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ADHESIVOS Y MADERA MODIFICADA TERMICAMENTE

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ADHESIVES AND THERMALLY MODIFIED WOOD

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Resumen

La modificación térmica de la madera es una alternativa tecnológica a la impregnación química que permite mejorar la durabilidad y estabilidad dimensional de la madera. Como ventaja principal frente a la impregnación, la madera modificada es, desde el punto de vista ambiental, superior. Permite un uso responsable y sostenible del recurso. Sin embargo, la modificación térmica genera cambios en propiedades físicas y químicas que pueden ser negativas en algunos usos. Tal es el caso de la pérdida de resistencia física, lo que hace a esta madera modificada inapropiada para algunos usos estructurales.

El presente trabajo se centra en el estudio de las propiedades físicas y químicas de la superficie de la madera térmicamente modificada. Estas propiedades tendrán importancia en el desempeño y aplicabilidad de adhesivos en madera modificada. Madera de *Pinus taeda* y *Eucalyptus grandis,* producidas en Uruguay, fueron sometidas a 200 °C en una atmósfera de nitrógeno por 3 horas.

Se estudió la pérdida de masa, el cambio en el pH y las modificaciones química. Posteriormente, se realizó la caracterización de la superficie de la madera mediante microscopía óptica, estudios de higroscopicidad y humectabilidad. Finalmente, se llevó acabo el ensayo comparativo entre madera modificada y sin modificar con adhesivo de poliuretano y con adhesivo de emulsión de polímero de isocianato (EPI)

La pérdida de masa, así como los cambios químicos, fueron más significativos en *E. grandis*. Sin embargo, para ambas especies se observaron cambios relevantes en la higroscopicidad, así como en la humectabilidad. El ensayo con adhesivo de poliuretano fue considerado exitoso para *P. taeda* y se concluye que existe potencial para el desarrollo de productos con poliuretano y *P. taeda* térmicamente modificado. Por otro lado, la madera de *E. grandis* modificada térmicamente no alcanzó un desempeño aceptable con este adhesivo y en las presentes condiciones de tratamiento. En cambio, para el adhesivo EPI, el desempeño fue considerado no satisfactorio para ambas especies.

Abstract

A technological alternative for chemical impregnation of wood, is thermal modification, which improves wood durability and dimensional stability. The main advantage of thermal modification is that the wood produced is superior from the environmental point of view. It makes possible a responsible and sustainable use of this resource. However, thermal modification has negative effects on physical and chemical properties that affects certain uses of wood. Such is the case of physical resistance, which makes thermally modified wood not proper for some structural uses.

The present work is focused on the study of physical and chemical properties associated to the surface of thermally modified wood. These properties have impact on the performance of adhesives applied on wood. *Pinus taeda* and *Eucalyptus grandis* wood, both produced in Uruguay, were heated at 200°C for 3 hours in a nitrogen atmosphere.

Mass loss, pH changes and chemical modifications were studied. Furthermore, surface characterization of wood was realized by light microscopy, hygroscopicity and wettability studies. Finally, a comparative test was performed with non-modified and modified wood, with a polyurethane adhesive and an emulsion polymer isocyanate adhesive (EPI).

Mass loss, as well as chemical changes, were more significant in *E. grandis.* However, for both species, important changes on hygroscopicity and wettability were observed. The polyurethane adhesive test was successful for *P. taeda* and it was concluded that there is potential to develop products with thermally modified wood and polyurethane. On the other hand, polyurethane did not achieve an acceptable degree of performance on thermally modified *E. grandis.* For the EPI adhesive, performance was considered not satisfactory for both species, after thermal modification.

Preface

This work was conducted by Ignacio Di Pascua and supervised by Professor Dr. Andrés Dieste and Professor MSc. Leonardo Clavijo, who helped with the experimental design, interpretation of the results and the writing of the present document.

The work was carried out in the Forest Process Engineering group, in the Chemical Engineering Institute at the Faculty of Engineering, University of the Republic, Montevideo, Uruguay. Shear test was performed in the Material Testing Institute at the Faculty of Engineering, University of the Republic, Montevideo, Uruguay.

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1. INTRODUCTION

Wood is a renewable material with a vast potential for use in various areas. Wood have been used since the very beginnings of mankind and is nowadays essential for the development of substitute products for oil derivatives, iron, concrete, and other non-renewables. Actually, general conditions in forest products markets are positive and consumption rates of sawnwood and wood-based panels have been increasing since the global crisis of 2008 (FAO 2018). Wood harvested from certified planted forest, managed in a sustainable way, is considered a renewable material. Though, the productive chain of wood products is large, and the economic and environmental impacts of manufacturing top value-added products is relevant. For this reason, it is necessary to develop and implement technologies and sustainable ways of producing wood derivatives.

Despite the many useful properties, wood has two main disadvantages regarding it use in construction and exterior uses. The first one, as a natural product, it is biodegradable and prone to microorganisms, fungal and insect attack. Secondly, as it is a hygroscopic material, moisture content of wood will vary according to air humidity leading to dimensional changes. Dimensional instability is critical for certain purposes, such as load bearing uses. Traditional wood preservatives like creosote, pentachlorophenol, and heavy metal-based systems, like CCA (cromated copper arsenate) have been used to prevent biological attack. The use of these preservatives is criticised due to their negative impact on the environment, caused principally by leaching of hazardous components (Gosselink et al. 2004) during final disposal. Furthermore, it does not solve the problem of dimensional stability and, not all wood species can be deeply impregnated.

New preservatives and other methods have been studied to increase the biological resistance of wood and to enhance wood dimensional stability. Wood modification is any chemical, mechanical, physical or biological method to alter the properties of the material (Sandberg, Kutnar, and Mantanis 2017). Thermal modification is the most advanced modification process for alternative wood preservation and dimensional stability increase (Zauer et al. 2014). During this process, wood is heated in absence of oxygen so chemical reactions occurs in the compounds of it. No chemicals are necessary in the process, only energy to heat and a medium to remove oxygen. After thermal modification, besides the mentioned advantages, there is a significant reduction of wood mechanical properties such as modulus of rupture and modulus of elasticity. This is a problem regarding structural uses of thermally modified wood.

Adhesives not only have historically been a fundamental element in the development of the wood industry but also, they are essential for an efficient use of the material. Adhesives transfer loadings and stresses between the components, enhancing the stiffness and hardness of wooden products, depending strongly on the strength of the bonding between the adhesive and the wood (United States Department of Agriculture 2010). Adhesives expands the universe of wood use: wood engineered products such as cross laminated timber (CLT), laminated veneer lumber (LVL) and glue laminated timber (GLULAM) are of importance, especially for the development of structural wood. It is of strategic importance to research and develop construction-grade products and engineered forest products as they “are some of the highest value products from trees” (Ramage et al. 2017). The use of adhesives in thermally modified wood, may counter the negative effects on the mechanical properties caused by the treatment. However, the changes associated to thermal modification, namely the structure and chemistry of the wood, might negatively affect adhesion.

1.1 Hypothesis and objective

After thermal modification, physical and chemical modifications occur on wood. These changes result in an inactivation of the surface making it more hydrophobic, reducing wettability and negatively affecting adhesive bonding.

The present research work is focused on evaluating the behaviour of thermally modified wood regarding adhesion. *Pinus taeda* and *Eucalyptus grandis* wood was selected as they are widely produced in Uruguay and both presents great potential to became products with greater added value, such as wood engineered products and thermally modified wood (A. Dieste et al. 2018). Both, thermal modification and adhesive performance, are highly dependent upon wood specie. Thus, research on national wood is essential on the way to develop new products and technologies.

2. LITERATURE REVIEW

2.1 Introduction

The objective of this chapter is to present the theory and literature about thermal modification of wood and how changes that occurs on wood affects the performance of adhesives. It is necessary, first, to introduce and describe wood anatomy and chemical composition. As the investigation is focused on wood species produced in Uruguay, a brief description of *Pinus taeda* and *Eucalyptus grandis* is presented. After this, theorical background regarding thermal modification is presented, as well as previous investigations about thermal modification on the species mentioned above.

In the second half of the chapter, adhesives and their importance regarding wood usage is presented. The most important type of adhesives, their functionality and specifications are introduced. Next, important properties of wood that influence adhesion are recounted and how they are affected after thermal modification. Finally, theory of the surface characterization, basis of the present investigation, is exposed.

2.2 Wood

Wood have played “an important role in human activity since before recorded history”. The importance of it lies in the fact that their useful properties are unique: recyclable, renewable, biodegradable, shock resistant, bendable and stable (Rowell 2005). Wood, and its derivatives, can be transformed into chemicals, burned as fuel, or used as a structural material.

Wood is a complex composite material, built up of compounds connected with each other. The quality and quantity of these compounds vary between species, between trees and within the tree itself (Popescu 2017). As an organic material, it contains mostly carbon and oxygen.

Table 2.1 Elementary composition of wood (Sixta 2008)

Element	**Content (%)**
C	49
H	6
O	44
N	<1
Na, K, Ca, Mg, Si	<<1

In all wood species this elements form macromolecules which represent the main cell wall compounds of cellulose, hemicellulose and lignin (Sixta 2008). Wood is divided primarily in two classes: softwood – that comes from gymnosperms (conifers in general) and hardwood – that comes from angiosperms (Popescu 2017). They, fundamentally, differ in proportions and composition of lignin and hemicellulose, while cellulose is a relatively uniform component of all woods (Sixta 2008).

Table 2.2 Wood main components (Sixta 2008)

	Content (%) Softwoods	**Content (%) Hardwoods**
Cellulose	40-44	40-44
Hemicelluloses	30-32	15-35
Lignin	25-32	18-25

2.2.1 Cellulose

Cellulose is a lineal and homogenous polysaccharide built up of monomeric units of β-D-glucopyranose (Sixta 2008) . The degree of polymerization depends on the wood specie (Hill 2006) and can be about 10,000.

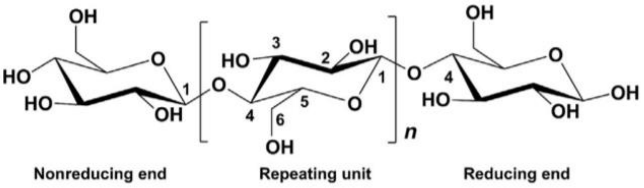


Figure 2.1 Cellulose (Zhou, Broadbelt, & Vinu, 2016)

Even though the structure of cellulose seems rather simple, the supramolecular organization turns cellulose on a complex substance. Glucose residues contains three hydroxyl groups which allows cellulose to form intermolecular hydrogen bonds which are responsible for many cellulose properties (Sixta 2008). Also, they determine it chemical reactivity and water sorption phenomena of wood (Popescu 2017).

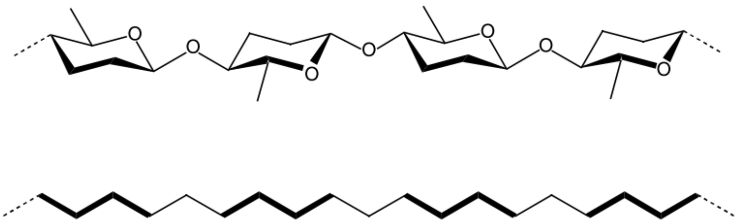


Figure 2.2 Spatial disposition of cellulose (Hill 2006)

2.2.2 Hemicellulose

Different from cellulose, hemicellulose are heteropolysaccharides consisting of several sugar monomers. They are not linear, form branches and have lower molecular weight. Sugar monomers can be divided into groups such as pentoses (xylose and arabinose units), hexoses (glucose and mannose units), hexuronic acids (glucuronic acid) and deoxy-hexoses (rhamnose units) (Sixta 2008). Some hemicelluloses are homopolymers (xylans) while others consist of two or more units (such as glucomannans). The high amount of available OH groups give the hemicellulose more reactivity and less thermal stability (Hill 2006). Due to their amorphous nature, hemicellulose contain the greatest part of available hydroxyl groups of wood (Popescu 2017). Hemicelluloses, act like a binder between the highly polar cellulose ant the less polar lignin (Popescu 2017).

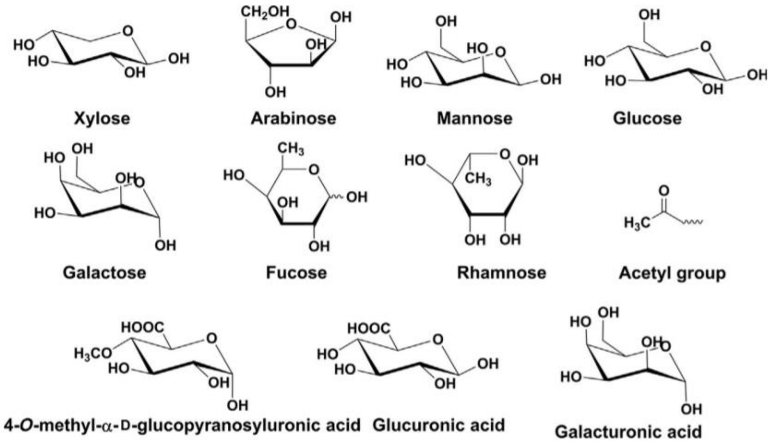


Figure 2.3 Hemicellulose monomers in wood (Popescu 2017)

Table 2.3 Chemical composition of softwood and hardwoods (Sixta 2008)

Specie	Cellulose (%)	Lignin (%)	Glucomannan (%)	Glucuronoxylan (%)
Softwood	40 - 44	26 – 30	14 - 20	6 – 11
Hardwood	40 - 44	20 – 25	1 - 4	18 – 30

Analysing the difference of chemical composition between softwoods and hardwoods is noticeable that the main difference is the type of hemicellulose. In softwoods glucomannan is the main hemicellulose, even though the quantity of glucuronoxylan is considerable. On the other hand, hardwoods have less glucomannan, and a relative higher amount of glucuronoxylan.

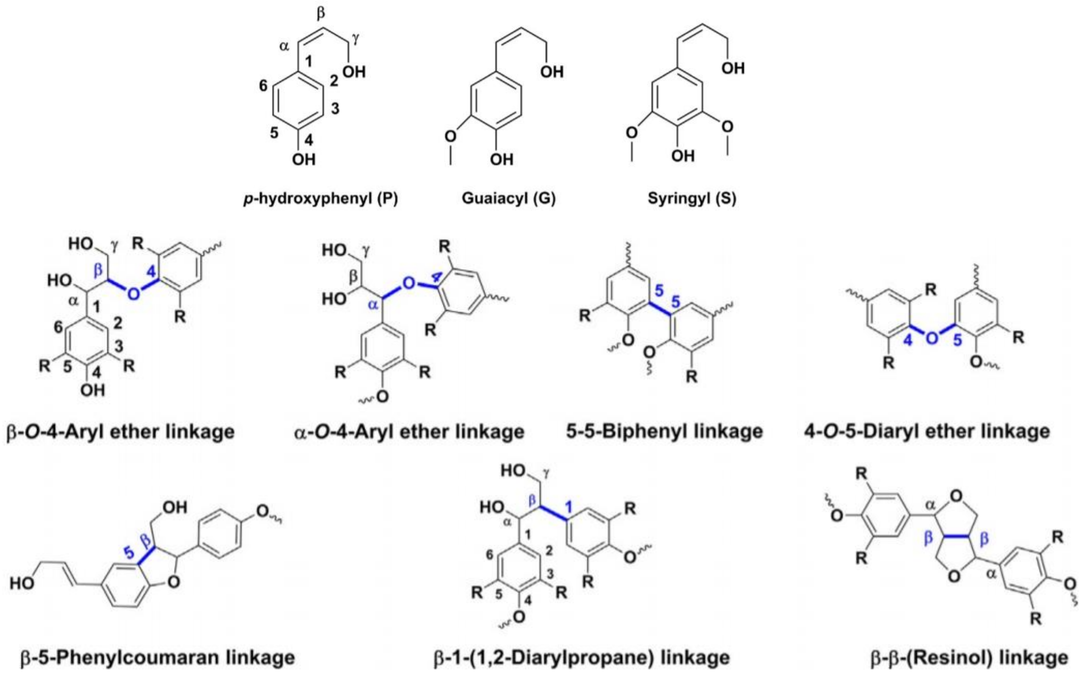
Table 2.4 Components of the hemicelluloses in softwood and hardwood (Sixta 2008)

	Pentose		**Hexose**		
Specie	Xylose	Arabinose	Galactose	Mannose	Acetylated
Softwood	5.0 - 7.6	1.0 - 2.0	1.0 - 6.0	8.1 - 13.6	1.4
Hardwood	15.0 - 25.0	0.4 - 1.0	0.7 - 1.0	0.9 - 3.8	3.5

As shown in Table 2.4, softwoods have a high proportion of mannose units and more galactose units. Instead, hardwoods have a high proportion of xylose units and more acetyl groups than softwood (Sixta 2008).

2.2.3 Lignin

Lignin is a complex three-dimensional amorphous polymer. It is an important component of wood, accounting 25-32% of its total dry weight (Popescu 2017). It consists mainly of phenylpropane – guaiacyl, syringyl and p-hydroxyphenyl units linked together by aryl ether interunit linkages and carbon-carbon bonds (Popescu 2017). There is no defined structure of lignin and it low content of hydroxyl groups contributes to it low reactivity (Hill 2006). Lignin contributes to wood mechanical properties, water transport and to biological durability.



p-hydroxyphenyl (P)

Guaiacyl (G)

Syringyl (S)

β-*O*-4-Aryl ether linkage

α-*O*-4-Aryl ether linkage

5-5-Biphenyl linkage

4-*O*-5-Diaryl ether linkage

β-5-Phenylcoumaran linkage

β-1-(1,2-Diarylpropane) linkage

β-β-(Resinol) linkage

Figure 2.4 Components of the lignin in softwood and hardwood (Sixta 2008)

2.2.4 Extractives

Extractives substances are non-structural compounds as they do not have significant influence on mechanical properties (Popescu 2017). They fulfil functions of energy reserves, anti-fungal and anti-bacteria agents. Extractives are aromatic and aliphatic chemical compounds such as resins, tannins, dyes, lignans, glucosides, terpenes, alcohols, fats and waxes. They can reach up to 2-8% total dry mass of wood, depending on the specie. (Popescu 2017)

2.2.5 Porosity

Wood is a porous material and its pore structure affects its behaviour more than any other characteristics (Ding et al. 2008). Porosity can be related to wood density, permeability, stability, strength, thermal and dielectric properties. Pore size of the wood cell are important for the movement and transport of water and biological function within trees (Grigsby et al. 2013b).

Wood microstructure and porosities vary widely according to wood type and specie. Although, they can be classified into three groups: perforated, semi-open and isolated. Perforated pores (Figure 2.5 A, B, C) are two-end open cutting cells, porous middle lamella and fibres connected laterally via pits. Pores classified semi-open (Figure 2.5 D, E, F) are closed-end pores and includes pits as openings, aspirated pits and cutting fibres. Finally, isolated pores (Figure 2.5 X, G) do not have connection to neither interior nor exterior surfaces. These voids are caused by cell-wall collapse during wood drying (Ding et al. 2008).

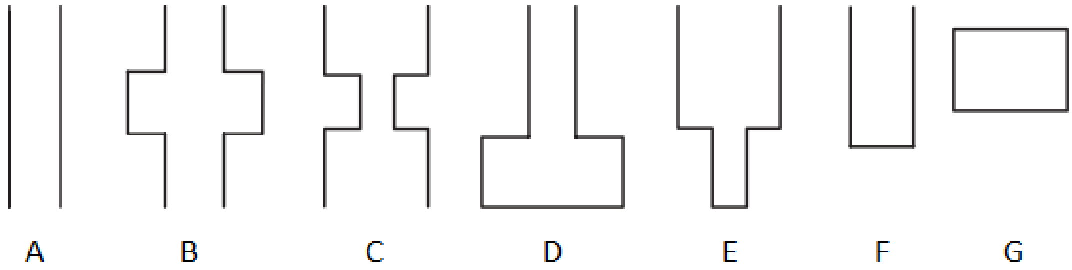


Figure 2.5 Different pore geometry (Ding et al. 2008)

Pores are observed in hardwoods due to the existence of vessels, structure specialized in water conduction. Vessels may occur solitary or in groups up to four pores. In different species, vessels vary greatly in size and distribution. So, the term porosity is used to differentiate wood species. There are three types of porosity (Sixta 2008):

- Ring-porous woods that vary size of vessels within one growth increment.
- Semi-ring-porous woods are characterized by gradual changes in one growth increment.
- Diffuse-porous woods, on the other hand, have nearly the same diameter through on growth increment.

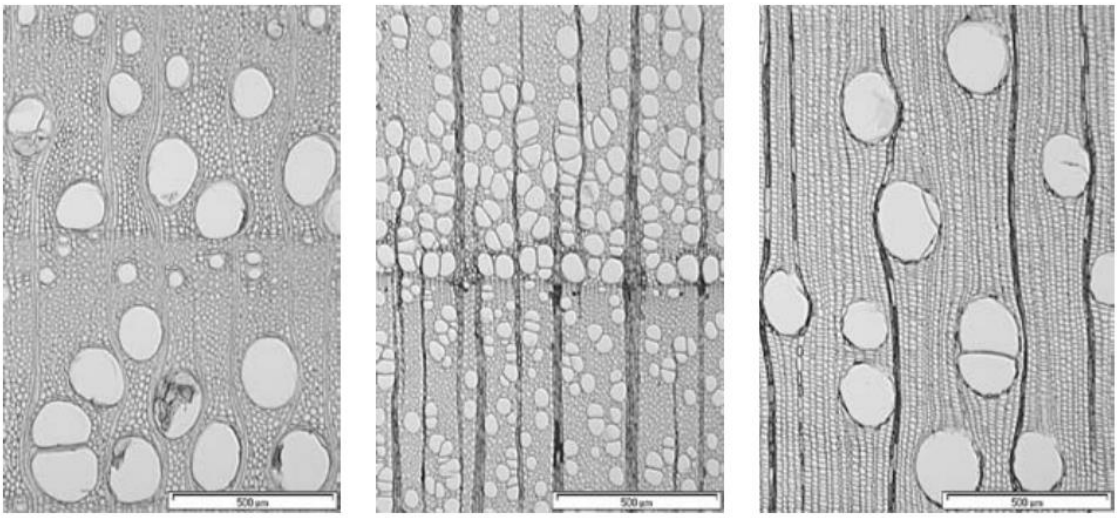


Figure 2.6 From left to right: Ring-porous, semi-ring porous, and diffuse porous hardwoods. Images obtained by light microscopy (Sixta 2008)

2.3 Wood Structure and Morphology

Trees can be divided in two big groups: those that produce flowers and enclosed seeds named angiosperms, and others which produce uncovered seeds called gymnosperms. Wood obtained from each group differs in its properties; angiosperm wood is classified as hardwood while softwood comes from gymnosperms (Ramage et al. 2017). These traditional terms (softwood and hardwood) have no general relation between hardness and softness and might be ambiguous in some cases as there are some hardwoods that are softer than softwoods.

Trunk is composed of various materials in concentric bands (Figure 2.7). Outer bark provides mechanical protection to tree and limits water evaporation. Inner bark (phloem) is the tissue through which sugars produced by photosynthesis are translocated from the leaves to the roots. Between the bark and the wood, the vascular cambium is responsible for producing both tissues. Sapwood is the active part, responsible for conducing the water (sap) through all the tree, that has not yet accumulated dark-coloured chemicals that set the nonconductive heartwood. Finally, the pith in the centre of the trunk is what remains from the early growth of the trunk before the wood was formed.

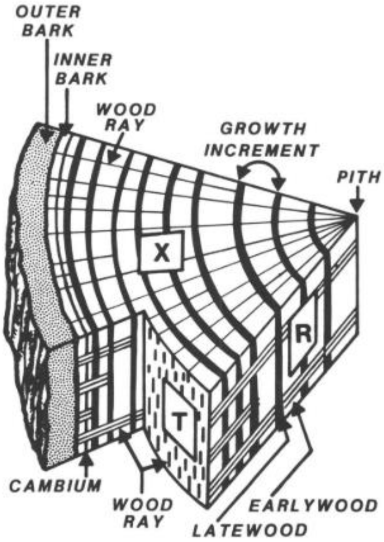


Figure 2.7 Representation of a trees cross section. X represents transverse plane, T tangential surface and R radial section. (Russell and Richard 1984)

Tree growth is related to variations in local climate, especially, to the supply of available water (Russell and Richard 1984). This situation is reflected in a visible change in the type of wood, as a detectable growth increment appears with the formation of a growth ring o annual ring (Russell and Richard 1984). Within a growth ring there are three patterns: no change in cell wall pattern, gradual reduction of the inner diameter of conducing elements from the earlywood (or springwood) to the latewood (or summer wood) and a distinct change in the inner diameter of conducing elements across the ring. Annual rings are more pronounced in softwoods (Popescu 2017). Earlywood in softwoods, are thin-walled and have wide radial diameters. As spring passes to summer, the fibres develop thicker walls, either abruptly or gradually, depending on the specie. These changes results in a latewood denser and harder. Latewood have also darker colour than earlywood. On the other hand, for most hardwoods, fibre morphology and wall thickness are similar within an annual ring. In this case, growth increments are distinguished by changes in vessel or pore diameters, and its magnitude depends on wood specie.

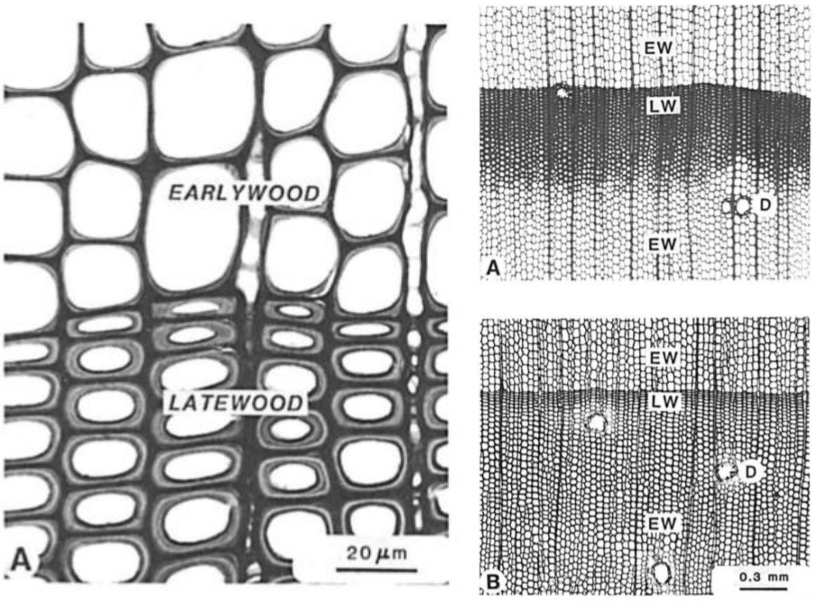


Figure 2.8 Left side: transition from earlywood to latewood in softwood. Right side: Different transitions in softwoods annual rings (Russell and Richard 1984)

Of the three cell wall components, cellulose form elementary fibrils alternating crystalline and amorphous regions and they aggregate in microfibrils between which the lignin and hemicelluloses are deposited (Sixta 2008). Hydrogen bonds are formed between hydroxyl groups of cellulose, lignin and hemicellulose and chemical bond between α-C atoms of lignin and hydroxyl groups of hemicelluloses. This results in a close and irregular network (Sixta 2008).

Anatomically, softwoods have simpler structure than hardwoods, with less classes of cells forming the xylem (Sixta 2008). Tracheids are the predominant cell type in softwoods. They are positioned longitudinally and have a length of 2-4 mm long and 30 μm width. Tracheids fulfil structural and water conducting functions (Ramage et al. 2017). Also, making up 6-10% wood volume, there is another type of cell named parenchymal. They are positioned radially within the trunk and can carry various substances, like resins for example. (Ramage et al. 2017).

In contrast, hardwoods have two primary types of wood cells: fibres, that constitutes 50% of wood volume and provides structural strength; and water conducing vessels which represents 30% of wood total volume. The dimensions of fibres are 1-2 mm long and 15 μm wide, while vessels are on average 0.2-1.2 mm long and 0.05-0.8 mm in diameter. Parenchymal cells are also present and the function is similar to softwoods (Ramage et al. 2017; Sixta 2008).

