized using lignin previously precipitated and silanized, an industrial extraction residue, and an inorganic additive. To find the best-performing resin, several formulations were synthesized, by varying the reaction time, the temperature, the ratio between lignin and residue, and the type and quantity of inorganic additive. After synthesis of the different resins, chemical characterization (FTIR) and thermal characterization (TGA) were carried out to determine preliminary resin performance. Spectral differences were observed according to the different formulations synthesized. At thermal level, the usefulness of adding organic compounds was highlighted. Moreover, the results also showed a better thermal resistance when using an excess of silanized lignin.

In the following of this chapter, the application of the resins on wood was presented. Various tests were then carried out to assess the performance of the resins applied to wood.

## IV. 3. Application of resins to wood and performance characterization

In the first part of this chapter, the synthesized resins were impregnated onto the wood samples. This method ensures that the quantity of resin is constant between samples and homogeneous across the piece of wood. Positive results were obtained during performance evaluation of the wood samples. As a result, the impregnation process was adopted and optimized in this section. Indeed, a study on the required cycles of impregnations to obtain maximum impregnation was carried out.

The second part of this chapter was dedicated to the characterization of resin-impregnated wood samples. Tests were carried out on resistance to water, fire, outdoor conditions (UV, humidity), and fungi. These experiments provided an overview of the performance provided by the resin to the wood. All these results are presented below.

### IV. 3. 1. Impregnation method

#### IV. 3. 1. 1. Experimental procedure

In this section, *Pinus pinaster* samples (sapwood) were used as a support for resin impregnation. Sample sizes of  $(125 \pm 5) \times (13.0 \pm 0.5) \times (3.5-4.0)$  mm were used. Impregnation was carried out by immersing the samples in the resin for 3 min, followed by drying at room temperature for 2 min. These two stages correspond to a complete cycle. To determine the number of cycles required for a maximum resin impregnation, from 1 to 8 cycles were carried out. A representation of the system used is shown in Figure IV-7. The resin used for this experiment was BL0 and a triplicate of samples for each number of cycles was performed.

The weight percent gain (WPG) was determined for each sample. This value represents the mass of resin impregnated on the wood and was calculated using the following formula:

$$\text{WPG (\%)} = \frac{m_{\text{wood} + \text{resin}} - m_{\text{wood}}}{m_{\text{wood}}} \times 100$$

$m_{\text{wood}}$ : mass of dry wood sample before impregnation (g)

$m_{\text{wood} + \text{resin}}$ : mass of dry wood sample after impregnation (g)



*Figure IV-7 - Installation used to dip wood samples in resin*

### **IV. 3. 1. 2. Results and discussion**

The results obtained for WPG percentage as a function of the number of cycles performed are shown in Figure IV-8. In some cases, the standard deviations obtained are important, but it is still possible to identify a trend. Indeed, an increase in WPG percentage can be observed until the third immersion cycle. Beyond that, a plateau is reached, meaning that more resin cannot be impregnated into the wood. Three immersion cycles were then enough to achieve a maximum impregnation. This observation was also observed visually during the experiment. Indeed, after the third immersion, the resin flowed more abundantly from the sample when it was removed before the drying step. Nevertheless, it is important to note that this study on the number of impregnation cycles required was carried out using only one formulation. Depending on the composition of the resin, results can vary, with more or less effective impregnation.

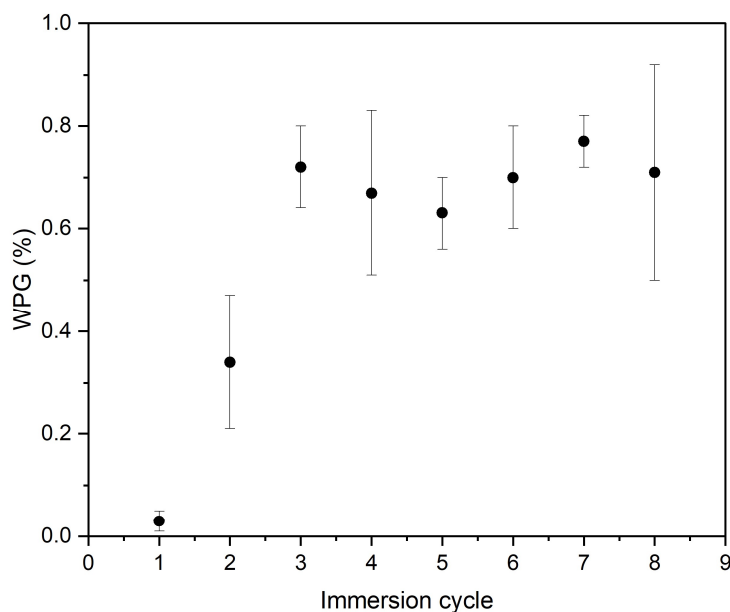


Figure IV-8 - WPG evolution as a function of the number of immersion cycles

This small part of the chapter was dedicated to the study of the number of cycles required to obtain a maximum impregnation of the resin on the wood samples. The results showed that three immersion cycles were sufficient to achieve a maximum rate of impregnation. Therefore, for the remainder of this work, three impregnation cycles consisting of 3 min of immersion followed by 2 min of drying at room temperature were carried out. Optimal optimization was performed on the initial formulation. Depending on the resin composition, the number of cycles required can differ. However, to compare these formulations, all wood samples were impregnated using the same protocol.

## IV. 3. 2. Performance of impregnated wood

### IV. 3. 2. 1. Experimental procedure

The resin-impregnated wood samples were subjected to various tests to determine the resulting preservation properties. Assessments of contact angle, fire resistance, accelerated aging, and biological durability were carried out, and descriptions of the device and conditions were reported in Appendix 2. 4. However, some additional information is given in the following paragraphs.

For water resistance, assessed by measuring the contact angle of the samples, three contact angle measurements per sample were carried out.

Fire resistance was assessed using a device complying with the ASTM D635. Tests were carried out on the initial resin (BL0), on resins in which the inorganic part (used for fire resistance) was modified (BL\_AP10%, BL\_M5%, BL\_M10%, and BL\_0%), and on resins with a different LOm/PR ratio (BL\_r1 and BL\_r2). The latter were chosen to compare the thermal resistance of resins as a function of composition. A sample of raw wood was also analyzed. For all formulations, triplicate samples were tested.

Resistance to external conditions was assessed using an accelerated aging chamber complying with the standard EN 927-6 with some modifications. According to this procedure, samples need to be subjected to various conditions (humidity, heat, UV, spraying) for a period of 12 weeks. Due to time constraints, the samples were removed from the chamber after 8 weeks, i.e. 1344 hours of exposure. Although the standard was not respected, this experiment provides an initial assessment of the outdoor resistance of the resin. The following resins were used for this test: BL0, BL\_r1, BL\_r2, BL\_M10%, and BL\_AP10%. In this case too, each formulation was impregnated on three wood samples. Photos and color measurements were recorded every week.

Standard EN 113-1 with some modifications was used to determine the biological durability of the resin. In this case, the wood samples should be left in the culture medium for 16 weeks. However, due to time constraints and to get an initial idea of the effectiveness of the resin to prevent the development of fungi on the wood surface, the samples were removed after 7 weeks of incubation. Fungal resistance was assessed on two resins: BL0 and BL\_M10%. BL0 was chosen because it was the initial formulation. BL\_M10% was selected because the replacement of the inorganic part present in BL0 (AP) by a biosourced inorganic additive (MMT) would be interesting in the development of a material as biobased as possible.

## **IV. 3. 2. 2. Results and discussion**

### Evaluation to water resistance

The water resistance of the samples was assessed by measuring the contact angle. The results obtained are shown in Figure IV-9. In this graph, resins where only the inorganic part was modified are not shown. Measurements were carried out, but no large differences or trends were observed compared with BL0 resin. As these resins have been synthesized to determine

their influence on thermal properties, they will be studied in greater depth during the presentation of fire test results.

Overall, an increase in contact angle can be observed for all the resins presented, compared with the contact angle obtained with raw wood. Then, the results show that a reaction time of one hour led to a slight decrease in contact angle. The same observation was made when the temperature was increased. During this increase in temperature, compounds can be degraded, causing a decrease in contact angle. For BL\_r1, the extraction residue (PR) was in excess, whereas for BL\_r2 it was the modified lignin (LOm) that was in excess. Based on the results obtained, it can be concluded that modified lignin provided a better contact angle to the formulation and therefore a better hydrophobicity of the surface. These results were in line with previous studies, which also obtained a considerable improvement in contact angle after lignin modification with amino-silane [173], [178]. It is also important to note that BL\_0%, a resin without inorganic additives, was the formulation with the best contact angle. The addition of this additive resulted in a slight reduction in contact angle. Finally, for all the samples analyzed, it is possible to observe a decrease in contact angle over time. With the exception of untreated wood, for which a important reduction was observed after 10 sec, this decrease was more or less the same for all resins. Indeed, the decrease in contact angle was around 31.07 ° for raw wood, whereas it was 8.44 ° for resin impregnated samples.

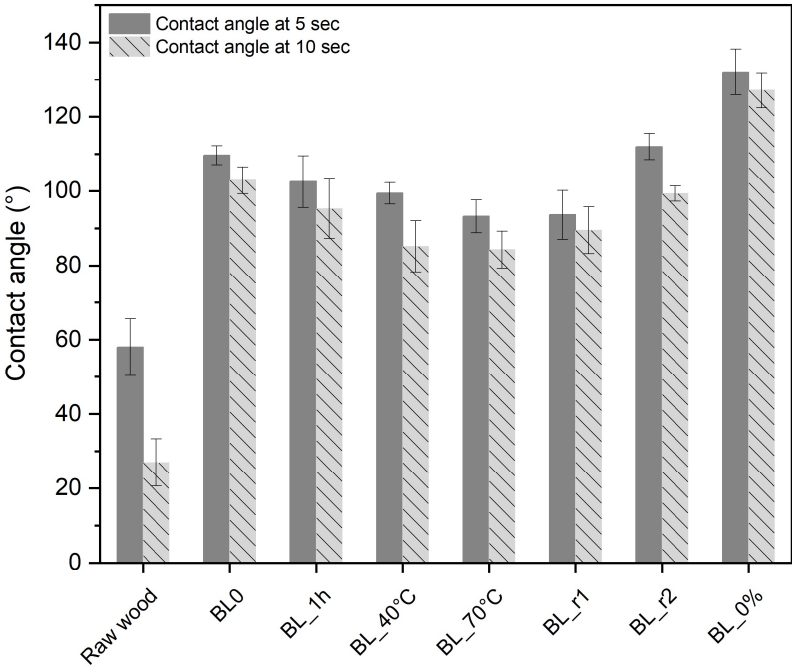


Figure IV-9 - Contact angle measured for resins with different synthesis parameters

### Evaluation to fire resistance

Figure IV-10 shows the burning rate and photos of the samples after the fire tests. It is possible to observe an improvement in fire resistance for the majority of samples. Increasing the percentage of inorganic part (BL\_AP10% and BL\_M10%) strangely did not lead to a decrease in burning rate. Furthermore, it can be observed that replacing the commercial inorganic additive (AP) with the biobased additive (MMT) resulted in a slight increase in combustion speed. This observation can also be made with the photos shown in Figure IV-10, where a greater length of wood sample was burned when using MMT. In the case of resin without inorganic additives (BL\_0%), a complete combustion of this sample was observed, with a much higher burning rate than for raw wood. This surprising result shows that, on the one hand, resin alone had no fire-protective properties and, on the other, it increased combustion compared with raw wood. Finally, the results obtained for the BL\_r1 and BL\_r2 demonstrated very good fire resistance for the first. Indeed, only a small portion of the length was burnt, at a very low burning rate. This resin corresponds to the formulation with a LOM/PR ratio of 20/80. This result may be due to the presence of suberin in PR and confirms the hypothesis of Trovagunta and Hubbe [189] concerning the possible use of suberin combined with lignin to obtain a fire-resistant material. The results of BL\_r2 indicated a notable burn length and burning rate, suggesting that the silane added to the lignin does not necessarily provide fire protection for the resin. This result was not in line with the results obtained in previous studies, which showed that APTES modification of lignin not only improved water resistance, but also provided thermal resistance to the resin [173], [178], [196]. Furthermore, the results obtained here were also not in agreement with the results obtained at the TGA, where a better thermal resistance was measured for samples containing a higher amount of LOM (BL\_r2).



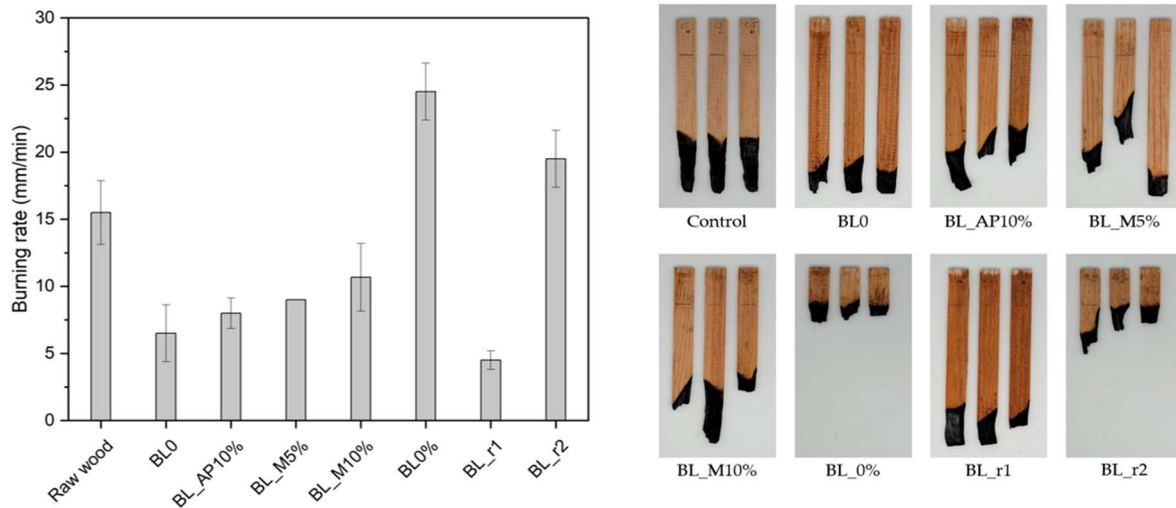


Figure IV-10 - Burning rate of samples (left) and photos of burnt samples after fire tests (b)

### Evaluation of resistance to accelerated ageing

Photos and color measurements taken every week are shown in Figure IV-11 and IV-12, respectively.

Visually, it is possible to observe an alteration in the resin from the first week for all samples, with an increase in this alteration over the weeks until complete elimination of the resin on the sample. After that, degradation of the wood sample is visible. In addition, it is possible to visually observe a few cracks in the samples for raw wood and BL\_r2. These cracks appeared during the first week, indicating that water had penetrated the wood during the spraying stage, followed by drying with UV light, resulting in cracks.

Differences in sample color over the weeks can be observed for the part not exposed to UV light, and can be explained by differences in humidity. Indeed, during spraying, water can slip between the plates holding the sample and the sample itself, and flow along the sample; as this part was not subsequently exposed to UV light, the water presents in this area did not dry out and became trapped there.

Figure IV-12 shows the parameters  $L^*$ ,  $a^*$ ,  $b^*$ , and  $\Delta E$  over the weeks of exposure. It is possible to observe an increase in  $L^*$  indicating a lighter sample, as can be seen in the photos. This increase can be observed for all samples, with slightly different values due to the initial color of the sample. However, after 4 weeks of exposure, the values became similar and the increase continued. For  $a^*$  and  $b^*$ , a decrease in these parameters is visible, with, as for  $L^*$ , a slight variation in values until 4 weeks of exposure. Finally, the graph presenting the color change

of the sample before and after 8 weeks of exposure ( $\Delta E$ ) shows a similar evolution for all samples. Three groups were present: BL\_r1, raw wood, and the other resins. This difference in values was due to the difference in sample color from the beginning. Indeed, in Figure IV-11 it is possible to see that BL\_r1 had a darker color, while raw wood appeared to be the lightest sample. Considering that the final color was the same for all samples, the  $\Delta E$  is greater for BL\_r1 and smaller for the untreated wood.

As a result, all this information indicated that the resins synthesized in this work did not protect the wood against UV radiation. Furthermore, it was not possible to determine the superior resistance of one resin compared to another. It should also be important to note that the exposure time in this case did not correspond to the exposure time indicated in the standard, however, a longer exposure would simply lead to a further degradation of the wood without being able to give any additional information on the protection provided by the resins.

Color measurements were also recorded on the area not exposed to UV radiation before and after the 8-week exposure. It was mentioned earlier that water could stagnate in this area. The purpose of this measurement was to assess the effect of humidity and run-off water on the resin. The color difference results ( $\Delta E$ ) are listed in Table IV-3. It is possible to observe lower values for the resins than for the formulations. In addition, it should also be noted that the values are all below 7 indicating little color change. For exposed parts,  $\Delta E$  values after 8 weeks of exposure were above 30. Finally, the lowest value was observed for BL\_r2 resin. This result was consistent with the excellent values obtained from contact angle measurements.

There are no calculations to correlate accelerated aging time with outdoor time. Too many variables need to be considered, such as geographic zone, altitude, seasonal variations, sample orientation, and many others. However, this device allows samples to be compared and provides information on the resistance of the material to harsh environmental conditions.