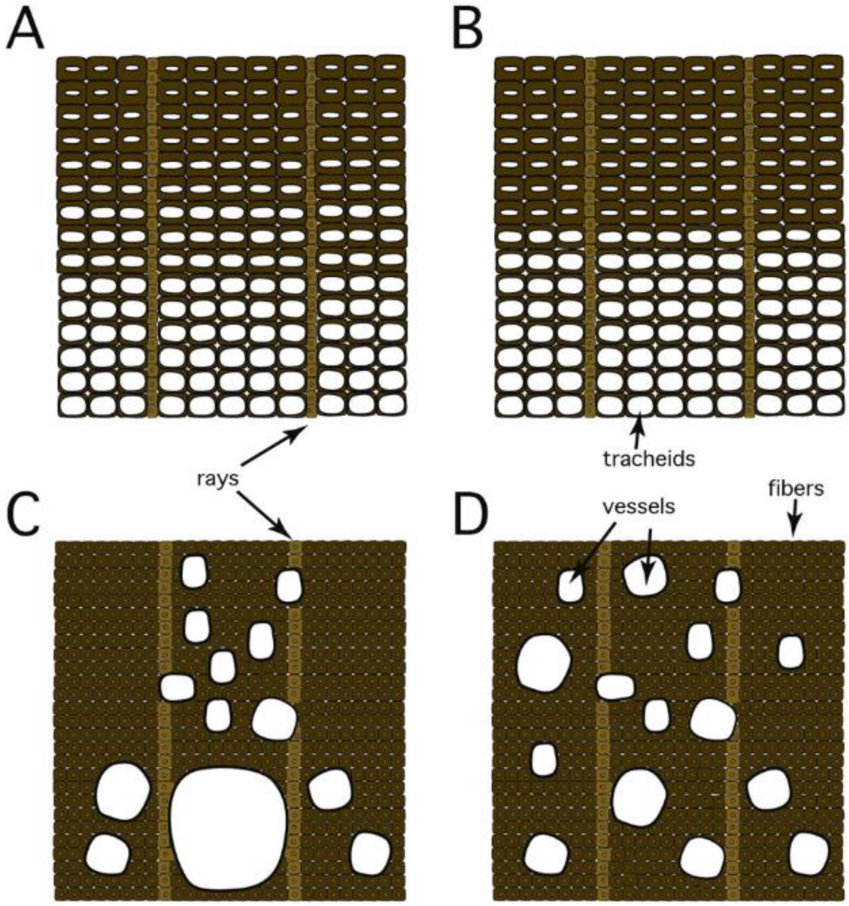


Figure 2.9 Different wood structures: Annual ring of gradual transition conifer (A), abrupt transition conifer (B), ring porous hardwood (C) and diffuse porous hardwood *(Ramage et al. 2017)*

The structure of cell wall is a mayor determinant of strength and mechanical properties (Ramage et al. 2017). Cell size, wall thickness and vessel diameter vary greatly, depending on growing speed and conditions. Between two adjacent cells, exists a region called middle lamella. This, a highly lignified region with also a high amount of pectin, which bonds the cell walls within the tissue organization (Ramage et al. 2017).

2.3.1 *Pinus taeda*

Ordinally called pine, characterized by tall trees with evergreen foliage leaves in the shape of needles, it is a kind of gymnosperm (softwood) that may be found in almost any terrestrial habitat. They are of great ecological importance, as a major component of many temperate forests and for their economic significance as a source of timber, pulp, paper, nuts, seeds, resins and construction materials. Pinaceae are among the largest families of conifers, comprised of 11 genera including 225 species which 110 of them are considered true pines belonging to the genus *Pinus*. The high degree of genotypic variability observed in the genus Pinus is reflected on the different properties across the regions (Ioannou et al. 2014).

Figure 2.10 *P. taeda* plantation (source: data.fao.org)

Figure 2.11 *P. taeda* wood

Pinus taeda is original from the southeast of United States. The sapwood is identified for being yellowish white and the heartwood as reddish brown. *P. taeda wood* is characterized for being stable in service and with low natural durability, being susceptible to microbiological and fungal attack. It can be submitted to fast drying conditions, with low tendency for deformation, cracking and split. Also, *P. taeda* wood presents good conditions for planning, is easily workable and respond appropriately to adhesives, being possible its usage in engineered wood products.

In Uruguay, there are 164,000 ha planted with pine, concentrated at the North of the country, growing at a rate of 18-20 $m^3ha^{-1}year^{-1}$. There is a relevant potential supply of pine logs (3.000.000 m^3 $year^{-1}$ in 2019) but unfortunately, half of them are exported without further added value (A. Dieste et al. 2019). It exists then, a great opportunity for developing a pine wood-based industry in Uruguay.

Table 2.5 Annual production of pine products in Uruguay,2018. (A. Dieste et al. 2019)

Product	**Annual Production (m^3 x 10^3)**	**Products sales (USD x 10^6)**
Boards	580	180
Plywood	240	72
Logs	1,600	64
Biomass	456	9

2.3.2 *Eucalyptus grandis*

The genus *Eucalyptus* contains about 500 species which are original from Australia (Annexe and Dadswell 1972). As many *Eucalyptus* species, this hardwood is of commercial importance and have been planted in many parts of the world. In fact, the remarkable adaptability of eucalyptus in addition to their fast growth, made these species to become the most widely planted hardwood across the world (Myburg et al. 2014). This wood is characterized for been slightly hard and resistant, but also smooth and flexible. Heartwood presents pink or reddish coloration. In Australia and South Africa, *E. grandis* from long cycle plantation is used in construction. On the other hand, short cycle plantation wood present problems of bent and cracking when drying and veneering (Vallejo, A. and Zapata, F. 2018).

Figure 2.12 E. grandis plantation

Figure 2.13 E. grandis wood

The use of *E. grandis* lumber in most added value products is limited due to its high dimensional instability, high growing tensions, low durability and difficult of preservation (Batista et al. 2016). Developing sustainable treatments with low impact on environment that counter *E. grandis* wood defects will increase the potential usage of *E.grandis* in high value products (Amilivia et al. 2017; Cantera 2020). Several studies have shown that eucalyptus wood has a great potential for thermal modification (Batista et al. 2016), by improving the limitations on it use.

In Uruguay 13 x 10^6 m^3 of eucalyptus were extracted in 2018, corresponding to 81% of total wood extraction. (Boscana and Boragno 2019), and most of its are used to produce short-fibre pulp. There are approximately 700,000 ha of planted *E. grandis*, growing at a rate of 25-30 $m^3ha^{-1}year^{-1}$ (Cubbage et al. 2020)

Table 2.6 Annual production of eucalyptus products in Uruguay,2018. (Boscana and Boragno 2019)

Product	**Annual Production (m^3 x 10^3)**
Boards	231
Panels	251
Plywood	198
Pulp	2543

2.4 Thermal modification

Even though several alternative and substitute artificial materials have been developed, a rise on wood (and its derivatives) demand on global markets is expected (FAO 2018). So, developing sustainable ways of production and wood preservation is needed to mitigate environmental impacts associated with the wood industry.

The increase in fast growing species plantation, such as *P. taeda* and *E. grandis*, makes necessary to modify or treat this kind of wood to enhance mechanical properties and its natural durability. This contributes to the possibility of using wood from fast growing plantations in certain uses attributed to tropical woods from natural forests, such as construction and furniture.

In Uruguay, the most extended wood preservation method is chemical impregnation with CCA (chromated copper arsenate). Even though CCA solution is highly toxic, impregnated wood does not imply health risks during its usage. However, the biggest drawback is at the time of final disposal, because impregnated wood degradation process release CCA components to the environment (Dieste 2014). Furthermore, *E. grandis* wood presents difficult towards an appropriate impregnation, which makes this process ineffective (Vivian et al. 2012). So, is explicit the importance of using sustainable alternatives for methods of preservation that, at the same time, improve dimensional stability of wood. Thermally modified wood emerged as a possible substitute of tropical woods and impregnated woods (Widmann et al. 2013).

Thermal modification process consists of heating wood in absence of oxygen to change chemical and physical characteristics of it. Thermal modification is invariably performed between the temperatures of 180°C and 260°C (Hill 2006). It was developed in Europe in the 1990s, and several methods have been implemented, differentiated by the way oxygen is displaced to avoid oxidative process (Johansson 2008):

- **ThermoWood process**: heating in an atmosphere of overheated steam.
- **PLATO process**: several steps, involving saturation of wood with water and heating in an atmosphere of steam.
- **Rectification**: nitrogen is used to displace oxygen.
- **Les Bois Perdure**: green wood is heated, and oxygen is displaced with the water vapour generated during wood drying.
- **Oil treatment**: oil is used as heating medium and to eliminate oxygen.

The chemical and physical modifications occurring on wood are strongly dependant on the process variables, including the following (Hill 2006):

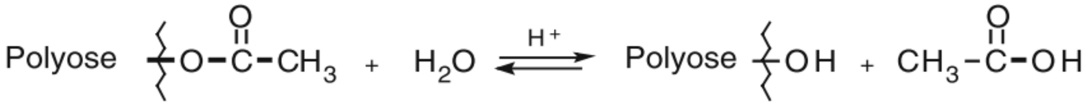
- Time and temperature of treatment.
- Atmosphere.
- Pressure.
- Wood specie.
- Moisture content of wood.
- Specimen dimensions.
- Use of catalysts.

The properties of thermally modified wood are highly dependent upon the thermal treatment employed, but in general, the induced chemical changes and physical and biological properties include (Hill 2006):

- Improved dimensional stability
- Reduced hygroscopicity (decrease in equilibrium moisture content and reduced wettability)
- Improved resistance to microbiological attacks.
- Reduction in impact toughness, modulus of rupture and work to fracture.
- Reduced abrasion resistance.
- Formation of cracks and splits.
- Darkening of wood natural colour.

2.4.1 Chemical reactions during thermal modification.

In thermal modification, changes in chemical structure of the wood is caused by autocatalytic reactions on the cell wall constituents (Medved and Kutnar 2013; Tjeerdsma and Militz 2005). This changes begin to manifest at temperatures above 150°C (Gonultas and Candan 2018). The grade of modification strongly depends on the applied temperature, atmosphere, pressure as well as wood specie and humidity. Until 100°C wood components are very stable, however, polysaccharides degrade fast as temperature increases. In order of reactivity, hemicellulose are most affected followed by cellulose and finally, lignin (Gonultas and Candan 2018). Initially, carbonic acids (such as acetic acid) are formed by rupture of acetyl groups in hemicelluloses (Medved and Kutnar 2013; Tjeerdsma and Militz 2005).



$$\text{Polyose}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O \overset{H^+}{\rightleftarrows} \text{Polyose}-OH + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Figure 2.14 Autocatalytic formation of carbonic acids (Tjeerdsma and Militz 2005)

So, the amount of carbonic acids synthetized depend on the quantity of acetyl groups present in wood. Hardwoods, have more acetylated groups (Table 2.4) thus, more carbonic acids are generated catalysing even more thermal modifications reactions (Tjeerdsma and Militz 2005). Within hemicelluloses, pentoses are degraded more easily than hexoses (Nuopponen et al. 2004). As shown in Table 2.4, hardwoods contain higher amount of pentoses than softwoods. As a result of these two facts, hardwoods are expected to have higher grades of modification compared to softwoods.

Then, depending on the concentration of carbonic acids and thermal modification temperature, hemicelluloses are hydrolysed into oligomers and monomers (Medved and Kutnar 2013). In particular, monomers (pentoses and hexoses), by dehydration reactions, form aldehydes such as furfural and hydroxymethylfurfural (Tjeerdsma and Militz 2005). These reactions contributes to an increase in C=O groups (esterification) and a decrease in hydroxyl groups existing in wood, which explains in part the less affinity to water of thermally modified wood (Esteves et al. 2013).

It is likely that minor thermal degradation of cellulose take place at relatively low temperatures, though, at a much slower rate than hemicelluloses. Cellulose crystallinity changes with temperature, due to the degradation of amorphous parts up to 200 °C (Esteves and Pereira 2009). Amorphous regions of cellulose are more susceptible to thermal degradation and exhibit a similar reactivity to those hexose components of hemicelluloses (Hill 2006). On the other hand, crystalline cellulose degrades in temperatures above 300°C (Hill 2006).

Temperature triggers the rupture of lignin ether link between monomers resulting in an increase on phenolic groups. This increase enhances the reactivity of lignin, causing auto condensation reactions (cross-linking) and condensation with aldehydes. Cross-linking is another important factor that contributes to the hydrophobic condition of thermally modified wood (Esteves et al. 2013).

Extractives, in general, possess much lower decomposition temperatures. Substances like lipids, resins, gum, starch, and simple metabolic intermediates, which influence surface properties, may be changed or decomposed at low (<130 °C) temperature. New compounds emerge that does not affect mechanical properties, but modify the wood-water relationship characteristics (Venson et al. 2016). Above 160°C, fats and waxes migrates from the centre of the wood, and it is reported that at 200°C resins acids were no longer found in the centre and have completely migrated to the surface, in Scots pine.

Finally, a typical characteristic of thermally modified wood is its darker colour. The process of thermal degradation forms dark brown quinones after oxidation of phenolic compounds. Some of them contributes with antibacterial and antifungal properties (Ziglio et al. 2017; Lopes et al. 2018).

In summary, in thermally modified wood the percentage of carbon increases while percentage of oxygen and hydrogen decrease.

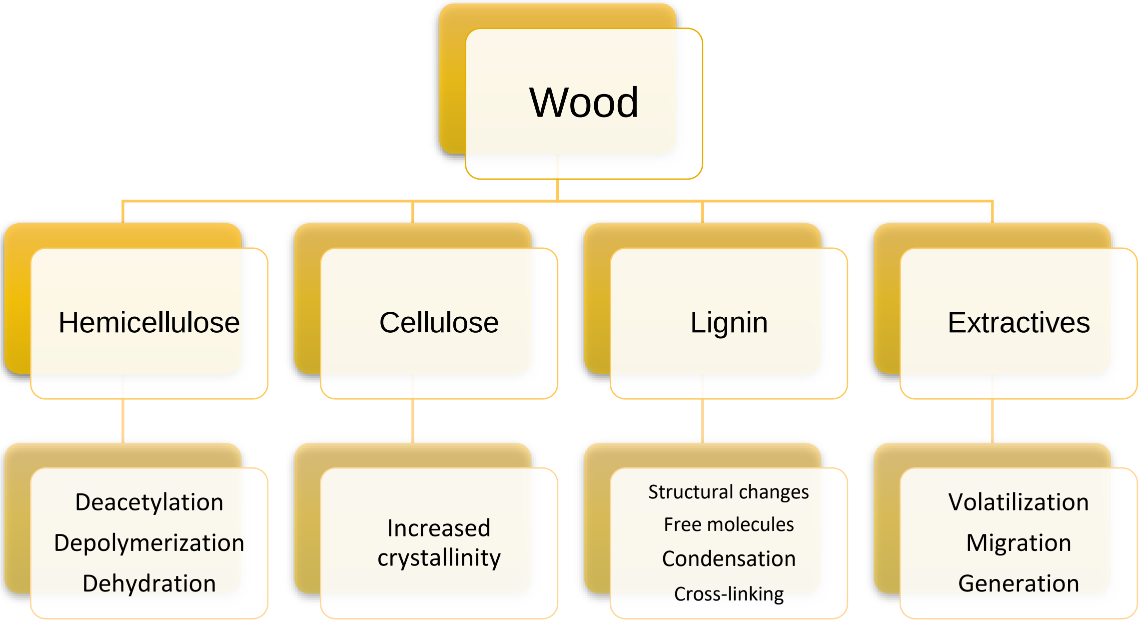


Figure 2.15 Chemical changes after wood thermal modification (Esteves and Pereira 2009)

2.4.2 Physical changes in thermally modified wood

2.4.2.1 Mass loss

Mass loss after thermal modification occurs, and the amount of it depends on temperature, time and wood specie (Hill 2006):

Table 2.7 Modification parameters affecting mass loss (Hill 2006)

Low rate of mass loss	**High rate of mass loss**
Inert atmospheres	In air
Open systems	Closed systems
Dry conditions	Wet conditions
Softwoods	Hardwoods

Dimensional changes are in general smaller than mass loss, thus, after thermal modification there is a reduction in density of the wood.

2.4.2.2 Anatomical structure

The anatomical structures are also affected by the thermal modification. Thermally modified wood becomes more brittle, having lower bending and tensile strength, principally, because of the degradation of hemicelluloses and the stresses caused by radial cracks (Ramage et al. 2017). Furthermore, between different cell wall layers and at the corners of cells radial cracks are observed (Ramage et al. 2017). Softwoods species, with annual rings and/or an abrupt transition from earlywood into latewood were sensitive to tangential cracks (Boonstra 2007). It is reported that treated radiata pine and red cedar resulted in a more open and permeable wood structure (Boonstra 2007; Jones 2011).

In hardwoods, thermal modification did not reveal damage to the ray parenchyma pit membranes, bordered pits and large window pit membranes and there were no reports of damaged fibrils. On the other hand, hardwoods are sensitive to collapse of vessels and deformation of fibres near vessels (Boonstra 2007).

2.4.2.3 Mechanical properties

Thermal modification results in a reduction in strength, toughness, and abrasion resistance. Strength reduction is proportionate to mass loss and strongly influenced by modification conditions: losses are higher in closed systems and in air conditions (Hill 2006). In general, hardwoods exhibit higher strength losses than softwoods under the same conditions (Hill 2006).

Several studies have shown that in short treatments there is an increase in wood modulus of elasticity (MOE). As time and temperature increases, the MOE decrease so as bending strength and modulus of rupture (Hill 2006).

These mechanical properties reduction are attributed to the degradation of the hemicelluloses, resulting in damage to the cell wall (Jones 2011).

2.4.2.4 Equilibrium moisture content

The basis of thermal modification of wood, and the main effect of it, is the decrease in the equilibrium moisture content (EMC) (B. M. Esteves and Pereira 2009). As most physical properties, this improvement depends on temperature, atmosphere, time, and wood specie. Several authors confirmed that 100 °C is the minimum temperature to reduce EMC.

Decrease in EMC is consequence of many variables, and this is the reason why comparing results is difficult. Less water is absorbed by the cell wall after heat treatment as a result of chemical change, with a decrease of hydroxyl groups (Esteves and Pereira 2009). Also, some authors concluded that the increase of cellulose crystallinity enhance inaccessibility of hydroxyl groups to water molecules (Boonstra 2007). There is evidence that polycondensation reactions in lignin, resulting in cross-linking, also contributes to the decrease of EMC (Tjeerdsma and Militz 2005). It is also reported that during thermal modification the microporosity of the wood changes, being proportional to temperature process and affecting water absorption (Šernek, Kamke, and Glasser 2004).

2.4.2.5 Dimensional stability

Increase in dimensional stability occurs after thermal modification, and its strongly related to the decrease of EMC (Esteves and Pereira 2009). As less water is absorbed by thermally modified wood, minor is the effect of swelling (or shrinkage) associated to moisture content changes. The increase in dimensional stability for heat-treated wood is mainly due to the decrease of wood hygroscopicity in view of the chemical changes (Esteves and Pereira 2009). But also, structural changes occurring on wood contributes to the improvement of dimensional stability. Cross-linking formation in lignin is an important factor for the enhanced dimensional stability (Hill 2006). Increase in crosslinks generates a more rigid structure, so cellulose microfibrils have less possibility to expand and to absorb water, explaining the decrease of the equilibrium moisture and the improvement of the dimensional stability (Esteves and Pereira 2009)

2.4.2.6 Durability

Thermal modification improves the decay resistance to biological attack, with different performance upon the type of treatment (Cantera

2020). However, it does not improve the resistance to rot when thermally modified wood is in contact with soil.

Tjeerdsma (2002) reported a correlation between the hygroscopicity and the increased decay resistance. In general, it is accepted that the fungal enzymatic system does not recognize thermally modified wood as a substratum and, therefore, does not degrade it (Esteves and Pereira 2009). Finally, there is also evidence that biocidal chemicals are formed during thermal modification, inhibiting microorganism growing (Hill 2006).

2.4.2.7 Wettability

It is reported that wettability of thermally modified wood decreases with treatments between 130°C and 210°C, reaching a maximum at 190°C (Esteves and Pereira 2009). According to Esteves and Pereira, the main reason is due to the formation of degradation compounds. On the other hand, Hakkou et al. (2005) reported that there was no relationship between wettability and mass loss or extractive content. In the same way, Pétrissans et al. (2003) suggested that one of the possible reasons for hydrophobic properties could be the increase of cellulose crystallinity. Furthermore, conformational arrangement of wood biopolymers resulting from the loss of residual water or, more probably, from the plasticization of lignin is other explication for wettability change (Esteves and Pereira 2009). The great variety of possible reasons, and the different effects, demonstrates that wettability changes are strongly dependant on modification conditions and, specially, wood species.

2.4.3 Thermal modification in *E. grandis*

It is reported (Batista et al. 2016) that temperatures of modification bellow 180°C are not high enough to cause mass loss due to degradation of cellulose. Above 180°C hemicellulose degradation (up to 25%) is higher compared to lignin degradation, resulting in a higher proportion of lignin in the cell wall, thus increasing apparent content of lignin. Because xyloses, main sugar of hardwood cellulose, are more easily degraded than other sugars. Non-modified wood presents the lowest relative concentration of extractives (2.22%), amount that increases with treatment temperature till 160°C (5% of extractives) and then slightly decrease due to volatilization of decay compounds. This increase in total extractives occurs by hemicellulose degradation. *E. grandis* have small amounts of water-soluble extractives and higher concentration of steroids, fatty acids, esters and long chain alcohols. After thermal modification, most of the original extractives disappear and new ones are generated, mainly apolar ones (Esteves et al. 2008; Batista et al. 2016).

Degradation of hemicellulose causes the desirable property changes such as dimensional stability and resistance to biological degradation, thus losing mechanical strength. In fact, there is a significant reduction of bending strength, and a minor decrease of modulus of elasticity and compression strength given the smaller degradation of cellulose and lignin (Esteves et al. 2008). Due to thermal modification above 160°C, cellulose crystallinity increases as amorphous cellulose degrades. This results in an enhanced inaccessibility of hydroxyl groups to water molecules contributing to a further decrease of equilibrium moisture content (Esteves et al.2008). Also, ether linkages of lignin are cleaved and the free phenolic hydroxyl and carbonyl groups bond with carbohydrates via crosslinking (Batista et al. 2016).

Studies have concluded that 80% of gaseous emissions during thermal modification were acetic acid, furfural, furfuryl and terpenes (Batista et al. 2016).

2.4.4 Thermal modification in *P. taeda*

In *P. taeda*, and softwoods in general, mass loss associated with thermal modification is lower than in hardwoods because hexoses (the main hemicelluloses in softwoods) are not as easily degraded as pentoses (Nuopponen et al. 2004). For Pine, a 3% mass loss is considered the least mass loss necessary to improve wood properties and above 6% modification conditions are severe (Esteves et al. 2011). During thermal modification pine hemicelluloses were the first to degrade, even for small mass loss (0.4%) (Esteves et al. 2011). It is reported that cellulose is only significantly attacked during modifications that represent mass loss of above 6.7%, when levoglucosan presence in the wood extractives are noticeable

(Esteves et al. 2011). So, relative content of cellulose is expected to increase after *P. taeda* thermal modification. For lignin, even for mass loss of 0.4%, there are reports of phenolic compounds in the dichloromethane extract which indicates some extent of lignin degradation (Esteves et al. 2011). As in thermally modified *E. grandis*, there is an increase in total extractive content with process temperature, reaching a maximum and a further decrease due to volatilization at higher temperatures. In non-modified pine, extractives are mainly polar and in the range of 3-4%, while reaching a maximum of 7.8% in thermally modified wood with a 3-4% mass loss. Melting points of softwood triglycerides and waxes range from -13 °C to 90 °C, thus it is possible that they can flow and migrate through the wood (Nuopponen et al. 2003). It is reported that from 120 to 200 °C waxes and fats migrates from the resin channels, and above 200-220°C they begin to volatilize and disappear from the wood (Nuopponen et al. 2003, 2004)

2.5 Wood adhesives.

The connection between the development of the society and the usage of adhesive has always been strong. Since the Neolithic, around 6100 BC, men and women used collagen adhesives made from animal skin, to produce sculptures, baskets, containers and tools (Johansson et al. 2002). Adhesives not only have historically been a fundamental element in the development of the wood industry but also, they are important for an efficient use of the material. Glued materials in the wood-based industry developed in the early XX century, mainly as boards and veneers. Nowadays, adhesives are used to glue woods to a variety of material such as steel, aluminium, concrete, glass and polymers, expanding the number of possibilities and putting new demands on adhesive characteristics (Johansson et al. 2002).

Adhesion is defined as the state in which two surfaces are held together by interfacial forces that may consist of valence forces or interlocking action. Bonding is the joining of two substrates using an adhesive (Kumar and Pizzi 2019). The American Society for Testing and Materials (ASTM) defines an adhesive as a substance capable of holding materials together by surface attachment.

Adhesives allows to transfer loadings and stresses between the components, enhancing the stiffness and hardness of wooden products. This increase depends strongly on the strength of the bonding between the adhesive and the wood (United States Department of Agriculture 2010). There are three basic mechanism of adhesion (Kumar and Pizzi 2019):

- **Specific adhesion**: bonding due to chemical reaction.
- **Mechanical adhesion**: mechanical anchorage.
- **Effective adhesion**: combination of specific and mechanical.

Specific adhesion involves bonding by chemical interaction as a result of molecular attraction. Hydrogen bonds and dipole-dipole interactions are the strongest, followed by apolar interactions such as van der Waals forces. On the other hand, mechanical adhesion or interlocking occurs when an adhesive penetrates the porous substrate and solidifies in the pores. In wood, a combination of both mechanism of adhesion are involved.

Cohesion is the attraction of molecules and groups within the adhesive (or other material) that holds the adhesive molecules together (Kumar and Pizzi 2019). Combination of both, adhesion and cohesive strength, will determine the effectiveness of the bonding. Failure of the bond will occur if either adhesive separates form the substrate (interfacial adhesion failure) or the adhesive breaks apart (cohesive failure) (Kumar and Pizzi 2019). It is desirable to achieve an adhesive bond in which, adhesion and cohesive strength, is higher than the cohesive strength of the wood itself.

The process of wood adhesion consists of 4 stages:

- **Application of the adhesive:** the adhesive is spread on the bonding surface of the wood (in one or both) by a roller, aspersion or drip.
- **Substrate union and pressing**: pressure is applied (cold pressing or hot pressing) so the wooden parts get in contact and the adhesive penetrates into the wood.

- **Hardening**: pressure is maintained until the adhesive line reaches the necessary hardness to maintain the substrates in place.
- **Curing**: pressure is released, and the wood product is stored in a controlled moisture and temperature condition so the bonding line develops its final resistance (may range between hours and days)

Actually, there are multiple wooden products that require the use of adhesives: plywood, medium density fibreboards (MDF), oriented strand board (OSB) panels, glued boards, frames, architectural wood, doors, windows, furniture, musical instruments, roofs, floorings and many others. (Ülker 2016).

Figure 2.16 Particleboard

- **Particleboard:** panel composed of wood or other lignocellulosic materials in the form of chips, flakes, splinters, strands, shivers, etc, agglomerated by an adhesive. They were developed to utilize the residues produced in the wood industry. Particleboards are used in floors, shelving, walls, doors, furniture and insulation.

Figure 2.17 Plywood

- **Plywood**: panel composed by several layers bonded by an adhesive and assembled under pressure to obtain an angle of 90° between the grain direction of adjacent layer. Layers are usually thin sheets of wood, from 0.3 mm to 6.5 mm. There are interior, exterior, and structural types of plywood according to the characteristics of the adhesive.

Figure 2.18 Medium density fibreboard

- **Medium density fibreboard (MDF)**: consist of fibres and fibre bundles glued together. It has higher density than dry wood, an average 750-850 kg/m^3. It is a relatively homogeneous structure and is used for furniture, mouldings, wall panelling and flooring.

Figure 2.19 Oriented Strand Board

- **Oriented strand board (OSB):** consist of layers of longitudinally and transversely oriented strands glued together. The physical properties are suitable for housebuilding and structural applications. They are widely used, also, for packaging.

Figure 2.20 Glued laminated timber

- **Glued laminated timber (GLULAM):** is a structural material composed of adhesive bonded solid timber laminations. Glulam is manufactured in the shape of beams, arches and columns with rectangular section. The thickness of the laminations range from 20 to 50 mm.

The great variety of wood species, and the diverse range of existent adhesives, complexes generalization. However, a common characteristic of all them, is that the ability of the adhesive to spread and penetrate the wood, directly influence the viability of using it as a wood adhesive (Ülker 2016). Mechanical anchorage will only be effective if the adhesive penetrates beyond the wooden surface, trespassing even the wood cells. Also, water-resistant bonds develop when the adhesive flows deeply into cell cavities, influencing the resistance of the adhesive (United States Department of Agriculture 2010). The pressure applied will also determinate the degree of penetration in the wood. Higher pressures will benefit a deep penetration. However, an excessive pressure applied can result in overpenetration causing thin and weak bond line. Penetration of the adhesive is categorized as:

- **Gross penetration**: adhesive flows through pores and capillaries of the wood structure.
- **Penetration into wood cells**: adhesive diffuse inside the cells.

Attractive forces between the adhesive and wood contribute to adhesion. Despite that some adhesives form covalent bonding with wood components, there is no evidence that this kind of bond are significant to the strength of the adhesion. However, intermolecular attractive forces, such as Van der Waal’s forces, dipole-dipole forces, and hydrogen bonding, occur so frequently that they must be very important (United States Department of Agriculture 2010).