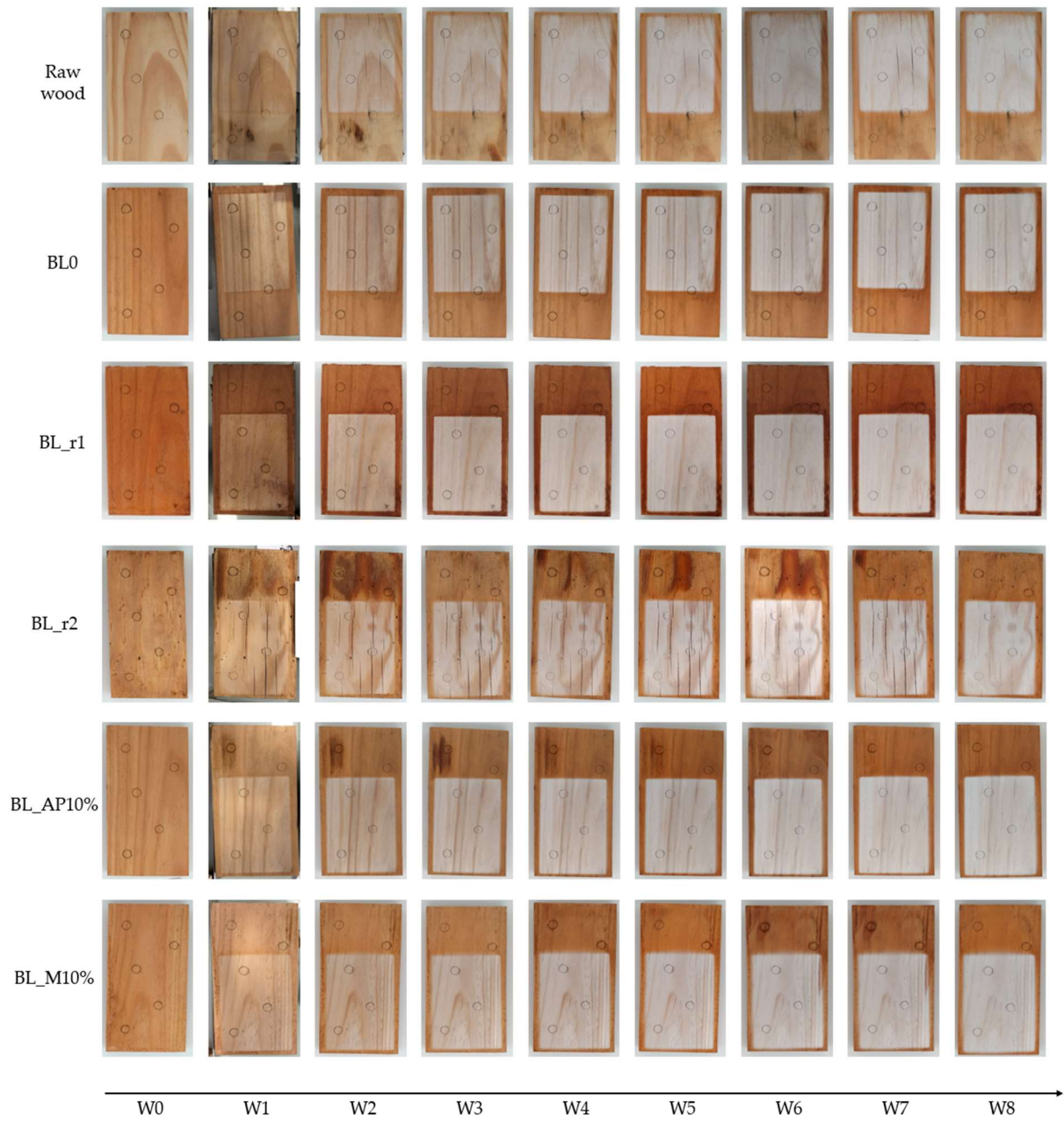


Figure IV-11 - Weekly sample images during accelerated aging (W0: before exposure, W1: after one week of exposure, etc.)

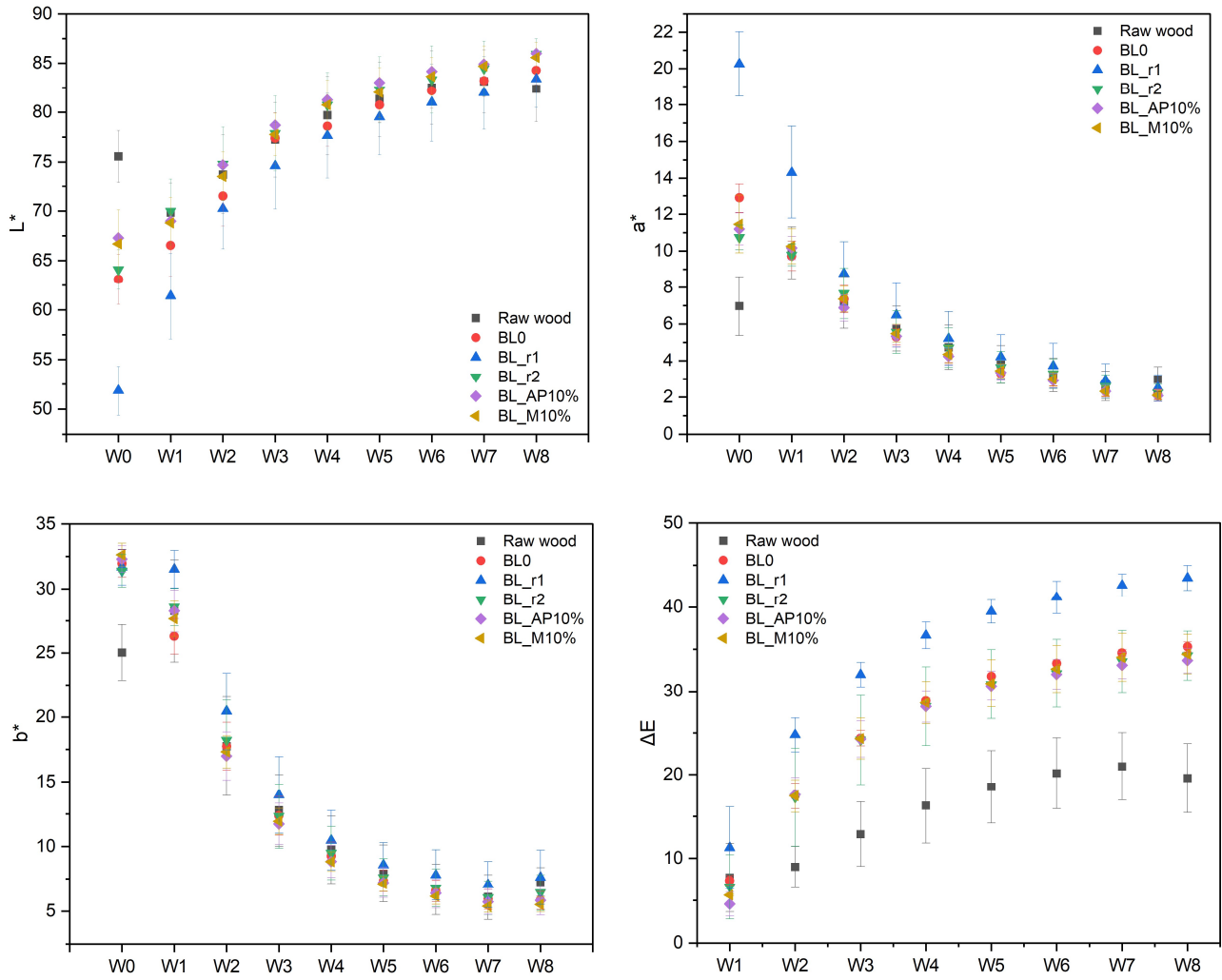


Figure IV-12 - Evolution of  $L^*$ ,  $a^*$ ,  $b^*$ , and  $\Delta E$  parameters over weeks of exposure (W0: before exposure, W1: after one week of exposure, etc.)

Table IV-3 -  $\Delta E$  values for color comparison before and after 8 weeks of exposure for the UV-protected part.

	Raw wood	BL0	BL_r1	BL_r2	BL_AP10%	BL_M10%
$\Delta E$	$9.64 \pm 2.00$	$4.99 \pm 2.75$	$4.66 \pm 1.00$	$3.60 \pm 0.44$	$6.81 \pm 0.45$	$5.42 \pm 1.88$

### Evaluation of fungal resistance

The results of the biological sustainability assessment are presented in Table IV-4.

The moisture content reported corresponds to the content of the samples at the end of the 7-week incubation period, before being oven-dried. According to Appendix 2. 4. 3, the amount of mass loss must be corrected by the correction factor obtained with the uninoculated flask. No mass loss was recorded for samples in uninoculated flasks. Therefore, the correction factor was 0. Regarding *Trametes versicolor* fungus, in comparison with the results obtained for raw wood, it is possible to observe a decrease in the moisture content at the end of exposure for both resins. However, it should be noted that this reduction is more important for BL0 resin. Indeed, the difference in moisture content between raw wood and BL\_M10% is very small (36.71% and 33.65%, respectively). A lower loss of mass compared to untreated wood can also be observed for BL0. On the contrary, mass loss is higher for BL\_M10% than for raw wood. Then, concerning the *Rhodonia placenta* fungus, BL0 resin exhibits a lower moisture content and mass loss than the raw wood. For the bottle containing BL\_M10% resin, a very high moisture content can be observed for both the raw wood and the impregnated samples (81.44 and 97.46%, respectively). The mass loss observed was higher for raw wood.

The large amount of moisture present at the end of the BL\_M10% formulation in the presence of *Rhodonia placenta* seems to indicate a better test efficiency. For this reason, a comparison between the different culture flasks studied was not possible. A poor growth of fungi can alter the results. However, within the same culture flask, it can be observed that wood samples impregnated with BL0 show slight resistance to the two fungi studied, while those impregnated with BL\_M10% show greater mass loss with *Trametes versicolor* and less with *Rhodonia placenta*.