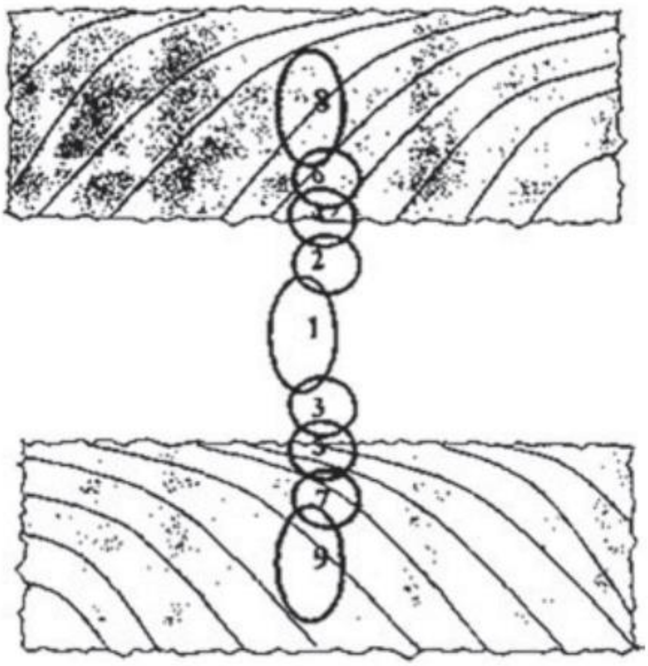


Figure 2.21 Links in adhesive bonding *(Kumar and Pizzi 2019)*

Figure 2.21 summarize the interactions occurring, as a series of chain links, with the weakest link being the site of the failure:

1- adhesive cohesion

2, 3 - intra adhesive boundary layer

4, 5 - adhesive-wood interface

6, 7 - adherend subsurface

8, 9 - wood

Adhesives become solid through one of the following three mechanism (United States Department of Agriculture 2010):

- Evaporation or diffusion of the solvent.
- Cooling.
- Polymerization.

Synthetic adhesives become industrially produced in the 1930s. They can be classified in two big groups:

- **Thermoplastics**: long chain polymers that flow when heated. In general, they are not resistant to heat, climate conditions and load. Examples of these are polyvinyl acetate, elastomeric, contact adhesive and hot melts.
- **Thermosetting**: they are polymers that undergo irreversible changes after curing. The resulting cross-linked structure can be resistant, can support moisture and they may be rigid enough to support high and long-term static load. Examples of thermosetting are phenol-formaldehyde, urea-formaldehyde, isocyanates and epoxy.

Adhesives are often formulated with a mix of active chemical substances and inert (fillers) materials. Solvents, water or organic ones, dissolve and disperse the adhesive polymers, and helps in wetting and penetration of the adhesive. Reinforcing fibres, inert organics, are used to enhance mechanical properties conferring strength and impact resistance to the bond. Fillers, organic and inorganic, are frequently used to control spreading and penetration. Also, certain chemicals are added to plasticize adhesive polymers, enhance tackiness, improve heat resistance, or lower costs. Finally, catalysts are used to accelerate curing, and to reduce pressing time. (United States Department of Agriculture 2010)

2.5.1 Types of adhesives

2.5.1.1 Phenol-formaldehyde

Phenol formaldehyde (PF) resin was developed in the late nineteenth century, but commercially developed and used in wood products in the 1930s. In general PF resin is used in the manufacture of plywood and engineered wood products. The main advantage of PF is its high resistance to moisture and low cost (Ormondroyd 2015).

Two manufacturing routes are industrially used to produce PF: Novolac process and Resol process. In the panel industry the Resol PF is predominantly used (Ormondroyd 2015). Resol resins are produced from phenol and formaldehyde under alkaline conditions (Kumar and Pizzi 2019). Depending on the molar ratio of formaldehyde to phenol (1.6:1 to 2.5:1), different strength and structure of the cured resin will result: higher proportion of formaldehyde to phenol is used for stronger cross-linked structure. On the other hand, Novolac resins are produced with phenol in molar excess using acid catalyst.

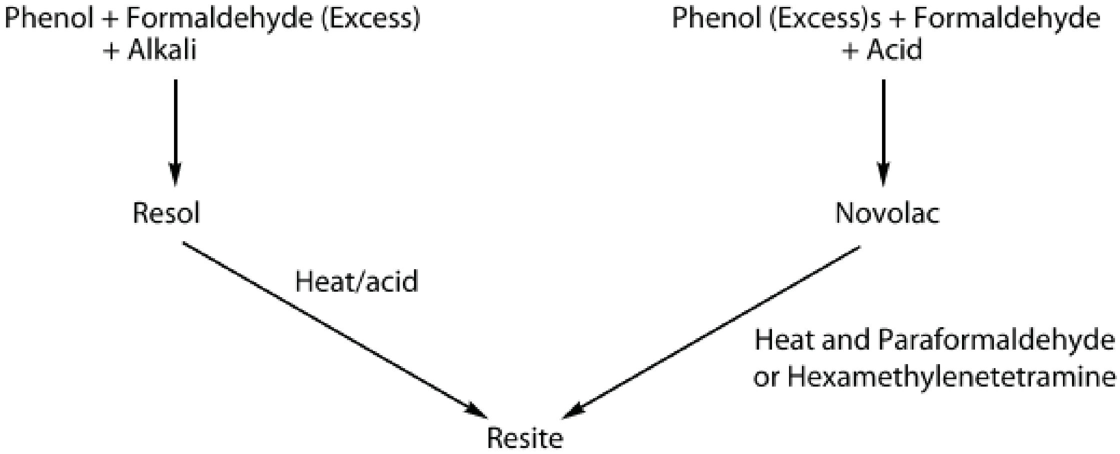


Figure 2.22 Resol, Novolac and Resite *(Kumar and Pizzi 2019)*

Resol-type resin are made in situ before application on the wood substrates. Components are mixed, sodium hydroxide is added, and temperature is kept under 95°C to 100°C for 1 to 8 hours, depending on pH and phenol/formaldehyde ratio. Reaction between phenol and formaldehyde is highly exothermic, and proper control of temperature is very important to avoid solidification of the resin(Kumar and Pizzi 2019). Resol molecule (intermediate quinone methide) contains reaction methylol groups, and on heating, the molecules combine to form larger molecules, gel and form the solid state of the resin, called Resite (Ormondroyd 2015). Temperatures of 110°C are used at low-hot press and 130°C for high hot-press (Kumar and Pizzi 2019).

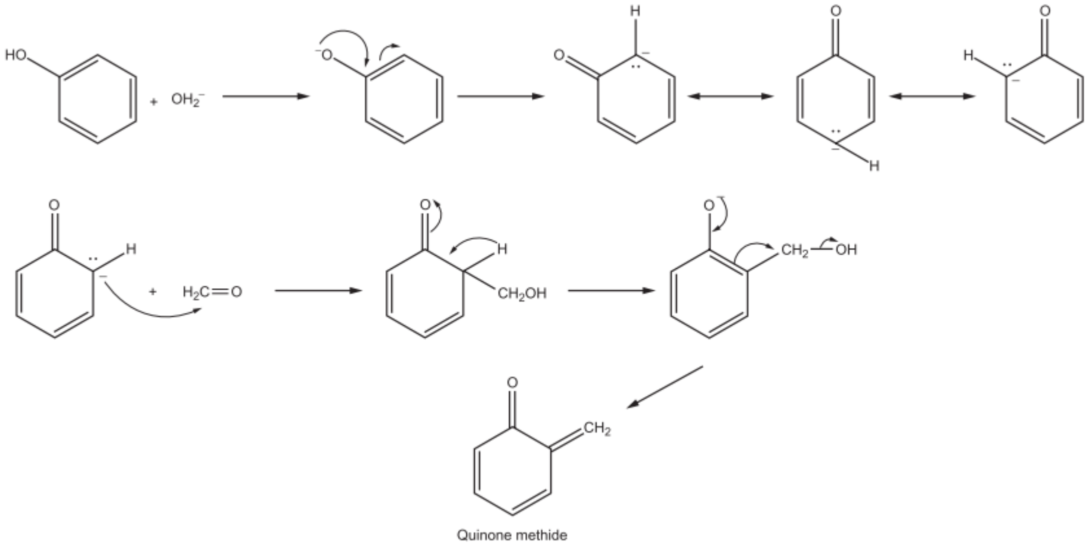


Figure 2.23 Formation of quinone methide molecule *(Ormondroyd 2015)*

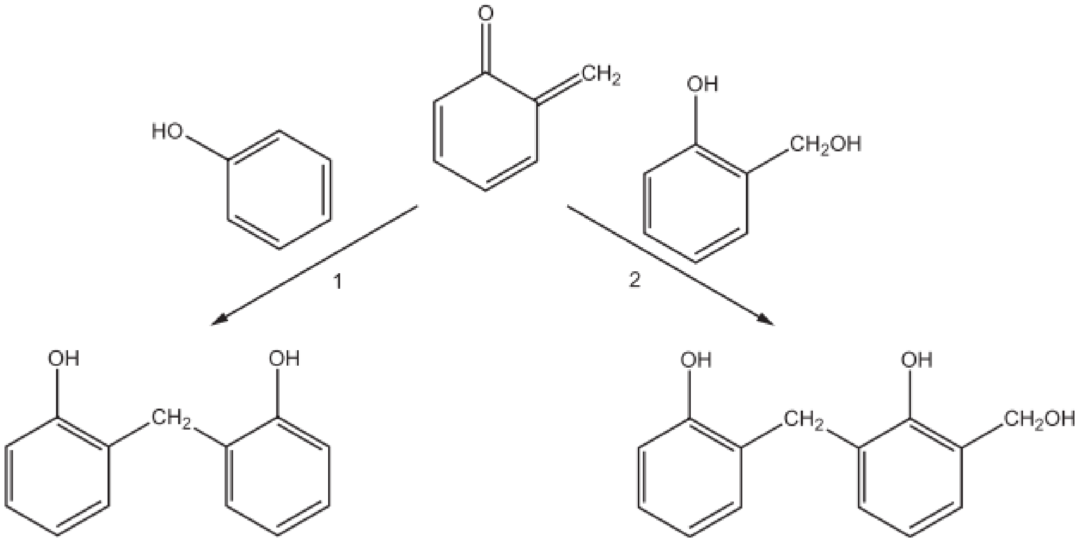


Figure 2.24 Formation of PF resin *(Ormondroyd 2015)*

2.5.1.2 Formaldehyde resins

The formaldehyde resins of aminoplastic resins, are the most important class of adhesives in the wood based panels industry (Pizzi and

Mittal 2010). They are used specially to produce particleboards, MDF, OSB, plywood, and to a lesser extent in furniture.

The condensation resin based on formaldehyde is formed by the reaction of formaldehyde with various chemicals like urea, melamine, phenol, resorcinol or by a combination of these substances (Cruz et al. 2002):

- UF urea – formaldehyde resin.
- MF melamine – formaldehyde resin.
- MUF melamine – formaldehyde co-condensation resin.
- mUF melamine fortified UF resins.
- MF + UF mixture of a MF and a UF resin.
- MUPF, PMUF melamine-urea-phenol-formaldehyde resin.

The most important parameters for aminoplastic resins are (Pizzi and Mittal 2010):

- Type of monomers used
- Relative molar ratio of monomers
- Purity of the materials
- pH, temperatures, catalysts, sequence of addition and duration of steps.

In general, they are delivered as a liquid consisting of linear branched oligomeric and polymeric molecules in aqueous solution and partly as dispersion of molecules in these aqueous solutions. During the hardening and gelling process they convert to insoluble and form a three dimensionally cross-linked network (Cruz et al. 2002).

Reaction of urea and formaldehyde is divided into two stages. The first, is alkaline condensation to form mono-, di-, and trimethylolureas. The second one, is an acid condensation of the methylolureas to form the cross-linked resins (Ormondroyd 2015).

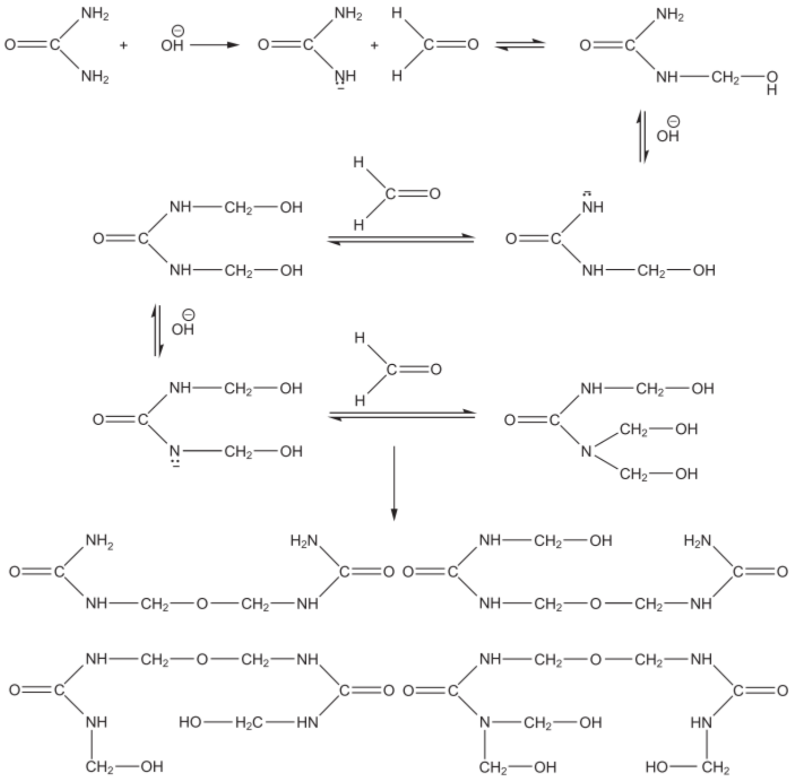


Figure 2.25 Condensation of urea and formaldehyde (Ormondroyd 2015)

Temperatures of 75-100 °C are used at pressing for curing. Also, fast process at 130-150 °C is used to catalyse hardening and curing (Brydson 1999). The UF resin is mainly used for interior boards (dry conditions) as UF-bonds have low resistance to humidity, water and exterior conditions. To improve this, melamine and phenol are added for exterior uses.

2.5.1.3 Polyvinyl Acetate

Poly(vinyl acetate) or PVAc is a very important thermoplastic adhesive, especially used in carpentry and furniture. It is a water-based dispersion of a polymer (or more than one). The mechanism of cohesion and adhesion, comes from polymerization after water removal by penetration into the wood substrate or by evaporation (Cruz et al. 2002; Pizzi and Mittal 2010)

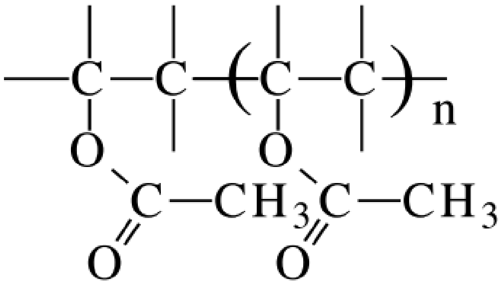


Figure 2.26 Polyvinyl Acetate (Cruz et al. 2002)

There can be various formulations, differing in viscosity, drying speed, colour, flexibility or brittleness, hardness and smoothness. Also various grades of water resistance can be achieved, especially through the addition of comonomers such as acrylic acid esters, dialkylfumarates and ethylene (Pizzi and Mittal 2010). PVAc is not suitable for load bearing applications and structural elements.

2.5.1.4 Polyisocyanates

They have been used in the wood-based panel industry for more than 35 years (Cruz et al. 2002; Pizzi and Mittal 2010). However, they still have a low market value in the woodworking industry compared to systems based on UF, MUF, or PF-resins (Cruz et al. 2002). The main advantage of polyisocyanates is that they form water resistant bonds, which compensates its high price, especially in structural products exposed to humid or exterior conditions. Because of this, polyisocyanates are extensively used to produce exterior-grade products such as particle board, oriented strand board (OSB), laminated strand lumber (LSL), medium density fibreboard (MDF) and other wood engineer products (Cruz et al. 2002).

It is common to name polyisocyanates as polyurethanes (PUR) in general. The two main components of this adhesives are polyols and isocyanates. The main isocyanates are diphenylmethane-diisocyanate (MDI) and the polymeric diphenylmethane-diisocyanate (PMDI).

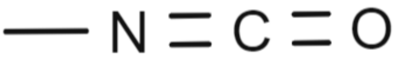
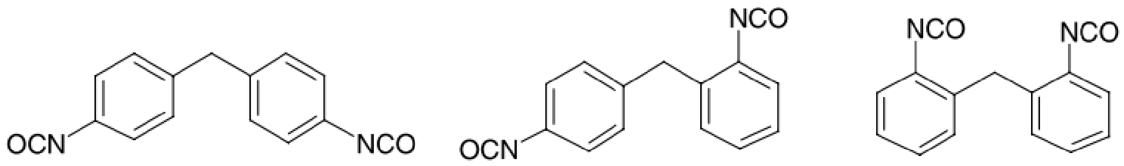


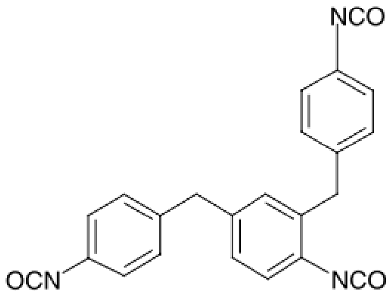
Figure 2.27 Isocyanate group



4, 4´ - MDI

2, 4´ - MDI

2, 2´ MDI



Triisocyanate

Figure 2.28 Main isocyanates in polyisocyanates adhesives

Several reactions can occur during hardening of the adhesive with a wooden substrate. The most important one is with water, forming a cross-linked polyurea network and carbon dioxide (Cruz et al. 2002):

$$2\,\mathrm{R-NCO} \;+\; \mathrm{H_2O} \;\longrightarrow\; \mathrm{R-NH-CO-NH-R} \;+\; \mathrm{CO_2}$$

Gas liberation due to carbon dioxide cause foaming of the bondline, which directly affects the strength and water resistance properties of it (Pizzi and Mittal 2010). Water is necessary, in the wood structure and/or the surrounding air, to form a strong bond. Even though, high amounts of water content may lead to excessive foaming.

Also, another hardening reaction that occurs, is the formation of the urethane bonding by reaction of an isocyanate group and an hydroxyl from the adhesive itself or from the wood substrate (Cruz et al. 2002; Pizzi and Mittal 2010):

$$\mathrm{R-NCO} \;+\; R'-OH \;\longrightarrow\; \mathrm{R-NH-CO-O-R'}$$

As expected, if high number of covalent bonding between wood and the adhesive is achieved, stronger and more resistant would be the bonding. However, some investigations have shown that the amount of covalent bonds is very small or not existent under industrial production conditions (Cruz et al. 2002). The main mechanism of bonding between wood and the adhesive is mechanical anchoring, as polyisocyanates adhesives not only penetrates the macroscopic hollows of the wood substance, but also penetrates the polymer structure of the wood (Pizzi and Mittal 2010). However, overpenetration can cause starved glue lines so, pressure applied during hardening is of importance. Finally, branching reactions occur between the urea structure and isocyanates contributing to the curing of the bond line (Cruz et al. 2002):

$$\mathrm{R-NH_2} \;+\; O=C=N-R' \;\longrightarrow\; \mathrm{R-NH-(C=O)-NH-R'}$$

2.5.1.5 EPI – Emulsion Polymer Isocyanate adhesive

EPI adhesives are two-component water-based emulsions cured with an isocyanate cross-linker. In general, they have good bonding with most wood species and have the advantage that they can cure at room temperatures in a short period of time. Due to the resistance to high moisture environment, EPI is used for the production of solid wood panels of different type, parquet, windows frame, furniture parts, plywood, finger joints and production of load-bearing constructions (Grøstad and Pedersen 2010). The chemical description of the two components is detailed below:

- **Water based component**: consist of water, PVA (poly (vinyl alcohol)), fillers, defoamers, dispersing agents and biocides.
- **Cross-linking agent**: isocyanate with two or more NCO groups which may cross-link the adhesive system (Grøstad and Pedersen 2010). Generally, the polymeric diphenylmethane diisocyanate (pMDI) is used.

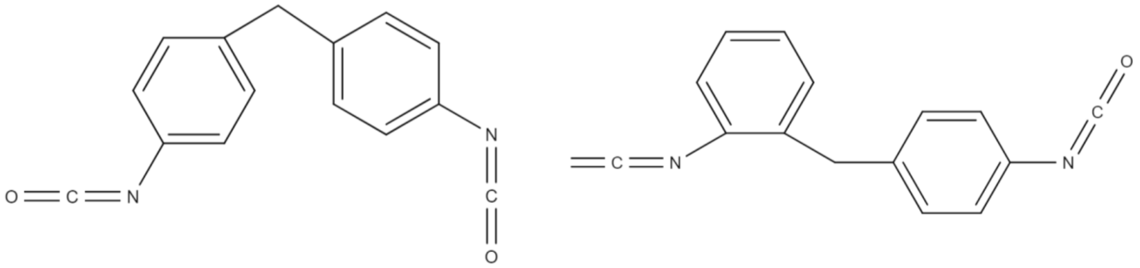


Figure 2.29 Structure of diphenylmethane diisocyanate (MDI) isomers

The mechanism of reaction involves several steps. The isocyanate will react with hydroxyl groups (available in PVA and in a small account in wood) to give urethane linkage. Isocyanate will also react with water of the adhesive itself resulting in the formation of urea. EPI adhesives share characteristics with both thermosetting and thermoplastic adhesives (Grøstad and Pedersen 2010). The mechanism is detailed below(Grøstad and Pedersen 2010):

- Water migrate away from the glue line.
- Coalescence of PVA to form a film.
- Reaction of isocyanate with water.
- Reaction of isocyanate with other molecules of isocyanate.
- Reaction of isocyanate with hydroxyl groups (and other hydroxyl-functional groups) available in PVA.
- Reaction of isocyanate with functional groups in the polymer.
- Reaction of isocyanate groups with hydroxyl groups on the wood cells.

The final properties of the bonding are determined by the amount of isocyanate used. Higher amounts of cross-linker and a proper mixing is of most importance for moisture resistance and a durable bond. Although, pot-life (time after mixing before the adhesive has too high viscosity) is shorter when higher amounts of cross-linker are used (Grøstad and Pedersen 2010). Another property of EPI is that CO_2 is formed during reaction of isocyanate with water, causing the glue-mix to foam. The amount of foam increases with the rate of free isocyanate, so anti foaming agents are added in order to avoid defects in glue line. Also neither film formation nor the cross-linking of the isocyanate is pH-dependent. (Grøstad and Pedersen

2010). Finally, since curing does not require heat, the process to manufacture products would be less expensive compensating the high cost of this adhesives.

2.5.1.6 Epoxy adhesives

An epoxy adhesive is a copolymer formed by an epoxy resin and a polyamine hardener (Kothe et al. 2014). Before polymerization happens, the resin is constituted of short chain polymers with an epoxy group at the end (Kothe et al. 2014). In general, as mentioned, it is a two-component adhesive but there are some of one component that gets activated through heat. The reaction of hardening begins when the epoxy and the polyamine are mixed. The epoxy group reacts with the polyamine and other epoxy group to form a crosslinked polymer as shown in Figure 2.30. (Kothe et al. 2014)

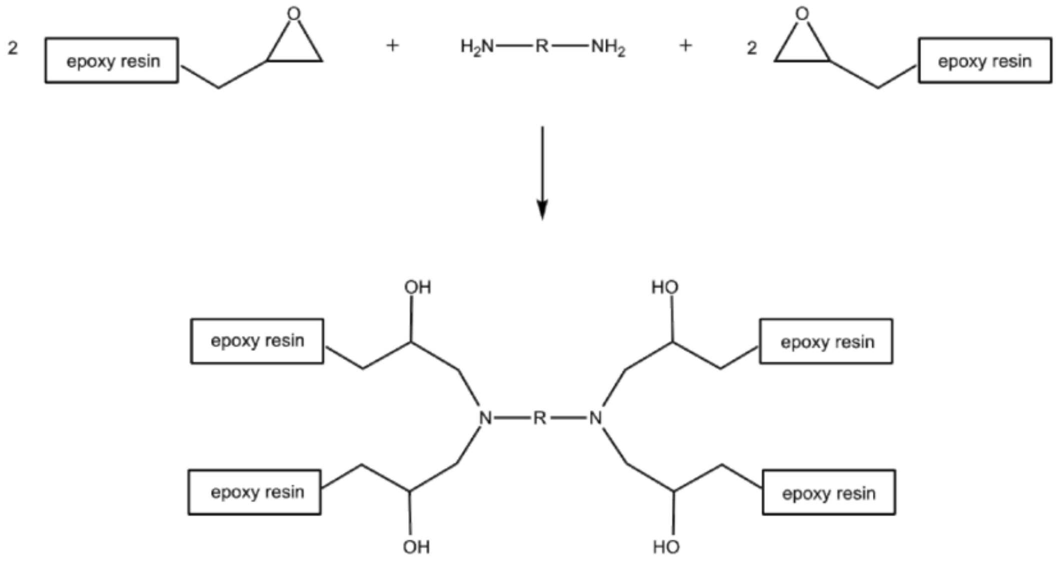


Figure 2.30 Polymerization of the epoxy adhesive. (Kothe et al. 2014)

Even though epoxies are minor wood adhesives (Frihart 2005), they have some interesting advantages: room temperature curing and low pressures are required. Epoxies have the widest formulation and curability of any adhesives due to the great variety of commercial epoxies adhesives. As the main type of commercially available epoxies are two-component system, when applied in wood, one component may be preferentially absorbed into and adsorbed onto the wood (Frihart 2003). So, the altered ratio of components would reduce the strength of the adhesives at the surface (Frihart 2003).

Epoxies are generally classified as adhesives not suitable for exterior wood bonds (Frihart 2005). This, according to many studies, is because failure occurs when the strain from wood swelling exceeds the ability of the interphase region to dissipate this force through the wood or adhesive when the wood is exposed to exterior conditions. The improved dimensional stability of thermally modified wood might enhance the exterior aptitude of the epoxy adhesives (Frihart 2005).

2.5.2 Cost of adhesives

Table 2.8 shows the different types of wood adhesives, their usage specifications, and their cost per unit of wood surface[1].

Table 2.8 Adhesives specifications and cost for glued laminated timber

Adhesive	**Ratio[2] (g/m^2)**	**Temp (°C)**	**Press (kg/cm^2)**	**Pressing (hours)**	**Curing (days)**	**Exterior use**	**Cost[3] (U$S/m^2)**
PF	220	80-150	10	0.08-0.16	4-7	Yes	0.3
UF	220	75-150	10	0.08-0.5	3-7	No	0.2
PVAc	220	25	8-10	0.5	7	Yes/No	0.3
PUR	200	25	8-10	1	7	Yes	0.6
EPI	200	25	8-10	1-2	7	Yes	0.9
Epoxy	160	25	Low	1	7	No/Yes	1.2

2.5.3 Influence of wood properties on bonding

According to Gillespie (1980), the strength of a glued joint depends on the weakest of five elements: wood surface, wood subsurface, interface, boundary layer and adhesive. The most critical bonding area in a glueline is the interphase: composed by both adhesive and wood (Cruz et al. 2002). Thus, chemical and physical properties of wood and the adhesive will determine the strength of the joint.

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[1] Information from commercially available adhesives

[2] Might change according different formulations and manufacturers

[3] Only taking in account the amount of adhesive necessary. Calculated by a mean price of consulted suppliers

Wood surface is extremely important to a satisfactory bonding (United States Department of Agriculture 2010). It should be smooth, flat, free of machine marks and other irregularities; free of burnishes, exudates, oil, dirt, dust and debris (Cruz et al. 2002). Surfacing or resurfacing, at least 24 hours before applying the adhesive, is necessary to remove dust, extractives and unevenness that may occur from moisture changes.

2.5.3.1 Roughness

Roughness of wood surface is result of the inherent anatomy of wood. Vessel elements, ray cells, and resin channels create openings or porosity at the wood surface. This is positive, as it adds surface area, improves penetration and interlocking of the adhesive. On the other hand, air can be trapped and good contact between opposite wood faces is difficult to achieve because of the surface roughness affecting negatively adhesive performance (Cruz et al. 2002). Parallel and flat surface allows adhesive to flow and form a uniform layer. Abrasive planning will crush cells, reducing the surface resistance, resulting in a weaker bond and is not recommended for structural joints.

2.5.3.2 Surface chemistry

Drying and heating deteriorates the wood surface by forcing extractives to diffuse to the surface, reorienting molecules and closing pores of cell walls. In particular, fatty substances and waxes might interfere in bonding (Pizzi and Mittal 2010). Extractives may also affect adhesive reactions, if they have a strong acidic or alkaline nature.

As attractive forces – Van der Waal`s, dipole-dipole, hydrogen bonding - between molecules of adhesive and wood contribute greatly to adhesion, chemical composition of wood will influence the strength of the bond (United States Department of Agriculture 2010). Different types (softwood and hardwood) and species will, logically, have heterogeneous behaviours towards different adhesives.