Table IV-4 – Final moisture content and mass loss for samples subjected to fungal resistance tests.

		Impregnated wood		Raw wood	
		Final moisture content (%)	Mass loss (%)	Final moisture content (%)	Mass loss (%)
Flask 1	<i>Trametes versicolor</i> + BL0	28.00 ± 2.87	6.74 ± 1.49	34.66	9.12
Flask 2	<i>Trametes versicolor</i> + BL_M10%	33.65 ± 2.29	9.32 ± 1.31	36.71	8.29
Flask 3	<i>Rhodonía placenta</i> + BL0	30.57 ± 1.64	4.62 ± 2.17	38.84	5.96
Flask 4	<i>Rhodonía placenta</i> + BL_M10%	81.44 ± 7.40	7.05 ± 1.54	97.46	8.14

### IV. 3. 3. Conclusion

In this section, the various resins previously synthesized and impregnated on wood samples were characterized for their performance.

Firstly, a study to determine the optimum number of cycles required to achieve maximum resin impregnation in wood samples was conducted. The results indicated that three immersion cycles were sufficient to achieve the highest rate of impregnation.

Then, the results of the contact angle measurements show that all the resins synthesized achieved a higher contact angle than the one measured on the raw wood sample. Moreover, the best formulations were BL0, BL\_r2, and BL\_0%. Secondly, fire test results showed very good results for BL0 and BL\_r1 resins, indicating an influence of the presence of suberin on thermal resistance. Regarding the UV resistance, a high UV sensitivity of the resins was observed after the first week of exposure. However, additional tests demonstrated that the resin was resistant to several cycles of humidity and the water passing over the samples. Finally, biological durability tests showed a slight resistance of BL0 resin and a similar behavior of BL\_M10% and raw wood towards both types of fungus. These results should be

considered with precaution, as the required time was not respected and poor fungal growth may have occurred in culture flasks. In addition, new experiments need to be carried out with, for example, the formulation containing a large amount of extraction residue, since excellent antioxidant properties were obtained during characterization.

## IV. 4. Chapter conclusion

This chapter was dedicated to the synthesis of different resins, the application of these resins to wood and the characterization of the performance provided to the wood. Firstly, the resins synthesized during the visit to Slovenia were presented. They were synthesized using lignin modified with trichlorododecylsilane. Chemical modification with this silane resulted in an important surface hydrophobicity. This research also confirmed the usefulness of adding an inorganic additive to improve the thermal resistance of resins. Moreover, the use of this biobased additive also gave positive results, suggesting that it could be considered in resin formulation. The plasma treatment used to improve resin adhesion to the wood surface had demonstrated its effectiveness. However, the excellent results obtained on non-plasma-treated samples enabled this extra step to be discarded.

In the second part of this chapter, resin syntheses were carried out, using in this case lignin silanized with APTES. During resin synthesis, several parameters were studied (reaction time, temperature, the ratio lignin/residue, and the type and quantity of inorganic additive). Rapid characterizations performed demonstrated an improvement in thermal properties when inorganic compounds were added, or when silanized lignin was used in excess.

The third part of this chapter was devoted to the application of these resins to wood. The impregnation used in the first part of this chapter provided favorable results. This type of application ensures a homogeneous quantity of resin both on the sample and between samples. In this section, between 1 and 8 impregnation cycles were performed. The results showed that 3 cycles of 3 min immersion followed by 2 min of drying at room temperature provided a maximum impregnation.

Finally, the last part of this chapter presented the tests carried out to determine the performance of resin-impregnated wood samples. The contact angle measurements revealed that the resins overall were strongly hydrophobic, with a contact angle around 1.5 times greater than raw wood. Furthermore, the resin containing no inorganic additive achieved a higher contact angle than all the others. Fire-resistance tests demonstrated the effectiveness of the initial resin (BL0) as well as the resin composed of excess suberin (BL\_r2). The resins presented no UV resistance. Finally, fungal resistance tests showed that BL0 was slightly resistant to the two fungi studied. The combination of all these results suggests that either the initial (BL0) resin or the resin composed of excess suberin (BL\_r1) are a suitable basis for the development of a wood preservative.





# Chapter V - Conclusion and perspectives



## V. 1. General conclusion

The main objective of this thesis was to develop a biosourced and multifunctional resin for wood preservation based on biobased and local resources.

To this end, the first chapter presented the composition of wood and its vulnerabilities to various degradation agents such as water, fire, microorganisms, and external conditions (UV, humidity, water). In this section, various existing protection methods were also presented. These methods can be divided into two groups. The first involves the addition of chemical preservatives such as woodstains, varnishes, or resins. The second group involves the modification of wood using a chemical reagent (chemical modification) or heat (thermal modification). However, the majority of compounds used in the above-mentioned methods use toxic compounds, some of them are now subject to regulations. For this reason, in this chapter a section on the regulations was presented, followed by current research proposing alternatives to existing products, with the aim of developing preservatives as environmentally-friendly as possible.

The second chapter of this thesis was devoted to the study of a resin previously developed by a previous PhD student. This resin, based on lignin and tannins, was produced to be used as a coating to protect wood against fire. In the case of this thesis, the resin must also protect the wood against photodegradation, water, and microorganisms. The development of a resin formulated by targeting the provision of multifunctional wood protection was thus studied. As a result, this previous resin was used as the basis for the development of new multifunctional formulations. To this end, the first part of this chapter was devoted to an investigation of the protection provided by this resin to wood in addition to fire resistance. The first part of this chapter presents the synthesis of this resin, involving the glyoxalation of lignin. This modification method added hydroxyl sites to the lignin surface, enhancing its reactivity with other compounds. The resin was then synthesized from three main compounds: modified maritime pine lignin, mimosa tannins, and an inorganic additive (organically modified montmorillonite). The latter was added to improve the thermal resistance of the resin. After application of the resin to wood samples, rapid water resistance tests showed considerable sensitivity of the resin to water. The passage of water led to complete solubilization. As a result, the resin had to be improved. For this, the first modification was to remove from the formulation the mimosa tannins from Brazil, which were already widely used and did not fit into the desired circular economy context. Then, the

addition of hydrophobic compounds such as beeswax or rosin to reduce water sensitivity was studied. Another alternative to improve this property was to use urea-formaldehyde resins rather than phenol-formaldehyde resins, replacing the phenol with glyoxal and using lignin to make a urea-lignin-glyoxal resin. All these different resins were synthesized and applied to wood before being subjected to water resistance tests. The results showed that the application of water to the coated wood samples also resulted in a complete leaching of the resin.

The third chapter of this thesis focused on the presentation of new raw materials used in the development of innovative resins. Indeed, because of the poor results obtained in the previous chapter, an analysis of each compound involved was carried out. Firstly, the mimosa tannins previously used have already been discarded, as they are already highly valorized in the industry. However, the by-product obtained by companies after extracting the tannins is not currently valorized. A complete characterization of this residue was presented in this chapter and the results obtained revealed a large amount of suberin ( $\approx 50\%$ ) which can bring a hydrophobic character to the resin. Moreover, this by-product derived from maritime pine bark also proved a very good antioxidant property. Secondly, the lignin previously used was an organosolv lignin. Although this type of extraction process produces high-purity lignin, the lignin was replaced by kraft lignin precipitated from black liquor from a local paper mill. This choice was made to be in line with the valorization of local resources. This precipitation was carried out using various organic acids, rather than the sulfuric acid generally used. The various characterizations carried out on these lignins resulted in high-purity lignins with suitable properties for future uses. Precipitation with oxalic acid offered a good compromise between the yield obtained, the quantity of acid used, the purity, and the properties of the lignin. A modification of this lignin was then carried out using a silane instead of glyoxal in this chapter. This change was decided because the addition of hydroxyl sites to the lignin surface can lead to undesired hydrophilicity. The two types of silanization successfully carried out were presented in this chapter. Analyses demonstrated an improvement in the thermal properties of lignins after modification.

The fourth and final chapter of this thesis presented the synthesis and application of various resins on wood. The synthesis was carried out using silanized lignin, residue from extraction, and inorganic additive. Various parameters such as reaction time, temperature, lignin/residue ratio, and type and quantity of inorganic additives were studied. Plasma treatment of the wood prior to resin application was also studied. In addition, in this chapter the application of resins to wood was carried out by impregnation. A study of this impregnation was therefore

conducted and the results obtained indicated an optimized impregnation for three cycles (1 cycle = 3 min impregnation + 2 min drying at room temperature). Performance characterization of the impregnated wood samples initially showed that plasma treatment was effective, but excellent results were obtained without it. Consequently, this additional step was omitted from the resin development process. Then, contact angle measurements indicated that the resins synthesized were highly hydrophobic for all the formulations studied. Fire-resistance tests showed an improvement in this resistance for some formulations, notably those containing an excess of extraction residue and therefore of suberin. For resins exposed to UV radiation, surface weathering was observed from the first week, indicating high sensitivity of resins to external conditions. Regarding biological durability tests, a slight resistance to fungi was observed for one resin, but a better growth of fungi or a longer inoculation period would certainly provide more relevant results. It is therefore impossible to make any conclusions about the biological protection of the synthesized resins.

In conclusion, the resin synthesized at room temperature for 24 h with an equivalent quantity of lignin and residue, or with an excess of residue, offered a good compromise between the performance obtained and an unconstrained synthesis. The addition of the organic compound was particularly positive, as an improvement of the fire resistance was observed. Despite the slightly lower performance of the biobased inorganic additive, its use would enable to obtain an inexpensive biosourced resin.

## V. 2. Perspectives

All the work carried out in this thesis has provided encouraging results for the development of a wood preservative. However, there are still a number of adjustments to be made before that a multifunctional resin can be obtained:

- Isolation of the suberin contained in the extraction residue. Indeed, the addition of this by-product has demonstrated a beneficial effect on resin protection against fire and water. Considering that this improvement is due to the presence of suberin in the residue, isolating the suberin a priori would possibly provide the desired protection without having a possible undesirable effect due to the other compounds present in this by-product.
- Use new inorganic additives to enhance fire resistance with biobased products. The use of POSS (polyhedral oligomeric silsesquioxanes), for example, could be investigated.
- Improve fire-resistance tests by measuring a larger number of samples to limit standard deviations.
- Further research and experimentation are needed to improved UV resistance and a comprehensive wood durability experiment must be carried out.
- Optimization of the formulation to obtain a multifunctional resin with the desired performance, keeping in mind the context of the circular economy and environmental considerations.
- Perform a complete life-cycle assessment to determine the environmental impact of the synthesis, use and end-of-life of the resin.

# Appendices





# **Appendix 1: Instrumental techniques**

## **1. 1. Spectroscopic techniques**

### **1. 1. 1. Fourier Transform Infrared spectroscopy (FTIR)**

Fourier Transformed Infrared (FTIR) analyses were performed using a Jasco FT/IR-4700 infrared spectrophotometer equipped with an ATR (Attenuated Total Reflection) unit (Jasco, Spain). Measurement were carried out in absorbance mode with 64 scans and a resolution of 4 cm<sup>-1</sup> from 4000 to 400 cm<sup>-1</sup>.

### **1. 1. 2. Ultraviolet spectrophotometer (UV)**

Absorbance was measured using a UV-Visible spectrophotometer (Secoman, France). Different wavelengths were used depending on the protocol used.

## **1. 2. Thermal techniques**

### **1. 2. 1. Thermogravimetric analysis (TGA)**

Thermogravimetric analysis was conducted using a Q500 thermogravimeter (TA Instrument, US). Between 5 and 10 mg of solid was heated from 30 to 800 °C at a heating ramp of 10 °C/min under a nitrogen flow rate of 40 mL/min.

In the case of ash determination with this technique. After temperature rise to 800°C as described above, the nitrogen flow was replaced by an oxygen flow at 60 mL/min. In this way, calcination of the solid occurred before the temperature decrease.

### **1. 2. 2. Differential Scanning Calorimetry (DSC)**

Differential Scanning Calorimetry was performed with a Q20 calorimeter (TA Instrument, US). Sample with a mass between 5 and 10 mg was added to a standard aluminum pan. First, the sample was heated under 105 °C with a heating rate of 10 °C/min. A one-minute isotherm was performed at 105 °C followed by a cooling step to -50 °C at 10 °C/min. After, that the sample was heating from -50 °C to 250 °C at a heating rate of 10 °C/min. All these steps were performed under nitrogen atmosphere.

## **1. 3. Chromatography techniques**

### **1. 3. 1. High Performance Liquid Chromatography (HPLC)**

The HPLC used for carbohydrates determination was a Jasco LC Net II/ADC chromatograph (Japan) equipped with a photodiode array detector (MD-2018Plus) and a refractive index detector (RI-2031Plus). The column working with a flow rate of 0.6 mL/min at 50 °C was an Aminex HPX-87H (300 × 7.8 mm) (Bio-Rad Laboratories, USA). The injection volume was 20 µL and 0.005 M H<sub>2</sub>SO<sub>4</sub> solution was used as mobile phase.

### **1. 3. 2. Size Exclusion Chromatography (SEC) for lignin characterization**

Lithium bromide (LiBr) was purchased from Panreac and N, N-Dimethylformamide (DMF) was obtained from Fisher Scientific.

SEC was performed using a Jasco LC-Net II/ADC (Japan) to determine the weight average molar mass ( $M_w$ ), the number average molecular weights ( $M_n$ ), and the polydispersity index ( $\mathcal{D}$ ) of lignin samples. The apparatus was equipped with a refractive index detector (RI-2031Plus) and two Polar-Gel-M columns (300 × 7.5 mm). The analysis was performed at 40 °C using N, N-dimethylformamide (DMF) with 0.1% of lithium bromide (LiBr) at a flowrate of 0.7 mL/min and 20 µL of injection volume. The solution injected was prepared by dissolving 25 mg of lignin in 5 mL DMF.

### **1. 3. 3. Size Exclusion Chromatography (SEC) for residues characterization**

The weight-average molar mass ( $M_w$ ), number-average molecular mass ( $M_n$ ) and polydispersity index ( $\mathcal{D}$ ) of the samples were determined using size exclusion chromatography (SEC) with NaOH solution as eluent. Measurements were performed on an Ultimate 3000 system (Thermoscientific, US) equipped with a diode array detector (DAD). The system also included a multi-angle light scattering detector (MALS) and a differential refractive index detector (DRI). Three Tosoh columns (G4000PW-2\*G3000PW (7.8 × 300 mm)) (exclusion limits from 200 Da to 300,000 Da) were used to separate polymers at a flow rate of 1 mL/min. Column temperature was maintained at 25 °C. Ethylene glycol was used as a flow marker and polystyrene sulfonate as a standard.

## 1. 4. Others techniques

### 1. 4. 1. Contact angle

The contact angle was used to measure the hydrophobicity of the resin-coated wood surface. Measurement was performed using an optical tensiometer (Theta Flow, Biolin Scientific) equipped with a camera. The "sessile drop" method in air at room temperature was followed by drops of 5  $\mu\text{L}$  of distilled water. Three measurements were performed on each sample.

### 1. 4. 2. Color measurement

Color measurements on wood samples were carried out using a spectrophotometer (X-rite, Ci6X). A minimum of three measurements were recorded on each sample.

Color was expressed using the CIELAB color space, which comprises 3 parameters:  $L^*a^*b^*$ . The first,  $L^*$ , gives an indication of lightness:  $L^*$  close to 100 corresponds to a light sample, while  $L^*$  close to 0 indicates a dark sample. The parameters  $a^*$  and  $b^*$  provide information on color:  $a^*$  indicates variation on the green-red axis and  $b^*$  on the blue-yellow axis.

The color difference between two samples or two states of the same sample can be calculated with the parameter  $\Delta E$  according to the following formula:

$$\Delta E = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2}$$

$$\Delta a^* = a_2^* - a_1^*$$

$$\Delta b^* = b_2^* - b_1^*$$

$$\Delta L^* = L_2^* - L_1^*$$

## Appendix 2: Procedure

### 2. 1. Black liquor characterization

#### 2. 1. 1. Density

The density was determined by measuring the weight of a known volume of liquid.

#### 2. 1. 2. Total dry solids content (TDS)

Total dry solids content was calculated as follows: 5 ± 0.001 g of liquid fraction ( $m_0$ ) were weighed into a tared and dry crucible ( $m_1$ ). The crucible containing the liquid fraction was placed in an oven at 105 ± 3°C for 24 hours. At the end, the crucible was placed in a desiccator to cool and then weighed until it reached a constant mass ( $m_2$ ).

The following formula was used to determine the TDS value:

$$\text{TDS (\%)} = \left( \frac{m_2 - m_1}{m_0} \right) \times 100$$

$m_0$ : weight of the dried crucible (g)

$m_1$ : weight of the liquid fraction (g)

$m_2$ : weight of the crucible after the oven (g)

#### 2. 1. 3. Ash, volatile matter, and fixed carbon

Volatile matter, fixed carbon, and ash contents were determined using a calcination furnace (Carbolite Gero, Germany). First, 0.25 g of solid ( $m_0$ ) were weighed into a tared and dry crucible ( $m_1$ ). The crucible and solid were placed in an oven for 24 h at 105 ± 3 °C. It was then placed in a desiccator to cool and weighed until a constant mass ( $m_2$ ) was obtained. The crucible with the lid was heated in the calcination furnace at 575 °C for 10 min. Once this stage was completed, the crucible was put back in the desiccator and weighed after cooling ( $m_3$ ). The crucible was then placed back into the calcination furnace at 575 °C without the lid, until all the powder had turned grey. At the end, it was once again transferred to a desiccator and weighed ( $m_4$ ).

The different contents were determined as follow:

$$\text{Humidity (\%)} = \frac{m_0 - (m_2 - m_1)}{m_0} \times 100 \quad \text{Volatile matter (\%)} = \frac{m_2 - m_3}{m_2 - m_1} \times 100$$

$$\text{Ash (\%)} = \frac{m_4 - m_1}{m_2 - m_1} \times 100$$

$$\text{Fixed carbon (\%)} = 100 - [\text{Humidity (\%)} + \text{Volatile matter (\%)} + \text{Ash (\%)}]$$

#### 2. 1. 4. Quantitative acid hydrolysis (QAH)

Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was purchased from Thermoscientific.