2.5.3.3 Density

Wood density is an intrinsic property of each specie and is determined by cell structure. High-density wood has thick walls and small lumen while low density wood has thin walls and large lumen (United States Department of Agriculture 2010). Higher density wood contains more material per unit of volume and can withstand more load. Based on the density at 12% moisture content, there are several groups proposed (Popescu 2017):

Table 2.9 Different groups of wood classified by density

Group	**Density (kg/m^3)**	**Species**
Very heavy wood	> 800	Yew, box, ebony
Heavy wood	710 - 800	Locust, beech, oak
Moderately heavy wood	600 - 710	Birch, maple, larch
Light wood	510 – 600	Juniper, chestnut, mahogany
Moderately light wood	410 - 500	Pine, spruce, fir
Very light wood	< 400	Poplar, white pine

The strength of the adhesive bonds increases up to a density range of 700-800 kg/m^3 and decrease rapidly above it. As wood density increases, high strength joints with high wood failure are more difficult to achieve (United States Department of Agriculture 2010). Wood failure is the percentage of the total failure area of the bond when submitted to test. High wood failure values mean that strength of the piece is not reduced because of the quality of the bondline, or in other words, the weakest part of the bond is the wood itself. Several reasons are behind the difficult regarding the use of adhesives for high density woods. Thicker cell walls and less lumen volume cause that adhesives to not penetrate easily into wood and mechanical interlocking is reduced (Cruz et al. 2002). High density woods “tend to swell and shrink more with changes in moisture content than do low density woods”(United States Department of Agriculture 2010), so, bondline might be subdued to severe stresses (Cruz et al. 2002).

2.5.3.4 Moisture content

Wood moisture content influences several important processes such as wetting, flow of the adhesive, penetration into the wood surface, and hardening of the adhesive. Low moisture content can cause a quick dry out of the glue spread as well as wetting problems. On the other hand, high moisture contents can lead to high flow and enhanced penetration causing starved glue lines (Pizzi and Mittal 2010).

Water has strong attraction to wood, especially through hydrogen bonding with hydroxyl groups. When wood is below the fibre saturation point (around 30 % in moisture content) changes in moisture content derives in dimensional changes. If moisture content decrease, wood will shrink and when moisture content increases it will swell. Because of this reason, the best results are obtained by using wood which at the time of gluing is as far as possible the same as it will reach when exposed to the conditions in which it will be used (Cruz et al. 2002). For interior wood, moisture content recommended is between 8 and 15 %, while for exterior use, moisture contents above 18% are expected.

Water content in wood is also important when hot pressing; high steam pressures can be generated, causing cracks and ruptures on the wood. Also, hardening of certain type of adhesives might be accelerated or retarded upon water presence (Pizzi and Mittal 2010).

2.6 Wood changes and its relationship with adhesion

Physical and chemical changes occurring in thermal modification have consequences regarding wood behaviour with adhesives. Phenomenon called surface inactivation is described in literature when wood is submitted to high temperatures, in process such as drying or thermal modification. An inactivated wood surface does not bond well with adhesive because the inactivation of the surface reduces the ability of the adhesive to properly wet, flow, penetrate and cure (Šernek et al. 2004). In other words, the ability to stablish intimate contact between molecules of wood and adhesive is reduced.

As adhesives requires a surface where it can be easily spread, reduction in the wettability of the wood after thermal modification negatively affects adhesion. It is reported that temperature process has a strong impact on wettability. The more severe the conditions of modifications are, the worst wettability properties of thermally modified wood results (Wang et al. 2015). Wettability of the surface is closely linked to the hydrophobicity of the material. Decrease in the amount of available hydroxyl groups and cross-linking reactions of lignin, generates a more apolar and hydrophobic wood structure, reducing wood wettability (Boonstra 2007; Wang et al. 2015).

Extractives also affects wood wettability and adhesive spreading. Most of them are hydrophobic and when they migrate to the surface, they act as a water repellent. Furthermore, extractives migration and generation during thermal modification may obstruct pit and pores (Nuopponen et al. 2003; Šernek et al. 2004), blocking sorption sites and affecting adhesive penetration and wood wettability. By these mechanism of inactivation, adhesives have more difficulties to spread and also to penetrate, and as consequence it will hind waterborne adhesives from adequately wetting the surface (Sernek et al. 2008).

Drying and thermal modification affects the porosity of wood. It is reported that during drying several amount of micropores are lost, being proportional to temperature process (Šernek et al. 2004). Thermal modification has different consequences on porosity, depending on process conditions and type of wood. In the case of pine and softwoods, thermally modified wood present a more open structure (Gosselink et al. 2004; Boonstra 2007) . On the other hand, in hardwoods, pore closure is evidenced (Zauer et al. 2014). Micropore closure affects adhesive penetration and wetting of wood. By limiting penetration, bond strength decreases, being of particular importance in adhesives where mechanical interlocking is relevant (Šernek et al. 2004).

Depending on the type of adhesive, changes in pH associated with thermal modification might retard or accelerate the curing of adhesives (Sernek et al. 2008). After thermal modification, due to the formation of acetic and formic acid, a drop in wood pH is expected. This increase in acidity, might neutralize alkaline hardeners (used for example in phenol-formaldehyde resins) and affecting adhesive hardening. Or, for example, it can accelerate the hardening of acid catalysed resins, such as urea-formaldehyde and melamine-formaldehyde (Sernek et al. 2008).

Due to the increase in acidity and lowering in pH of thermally modified wood, the material is reported to be more aggressive to all metals (Jermer and Andersson 2005). Screws and nails are the most common type of jointing for wood, especially in construction and furniture production (Gašparík et al. 2015). So, the decrease durability of screws and nails due to the acid residues in wood, added to the fact that there is a significant decreasing effect of thermal modification on screw direct withdrawal resistance (Gašparík et al. 2015), enhance the importance of adhesives as bonding material in the development of thermal modification technology.

The improvement on the dimensional stability of wood is a positive aspect regarding adhesive bond strength. Thus, stresses due to shrinking and swelling during cure of the adhesive or in usage are reduced, improving bonding performance (Sernek et al. 2008; Medved and Kutnar 2013)

2.7 Selection of adhesives for testing

The objective of this investigation is to determine the behaviour of thermally modified national wood towards adhesives used in the wood industry. So, in order to select the adhesives, the final use of the product must be set. Thermally modified wood is used in outdoors, exposed to humid condition and sun. Because of this, adhesives selected are reported to withstand changing conditions of moisture and temperature.

Furthermore, adhesives selected preferent should be used at low temperatures. Avoiding hot pressing and curing at high temperatures would be beneficial for wood, because it will prevent further deterioration of wood due to high temperature. Also, avoiding hot pressing would lower costs in an eventual industry use. Nowadays, there have been developments of high frequency (radio frequency) to shorter times of pressing and curing of hot-pressing adhesives. However, it is still an expensive technology.

On the other hand, the investigation is focused on structural use of thermally modified wood. As a result of the modification, mechanical properties of the wooden boards would be significantly affected. To counter this weakness, a possible alternative would be glued laminated timber or GLULAM, one of the oldest engineered wood products. It consists of two or more layers of boards bonded by an adhesive, thus, the dimension of the beam can surpass the size of the biggest possible board from a trunk. In fact, actual silviculture trend is to produce smaller trees in shorter period. Furthermore, in GLULAM is possible to combine different quality boards in the structure (United States Department of Agriculture 2010). In thermal modification, thickness of boards is a limiting factor, because modifying thick boards demands more heat and result in less uniform treatment (Widmann et al. 2013). GLULAM products require boards of less than 50 mm thick (United States Department of Agriculture 2010), so both process can be successfully combined.

For this kind of products, when thick boards or panels are used, thermoset adhesives are avoided as the heat transfer through wood is low (Mousavi et al. 2019). This, and to avoid even further degradation, is why the present investigation would focus on cold-set adhesives.

2.8 Surface characterization

The final use of the wood, and in the same way the quality of the product, is determined by the characteristic of the surface. This, are the integration of the chemical, physical and biological interactions of the materials that compose the wood (Medved and Kutnar 2013). For the study of the behaviour of adhesives, chemical and physical properties are of most importance. Investigate how thermal modification changes these properties is crucial to understand the compatibility of adhesives and thermally modified wood (Wang et al. 2015).

2.8.1 pH

The pH of the wooden surface will have a direct influence in the performance of the different adhesives, particularly in the hardening and curing speed. Acidity of wood originates mostly from acetic acid, but also from other substances in wood, such as formic acid and tannins (Popovic et al. 2016) which would depend on chemical composition of wood. Furthermore, acidity increases (pH drops) during drying and storage as degradation of wood compounds occur (Popovic et al. 2016). Regarding thermal modification, due to the formation of acetic and formic acid, drop of the pH values to 3.5- 4 (depending on the wood specie) is expected (Sernek et al. 2008). Due to the acid nature of the thermally modified wood, acid catalysed adhesives properties may be enhanced while adhesives that need an alkaline medium, such as urea-formaldehyde, would be weakened by this factor.

2.8.2 Chemical changes

Wood wettability, and the reactivity of it towards adhesives, depends on the chemical composition of the surface. In particular, oxygen containing chemical groups that are related to surface energy (Wang et al. 2015). In this way, it would be important to determine surfaces chemical changes associated with thermal modification, which compounds are affected and which new are generated. Furthermore, during thermal modification, hydroxyl groups are substituted for hydrophobic acetyl groups. It is possible to quantify these chemical changes by Fourier-transform infrared (FTIR) spectroscopy measurements. This is a fast analysis and only requires pulverized wood samples. Several authors report wood typical spectrum bands for 4000-400 cm^{-1}, in which is possible to identify functional groups and bonds according to it resonance frequency (Nuopponen et al. 2004; Esteves et al. 2013; Ozgenc et al. 2018).

2.8.3 Wood hygroscopicity

Wood is a hygroscopic material. Moisture content highly influence wood properties, and therefore the usability of wood in general (Nopens et al. 2019). Wood bonds with water by hydrogen bonds to the hydroxyl groups in cellulose and hemicellulose. However, not all hydroxyl groups are accessible to water molecules; some of this groups may not be available because they might be bonded with other molecules or because steric restrictions (Simpson 1979). So, hygroscopicity of wood is related to the available hydroxyl groups of its components, which directly affects surface reactivity regarding adhesion and wettability.

Figure 2.31 Sorption isotherms types

Several models of water sorption are described in literature. They describe the mechanism of how water is held in wood and also provides an equation through curve fitting of data (Simpson 1979). In particular, the type of sorption isotherms identifies the mechanisms involved. For gas-solid system, there have been identified five general types (Figure 2.31): type 1 is characteristic of a monolayer sorption of water molecules on the surface, in type 2 more than one layer of vapor is formed and the forces of attraction between the vapor and solid are large; in type 3 sorption is similar to 2 but forces of attraction are relatively small. Finally, type 4 and 5 are characteristic of adsorption limited by capillary condensation (Simpson 1979).

Equilibrium moisture content of a wet solid is defined as the moisture content when water vapor in the pores reaches an equilibrium state with the liquid water attached to the solid (Ouertani et al. 2014a). The grade of hygroscopicity reduction after thermal modification depends on modification parameters as temperature, time, atmosphere gas and pressure (Venson et al. 2016). Due to its high crystallinity, cellulose is less susceptible to high temperatures. However, amorphous regions of cellulose degrades. So, the proportion of crystalline cellulose increases resulting in less free hydroxyl groups accessible for water molecules (Venson et al. 2016).

2.8.3.1 Hailwood-Horrobin model

The Hailwood-Horrobin equation has been most frequently applied to describe sorption isotherms of wood (Olek et al. 2013). The model is based on the ideal solution theory, and assumes that the mixture consist of dry polymer, hydrated polymer, and dissolved water (Simpson 1979; Olek et al. 2013). For water sorption in wood, the one-hydrate model is (C. Skaar 1983):

$$\frac{a_W}{M} = A + B \cdot a_W - C \cdot {a_W}^2 \qquad [1]$$

M: Equilibrium moisture content

A,B,C: empiric parameters

At equilibrium, constant K_H is defined as the activities relations between dissolved water and dry wood; and K_D as dissolved water and vapor in the atmosphere. Also, apparent molecular weight of the wood per mole of sorption or hydration sites is W. These three constants are expressed as (C. Skaar 1983; Amilivia et al. 2017):

$$K_D = \frac{0.5(-B + \sqrt{B^2 + 4AC}}{A} \qquad [2]$$

$$K_H = 1 + \frac{B^2 + B\sqrt{B^2 + 4AC}}{2AC} \qquad [3]$$

$$W = 18\sqrt{B^2 + 4AC} \qquad [4]$$

Also, it is possible to quantify the first layer of vapor adsorbed to the surface of the wood (M_D) and the successive layers of adsorbed water (M_H) (C. Skaar 1983; Amilivia et al. 2017):

$$M = M_D + M_H \qquad [5]$$

$$M_D = \frac{18}{W}\left(\frac{K_D H}{1 - K_D H}\right) \qquad [6]$$

$$M_H = \frac{18}{W}\left(\frac{K_H K_D H}{1 + K_H K_D H}\right) \qquad [7]$$

To compare isotherms, equilibrium moisture content with air at 90% relative humidity ($M_{0.9}$) at each condition was determined according to the model, with their respective M_D and M_H.

2.8.3.2 Heat of sorption

It is possible to estimate the quantity of water molecules that are connected to hydroxyl groups within the wood matrix by the energy at which the adsorbed water bonds to the wood structure (Nopens et al. 2019). The adsorption of water is an exothermic process. Energies involved during this process are (Simpson 1979): energy released when water is adsorbed by the cell wall (Q_V) and the energy released when water vapor condenses to liquid (Q_O). The difference between these two quantities is the differential heat of adsorption (Q_L) which reflects the additional energy released, above heat of vaporization of water, when water is adsorbed by wood (Simpson 1979):

$$Q_L = Q_V - Q_O \qquad [8]$$

Heat of sorption of wood represents the theoretical minimum amount of energy required to remove a given amount of water from it (Wan et al. 2016). In other words, it is the heat that is produced when a gram of liquid water is adsorbed by a mass of solid. Sorption thermodynamics are complicated because the sorption enthalpy (heat) in a wood-water system, is a function of moisture content (Nopens et al. 2019). So, the heat of sorption is an indicator of the strength of the interaction between an adsorbate and the solid, in this case, water and wood. It is expected that after thermal modification, the heat of sorption would decrease indicating a "chemical inactivation".

Sorption isotherms depends on temperature: as temperature increases, the amount of vapor adsorbed at any given vapor pressure decreases (Simpson 1979). The differential heat of sorption can be estimated by the Clausius-Clapeyron equation [9] applied to the sorption isotherms at different temperatures, assuming that isosteric (constant coverage, in this case adsorption) heat of sorption is constant with temperature (Dieste et al. 2008; Ouertani et al. 2014a).

$$\frac{\partial \ln(P)}{\partial T} = \frac{Q_{st}}{R\,T^2} \qquad [9]$$

P: partial absolute pressure

Q_{st}: isosteric heat of sorption

T: temperature

R: gas constant

In particular, Clausius-Clapeyron applied to pure water results(Ouertani et al. 2014a):

$$\frac{\partial \ln\left(\frac{P}{P_0}\right)}{\partial T} = \frac{q_{nst}}{R\,T^2} \qquad [10]$$

Where P_0 is the saturation pressure of water vapour at temperature T, and q_{nst} is the net isosteric heat of sorption representing the difference between the isosteric heat and pure water vaporization energy. Integrating equation [10]:

$$\ln\left(\frac{P}{P_0}\right) = -\frac{q_{nst}}{R}\frac{1}{T} + constant \qquad [11]$$

By plotting sorption isotherms as $\ln(P/P_0)$ (analogous to ln(a_W)) at a given moisture content of wood vs $\frac{1}{T}$, q_{nst} can be calculated from the slope of the curve.

2.8.4 Wettability

Wettability is the preference of a liquid to be in contact with a solid. It is a measure of the capacity of a liquid to spread over a surface. In other words, “how a liquid spread on a solid substrate reflect intermolecular forces in the liquid-solid interface”, and it is essential for understanding how the thermal treatment influences the adhesion between wood substrate and adhesive (Wang et al. 2015). The wetting process by a liquid on a surface is complex due to the formation of solid-liquid interphase, penetration of the liquid through the solid surface and diffusion inside it. Thermal modification has effects on wettability, mainly, due to the resulting chemical changes. Understanding wettability and hydrophobic characteristics of thermally modified wood is important to optimize adhesion, establish adhesives compatibilities and develop composite materials (Dos Santos and Goncalves 2016). Contact angle measurements are an elegant way to determine the chemical characteristics of wood surfaces as it can be related to surface chemistry and morphology (Gindl et al. 2001). The wettability of a wood surface can be determined by measuring the contact angle between the wood surface and the liquid drop (Medved and Kutnar 2013). The intermolecular forces in the liquid-solid interphase are observed by the way the liquid spreads over a solid surface. When a drop of liquid falls over a surface, its spread, decreasing the contact angle (θ) in accordance to the wettability of the surface (Wang et al. 2015).

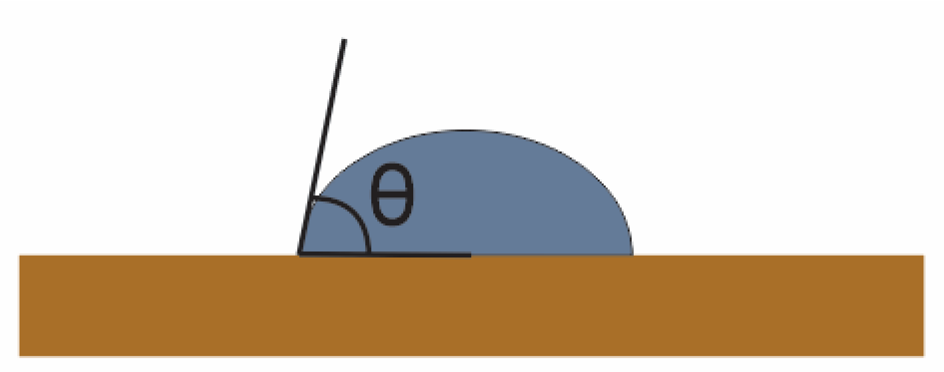

Figure 2.32 Contact angle of a drop in a surface

Due to the porosity of wood, the liquid will spread and at the same time be absorbed, so the contact angle and the volume of the drop will reduce over time (Wang et al. 2015). By measuring the contact angle over time, different levels of wettability can be compared. A dynamic wetting model was proposed by Shi and Gardner to better describe and quantify the spreading and penetration ability of liquids on wood surfaces. The model can be expressed as the following equation (Wang et al. 2015):

$$\theta = \frac{\theta_i \theta_e}{\theta_i + (\theta_e - \theta_i) \exp\left(\frac{K_\theta \cdot \theta_e \cdot t}{\theta_e - \theta_i}\right)} \quad [12]$$

θ: contact angle at t (s)

θ_i: initial contact angle

θ_e: equilibrium contact angle

t: wetting time (seconds)

K_θ: constant referred to the intrinsic relative contact angle decrease rate

2.8.5 Surface free energy

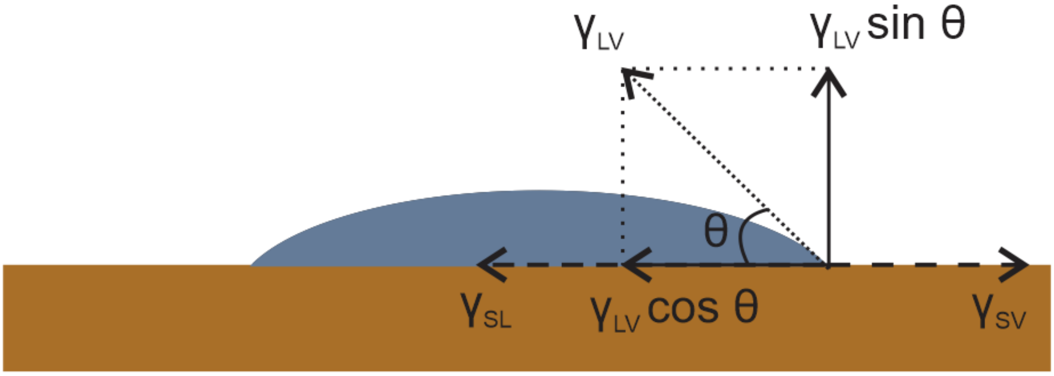

Figure 2.33 Surface free energy

The term surface free energy describes the excess energy in a solid surface compared to that of the bulk of the material. Surface free energy originates from the intermolecular interactions at the interface which includes van der Waals, hydrogen bonding and dipole-dipole interactions. Interactions between solid and liquid are determined by the surface free energy and the surface tension of the liquid. When the surface energy is high, liquids will wet it easily.

The surface free energy (γ) defines the solid-vapour (γ_{SV}), solid-liquid (γ_{SL}) and liquid-vapour (γ_{LV}) interphase. Additionally, the surface free energy can be divided in 2 terms [13]: apolar or diffusive (γ_S^d), originated from van der Waals forces, and polar (γ_s^p) which derivates mainly from hydrogen bonds (Dos Santos and Goncalves 2016).

$$\gamma = \gamma_s^d + \gamma_s^p \qquad [13]$$

According to Fowkes, Owens and Wendt it is possible to establish a general equation to represent the different components of γ :

$$\gamma_{SV} + \gamma_{LV} - \gamma_{SL} = 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + 2\sqrt{\gamma_{SV}^p \gamma_{LV}^p} \qquad [14]$$

So, combining equation [14] and Young equation [15] for stable and homogeneous surfaces:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \qquad [15]$$

$$\gamma_{LV}\,(cos\theta + 1) = 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + 2\sqrt{\gamma_{SV}^p \gamma_{LV}^p} \qquad [16]$$

Reorganizing the terms of equation [16]:

$$\left(\frac{\gamma_{LV}\,(cos\theta+1)}{2\sqrt{\gamma_{LV}^d}}\right) = \sqrt{\gamma_{SV}^d} + \left(\frac{\sqrt{\gamma_{LV}^p}}{\sqrt{\gamma_{LV}^d}}\right)\sqrt{\gamma_{SV}^p} \qquad [17]$$

Which corresponds to a linear equation with $\sqrt{\gamma_{SV}^{p}}$ slope and $\sqrt{\gamma_{SV}^{d}}$ as y-intercept. So, by measuring the contact angle for at least two liquids with different polarities, the surface free energy can be calculated.

2.8.6 Pore structure

Studying the pore characteristics is of relevance as pore volume, pore size distribution and porosity, are closed related to the physical and mechanical properties of wood (Ding 2009). Porosity and pore size distribution as well as of the various voids in the wood structure (e.g. pointed ends of the lumen, pit apertures, pit membrane voids) are modified.

The effect of thermal modification on pore structure and porosity may have different consequences depending on the wood specie, temperature and method of eliminating oxygen. For example, cell structure may collapse, increasing the pore size. Or extractives could migrate to the surface, occluding the pores. So, it is important to study the effects on porosity on the current modification process and the selected wood species.

It is reported, in heat treatment of pine (*P. sylvestris*), a formation of “a more open structure of wood” due to removal of wood constituents compared to untreated wood (Gosselink et al. 2004). The shrinking of the fibres results in an increase on amount and size of the pores. In other study, in pine wood species such as Scots, Ponderosa and Slash, thermal modification shows damages to ray parenchyma cells around resin canals after thermal modification (Boonstra 2007). These damages resulted in a very open and permeable wood structure. Boonstra reported that the open structure of modified pine revealed practical problems when applied in service conditions. Problems associated are moisture absorption and desorption, deformation, surface cracks, growth of fungi, and a permeable wood structure resulting in over penetration of paints and adhesives.

As the anatomical structure differs from softwood to hardwood, the effects of thermal modification on porosity is expected to be different. For hardwoods, heat treatment did not reveal damage to the ray parenchyma pit membranes, bordered pits and large window pit membranes (Boonstra 2007). In hardwood species, vessels are predominantly sensitive to collapse (Boonstra 2007). As vessels are responsible for conducting water and nutrients, the collapse of its affects permeability of the wood as well as reduce porosity. For certain species of hardwoods, a brown-red extractive is formed after thermal modification that is situated on the cell wall blocking pits and preventing the transport of air and moisture (Boonstra 2007); also reducing porosity and permeability.

Pore sizes within the ultrastructure of the wood cell are important for movement and transport of water and biological function within trees. After kiln drying of the wood, the network of pores decreases, resulting in smaller pore sizes (Grigsby et al. 2013b). This has direct implications in the performance of adhesives and coatings. In order to characterize pore size distribution in wood, thermoporosimetry using differential scanning calorimetry (DSC) is an emerging method and it has been demonstrated the applicability of the technique on solid wood (Dieste at al. 2009; Grigsby et al. 2013a). This method is based in the fact that absorbed water in hydrophilic materials is categorized as non-freezing bound water, freezing bound water, and unbound water. Non-freezing bound water corresponds to the first layers of water adjacent to the wood surface and does not freeze because these molecules have limited motion due to the interaction with the surface. On the other hand, freezing bound water “has thermodynamically different behaviour than unbound water and can be determined by an endotherm (melting of frozen water). This freezing bound water is stored by capillary condensation in the intermicellar and interfibrillar cavities of the cell wall” and also in small pores outside the cell wall (Zauer et al. 2014). Furthermore, due to the lower pressure at “curved interface in cavities”, water held in the capillaries has a depressed melting temperature. This depression can be related with the pore diameter, and is the principle of thermoporosimetry (Park et al. 2006). Finally, embedded free water in the lumen of the wood cells undergoes no melting point depression.

3. MATERIALS AND METHODS

3.1 Introduction

The objective of this project was to study the effects of thermal modification on Uruguayan wood (*Eucalyptus grandis* and *Pinus taeda*) and how these changes affects the effectiveness of adhesives. For this purpose, first, the surface of thermally modified wood was characterized. As *E. grandis* and *P. taeda* are different kinds of wood, the effects of thermal modification were expected to be different. So, each specie was analysed independently from the other. However, comparisons between them were made. After the surface was characterized, the next step was to test wood adhesives that are used in wood products and compare their performance before and after thermal modification. Finally, the obtained results of adhesives performance were linked with the determined surface properties, and an explanation for the changes on the adhesives performances were formulated.

3.2 Experimental design

Table 3.1 Experimental design

Stage	Activity	Determinations
1	Acquire of national produced wood	Density
2	Thermal modification	Mass loss
3	Surface characterization	pH, light microscopy, chemical changes, hygroscopicity, wettability, porosity
4	Adhesive test	Shear test

The experimental design for the present investigation is shown on Table 3.1.

First, national harvested wood was acquired from a local sawmill. *Eucalyptus grandis* and *Pinus taeda* kiln dried boards, of high quality, without knots were selected.

On the second stage, the boards were cut to properly fit in the stove, and they were thermally modified at 200°C in a nitrogen atmosphere for 3 hours. The mass loss, associated with the process, was determined for each wood piece.

After thermal modification, the next step was to study the changes that occurred on the surface of the wood. pH of it was determined, and, the surface was observed with optic microscopy to determine defects and extractives presence. By analysing the FTIR spectra, the chemical changes produced by thermal modification were studied. Wood water relations, and how it changes after the process, was determined with sorption isotherms. With contact angle measurements, it was possible to establish the wettability properties of modified and non-modified wood. To study the changes on the porosity of the wood, and the pore sized distribution, the differential scanning calorimetry technique was used.

Finally, the last stage was the selection and testing of the adhesives on thermally modified wood. Polyurethane and EPI adhesives were selected, as they are adhesives that are commonly used in the wood industry, and because heat is not needed to cure. Shear test of the glued wooden species were conducted following the ASTM D905 standard.

3.3 Thermal modification

To thermally modify wood a Cole Palmer model G05053-22 (USA) oven was used. In this oven, a nitrogen atmosphere (-0.8 barg) was generated to remove oxygen and avoid oxidation of wood. Condition of modification was 200°C during 3 hours for both species (*Eucalyptus grandis* and *Pinus taeda)*. This condition was selected according to previous studies by Cantera (2020). Boards of 47 x 10 x 2,5 cm were dried for 24 hours in a stove at 103°C before the process of modification. Humidity content of the boards before modification were determined by cutting a 2 cm piece of each board and drying them in stove (103°C) until constant weight. Six boards were modified in each run.

The modification process is detailed below:

- Warming of the boards at atmospheric pressure until 100°C.
- Vacuum was generated while warming continued.
- Once the vacuum was accomplished, gas nitrogen was injected until reaching -0,8 barg.
- Maintenance of 200°C for 3 hours.
- Due to the formation of volatile compounds, pressure rise. Vacuum must be generated regularly to remove reaction gases and new nitrogen must be supplied afterwards.
- Cooling in stove maintaining the nitrogen atmosphere.

The diagram of the equipment is presented below (Figure 3.1). Boards 1, 2, 3, 4, 5, 6, were identified and placed in the same order in each run. Two vacuum flasks with water were added in order to clean the gases of wood modification emissions and to remove odours.