Quantitative acid hydrolysis was used to determine acid-insoluble lignin (AIL or Klason lignin), acid-soluble lignin (ASL), and carbohydrates content, following the NREL TP-510-42618 standard. A first acid hydrolysis was conducted by mixing 300.0 ± 10.0 mg (m<sub>0</sub>) of sample with 3.00 ± 0.01 mL of a sulfuric acid solution (H<sub>2</sub>SO<sub>4</sub>) at 72%. The solution was placed in a water bath for 60 ± 5 min at 30 ± 3 °C, stirring every 5 to 10 min without removing sample from the bath. Sample was then removed from the water bath and diluted to 4% H<sub>2</sub>SO<sub>4</sub> concentration by adding 84.00 ± 0.04 g of water. The solution was placed in an autoclave for 1 h at 121 °C to conduct the second acid hydrolysis. At the end, the sample was vacuum filtrated using a filter crucible (n°3). The filtrate was captured and kept for the ASL and carbohydrates determination. The solid residue was washed with distilled water until a neutral pH, and was then placed to the oven at 105 ± 3 °C during 24 h and weighed (m<sub>1</sub>) to determine the AIL content.

$$\text{AIL (\%)} = \frac{m_1}{m_0} \times 100$$

m<sub>0</sub>: weight of initial sample (g)

m<sub>1</sub>: weight of acid-insoluble lignin (g)

For the ASL content, the filtrate was analyzed by UV-Visible spectroscopy using a V-730 UV-Vis spectrophotometer (Jasco, Japan) at 205 nm. The sample was diluted with a 4% H<sub>2</sub>SO<sub>4</sub> to have an absorbance in the range 0.1-0.8. An acid soluble lignin absorptivity value (ε) of 110 L. g<sup>-1</sup>.cm<sup>-1</sup> was used and the blank was done with a 4% H<sub>2</sub>SO<sub>4</sub>.

$$\text{ASL (\%)} = \frac{\text{UV}_{\text{abs}} \times V \times D}{\epsilon \times m_0 \times l} \times 100$$

$\text{UV}_{\text{abs}}$ : UV-Vis absorbance of sample

V: volume of filtrate (L)

D: dilution

$\epsilon$ : absorptivity ( $110 \text{ L} \cdot \text{g}^{-1} \cdot \text{cm}^{-1}$ )

$m_0$ : weight of initial sample (g)

l: pathlength of UV-Vis cell (cm)

The carbohydrates content was measured by analyzing the filtrate by High Performance Liquid Chromatography (HPLC) (Appendix 1. 3. 1).

## 2. 2. Lignin characterization

### 2. 2. 1. Total phenolic content

The Folin Ciocalteu reagent was purchased from Merck, dimethylsulfoxide (DMSO) from Sigma Aldrich, sodium carbonate from Honeywell, and gallic acid was obtained from Acros Organics.

The total phenolic content of precipitated lignin was determined using the Folin-Ciocalteu method [197] adapted for lignin. Firstly, 1 mL of Folin-Ciocalteu reagent was mixed with 0.2 mL of lignin solution at 2 g/L in DMSO and 2 mL of sodium carbonate solution (200 g/L in water). Then, 16.8 mL of water was added to previous solutions to reach a total volume of 20 mL, and they were placed in a water bath for 30 min at 40 °C. After that, the absorbance was read using a UV-Visible spectrophotometer (Secoman, France) at 750 nm. Calibration curve was done with gallic solutions (100-1000 mg/L) and the results are expressed as microgram of gallic acid equivalent per gram of dry lignin ( $\mu\text{g GAE/g dry lignin}$ ).

$$\mu\text{g GAE/g dry lignin} = \frac{C_{\text{GAE}}}{C_{\text{sample}}} \times 1000$$

$$\text{OH (\%)} = \frac{C_{\text{GAE}} \times n \times M_{\text{OH}}}{M_{\text{GA}} \times C_{\text{sample}}} \times 100$$

$C_{\text{GAE}}$ : concentration of gallic acid obtained by the calibration curve (g/L)

$C_{\text{sample}}$ : concentration of the lignin sample in DMSO (g/L)

n: OH number in gallic acid (4)

$M_{\text{OH}}$ : Molar mass of OH (17 g/mol)

$M_{\text{GA}}$ : Molar mass of gallic acid (170.12 g/mol)

### 2. 2. 2. Antioxidant activity

Dimethylsulfoxide (DMSO) was bought from Sigma Aldrich, methanol from Fischer Scientific, 2,2-diphenyl-1-picrylhydrazyl (DPPH) was purchased from Alfa Aesar, and Trolox and butylated hydroxytoluene (BHT) from Thermoscientific.

The antioxidant activity of lignin samples was assessed using the method described by Brand-Williams and his collaborators [198] with a few modifications. Lignin samples were dissolved



with DMSO at different concentrations (0-0.04 mg/mL). In test tubes, 3 mL of diluted lignin solutions were mixed with 3 mL of DPPH (39.4 mg/L in water). Test tubes were then placed in the dark for 30 min. Absorbances of solutions were read using a UV-Visible spectrophotometer (Secoman, France) at 517 nm. The blank was done with DMSO. Two commercial antioxidants, Trolox and BHT, were used as comparison. The same protocol mentioned above was used replacing DMSO by methanol and using a dilution between 0 and 0.1 mg/mL.

The inhibition percentage (I) was calculated with the following formula:

$$I (\%) = \frac{(A_0 - A_s)}{A_0} \times 100$$

A<sub>0</sub>: absorbance at the zero concentration (3 mL of DMSO + 3 mL of DPPH solution)

A<sub>s</sub>: absorbance of the lignin sample

The graph inhibition percentage versus concentration was then plotted and the concentration to inhibit 50% of the DPPH radical (IC<sub>50</sub>) was determined using the following formula:

$$IC_{50} (\%) = \frac{(50 - b)}{a} \times 100$$

a: slope of the tendency curve

b: interception of tendency curve

### 2. 2. 3. Quantitative acid hydrolysis (QAH)

Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was obtained from Thermoscientific.

Quantitative acid hydrolysis was performed to measure the acid-soluble lignin (ASL), acid-insoluble lignin (AIL or Klason lignin), and the carbohydrates content of precipitated lignins. The protocol used was the same as mentioned before in Appendix 2. 1. 4 with some modifications. First, 250.0 ± 5.0 mg of lignin were mixed with 2.50 ± 0.01 mL of H<sub>2</sub>SO<sub>4</sub> solution at 72%. The mixture was placed in a water bath at 30 ± 3 °C for 60 ± 5 min with a stirring every 10 min without removing the sample from the water bath. After this first acid hydrolysis, the solution was diluted with distilled water by adding 12% H<sub>2</sub>SO<sub>4</sub> until a total volume of 24.2 mL. Samples were then transferred in an autoclave for 1 h at 121 °C. After completion of this second acid hydrolysis, vacuum filtration was performed using a filtering crucible n°3. The filtrate was recorded for further analysis (ASL and carbohydrates content). The solid part was washed

several times with distilled water until a neutral pH was reached and was then put in an oven during 24 h at  $105 \pm 3$  °C.

The recovered filtrate was diluted with a 12% H<sub>2</sub>SO<sub>4</sub> solution before reading the absorbance as described for black liquor QAH. The determination of AIL and carbohydrates was carried out following the same procedure used for black liquor QAH.

## 2. 3. Residue characterization

### 2. 3. 1. Total phenolic content

Sodium carbonate, Folin reagent, and acetone were bought from Fisher Scientific and gallic acid was purchased from VWR.

Total phenolic content of residues extraction was performed using the Folin-Ciocalteu method [197] adapted for biomass. First, 500 mg of solid extract was dissolved in 30 mL of acetone solution (70% in water). Then, 0.5 mL of this aqueous extract was mixed with 2 mL of Folin reagent (10% in water) and 2.5 mL of sodium carbonate (75 g/L in water). The solutions were placed in a water bath for 5 min at 50 °C and then analyzed using a UV-Visible spectrophotometer. The absorbance was read at 760 nm and gallic acid solutions (0-100 mg/L) were used for calibration curve. The results obtained are expressed as milligrams of gallic acid equivalent (GAE) per gram of dry residue (mg GAE/g dry residue).

$$\text{mg GAE/g dry residue} = \frac{C_{\text{GAE}} \times V \times D}{m} \times 1000$$

$C_{\text{GAE}}$ : concentration of gallic acid obtained by the calibration curve (g/L)

V: volume of solution (0.03 L)

D: dilution factor

m: dry mass of residue (g)

### 2. 3. 2. Condensed tannins content

Acetone and methanol were obtained from Fisher Scientific. Vanillin and hydrochloric acid (37%) were purchased from Acros Organics and catechin from Sigma Aldrich.