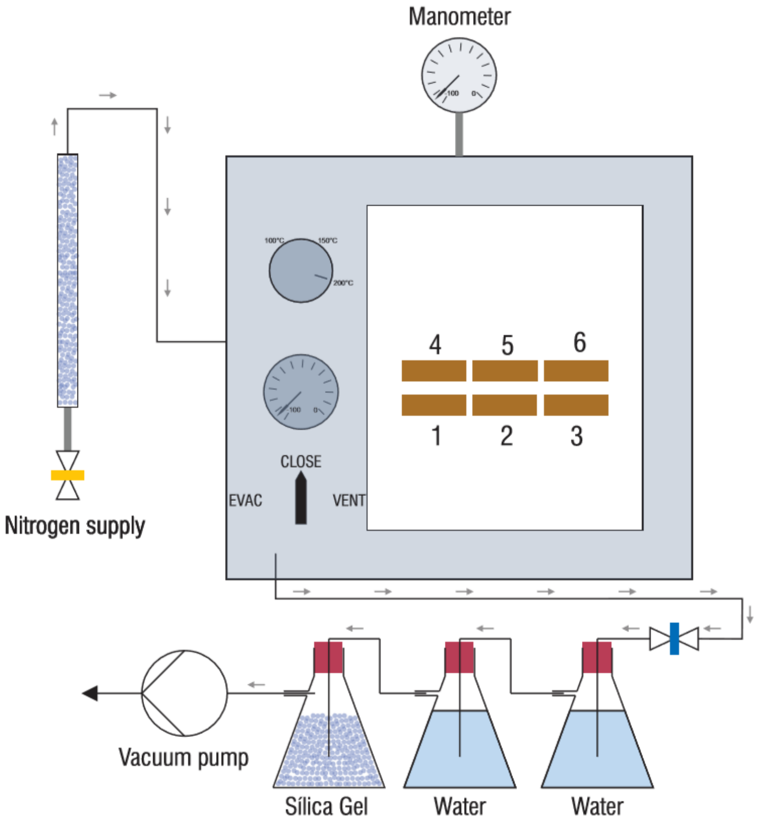

Figure 3.1 Scheme of equipment used in thermal modification

Each board was measured and weighted before modification to determine mass loss. The final mass of thermally modified wood must be corrected by humidity content, measured by same way as boards before modification (cutting a 2 cm piece).

3.4 Surface Characterization

3.4.1 pH measure of modified wood

To measure changes in pH of wood due to the thermal modification 12.0 g of sawdust (particles < 2 mm obtained with an IKA MF 10 basic grinder, China) from the wood surface were left to soak in 50 mL of distilled water for 24 hours. The extract was then filtered and analysed in the ph-meter (Oakton PH 700, USA) (Sitholé 2005). pH of each board, before and after the thermal modification was measured.

3.4.2 Light microscopy

Small blocks of modified and non-modified wood were cut form the wood sample´s surface and an Olympus IX53 inverted microscope was used with enlargements of 5x, 20x and 50x to observe changes.

3.4.3 Infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to determine changes in chemical composition of wood, focused on wood surface. FTIR spectra of wood from the four different wooden samples (sawdust obtained from the surface of unmodified and modified *P. taeda*, and unmodified and modified *E. grandis*) were determined in the range of 400 – 4000 cm^{-1} with a resolution of 4 cm^{-1}, collected from 32 scans (Özgenç et al. 2016). For each sample, three measurements were averaged to produce the corresponding spectrum. The equipment used was a Shimadzu IRAffinity-1S (Japan). Different bibliography report typical bands at different wavenumber (cm^{-1}) corresponding to vibrations of chemical bonds in wood (Nuopponen et al. 2004; Esteves et al. 2013; Ozgenc et al. 2018).

3.4.4 Wood hygroscopicity

Decrease in wood hygroscopicity, as consequence of thermal modification, is attributed mostly to the loss of sorption sites due to hemicellulose degradation as the most hygroscopic component of wood. Furthermore, the reorganization of the lignocellulosic complex and the formation of less hydrophilic substances are other factors that contributes to affecting the sorption behaviour of wood (Olek, Majka, and Czajkowski 2013).

Sorption isotherms, as the curves representing the equilibrium moisture content (EMC) versus water activity at a constant temperature, were determined by static-gravimetric method. Water activity (a_W) quantifies the presence of water and is defined as the ratio of the water vapour pressure exerted by a product to the vapour pressure of pure water.

Sample of 20 x 20 x 5 mm (long, width, thick) were taken from modified boards and non-modified wood (control samples). The surface of the samples corresponds to the board surface. First, samples were oven dried at 105°C for 24 hours and the dry mass of them were registered. Then, samples were exposed to controlled humidity conditions in order to determine the EMC for each one (Amilivia, Martínez, and Dieste 2017)(Medved and Kutnar 2013), in ascendant conditions of humidity. After reaching the equilibrium for each condition (approximately 5 days), weight of the samples was measured to determine the EMC.

With the EMC and the corresponding relative humidity condition (water activity) of surrounding air, the adsorption isotherm was defined. This isotherm was constructed for each specie (*E. Grandis* and *P. Taeda*) in both conditions (modified and non-modified). Adsorption behaviour was studied at a series of relative humidity (HR) at 25, 40, 50 °C in triplicate samples (n=3). Different relative humidity conditions were achieved in flasks containing the following saturated solutions:

Table 3.2 Water activity of different salt saturated solutions

Salt	**a_W**			**Reference**
	25 °C	**40° C**	**50°C**	
LiCl	0.114	0.105	0.100	(Bahar et al. 2017)
$MgCl_2$	0.329	0.313	0.304	
KI	0.689	0.661	0.645	(Arabhosseini et al. 2005)
NaCl	0.762	0.734	0.718	(Bahar et al. 2017)
KCl	0.855	0.806	0.777	
K_2SO_4	0.973	0.964	0.945	(Arabhosseini et al. 2005; Naphade et al. 2015)

3.4.4.1 Hailwood-Horrobin model

The experimental results from the adsorption isotherms were modelled according with the Hailwood-Horrobin model (section 2.8.3.1) (C. Skaar 1983; Amilivia et al. 2017). The equilibrium constants K_d and K_h were calculated with equations 2 and 3. K_d being the equilibrium constant between the dissolved water and the vapor in the atmosphere, and K_h the ratio of the activity of the hydrate (wood-water) to the product of the activities of the two reactants: dissolved water and anhydrate wood. The apparent molecular weight of a wood molecule capable of absorbing a water molecule, W, was calculated with equation 4. To compare isotherms, equilibrium moisture content with air at 90% relative humidity ($M_{0.9}$) at each condition was determined according to the model, with their respective M_D and M_H

3.4.5 Heat of sorption

To calculate the heat of sorption of the wood, before and after thermal modification, equation 11 (section 2.8.3.2) was used:

$$\ln\left(\frac{P}{P_0}\right) = -\frac{q_{nst}}{R}\frac{1}{T} + constant \qquad [11]$$

By plotting sorption isotherms as $\ln(P/P_0)$ (analogous to ln(a_w)) at a given moisture content of wood vs $\frac{1}{T}$, q_{nst} can be calculated from the slope of the curve.

3.4.6 Wettability

Three samples of modified and non-modified wood from *P. taeda* and *E. grandis* were cut. By an automatic pipette, a drop of approximately 8 μL of distilled water was dispensed on three random sites of the samples (Dos Santos and Goncalves 2016). The contact angle (θ), height (h) and diameter (d) of droplet was measured at 0, 4, 8,16, 32, 64 and 96 seconds after drop was dispensed on the surface (Wang et al. 2015). To measure this, a goniometer was manufactured, consisting of a magnifying glass, a camera, and an image processor software (imageJ).

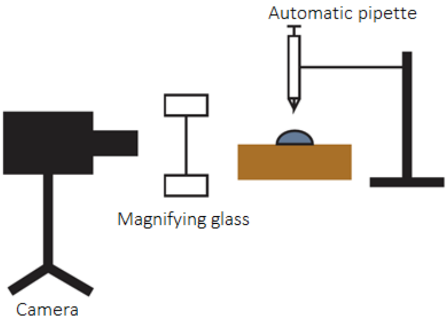

Figure 3.2 Goniometer

With the measured contact angle through time, the Shi and Gardner (section 2.8.4) wetting model was adjusted for each wood condition and so the model parameters were determined. With the initial slope ($WS_{\theta 0\text{-}4}$), initial wetting spread rate can be calculated and comparisons between conditions could be made.

$$\theta = \frac{\theta_i \theta_e}{\theta_i + (\theta_e - \theta_i)\exp\left(\frac{K_\theta \cdot \theta_e \cdot t}{\theta_e - \theta_i}\right)} \qquad [12]$$

θ: contact angle at t (s)

θ_i: initial contact angle

θ_e: equilibrium contact angle

t: wetting time (seconds)

K_θ: constant referred to the intrinsic relative contact angle decrease rate

3.4.6.1 Surface free energy

The contact angle of three different liquid was measured by sessile drop method. Drops of 8 µL (water, ethylene glycol and soybean oil) were dropped on 3 different positions of 3 different samples for each condition (*E. grandis* and *P. taeda* modified and non-modified*).* Through a goniometer the contact angle was measured after 4 seconds. By equation [17], as explained on section 2.8.5, the surface free energy was calculated for each type of wood:

$$\left(\frac{\gamma_{LV}\ (cos\theta + 1)}{2\sqrt{\gamma_{LV}^{d}}}\right) = \sqrt{\gamma_{SV}^{d}} + \left(\frac{\sqrt{\gamma_{LV}^{p}}}{\sqrt{\gamma_{LV}^{d}}}\right)\sqrt{\gamma_{SV}^{p}} \qquad [17]$$

By plotting equation [17] with the mean contact angle for each liquid and the dispersive and polar components of it (Table 3.3), the surface free energy of the wood can be estimated with the slope ($\sqrt{\gamma_{SV}^{p}}$) and the y-intercept ($\sqrt{\gamma_{SV}^{d}}$) of the linear equation.

Table 3.3 Surface free energy of test liquids with the apolar (dispersive) and polar components

Liquid	γ_{LV} **(mJ m^{-2})**	γ_{LV}^{d} **(mJ m^{-2})**	γ_{LV}^{p} **(mJ m^{-2})**
Water	72.8	21.9	51.0
Ethylene glycol	48.0	29.0	19.0
Soybean oil[4]	45.5	21.3	2.5

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[4] (Pan et al. 2018)

3.4.7 Thermoporosimetry

To determine pore size distribution, specimens of 5 mg were cut from the wood boards: modified and non-modified *P. taeda*; modified and non-modified *E. grandis.* The specimens were immersed in water for 24 hours, blotted with tissue and then weighed into the differential scanning calorimetry (DSC) pans, in this case aluminium hermetic pans (Grigsby et al. 2013b). The analyses were performed on a Perkin Elmer DSC 6000 (USA) with a Perkin Elmer Intracooler (USA) as the cooling equipment. Six replicates of each sample were used. After the measurements, the pans were re-weighed to ensure no water was lost. Finally, pans were punctured and dried in stove at 105°C until constant weight, in order to determine the total content of water. Temperature calibration of the DSC was performed with 5 mg of Mili-Q water.

Freezing bound water was determined by continuous melting (from -30°C to 15°C at a rate of 1°C/min). Overlapping peaks for freezing bound water and unbound water were separated by splitting the integrated areas of heat flow at the temperature of inflection between the peaks. Then, by subtracting the total freezable water (determined form integration of DSC thermogram) from the amount of water in the initial sample, the amount of non-freezing bound water could be calculated (Grigsby, Kroese, and Dunningham 2013; Park et al. 2006).

3.4.7.1 Pore size distribution

By measuring the amount of water that has it melting temperature depressed at each isothermal step, the pore size distribution was determined. In first place, samples were cooled to -30°C, maintained for 5 min and then raised to -20°C at 1°C/min. It is assumed that there is no melting in this range, so this step is used to determine the specific heat capacity (C_P) of the wet wood, which is considered constant with temperature (Park et al. 2006). Then, ramp to higher temperatures begin (-15, -10, -6, -4, -2, -1.5, -1.1, -0.8, -0.5, -0.2 and -0.1 °C) at a rate of 1°C/min (Grigsby, Kroese, and Dunningham 2013; Park et al. 2006). At each temperature, the sample was maintained at it until the heat flow returned to the baseline value (3 minutes). The relationship between pore diameter and the depressed melting temperature is described by the following equation, which is a case of the Gibbs-Thomson equation assuming that wood is not soluble and the pore shape is cylindrical (Park et al. 2006; Dieste et al. 2009; Grigsby et al. 2013b):

$$\Delta T = T_0 - T_m = \frac{-4T_0\gamma_{ls}\cos(\theta)}{D\rho H_f} \qquad [18]$$

T_0: melting temperature of water (273.15 K)

T_m: depressed melting temperature

γ_{ls}: surface energy at the ice-water interface (12.1 mJ/m^2)

θ: contact angle (assumed 180°C)

D: diameter of the pore

ρ: density of freezing bound water (assumed equal to unbound water,1000 kg/m^3)

H_f: specific heat of fusion of freezing bound water (334 J/g)

Thus, the equation reflects that in smaller pores the depression of melting temperature is larger. Applying the equation to the ramp of temperatures in the DSC, the diameter of pores evaluated in each step is showed in the table below (Park et al. 2006; Dieste at al. 2009):

Table 3.4 Relationship between melting temperature depression and pore diameter based on the Gibbs-Thomson equation (Park et al. 2006)

T_m (°C)	D (nm)
-15	2.6
-10	4.0
-6	6.6
-4	9.9
-2	19.8
-1.5	26.4
-1.1	36.0
-0.8	49.5
-0.5	79.2
-0.2	198
-0.1	396

Pore size distribution can be estimated by determination of mass of freezing water at each temperature of the ramp, corresponding to the water contained at each size of pore. Integrating DSC thermograms, using temperature as the x-axis, gives the total enthalpy (ΔH_{peak}) for each temperature step. To calculate the corresponding enthalpy of fusion (ΔH_{fusion}) for each pore diameter the sensible heat must be subtracted:

$$\Delta H_{fusion} = \Delta H_{peak} - m \cdot C_P \cdot \Delta T \qquad [19]$$

m: mass of the wet sample

Volume of water retained at each pore diameter, expressed by gram of dry wood is calculated as following (Zauer et al. 2014):

$$v = \frac{\Delta H_{fusion}}{H_f \cdot \rho \cdot m_s} \qquad [20]$$

v: volume of water retained (mm^3/g)

m_s: mass of dry sample (mg)

3.5 Shear test

To evaluate the quality of the bonding between modified wood and an adhesive, a shear test was carried out according to the ASTM D905 - 03 norm. This norm provides a method that is primarily intended as an evaluation of adhesives for wood and is suitable for product research and development, qualifying adhesive in accordance with certain product or performance specifications, and, for comparing and selecting adhesives

(ASTM International 2003). For this, glued pieces were submitted to compression efforts, parallel to the glue line.

Once wood was thermally modified, test specimens were manufactured. The blocks to be glued were cut from the same board. This specimens were designed according to current standards (ASTM International 2003) and to available test equipment (Figure 3.3). The blocks obtained from the original board were glued and pressed together. Pressing was carried out on an Amsler (Switzerland, 1960) press with a capacity of 10.000 kg. Upon pressure removal, joints were conditioned in a temperature-controlled room (20°C). After curing, specimens were tested. Shear tests were carried out with a Controls Pilot 4 (Italy) universal testing press with a capacity of 10.000 kg, applying load at a rate of 5 mm/min. In parallel, control specimens of unmodified wood were manufactured and tested, under the same conditions in order to compare bonding performance in modified wood and non-modified wood. Shear stress at failure in kilopascals, based on the bond line area, together with the estimated percentage of wood failure were reported. Wood failure is the area of wood surface that is damaged due to the shear stresses. This is an important factor, as wood failing, indicates that bonding between wood and adhesive is stronger than the wood itself. A total of 15 test specimens for the four different types of wood (unmodified *P. taeda*, modified *P. taeda*, unmodified *E. grandis* and modified *E. grandis*) were manufactured with each adhesive.

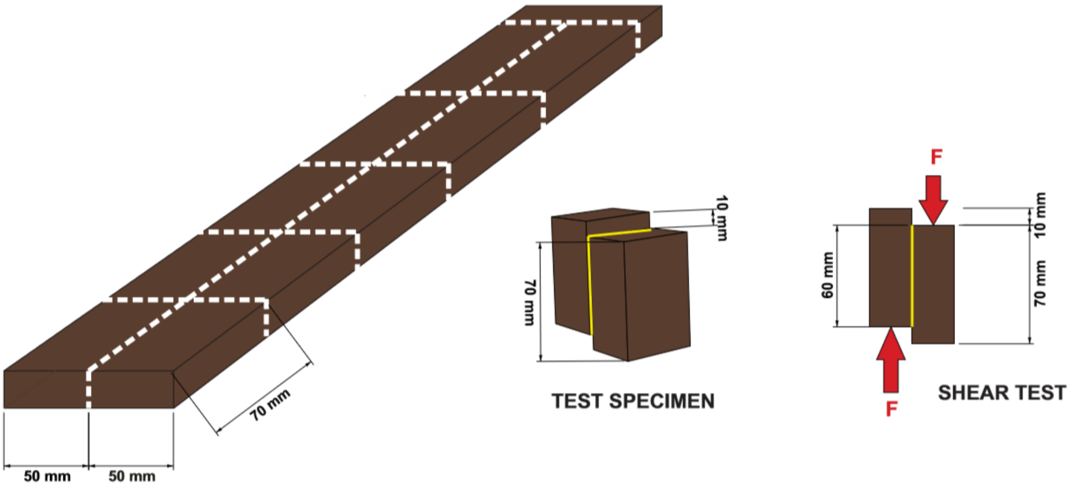

Figure 3.3 Manufacture of test specimen and representation of shear test. White lines represent saw cuts and yellow ones show the glue line

Wood boards were surfaced just prior gluing, with a sandpaper N° 220 in order to remove extractives and imperfections from the surface (Andromachi and Ekaterini 2018).

3.5.1.1 Polyurethane

Polyurethane adhesive selected was Afix PUR 351. The adhesive was applied at a load of 200 g/m^2 (according to the manufacturer) on one of the surfaces to be glued. After the wooden pieces were assembled, pressure of 10 kg/cm^2 was applied for *E. grandis* and 8 kg/cm^2 for *P. taeda*, for 1 hour. Glued blocks were left to cure for 7 days at 20°C before proceeding to the shear test.

3.5.1.2 Improved polyurethane

Based on the results obtained previously, gluing conditions were changed to improve performance, as following:

- The pressure applied for *P. taeda* was increased to 10 kg/cm^2 with the objective of enhancing adhesive penetration
- For modified and non-modified *P. taeda*, and modified *E. grandis* specimens, 0.2-0.3 g of water was added and dispersed on each surface to be glued (7.4 mg$_{water}$/cm^2). As polyurethane adhesive need water (in air or wood) to cure, the addition of water would counteract the lower water content on thermally modified wood.

3.5.1.3 EPI – Emulsion Polymer Isocyanate

EPI adhesive selected was Franklin Advantage EP-950A. The adhesive was applied at a load of 220 g/m^2 (according to the manufacturer) on one of the surfaces to be glued. After the wooden pieces were assembled, pressure of 11 kg/cm^2 was applied for *E. grandis* and *P. taeda*, for 1 hour. Glued blocks were left to cure for 7 days at 20°C before proceeding to the shear test.

4. Results and Discussion

4.1 Introduction

This chapter presents the results of the study on thermally modified Uruguayan *Eucalyptus grandis* and *Pinus taeda*, and the effects of this process in wood surface properties and wood behaviour towards adhesives

First, results on the variations of mass and pH due to thermal modification are presented. Differences of these parameters between P*.* *taeda* and *E. grandis* are discussed.

For surface characterization of wood before and after thermal modification, a series of experimental results are presented, namely: light microscopy, determination of chemical changes by FTIR spectrum, wood hygroscopicity and wood wettability.

Finally, polyurethane and EPI adhesives test results with thermally modified wood are presented. These results are then linked to the surface characterization, and the usage advantages and disadvantages of these adhesives are discussed.

4.2 Thermal Modification

For each thermal modification run, moisture content and density of every board were determined before modification so as the percentage of mass loss (dry base) due to the process (Table 4.1).

Table 4.1 Mass loss due to thermal modification

	Initial density (kg/m^3)	**Initial moisture (%)**	**Mass loss (%)**
P. taeda	464.3 ± 18.8	1.3 ± 0.6	3.7 ± 1.5
E. grandis	518.9 ± 43.4	0.8 ± 0.5	7.3 ± 2.0

Figure 4.1 Before and after thermal modification: *P. taeda* (left side) and *E. grandis* (right side)

As expected, under the same modification conditions (time and temperature) *E. grandis* shows higher grades of modification, according to the percentage of mass loss (7.3 % vs 3.7 %). This is explained by the fact that *E. grandis* (hardwood) have more acetylated groups and higher amount of pentoses than *P. taeda* (softwood), in which hexoses are predominant. More amount of acetylated groups in wood composition results in more generation of carbonic acids, catalysing even more thermal modification reactions (Tjeerdsma and Militz 2005). Within hemicelluloses, pentoses are degraded easily than hexoses (Nuopponen et al. 2004). Furthermore, as reactions in thermal modification are autocatalytic, more mass (higher density of *E. grandis* compared to *P. taeda*) stimulate and enhance reactions, thus increasing mass losses.

4.3 pH

The result of pH measure of the boards, after and before thermal modification is presented in the table below:

Table 4.2 pH measure of the boards before and after thermal modification

	Non modified pH	**Modified pH**	**pH variation**
P. taeda	4.44 ± 0.08	4.21 ± 0.08	0.23 ± 0.10
E. grandis	3.92 ± 0.10	3.73 ± 0.09	0.20 ± 0.11

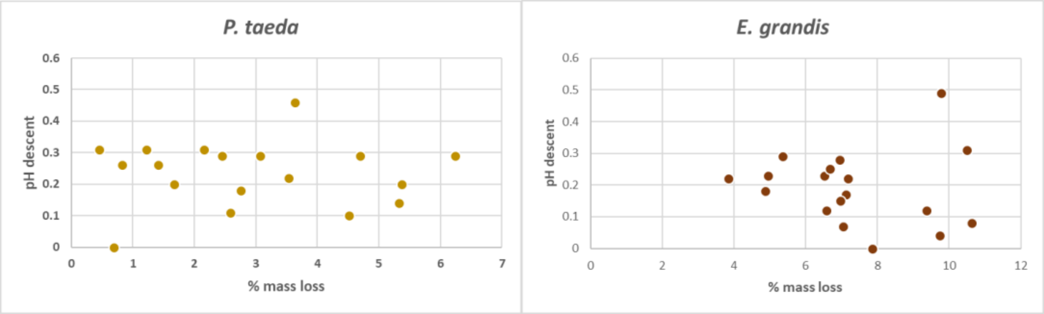

Figure 4.2 Distribution of pH descent vs % mass loss for *P. taeda* and *E. grandis*

Even though a drop in pH after thermal modification is observed for both species, there is no correlation with the mass loss percentage, at the present levels of modification (Figure 4.2). However, some interesting facts can yet be extracted. In first place, the acid nature of wood of *E. grandis* without modification is significant, compared to *P. taeda.* (mean pH of 3.9 and 4.4 of wood without thermal modification). The fact that *E. grandis* *(*hardwood) have more acetylated groups than *P. taeda* (softwood)(Sixta 2008) contributes to formation of more acetic acid during the drying process in the sawmill. Furthermore, drying process of *E. grandis* boards can last even 30 days with temperatures reaching 65°C (Vázquez 2016) which results in a higher rate of acetic acid liberation (Popovic et al. 2016). On the other hand, *P. taeda* board are kiln dried in higher temperatures (75-95°C), but for a maximum period of 1 or 2 days.

Even though modified *E. grandis* reaches more mass loss percentage - almost double compared to modified *P. taeda* - this does not reflect on pH descent as it is slightly higher in *P. taeda* (0.23 mean pH descent) in contrast with *E. grandis* (0.20 pH descent). This could give some evidence that *P. taeda* degradation by-products due to thermal modification are more acid, contributing more to pH drop than those of *E. grandis.* A possible explanation to this, might be that pine wood has a high amount of acid extractives compared to other wood species (Šernek et al. 2004).

4.4 Light Microscopy

4.4.1 *P. taeda*

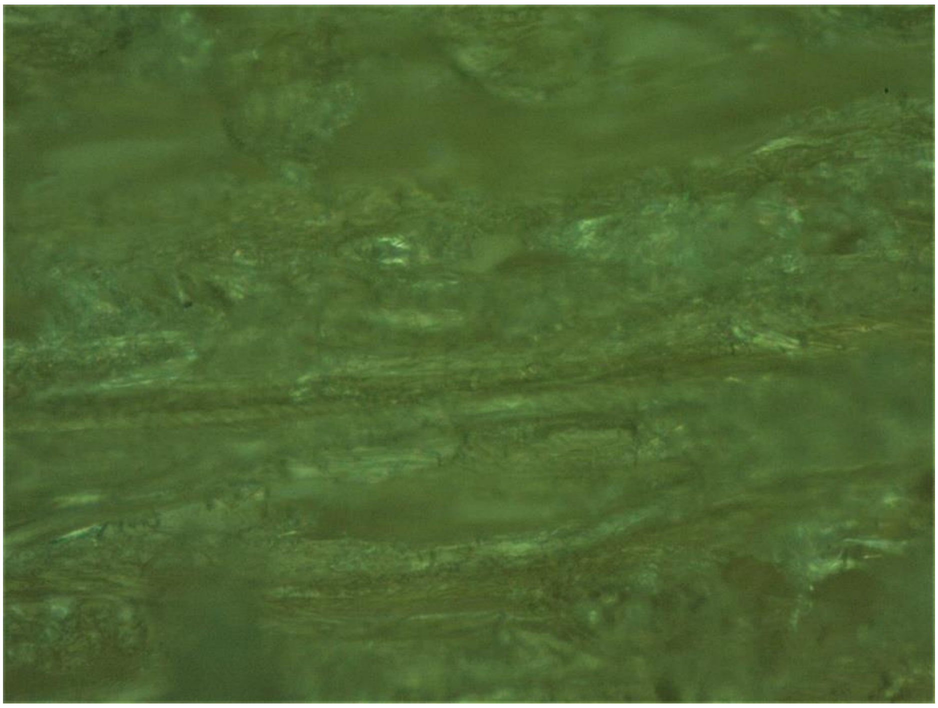

Figure 4.3 *P. taeda* surface (50x)

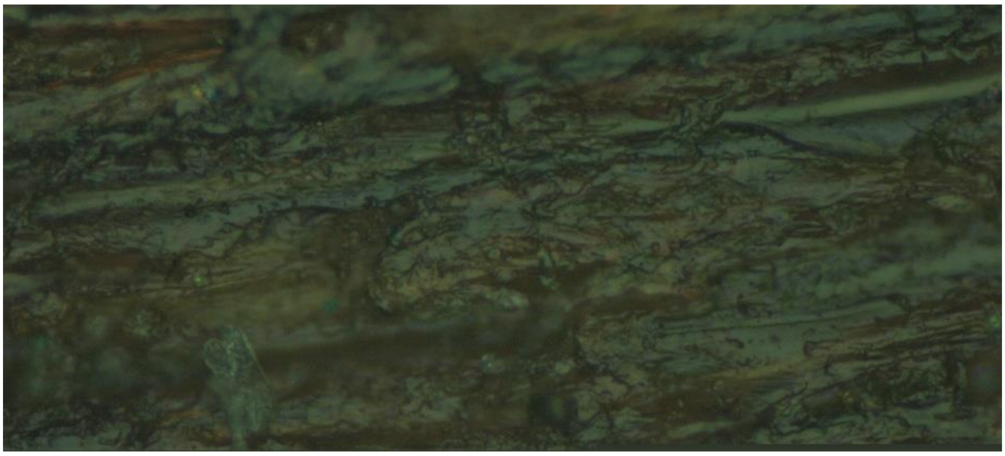

Figure 4.4 Modified *P. taeda* surface (50x) I

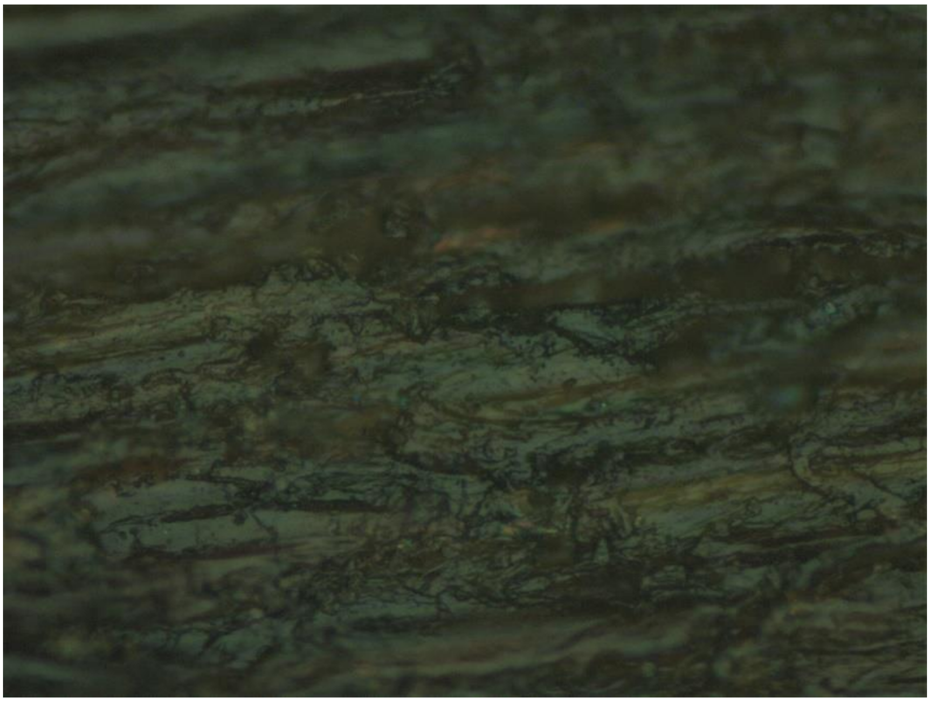

Figure 4.5 Modified *P. taeda* surface (50x) II

Different from non-modified (Figure 4.3), deformations and tangential cracks are observed after thermal modification. Large stresses occur between the earlywood and latewood tracheids “due to differences in shrinkage/swelling behaviour, resulting in these tangential cracks” (Boonstra 2007). Furthermore, a shining black substance, presumably resins and waxes, appear at the surface which evidence extractive migration to the surface