Content of condensed tannins was assessed with the vanillin method described by Broadhurst and Jones [199]. An aqueous solution of 300 mg of sample in 25 mL of acetone solution (70% in water) was prepared. Then, 0.5 mL of this sample solution was mixed with 3 mL of vanillin (4% in methanol) and 1.5 mL of concentrated hydrochloric acid. The mixture was then kept protected from light at ambient temperature for 15 min. Absorbances of solutions were read using a UV-Visible spectrophotometer at 500 nm. Catechin solutions (0-100 mg/L) were used

to do calibration curve. The results were obtained as mg of catechin equivalent per g dry residue (mg CE/g dry residue).

$$\text{mg CE/g dry residue} = \frac{C_{\text{CE}} \times V \times D}{m} \times 1000$$

$C_{\text{CE}}$ : concentration of gallic acid obtained by the calibration curve (g/L)

V: volume of solution (0.025 L)

D: dilution factor

m: dry weight of residue (g)

### 2. 3. 3. Hydrolysable tannins content

Methanol was purchased from Fisher Scientific while potassium iodate ( $\text{KIO}_3$ ) and tannic acid were obtained from Acros Organics.

The method described by Bossu and collaborators [200] was used to determine the hydrolysable tannins content. First, 0.25 g of residue was dissolved in 50 mL of methanol (80% in water). Agitation at ambient temperature during 6 h was performed before centrifugation for 10 min at 2000 rpm. The supernatant recovered was diluted five times with water. Then, 5 mL of a  $\text{KIO}_3$  solution (2.5% in water) were heated for 7 min at 30 °C before the addition of 1 mL of the previous diluted solution. The mixture was heated at 30 °C for 2 min more. Absorbances of solutions were read at 550 nm using a UV-Visible spectrophotometer. A calibration curve was produced using a 5000 mg/L solution of tannic acid in methanol. Dilutions from this solution (0-5000 mg/L) were made with distilled water. The results were expressed in mg of tannic acid equivalent per g of dry residue (mg TAE/g dry residue).

$$\text{mg TAE/g dry residue} = \frac{C_{\text{TAE}} \times V \times D}{m} \times 1000$$

$C_{\text{TAE}}$ : concentration of gallic acid obtained by the calibration curve (g/L)

V: volume of solution (0.01 L)

D: dilution factor

m: dry mass of residue (g)

### 2. 3. 4. Stiasny number

Acetone and formaldehyde (37%) were bought from Fisher Scientific and hydrochloric acid (37%) was a product of Acros Organics.

The Stiasny number was performed to evaluate the reactivity of tannins with formaldehyde. This test, described by Voulgaris and collaborators [201], was performed as follow: a solution of residue at 4 g/L in acetone solution (70% in water) was prepared. Then, 50 mL of this solution were poured in a round bottom flask and 10 mL of formaldehyde 37% and 2.5 mL of hydrochloric acid 10 mol/L were added. The mixture was heated under reflux for 30 min before to be vacuum filtrated using a filtering crucible n°3. After washing with water, the precipitate was dried at 105 °C in an oven until constant weight.

$$\text{Stiasny number (\%)} = \frac{m_1}{m_0} \times 100$$

m<sub>0</sub>: dry weight of the precipitate (g)

m<sub>1</sub>: dry weight of the initial residue (g)

### 2. 3. 5. Extractives content

Toluene and ethanol were respectively purchased from Alfa Aesar et Fischer Scientific.

Solvent extractives content was done using soxhlet equipment. First, 5.0 ± 0.1 g of residue were put into a cellulose cartridge and placed inside the soxhlet apparatus. Then, 150 mL of a mixture of toluene and ethanol (2/1, v/v) were poured into a round bottom flask previously dried and tared. The solvent solution was boiled to 150 °C to complete 24 extractions under reflux. After completion, the solvent was partially evaporated with a rotavapor and the round bottom flask was then put in an oven at 105 °C until a constant weight.

$$\text{Solvent extractives (\%)} = \frac{m_2 - m_0}{m_1} \times 100$$

m<sub>0</sub>: dry weight of the empty round bottom flask (g)

m<sub>1</sub>: dry weight of residue (g)

m<sub>2</sub>: dry weight of the round bottom flask at the end (g)

### 2. 3. 6. Suberin content

Sodium methoxide and chloroform were products of Alfa Aesar while methanol from Fischer Scientific. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and sodium sulfate were purchased from Acros Organics.

The content of suberin was performed by the method described by Pereira [202]. Briefly, 1.5 ± 0.1 g of residue was put into a round bottom flask previously tared and 250 mL of sodium methoxide (3% in methanol). The mixture was heated under reflux for 3 h. Then, the solution was vacuum filtrated and the precipitated was heated under reflux again with 100 mL of methanol for 15 min. The solution was on other time vacuum filtrated. Both liquid phases were combined and acidified to pH 6 using sulfuric acid (2 M). The solvent was evaporated using a rotavapor and the residue was suspended with 100 mL of distilled water before performing a liquid-liquid extraction three times with 200 mL of chloroform. Finally, sodium sulfate was added to dry the extract and then filtration and solvent removal were conducted before to put the round bottom flask in an oven at 105 ± 3 °C until constant weight.

$$\text{Suberin content (\%)} = \frac{m_2 - m_0}{m_1} \times 100$$

m<sub>0</sub>: dry weight of the empty round bottom flask (g)

m<sub>1</sub>: dry weight of residue (g)

m<sub>2</sub>: dry weight of the round bottom flask at the end (g)

### 2. 3. 7. Antioxidant activity

Butylated hydroxytoluene (BHT) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Alfa Aesar and methanol from Fisher Scientific.

Antioxidant activity of residues was evaluated by the stable radical DPPH method [203]. First, the residues were diluted with methanol between 0 and 0.05 mg/mL for pine residue and between 0 and 0.01 mg/mL for the oak residue. A commercial antioxidant, BHT, was used as the reference. Then, 3 mL of these previous residue solution or methanol (control) were mixed with 3 mL of DPPH (0.1 mmol/L in methanol). The mixtures were put in the dark for 30 min and the absorbance was read using a UV7 UV-Visible Spectrophotometer (Mettler Toledo, UK) at 517 nm. The blank was done with methanol.

The inhibition percentage (I) was calculated with the following formula:

$$I (\%) = \frac{(A_0 - A_s)}{A_0} \times 100$$

A<sub>0</sub>: absorbance at the zero concentration (3 mL of methanol + 3 mL of DPPH solution)

A<sub>s</sub>: absorbance of the lignin sample

The graph inhibition percentage versus concentration was then plotted and the concentration to inhibit 50% of the DPPH radical (IC<sub>50</sub>) was determined using the following formula:

$$IC_{50} (\%) = \frac{(50-b)}{a} \times 100$$

a: slope of the tendency curve

b: interception of tendency curve

### **2. 3. 8. Ash**

For the determination of ash content, the same protocol as mentioned for the black liquor characterization was used (Appendix 2. 1. 4).

## 2. 4. Characterization of resin performance on wood

### 2. 4. 1. Water resistance

Firstly, the water resistance of the resins was tested in accordance with the standard NF EN ISO 2812-4: « Determination of resistance to liquids - Part 4: Spotting methods » (December 2017).

In this standard, wood samples must be of the following dimensions: 150 x 100 mm. The sample was then placed at an angle of 30° to the horizontal. Drops were applied with a burette to the top of the sample over a period of 10 min; each drop fell at intervals of 1 to 2 sec. The liquid running down the wood was collected in a collection bottle. At the end of the 10 min, the sample was dried with a clean absorbent paper and observed with the naked eye. Figure 0-1 shows the experimental scheme and laboratory setup. .

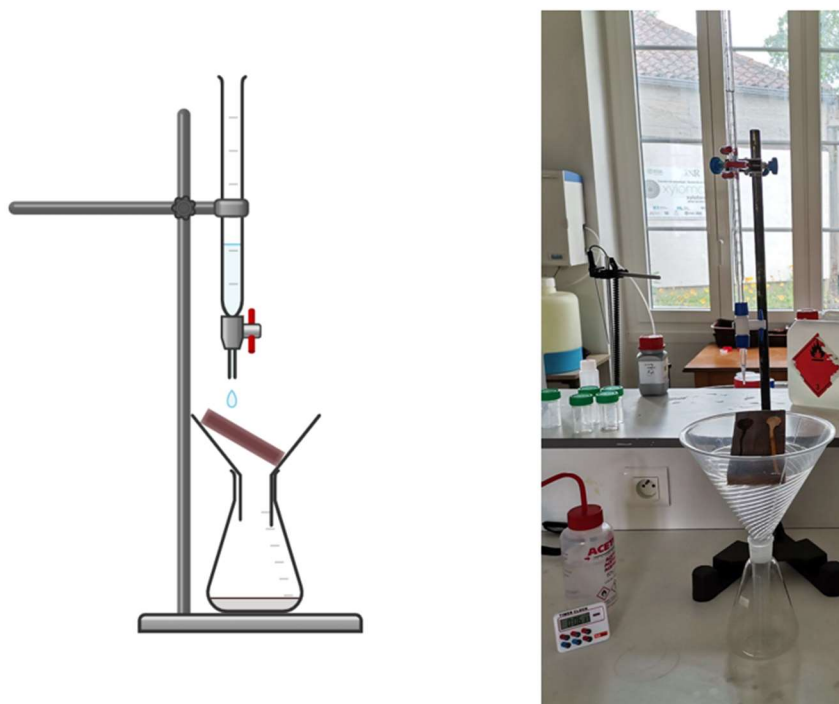


Figure 0-1 - Experimental scheme (left) and laboratory assembly (right)



## 2. 4. 2. Fire resistance

Fire tests were carried out according to the ASTM D635-2003 « Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position » using a horizontal/vertical flammability tester, UL94 (Fanyuan Instrument, China).