4.4.2 E. grandis

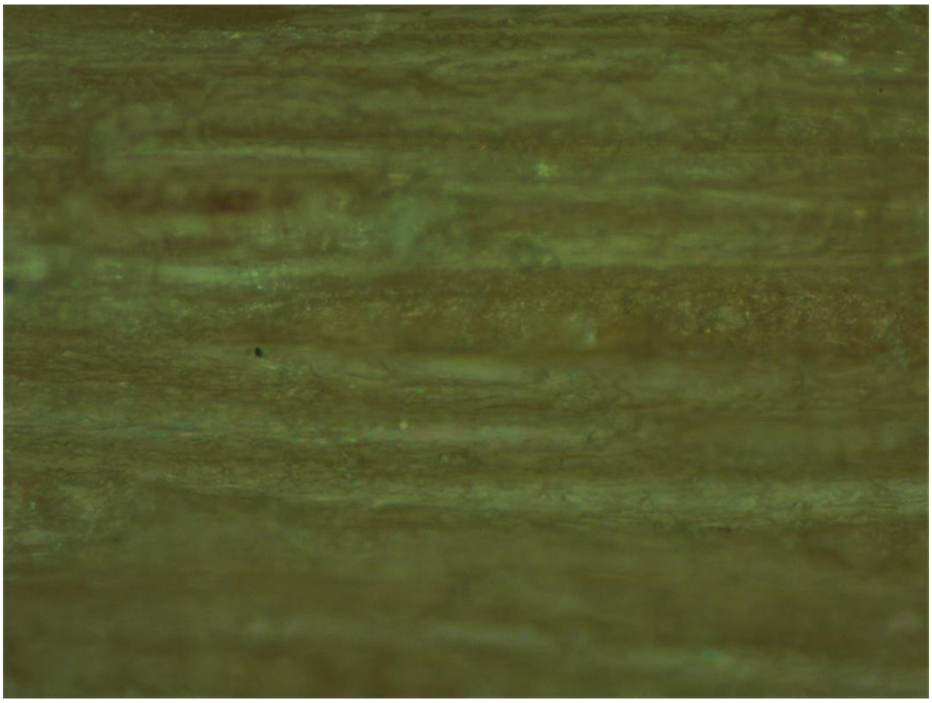

Figure 4.6 *Eucalyptus grandis* surface (50x)

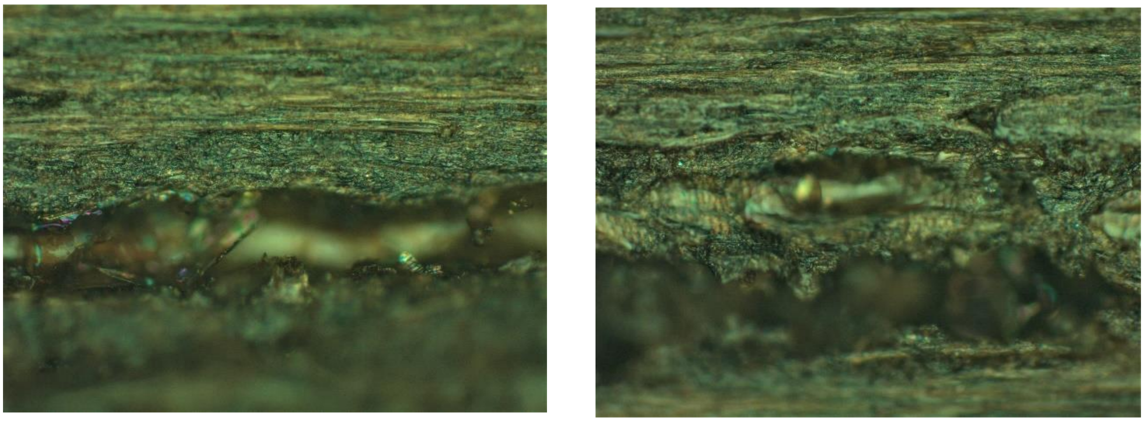

Figure 4.7 Cracks on modified *E. grandis* surface (20x)

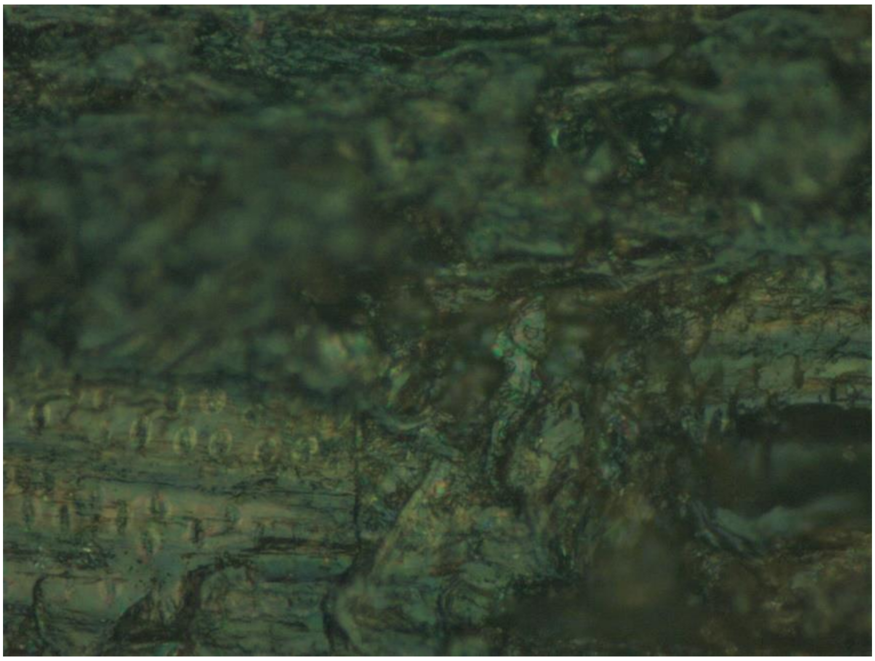

Figure 4.8 Modified *E. grandis* surface (50x)

E. grandis wood showed (Figure 4.6) some irregularities parallel to the fibres in it surface but no cracks or large deformations. On the other hand, after thermal modification, wood surface was significatively affected. Cracks and deformations appeared (Figure 4.7), and a more irregular and rougher surface resulted. A shining dark substance, extractive or degradation sub products, seems to be covering the wood surface (Figure 4.8).

Hardwoods species are reported to be sensitive to collapse of vessels and deformation of fibres (Boonstra 2007). The presence of tension wood, which have longitudinal shrinkage much larger than normal wood, and the shorter fibres, contributes to abrupt fracture. These abrupt fractures can lead to considerably different failure behaviour after impact or mechanical stress (Boonstra 2007). This might explain why thermally modified *E. grandis* wood surface is brittle, with low resistance to abrasion.

4.5 FTIR spectrum

4.5.1 *E. grandis*

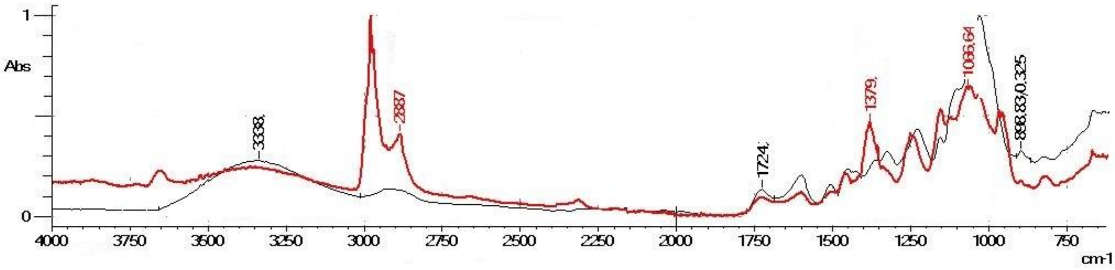

Figure 4.9 FT-IR spectrum for unmodified (black) and thermally modified (red) *E. grandis*

As expected, band at 3300-3400 cm^{-1} is significatively reduced due to the decrease in OH groups of thermally modified wood. Decrease of OH groups can be explained by thermal degradation but also by different amount of water contained on unmodified and modified wood (Lopes et al. 2018). This evidence the lower equilibrium moisture content (EMC) of modified wood.

Due to high temperatures, deacetylation occurs by cleavage of acetyl groups bonded as an ester group to the hemicellulose. In the FTIR spectrum, at 1720 cm^{-1} the absorption peak of the carbonyl groups of this ester appears (Tjeerdsma and Militz 2005). It is observed, an intensity reduction of the peak at 1720 cm^{-1} (corresponding to C=O in xylans) in modified wood, indicating a reduction of acetyl groups. This decrease in the absorption band at 1720 cm^{-1} leads to a decrease in the amount of absorbed water in cellulose (Ozgenc et al. 2018).

It has been reported that the band appearance at 1380 cm^{-1} corresponds to the condensation of lignin and the formation of lignin-carbohydrate complexes (Özgenç et al. 2016). The extent of these reactions is highly dependent on wood specie, especially on the type of lignin and hemicellulose composition. As it is observed in the *E. grandis* spectrum, during thermal modification the extent of lignin and carbohydrate condensation is occurring significantly.

Peak around 2900 cm^{-1} represents C-H stretch while the band at 1000 – 1100 cm^{-1} represents C-O stretching of alcohols and esters (Lopes et al. 2018). As observed in the spectrum there is an increase in the peak signal at 2900 cm^{-1} while the signal band at 1000 – 1100 cm^{-1} reduces. This may be explained by the fact that during thermal modification, C-O functional groups are cleaved, generating volatile compounds. The resulting wood, has more amount of C-H proportion than C-O, resulting in a less reactive material (Liu et al. 1998).

Band reduction located at 895-896 cm^{-1} indicates the decrease in C-H groups, associated with the loss of hemicellulose in modified wood (Ozgenc et al. 2016, 2018) and the lesser content of carbohydrate compared with lignin (Esteves et al. 2008, 2013.

4.5.2 P. taeda

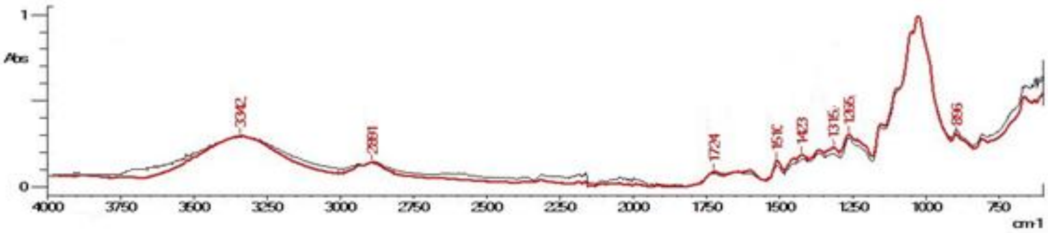

Figure 4.10 FT-IR spectrum of unmodified (black) and thermally modified (red) *P. taeda*

Spectrum of *P. taeda* shows less differences between unmodified and modified wood compared with *E. grandis*. As mass loss during thermal modification in *P. taeda* is less than in *E. grandis*, chemical changes occur in minor extension.

As in *E. grandis*, there is a decrease in OH groups after thermal modification (band at 3300-3400 cm^{-1}). Though, the fall in modified *P. taeda* is not as pronounced as in *E. grandis*. The fact that softwoods have more hexoses than hardwoods, causing a less reaction of hemicelluloses, explains the different extension of OH groups loss. Furthermore, the reduction of carbonyl groups (1720 cm^{-1}) is not clear in the spectrum, as there are no significant difference in the absorbance peak. It is reported that spectrum between 1730-1740 cm^{-1} in pine represents fats and waxes (Nuopponen et al. 2003). As there are no changes in the spectrum, volatilization of its did not occur.

Peak increase in 2900 cm^{-1} is not as clear as in *E. grandis*, so reactions of condensation between lignin and carbohydrates are not significant in *P. taeda.* Although, a relative lignification of the wood is occurring as there is a peak reduction at 895-896 cm^{-1} (C-H group decrease) indicating loss of hemicelluloses and also to the signal increase at 1510 cm^{-1} indicating more relative amount of C=C in lignin. Furthermore, increased peak signal at 1315 cm^{-1} is assigned to C-H vibration in cellulose indicating some extension of depolymerization (Lopes et al. 2018).

Finally, 1423 cm^{-1} signal increase indicates a relative higher cellulose crystallinity in modified *P. taeda* (Lopes et al. 2018). This is caused by two factors: degradation of hemicellulose and rearrange of amorphous regions of cellulose. This higher content of crystal cellulose, besides the degradation of OH groups, contributes to higher hydrophobicity of thermally modified *P. taeda* wood. Also, regarding adhesives, solvent “penetration in the amorphous region is faster than in crystalline regions” (Lopes et al. 2018).

4.6 Wood Hygroscopicity

Images below shows the sorption isotherms models at 25 °C for *P. taeda* and *E. grandis*, both unmodified and thermally modified.

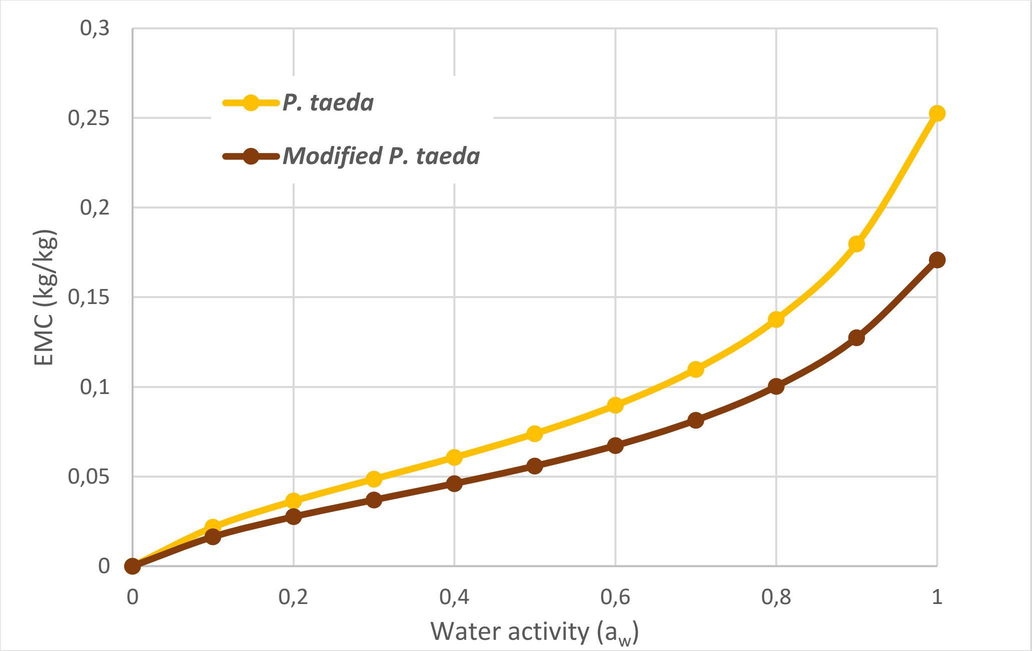

Figure 4.11 Sorption isotherm model of non-modified and modified *P. taeda* at 25 °C

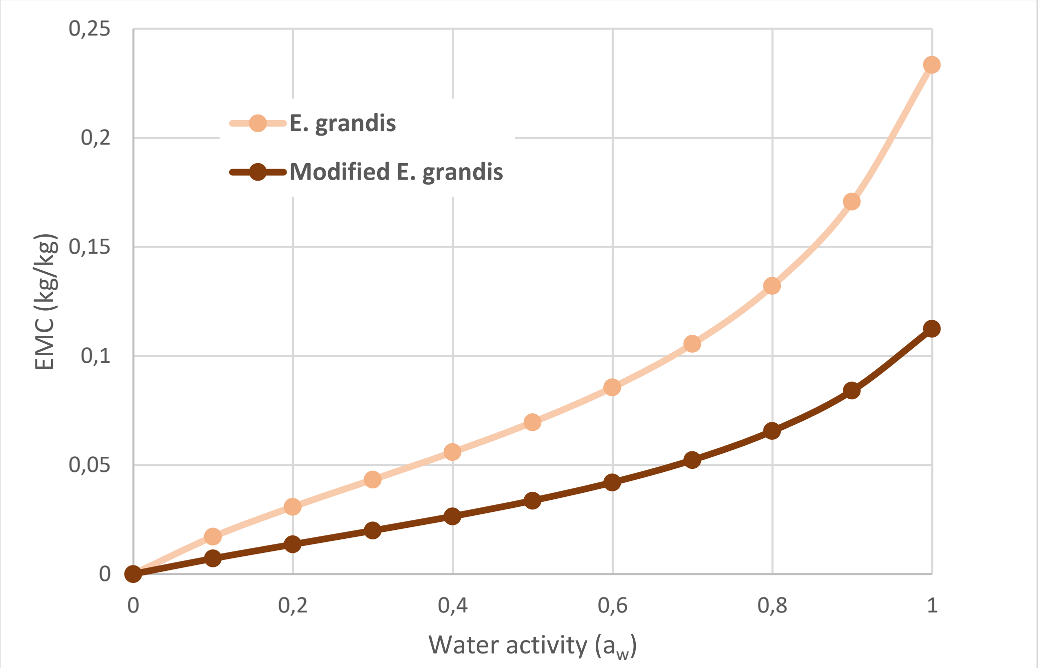

Figure 4.12 Sorption isotherm model of non-modified and modified *E. grandis* at 25 °C

Table 4.3 Hailwood-Horrobin model parameters and the correlation coefficient between the experimental data and the model (r)

Wood	A	B	C	K_d	K_h	W	M_d	M_h	$M_{0.9}$	r
P	3.45	12.72	12.22	0.791	5.65	327.39	0.136	0.044	0.178	0.976
TM-P	4.66	15.98	14.78	0.758	5.53	414.60	0.093	0.034	0.127	0.957
E	5.00	9.45	10.17	0.766	3.47	308.04	0.130	0.041	0.171	0.969
TM-E	13.07	11.27	15.45	0.738	2.17	550.32	0.065	0.019	0.084	0.965

Thermal modification reduced the hygroscopicity of both wood species as it can be observed in Figure 4.11 and Figure 4.12. For *E. grandis* changes on hygroscopicity are greater than in *P. taeda*.

As hydroxyl groups in wood bind water chemically (Simpson 1979), the reduction in the amount of OH groups due to thermal modification lowers the wood´s hygroscopicity capacity to adsorb water from the surrounding air (Venson et al. 2016). Also, equilibrium moisture content is also decreased by the fact that thermal modification (specially at temperatures higher than 200°C) reorganize the cellulose state to a more crystalline one (Olek et al. 2013). Cellulose molecules from crystalline regions have their hydroxyl groups bond with hydroxyl groups of adjacent cellulose molecules, holding it in a parallel arrangement (Simpson 1979) and transforming this OH into non-accessible to water. Regarding sorption, more crystalline regions of cellulose effectuates a further reduction in the available sorption sites (Olek et al. 2013). Furthermore, lignin is another wood component that contributes to hygroscopicity. Rearrangement and cross-linking of lignin with other wood components, consequence of thermal modification, cause a reduction of carbonyl groups which also are responsible for binding water (Olek et al. 2013). It is reported that cross-linking contributes to a stiffer matrix, which restrains the swelling of cell walls during adsorption, making sorption sites less available for bonding with water molecules. W coefficient, representing the apparent molecular mass of dry wood per sorption sites were higher after thermal modification. In other words, there was a remarkable decrease in the number of sorption sites in thermally modified wood. W obtained values for *P. taeda* and *E. grandis* were 327 and 308, respectively, while after thermal modification they were 415 and 550. The difference between species, after thermal modification, is significant. This fact can be attributed to the higher loss of hemicellulose (and higher mass loss) after thermal modification of *E. grandis*, as showed on the FTIR spectre.

On the other hand, K_d coefficient is the equilibrium constant between the dissolved water and vapor and in this case, lower than 1. This means that dissolved water had lower activity compared with liquid water (Olek et al. 2013). However, there were not significant changes in K_d after thermal modification. This means that the descend on moisture equilibrium content is related to the monomolecular sorption and highly dependent on the accessible sorption sites, as reported (Olek et al. 2013).

4.6.1 Isosteric heat of sorption

The isosteric heat of sorption was calculated from the sorption data determined through the thermodynamic model. The sorption isotherms are shown below. At constant water activity, EMC decreases as temperature increases. Higher temperatures promotes the migration of water molecules as they increase their energy level, becoming less stable and breaking away from the water-binding sites of the wood (Bahar et al. 2017). However, it is noticeable that EMC reduction with increasing temperature is smaller in *E. grandis* and is almost unchanged after thermal modification (Figures 4.13 to 4.16)

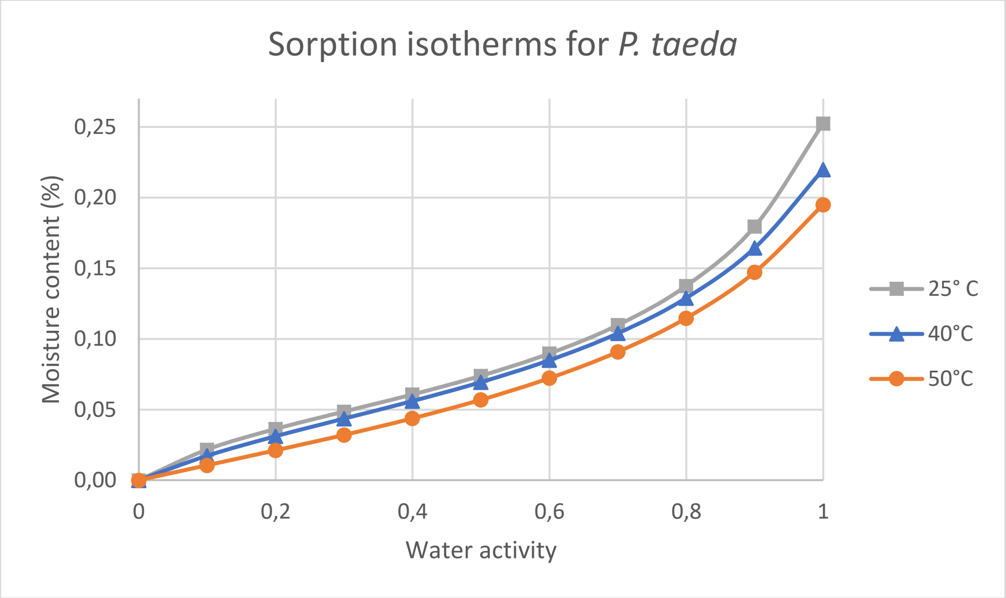

Figure 4.13 Sorption isotherms for *P. taeda*

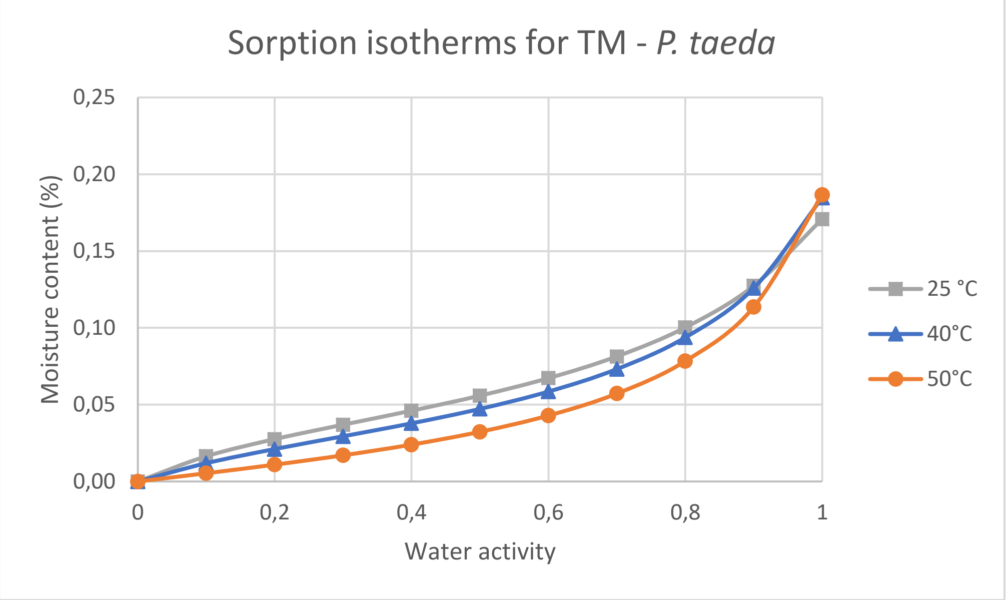

Figure 4.14 Sorption isotherms for thermally modified *P. taeda*

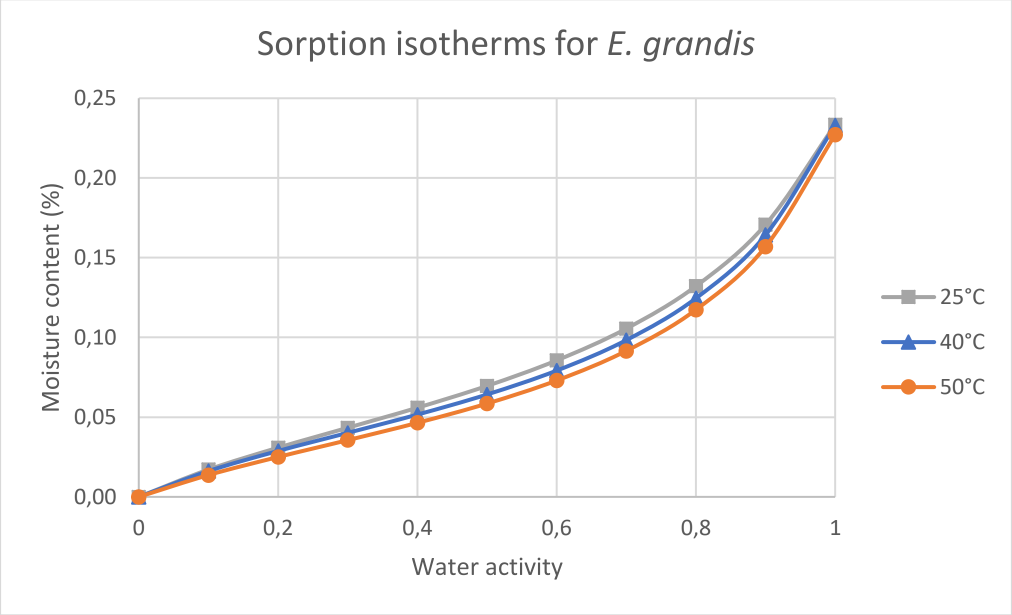

Figure 4.15 Sorption isotherms for *E. grandis*

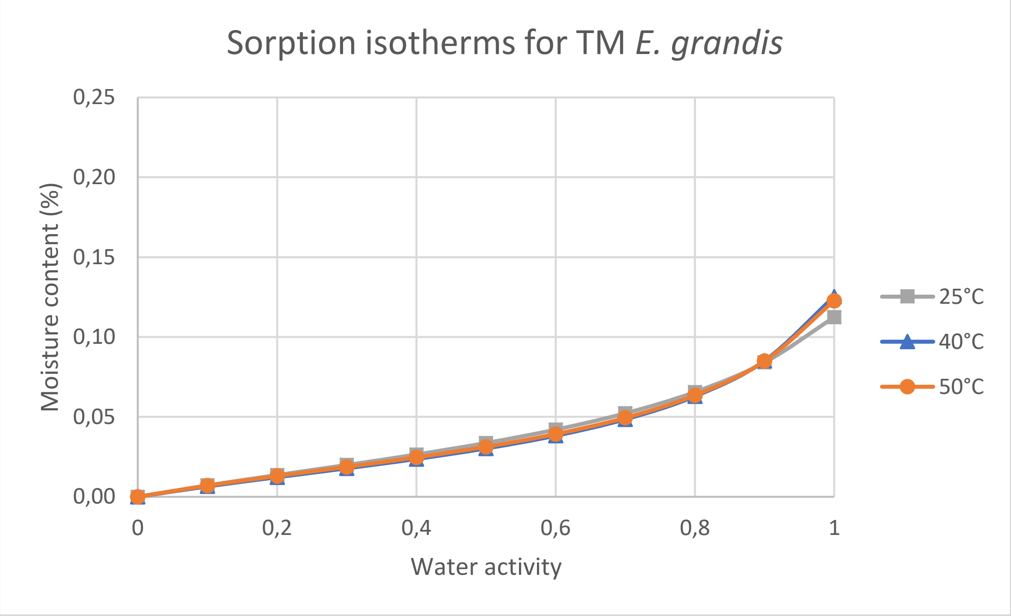

Figure 4.16 Sorption isotherms for thermally modified *E. grandis*

Isosteric heat of sorption was calculated from the slope of the plot of Ln (a_w) versus 1/T (K^{-1}) for each equilibrium moisture content, as showed on Equation 11. Figure 4.17 shows that net isosteric heat of sorption (q_{nst}) decreases with the increase of the EMC. The higher values at low moisture content are due to the existence of highly active sorption sites, which are firstly covered by water molecules. As moisture content increases, the most active sites become occupied and sorption occurs on less active sites, thus reducing heat of sorption and the strength of water-wood bonding (Figure 4.17).