The samples dimensions were  $(125 \pm 5) \times (13.0 \pm 0.5) \times (3.0-3.2)$  mm.

The first step was to mark two lines perpendicular to the longitudinal axis on the sample, at  $25 \pm 1$  and  $100 \pm 1$  mm from the end to be ignited. The sample was then placed on the support, inclined at  $45 \pm 2^\circ$  as shown in Figure 0-2. The burner is then switched on for 30 sec, starting the ignition of the wood sample. The timer was activated when the flame front of the sample reaches the 25 mm mark. If this mark was reached before the end of the 30 sec ignition time, the burner must be stopped and the timer started. The timer was then stopped when the flame front reaches the 2nd mark at 100 mm, or when the flame goes out. The burning rate can then be calculated by dividing the distance burned by the ignition time.

For each formulation, three wood samples were impregnated and tested.

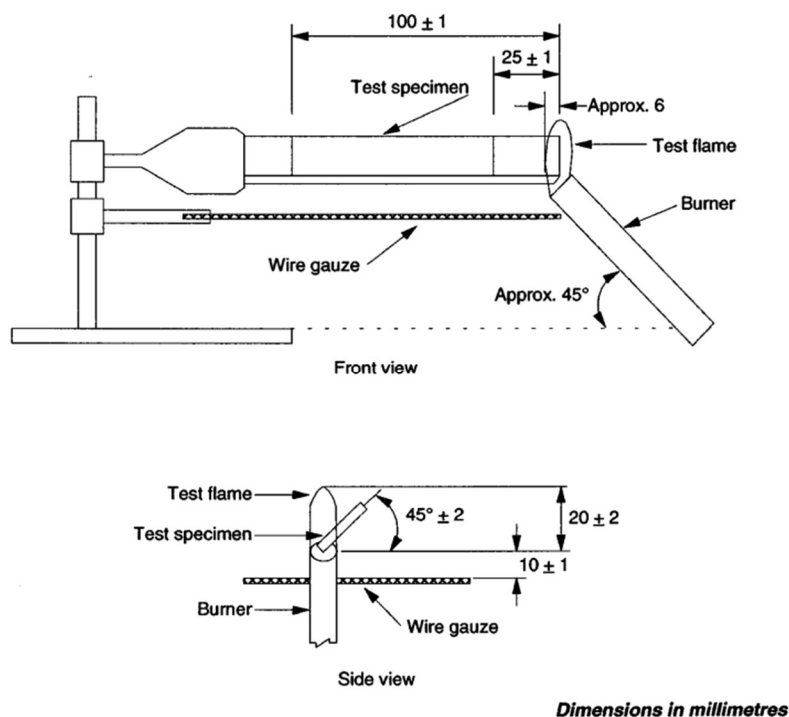


Figure 0-2 - Schematic representation of inflammation of the sample at  $45^\circ$  (source: ASTM D635)



Figure 0-3 - Photos of the instrument

### 2. 4. 3. Fungi resistance

The durability of wood against fungi was determined in accordance with NF EN 113-1 "Durability of wood and wood-based products - Test method against wood destroying basidiomycetes - Part 1: assessment of biocidal efficacy of wood preservatives" (December 2020), with a few modifications.

The fungi used in this test were *Trametes versicolor* and *Rhodonia placenta*. The culture medium was prepared according to the following protocol:  $40 \pm 0.5$  g of malt was mixed with  $20 \pm 0.5$  g of agar and 1000 mL of distilled water. The mixture was heated with stirring until complete dissolution. Then, 150 mL of this solution were introduced into the culture vessels shown in Figure 0-4. These were closed with a clean piece of cotton and autoclaved at  $121^\circ\text{C}$  for 20 min. Finally, the flasks were cooled in their final position of use.

The second step was to inoculate the culture flasks with the fungi mentioned above. After the culture media had been completely covered with fungi within two weeks, the resin-coated maritime pine (*Pinus pinaster*) wood (sapwood) samples were weighed and sterilized (20 min at  $121^\circ\text{C}$ ) before being introduced into the flasks. Sample dimensions were:  $(50 \pm 0.5) \times (25 \pm 0.5) \times (15 \pm 0.5)$  mm. In each fungus-inoculated flask, 3 test specimens of the same formulation and 1 control specimen (untreated wood) were placed. An uninoculated flask was also used to determine the influence of the culture medium on the sample, and consequently

the value of the correction factor. In this flask, 2 test specimens of each formulation were placed. The flasks were then placed in the culture chamber set at  $22 \pm 2$  °C and  $70 \pm 5\%$  humidity for 16 weeks.

At the end of the test, the test specimens were removed from the flasks and cleared of adhering mycelium before being weighed. They were then placed in an oven at  $105 \pm 3$ °C and weighed again until a constant mass was reached.

$$\text{Correction factor (\%)} = \frac{m_0 - m_1}{m_0} \times 100$$

$$\text{Corrected mass loss (\%)} = \left( \frac{m_2 - m_3}{m_2} \times 100 \right) - \text{Correction factor (\%)}$$

$m_0$ : dry weight of sample before being placed in uninoculated flask (g)

$m_1$ : dry weight of sample after being placed in uninoculated flask (g)

$m_2$ : dry weight of sample before being placed in fungus-inoculated flask (g)

$m_3$ : dry weight of sample after being placed in fungus-inoculated flask (g)

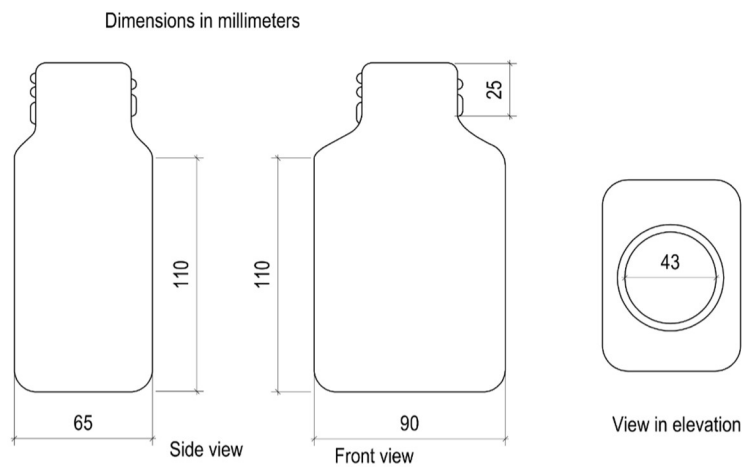


Figure 0-4 - Schematic representation of culture vessels (source: NF EN 113-1)

## 2. 4. 4. Accelerated aging

The accelerated aging of the resin was tested in accordance with NF EN 927-6: "Paints and varnishes - Coating materials and coating systems for exterior wood - Part 6: exposure of wood coatings to artificial weathering using fluorescent UV lamps and water" (October 2018), with a few modifications.

Accelerated aging of resin samples was evaluated using a QUV chamber (Q-LAB, USA) which reproduces the natural deterioration caused by sun, humidity, and rain.

Samples  $(150 \pm 2) \times (74 \pm 1) \times (18 \pm 1)$  mm were placed on the sides of the equipment as can be seen in Figure 0-5. Color measurements of the samples were carried out beforehand.

The cycle performed is shown in Table 0-1.

*Table 0-1 - One-week exposure cycle*

Step	Function	Temperature	Duration	Condition
1	Condensation	$(45 \pm 3) ^\circ\text{C}$	24 h	-
2	Subcycle 3 +4	-	cycles 3 + 4 (= 3 h) repeated 48 times (= 144 h)	-
3	UV	$(60 \pm 3) ^\circ\text{C}$	2.5 h	0.89 W/(m <sup>2</sup> mm) at 340 nm
4	Spray	-	0.5 h	6 L/min to 7 L/min. UV off

A complete cycle (steps 1 to 4) took 168 h, or 1 week. This cycle was repeated 12 times to reach a total exposure of 2016 h. Every week, color measurements were performed to follow the aging process and calculate the  $\Delta E$  (Appendix 1. 4.). Each formulation was applied to three wood samples. In addition, the color was measured at three different points on the sample, and always at the same location, thanks to pre-drawn markers.

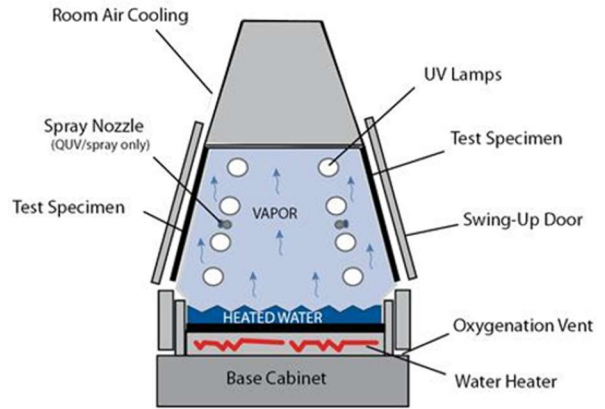


Figure 0-5 - Photos of the equipment used (left) and illustration of the inside of the QUV (right)

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