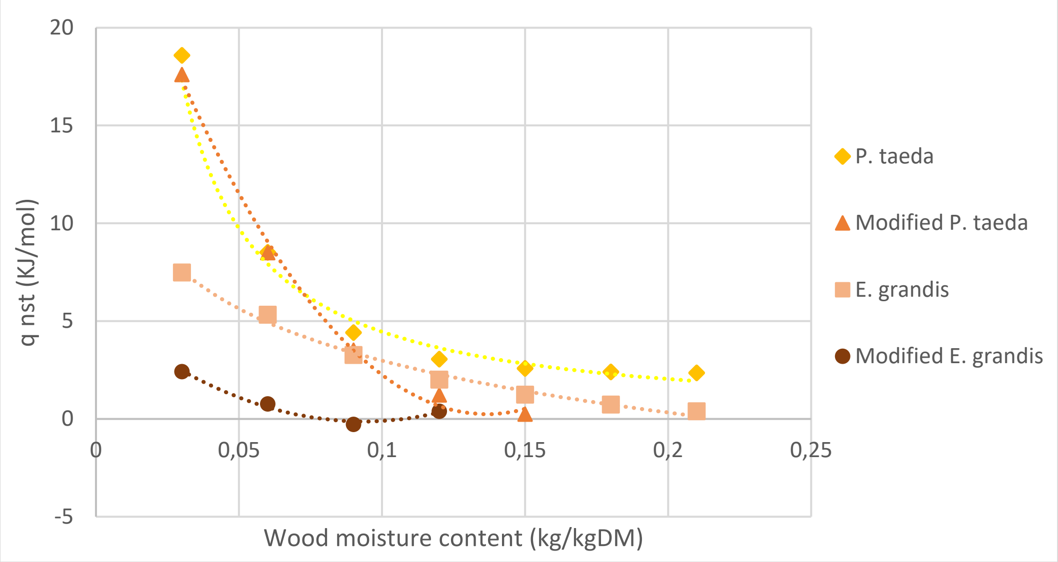

Figure 4.17 Isosteric heat of sorption vs wood moisture content

P. taeda presented higher values of heat of sorption specially at moisture contents below 10%. This is an indicator of strong water-surface interactions in *P. taeda* (Ouertani et al. 2014b), that even remains after thermal modification which presented almost the same values that of non-modified wood below 8% EMC. In contrast, for *E. grandis*, there is a significant decrease of the isosteric heat of sorption after thermal modification. This is consistent with the fact that *E. grandis* showed more significant losses in hemicellulose and specially OH groups due to thermal modification compared with *P. taeda* wood. These losses affected and reduced the sorption sites and had a negative effect on the strength of this sites. It can be concluded, then, that a certain degree of surface inactivation occurs on *P. taeda*, which is more significant in *E. grandis*. This could have effects also on the chemical interactions (and strength of the bond) between wood and adhesives, due to the elimination of OH and other polar groups.

4.7 Wettability

Figures 4.18 to 4.21 shows examples of photos of the water drop at different times and on different wood. It is noticeable, at simple view, the different water spreading behaviour between thermally modified and non-modified.

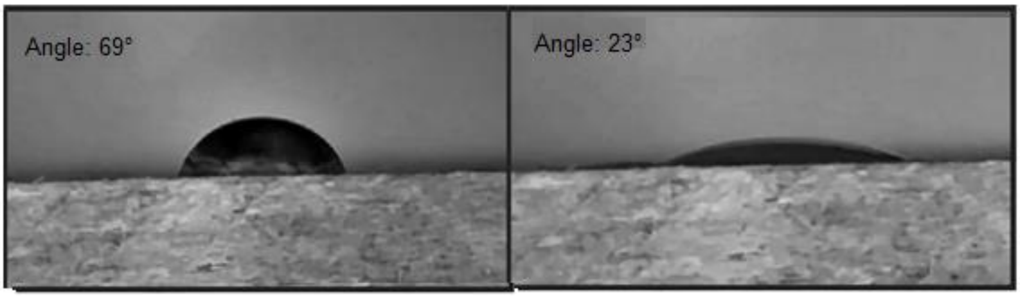

Figure 4.18 Contact angle with water at 4 and 96 sec in *P. taeda*

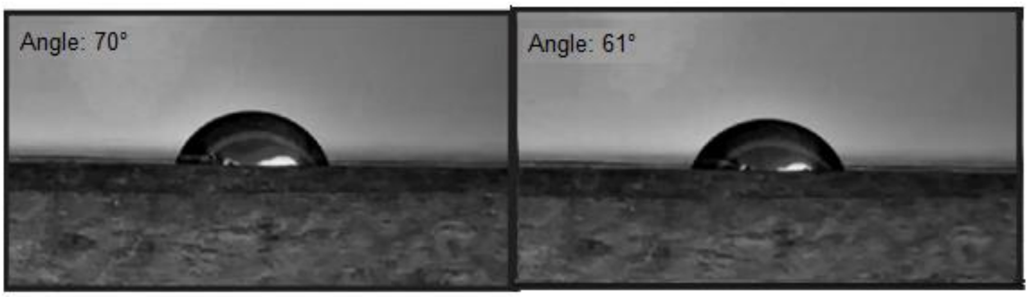

Figure 4.19 Contact angle with water at 4 and 96 sec in modified *P. taeda*

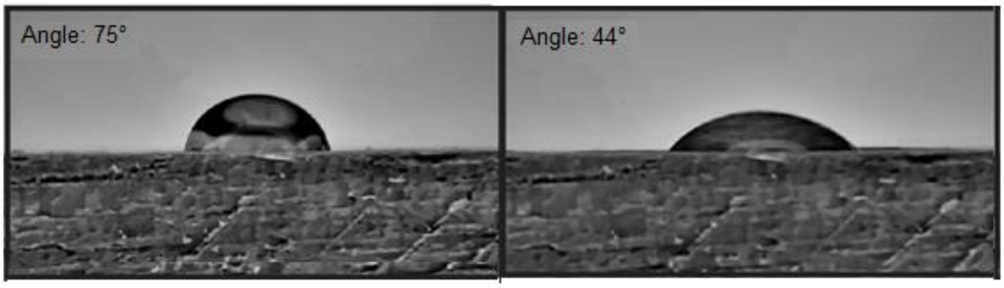

Figure 4.20 Contact angle with water at 4 and 96 sec in *E. grandis*

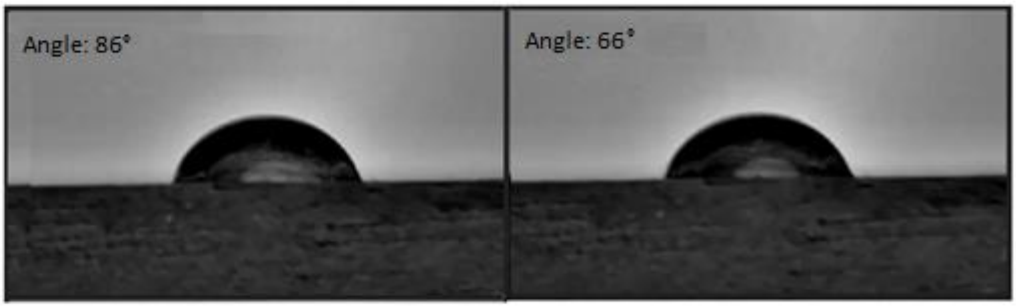

Figure 4.21 Contact angle with water at 4 and 96 sec in modified *E. grandis*

Experimental results of contact angle measurements and the Shi & Gardner fitted model are shown in Figure 4.22. In Table 4.5 model parameters are presented. The R^2, corresponding to the coefficient of relation, are over 0.95 which indicates that Shi & Gardner model is accurately predicting wetting of the modified and non-modified wood species. In this model, K_θ reflects the shape of the wetting curve. A high K_θ value indicates a non-linear curve with a high curvature, while a small K_θ suggests an inclination to a linear function.

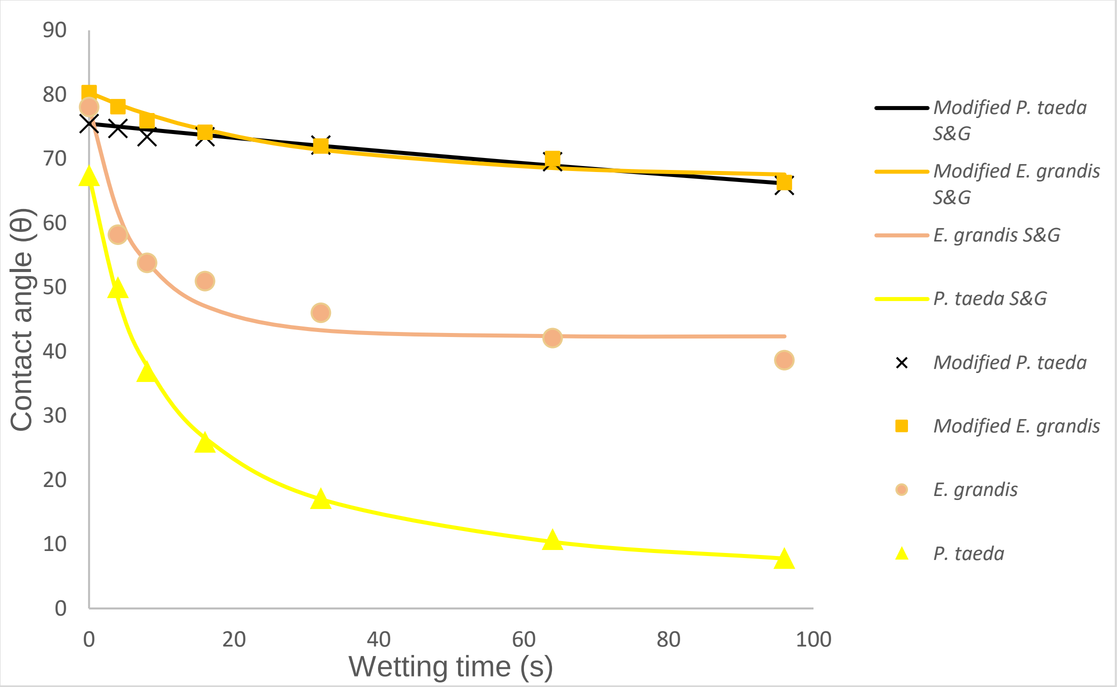

Figure 4.22 Experimental results of contact angle measurements and Shi & Gardner model.

Table 4.4 Contact angle (t= 4 seconds)

Wood	**Average contact angle (θ_i)**
P taeda	49.9 °
Modified *P. taeda*	75.5 °
E. grandis	58.2°
Modified *E. grandis*	78.1°

Table 4.5 Shi & Gardner model parameters

Wood	**K_θ**	**$WS_{\theta 0\text{-}4}$**	**R^2**
P. taeda	0.100	-4.775	0.999
Modified *P. taeda*	0.001	-0.113	0.979
E. grandis	0.080	-4.103	0.954
Modified *E. grandis*	0.006	-0.452	0.964

Modified *E. grandis*, as it presents the highest contact angle (Table 4.4), is the most water repellent. The contact angle is higher after modification indicating the more hydrophobic nature of the surface for both species. Furthermore, water absorption and spreading rate is significantly reduced after thermal modification, standing out the big drop in *P. taeda*. Modified *P. taeda* presents the lowest contact angle decrease rate (0.001) and the lowest $WS_{\theta 0-4}$ (-0.113).

Even though mass loss in modified *P. taeda* was lower than in *E. grandis*, the effects of thermal modification regarding wettability and water absorption were more significant in pine. Hakkou observed that there was not direct relation between contact angle evolution and sample weight loss, "indicating that change of wettability is not due to important chemical modifications like hemicellulose decomposition". In fact, Hakkou concluded that plasticisation of lignin, conformational reorganization and condensation reactions of it, explain the hydrophobic properties of thermally modified wood, even at low temperature modification were mass loss is not significant (Hakkou et al. 2005). FTIR analysis showed that lignin reactions are significant in thermal modification of *E. grandis* but not in *P. taeda*. So, lignin condensation and plasticisation were contributing to the water repellent properties of thermally modified *E. grandis.*

Nussbaum have previously stated that differences in wetting properties of different wood species originates from different extractive composition and functionality (Nussbaum 1999). In the same way, Sernek concluded that “migration of the extractives to the wood surface is a dominant mechanism, which explains the changes in the wood surface chemistry” responsible for surface deactivation (Šernek et al. 2004). For *P. taeda*, FTIR analysis showed that there was not an appreciable decrease on fats and resins content and, furthermore, studies shown that migration of its from resin channels is possible at temperatures below 200°C (Šernek et al. 2004). So, there is evidence to assume, that the significant deactivation of the thermally modified pine surface might be caused by the presence of fats, resins and extractives translocated from within the board to the surface.

For gluing two wood surfaces, a good wetting of it is a precondition. Wetting involves the value of the contact angle and penetration of the liquid into the wood. Contact angles greater than 90° lead to incomplete wetting, causing low bond strengths (Pizzi and Mittal 2010). In the present study, none of the species have contact angles greater than 90°, thus, the spreading of adhesives might not be negatively affected. On the other hand, penetration might be a problem when gluing thermally modified wood. As reflected in K_{θ} and $WS_{\theta 0\text{-}4}$, penetration of water is drastically reduced. In thermally modified *P. taeda*, penetration rate is several times minor than non-modified, and is even lower than thermally modified *E. grandis.*

In conclusion, thermal modification (at the present conditions, and in *E. grandis* and *P. taeda*) severally affects water penetration and hydrophobicity, being especially remarkable for *P. taeda*. To counter this effect and improve adhesion, higher pressures should be used when gluing thermally modified wood.

4.7.1 Surface free energy

Contact angle measurements with water, ethylene glycol and soybean oil for *P. taeda* and *E. grandis* are shown on Table 4.6. A first look to these results indicates that as the polarity of the liquid decreases (water > ethylene glycol > oil) so did the contact angle, evidencing the affinity of wood for apolar liquids. For water and ethylene glycol, it was observed an increase in the contact angle after thermal modification. On the other hand, for soybean oil, the contact angle decreases after thermal modification. There is, then, evidence that the polarity of the wood surface changed after being thermally modified.

Table 4.6 Contact angle measurement

	Water		**Ethylene glycol**		**Soybean oil**	
	Θ (°)	Standard deviation	Θ (°)	Standard deviation	Θ (°)	Standard deviation
P. taeda	49.9	13.3	27.6	8.4	27.0	8.9
Modified *P. taeda*	74.7	10.9	52.3	3.1	23.1	5.3
E. grandis	58.2	16.1	32.8	5.5	25.1	2.7
Modified *E. grandis*	78.1	9.8	49.7	7.4	19.3	4.9

Results confirmed the fact that *P. taeda* is a more hydrophilic wood than *E. grandis*, in the same way as shown in the previous wettability results.

However, after thermal modification differences between species were smaller.

Lineal regression of contact angle measurements and liquid properties, according to Equation 17, allowed surface free energy parameters to be estimated (Table 4.7).

Table 4.7 Lineal regression of Equation 17 and angle contact measurements, and calculated surface free energy of wood

	Slope	**y-intercept**	**R^2**	**γ^D_s (mJ m^{-2})**	**γ^P_s (mJ m^{-2})**	**γ_s (mJ m^{-2})**
P. taeda	4.91	5.04	0.973	25.37	24.16	49.53
Modified *P. taeda*	2.53	5.72	0.911	32.74	6.41	39.15
E. grandis	4.16	5.33	0.975	28.43	17.27	45.71
Modified *E. grandis*	2.11	6.04	0.955	36.47	4.44	40.91

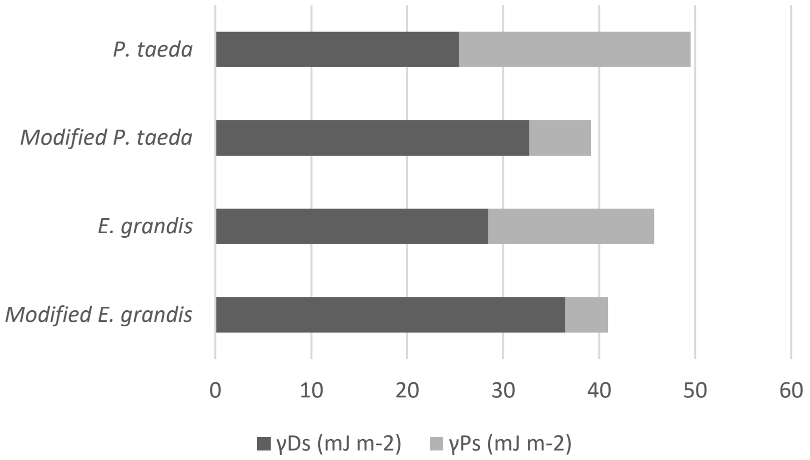

Figure 4.23 Surface free energy of *P. taeda* and *E. grandis* before and after thermal modification

Surface free energy was reduced, by 21% for *P. taeda* and 11% for *E. grandis*, after thermal modification. But, what is more important, in both species, the polar component (γ^P_s) decreases in detriment to the dispersive component ($\gamma^D{}_s$) indicating a transformation of the surface polarity (Figure 4.24).

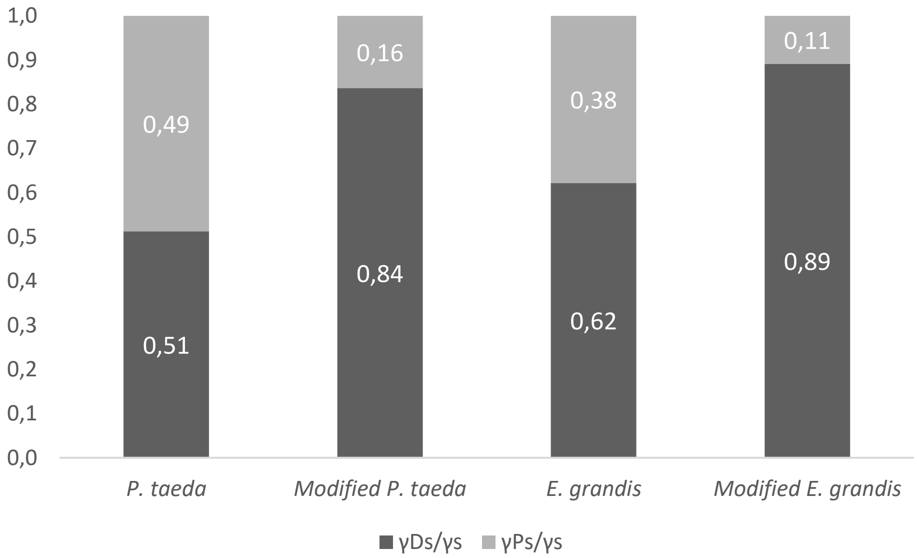

Figure 4.24 Relation between polar and diffusive components of the surface free energy

In *E. grandis* the diffusive component ascended from 62% to 89% of total surface free energy after thermal modification. As FTIR spectra indicates, chemical changes regarding loss of OH groups and acetyl groups, in addition to an increase in the relative amount of lignin (hydrophobic) and the formation of a cross-linked network between lignin and carbohydrates explains the modification of the wood surface to a more hydrophobic and less polar one.

In *P. taeda*, the diffusive (apolar) factor represents 51% of the surface free energy, while it is 84% on thermally modified *P. taeda.* Again, although % mass loss is half than *E. grandis,* polarity of *P. taeda* is relatively more affected by thermal modification. Referring to the observed chemical changes in FTIR spectra, which are less significant in *P. taeda* compared to *E. grandis*, increase of the hydrophobicity (decrease of polarity) of the surface is partially explained by the increase in the crystallinity of the cellulose (Lopes et al. 2018). But, as chemical changes are minor, migration of extractives, fats and waxes to the surface might be a significant factor too.

4.8 Thermoporosimetry

Shown in Figure 4.25 Thermogram of unmodified *P. taeda* (yellow) and modified *P. taeda* (brown)Figure 4.25 and Figure 4.26 are typical DSC thermogram for modified and unmodified wood. Differences between them are evident across the thermograms for each temperature step. Above -2°C, and for all thermograms, a broad endothermic absorption was observed. This absorption was attributed to the melting of free water present in lumens (Grigsby et al. 2013b). Because of this, it was not possible to determine the amount of bound water for pores above 9.9 nm, as there were not observable peaks in the thermograms.

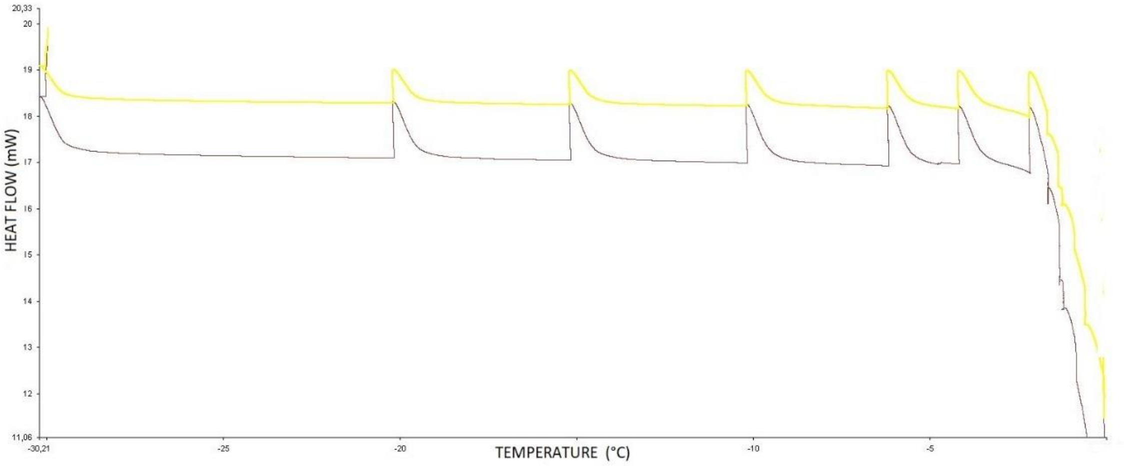

Figure 4.25 Thermogram of unmodified *P. taeda* (yellow) and modified *P. taeda* (brown)

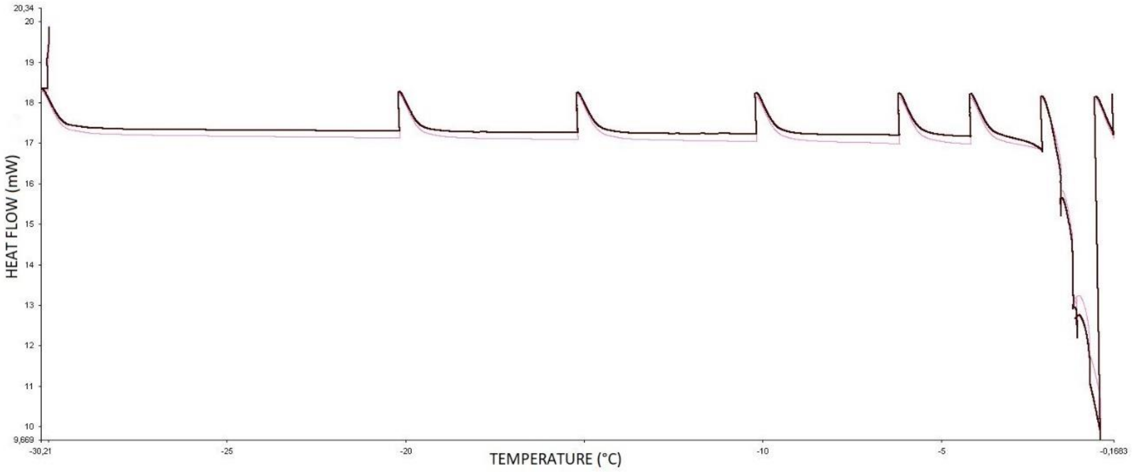

Figure 4.26 Thermogram of unmodified *E. grandis* (violet) and modified *E. grandis* (black)

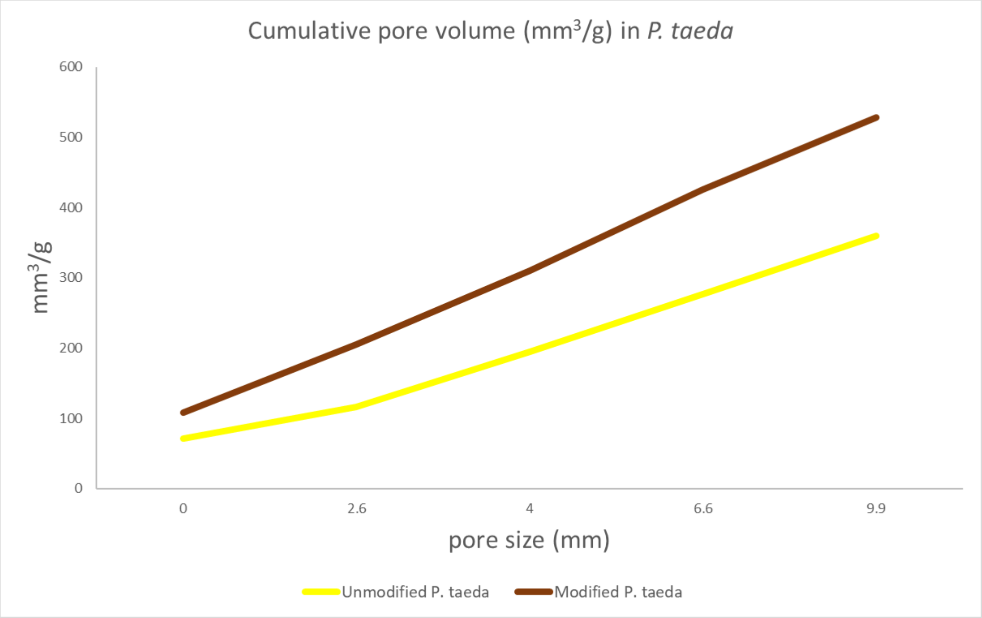

Figure 4.27 Cumulative por volume in *P. taeda*

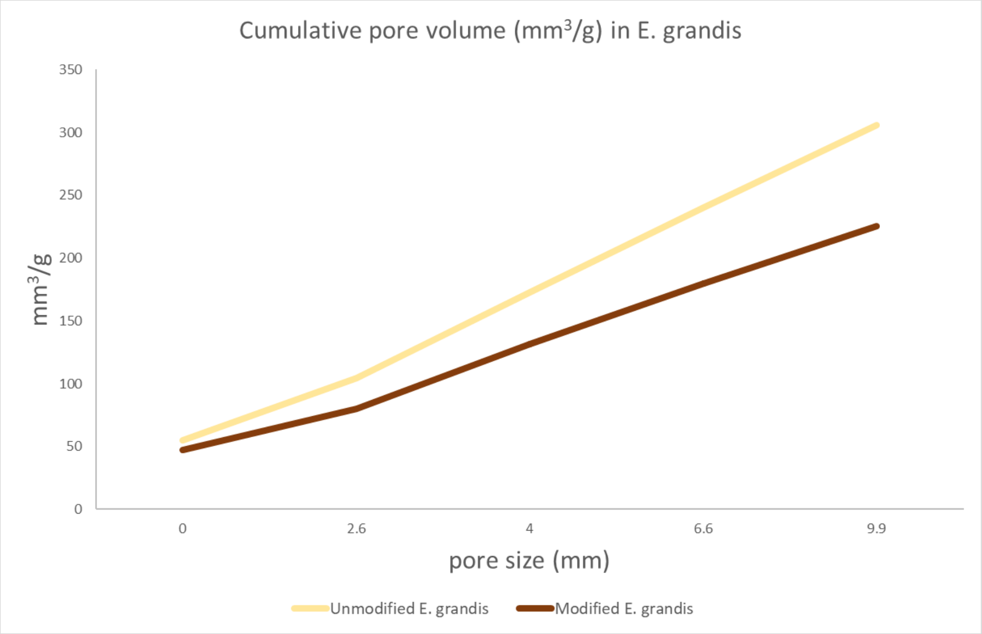

Figure 4.28 Cumulative pore volume in *E. grandis*

As shown in thermograms and in the respective graphics of cumulative pore volume (Figure 4.27 and Figure 4.28) for *P. taeda* and *E. grandis*, there are differences in the pore size distribution before and after thermal modification. Though, general behaviour differs in *P. taeda* and *E. grandis* as expected due to their different morphology.

In *P. taeda*, a significant increase in pore size distribution in pores less than 9.9 nm is observed after thermal modification. As reported for softwoods and pine species in general (Gosselink et al. 2004; Boonstra 2007) thermal modification results in a more open structure of the wood as reflected in the increase of pore size distribution. From microscopy studies performed by the mentioned authors, it was concluded that the increase in porosity was due to the damages to ray parenchyma cells around resin canals.

On the other hand, thermoporosimetry shows a contrary effect on porosity caused by thermal modification on *E. grandis*. In this case, there was a reduction in the pore size distribution. This coincide with previous studies in thermoporosimetry on hardwoods (Zauer et al. 2014). As reported by some authors, the reduce in porosity in hardwoods is attributed to shrinkage of lumens and cell walls (Boonstra 2007), flowing of lignin in the cell-wall pores and even by “closure of the skeletal substance of wood due to softening and subsequent solidification of lignin during thermal treatment” (Zauer et al. 2014). From these results, it can be concluded that capillary condensed water in the cell wall and nano pores outside the cell wall are lower in thermally modified *E. grandis*.

4.9 Shear test

Images below shows the equipment and the stages done to perform the shear test.

Figure 4.29 Pressing

Figure 4.30 Curing

Figure 4.31 Shear test

Figure 4.32 Device used for shear test

4.9.1 Polyurethane adhesive

Results of the shear test performed, shear stress at failure and % of wood failure, on modified and unmodified *P. taeda*, and *E. grandis* are shown in the Table 4.8

Table 4.8 Results of shear test with polyurethane adhesive (15 test samples)

	Shear Stress at failure (MPa)				**Resistance reduction (%)**	**Wood failure (%)**	
	Minimum	Maximum	Average	SD		Average	SD
P. taeda	5.45	9.31	7.50	2.98	59	39	26
Modified *P. taeda*	2.36	4.41	3.07	1.08		35	33
E. grandis	5.12	10.76	8.22	2.91	42	98	4
Modified *E. grandis*	2.90	7.61	4.79	1.81		82	23

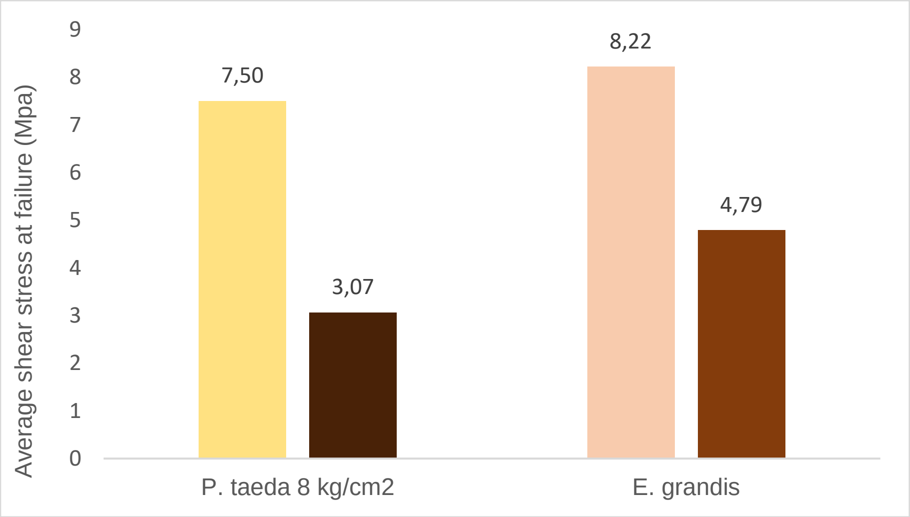

Figure 4.31 Average shear stress at failure between with polyurethane adhesive

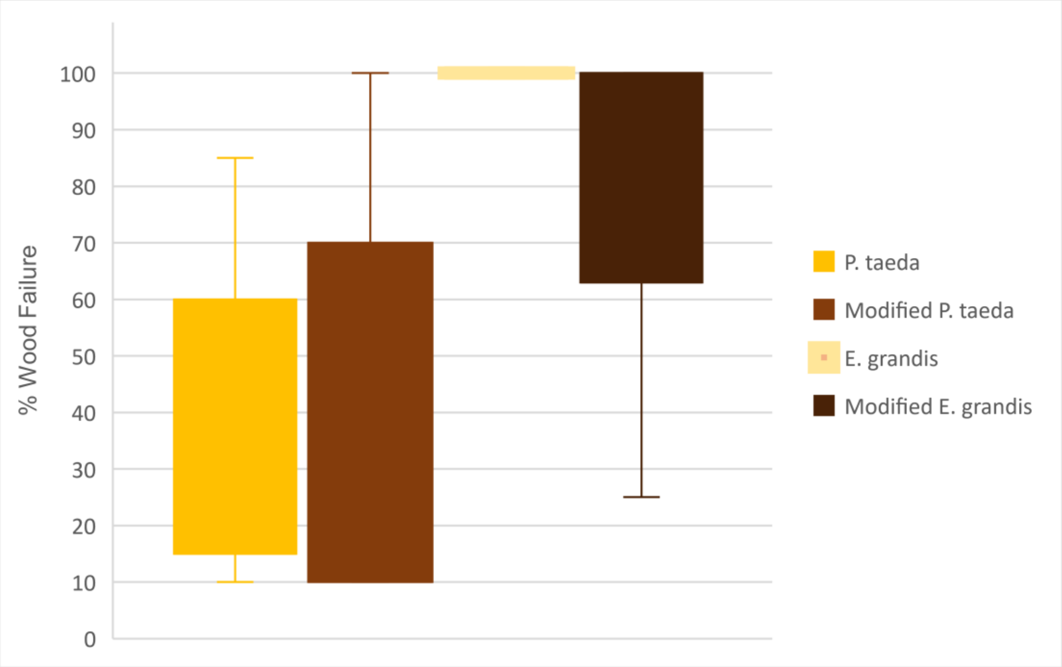

Figure 4.32 % wood failure after shear test with polyurethane adhesive

Differences between modified and non-modified wood adhesive performance was significant. Furthermore, there was also appreciable difference of the adhesive performance between *P. taeda* and *E. grandis*. As shown in Figure 4.31, there is a significant reduction on the average shear stress at failure after thermal modification. Moreover, as reflected on Figure 4.32, differences in behaviour in terms of % wood failure (% WF) are observed in *P. taeda* and *E. grandis.*

4.9.1.1 *P. taeda*

Focusing the analysis on *P. taeda*, the first conclusion regarding bonding is that for structural adhesion, % WF achieved was not satisfactory. Even though ASTM D 905 does not specify a minimum %WF, a similar norm (EN-392) indicates a minimum %WF of 90% (Steiger et al. 2010).

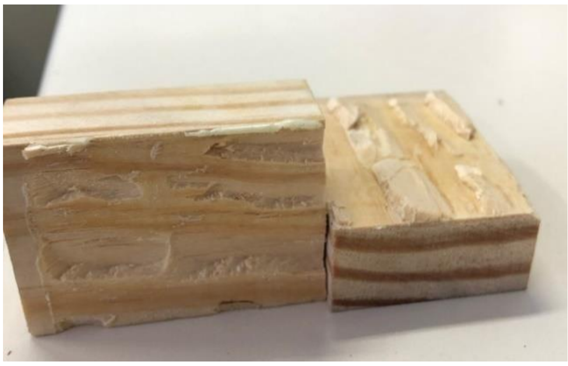

Figure 4.34 P. taeda test specimen after shear test

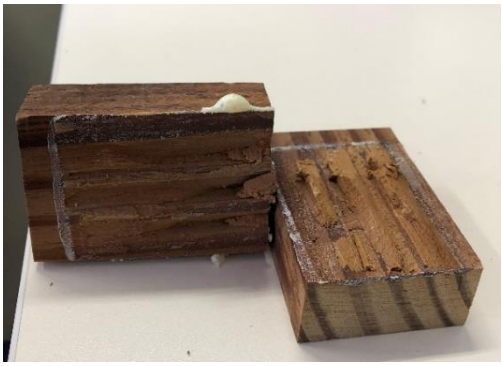

Figure 4.33 Modified P. taeda test specimen after shear test

In average, there are no significant changes in %WF after thermal modification (39% in non-modified and 35% in modified wood). Modified wood presented higher variation in %WF, even reaching 100 %WF in two test specimens. One common fact for most test specimens, is that wood failure occurs on the earlywood where the wood is less dense thus, less resistance.

Figure 4.36 Wood failure in earlywood in non-modified P. taeda

Figure 4.35 Wood failure in earlywood in modified P. taeda

Earlywood, as it has lower density, is more porous. This allows more adhesive to penetrate in this part of the wood, generating a better mechanical anchorage. The heterogeneity of the board surface in *P. taeda* had a negative effect on the bonding with polyurethane adhesive, as the bonding line have located weak areas. From this result, it was evident that penetration of adhesive was not satisfactory. To enhance polyurethane penetration, higher pressure needs to be applied at least to the same level of *E. grandis,* that is to say, 10 kg/cm^2.

As there are not significant differences in %WF between non-modified and modified *P. taeda*, the shear stress resistance reduction of 59 % due to thermal modification is explained mostly by the decay of wood mechanical properties, inherent consequence of the modification. However, as polyurethane needs a minimum content of water (rather in air or/and in wood) for the hardening reactions to occur, the different moisture content of modified and non-modified wood might also be affecting the strength of the wood-adhesive bond. As shown in the isotherms, there is a significant decrease on equilibrium moisture content after thermal modification. In this point, the hypothesis that adding water to the specimens should improve the bonding strength was set. In the following shear test, this hypothesis was taken into consideration.

4.9.1.2 *E. grandis*

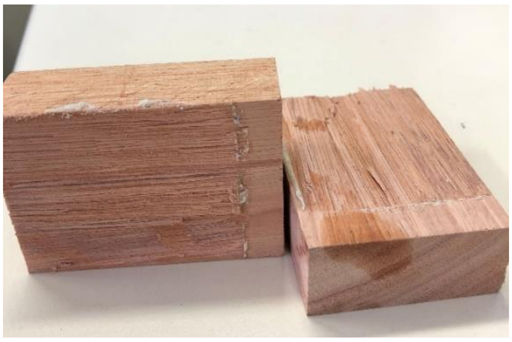

Figure 4.38 E. grandis test specimen after shear test

Figure 4.37 Modified E. grandis test specimen after shear test

On the other hand, %WF on *E. grandis* is higher and in satisfactory levels (Table 4.8). The adhesive penetration was acceptable indicating that pressure applied to *E. grandis* specimens was correct. Although, there was an appreciable reduction of this factor consequence of thermal modification.

Unlike *P. taeda*, *E. grandis* wood surface is homogeneous, resulting in an adhesion bond with no weak points. Also, shear stress resistance reduction of 42 % is less than in *P. taeda*. In this case, as % WF is minor in modified wood (Figure 4.32), the bond between adhesive and wood is weaker after thermal modification. So, this fact, in addition to the decay of mechanical resistance due to thermal modification, explains the decrease of the shear stress resistance. As *P. taeda*, the lower moisture content of thermally modified *E. grandis* might be negatively affecting the bond resistance. In the same way as in *P. taeda*, addition of water on the surface of the wood is discussed in the next section.

4.9.2 Improved Polyurethane adhesion

Results of shear stress at failure and wood failure, on modified and unmodified *P. taeda*, and *E. grandis* after polyurethane shear test (II) are shown in Table 4.9 Shear test (II) of polyurethane adhesive results.

Table 4.9 Shear test (II) of polyurethane adhesive results (15 test samples)

	Shear Stress at failure (MPa)				**Resistance reduction (%)**	**Wood failure (%)**	
	Minimum	Maximum	Average	SD		Average	SD
P. taeda	7.50	11.39	9.30	2.60	8	90	6
Modified P. taeda	4.58	11.88	8.57	3.62		91	11
Modified E. grandis	3.41	6.78	4.45	1.97	46[5]	100	1

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[5] Compared without water addition

4.9.2.1 *P. taeda*

The increase in the pressure during pressing improved the adhesion. It was clear, then, that in the first test with polyurethane adhesive penetration was insufficient. With the increase in pressure to 10 kg/cm^2, polyurethane penetrated deeper inside the wood and was able to bond strongly with it, as it is evidenced in higher levels of shear stress at failure and percentage of wood failure. After the improvements, polyurethane performed better in *P. taeda* than *E. grandis*. This agrees with previous investigations carried out with national woods and adhesives (Quagliotti 2008). Even, shear stress at failure in modified *P. taeda* (8.57 MPa) is higher than non-modified *E. grandis* (8.22 MPa).

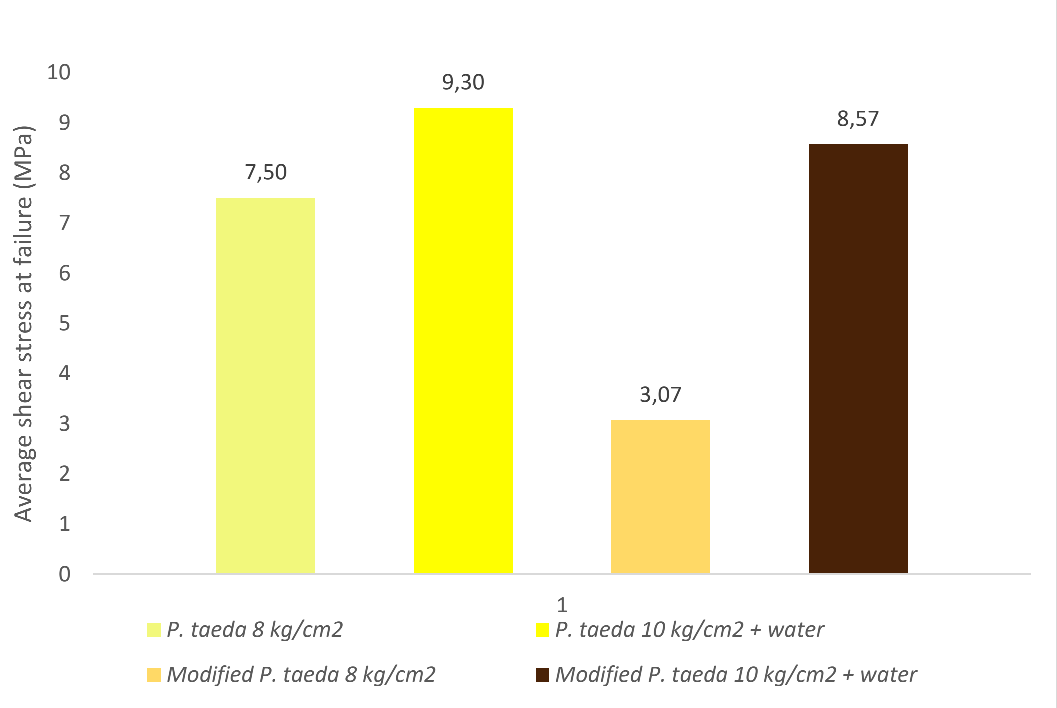

Figure 4.39 Average shear stress at failure in *P. taeda* after improvements

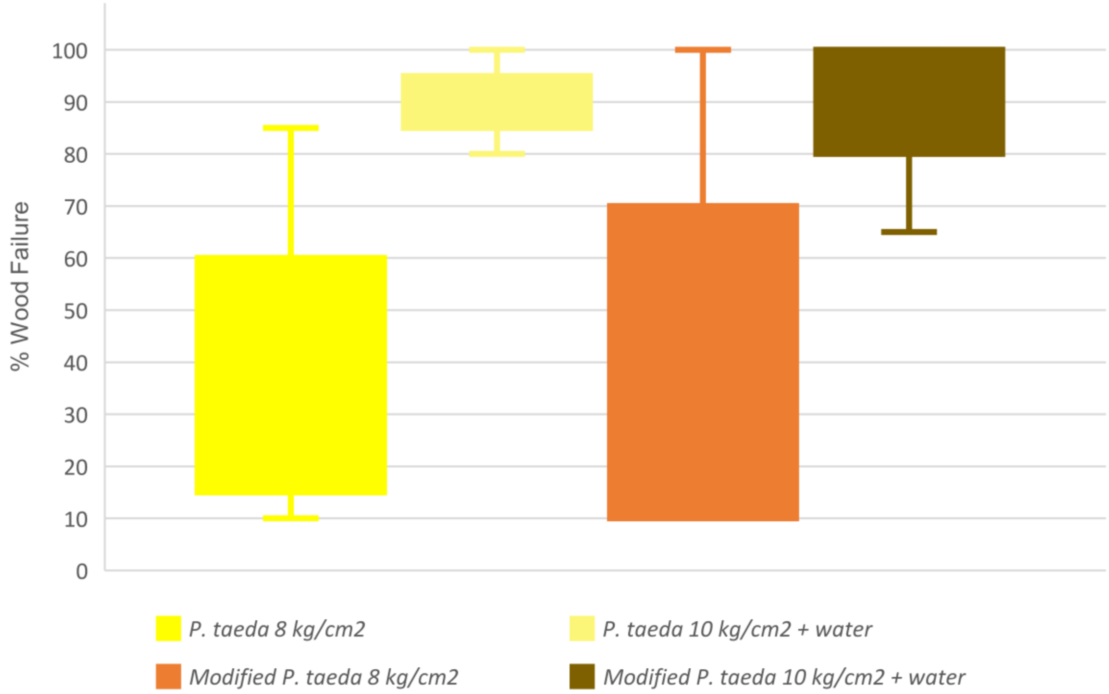

Figure 4.40 % Wood Failure after improvements in *P. taeda* adhesion with PUR

ANOVA test rejected the null hypothesis of equality of means of shear stress at failure. Comparison of the samples by Tukey test resulted in no significance statistical difference between *P. taeda* at 8 kg/cm^2, non-modified *P. taeda* at 10kg/cm^2 and modified *P. taeda* at 10 kg/cm^2. Tukey test results are shown on Table 4.10.

Table 4.10 Tukey test results for *P. taeda* with PUR adhesive

Conditions	**Shear stress at failure (MPa)**	**Group result of Tukey**
P. taeda 8 kg/cm^2	7.50	a
P. taeda 10 kg/cm^2 + water	9.30	a
Modified *P. taeda* 10 kg/cm^2 + water	8.57	a
Modified *P. taeda* 8 kg/cm^2	3.07	b

Shear stress resistance was substantially improved (Figure 4.39) as well as %WF (Figure 4.40) which is above 90%, for non-modified and modified wood: a value acceptable for structural adhesion. %WF remained invariable after thermal modification, which means that the physical resistance of wood is limiting the adhesion performance.

The resistance reduction of the bonding after thermal modification resulted in 8 %, which is an important improvement compared to the adhesion at 8 kg/cm^2 without the addition of water (59 % of decrease). This indicates that the polyurethane adhesive has a good mechanical anchorage with the wood, and, that the addition of water counters the reduction of the moisture equilibrium content and helped the polyurethane cure with good strength.

Figure 4.42 *P. taeda* test specimen after shear test II.

Figure 4.41 Modified *P. taeda* test specimen after shear test II.

4.9.2.2 E. grandis

The addition of water to the surface did not have improvements on the average shear stress at failure in the bonding (Figure 4.43). However, it had a positive effect on the %WF by increasing it to almost 100% (Figure 4.44).

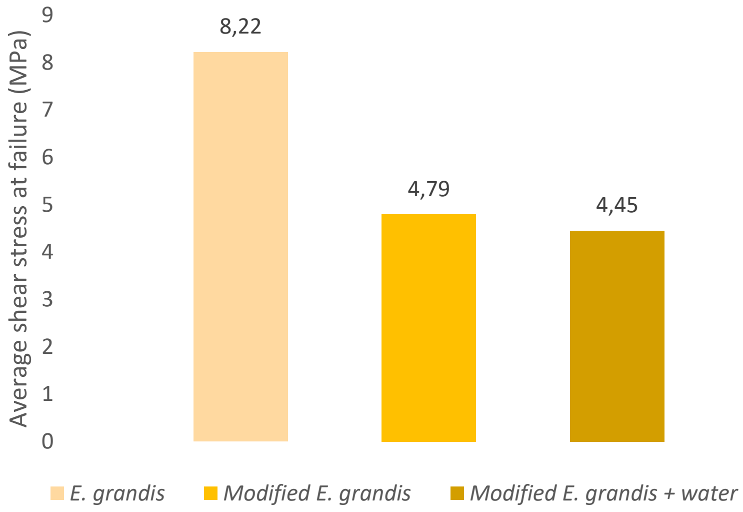

Figure 4.43 Average shear stress at failure after in *E. grandis* adhesion with PUR

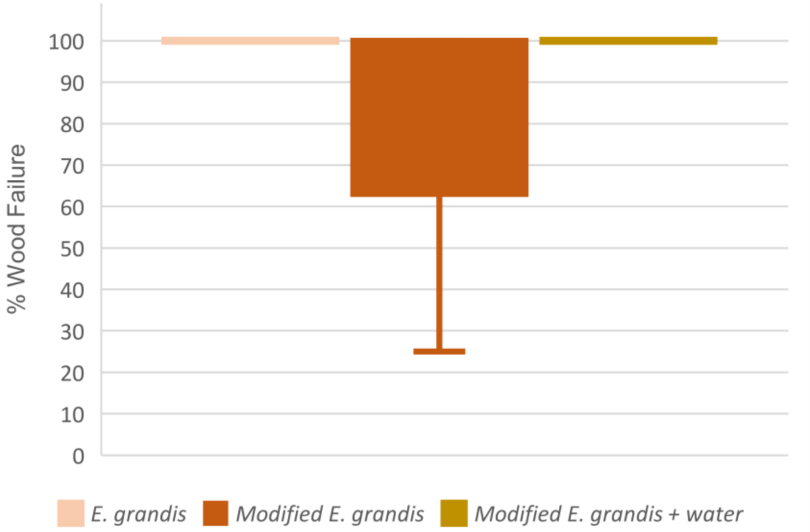

Figure 4.44 % Wood Failure after improvements in *E. grandis* adhesion with PUR

ANOVA test rejected the null hypothesis of equality of means of shear stress at failure. Comparison of the samples by Tukey test resulted in significant statistical difference between *E. grandis and modified E. grandis,* despite the addition of water. Tukey test results are shown in Table 4.11

Table 4.11 Tukey test results for *E. grandis* with PUR adhesive

Conditions	**Shear stress at failure (MPa)**	**Group result of Tukey**
E. grandis	8.22	a
Modified *E. grandis*	4.79	b
Modified *E. grandis* + water	4.45	b

Without water, there was evidence (by the reduction of the %WF) that the adhesive was less resistant after thermal modification. The addition of water helped the polyurethane spread easily and smoothly through the surface and contributed to the curing of the polyurethane. There was no evidence of adhesive strength reduction as %WF remained at 100%, indicating that the weakest point of the adhesion is the wood. For *E. grandis*, the decrease in the mechanical properties after thermal modification affects negatively, and in an important amount, the strength of the bond.

Figure 4.45 Modified *E. grandis* test specimen after shear test II (100% WF).

Shear strength parallel to grain ($f_{t,0}$), seems to be an important property of the wood affecting strength of the adhesive bonding. For non-modified wood, *E. grandis* has higher $f_{t,0}$ (14 MPa) than *P. taeda* (10-12 MPa) (Baño and Moya 2015). However, shear test showed that bonding in non-modified wood is stronger in *P. taeda*. This can be attributed to the fact that, as *P. taeda* is a softwood less dense than hardwood *E. grandis,* the adhesives penetrate deeper inside the wood resulting in a stronger mechanical anchorage with higher surface area. In other words, tensions are distributed in more fibres of wood for *P. taeda* enhancing mechanical anchorage.

4.9.3 EPI adhesive

Results of shear stress at failure and wood failure, on modified and unmodified *P. taeda*, and *E. grandis* after EPI shear test are shown in Table 4.12

Table 4.12 Shear test results of EPI adhesive (15 test samples)

	Shear Stress at failure (MPa)				**Resistance reduction (%)**	**Wood failure (%)**	
	Minimum	Maximum	Average	Standard deviation		Average	Standard deviation
P. taeda	5.39	13.73	10.21	2.92	50	90	5
Modified *P. taeda*	2.55	8.45	5.09	1.98		76	10
E. grandis	4.59	11.22	7.99	2.40	64	88	5
Modified *E. grandis*	1.55	5.51	2.86	1.26		44	16

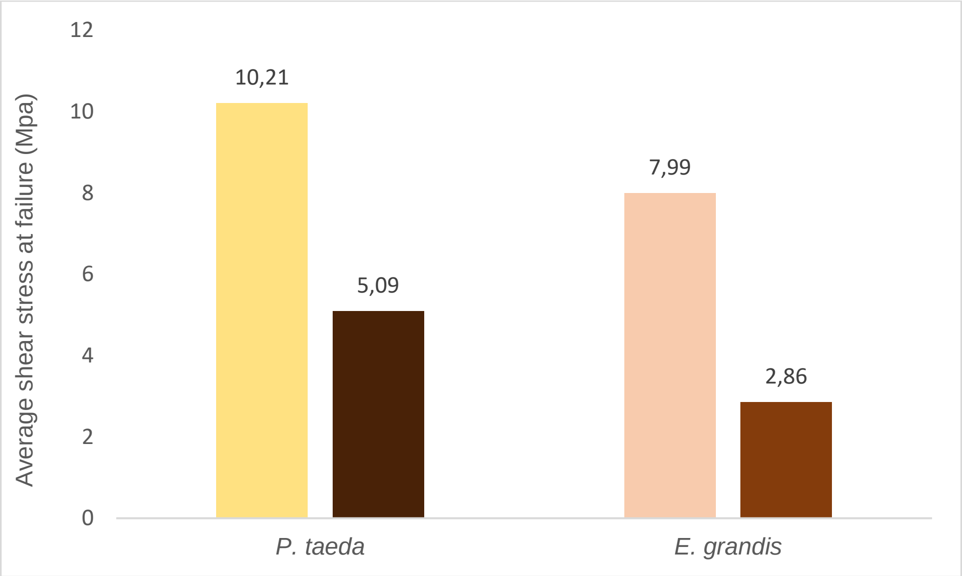

Figure 4.46 Average shear stress at failure between with EPI adhesive

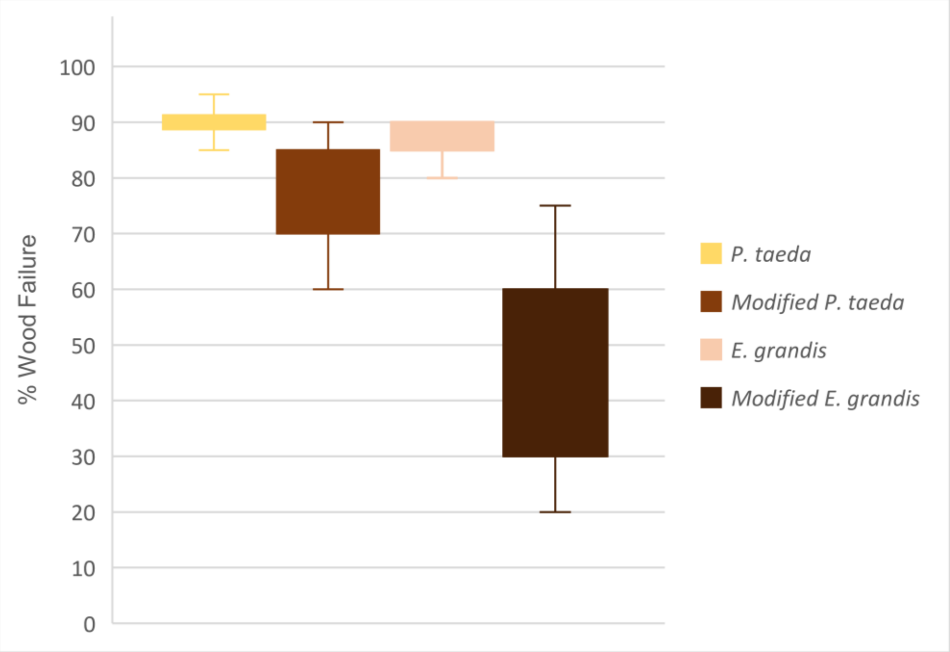

Figure 4.47 % wood failure after shear test with EPI adhesive

As shown in Figure 4.46, there was an important reduction on the average shear stress at failure after thermal modification. Furthermore, as reflected on Figure 4.47, differences in behaviour in terms of % wood failure (% WF) are observed after thermal modification in *P. taeda* and *E. grandis.* This could be explained by the fact that Emulsion polymer isocyanate adhesive has water on the PVA compound, and due to the water repellent properties of thermally modified wood, a weaker bond between wood and adhesive was formed.

4.9.3.1 *P. taeda*

EPI was confirmed as a suitable adhesive for *P. taeda* wood products, as it resulted in a high shear stress at failure (10.21 MPa) and 90% of wood failure thus performing even better than with polyurethane adhesive. These values make EPI a suitable adhesive for engineering wood products with national *P. taeda*. However, changes on wood after thermal modification decreased the effectiveness of EPI adhesive. ANOVA test rejected the null hypothesis of equality of means of shear stress at failure. Comparison of the samples by Tukey test resulted in significant statistical difference between *P. taeda* non-modified and modified wood.

The important reduction of 50% on shear stress resistance can be attributed mainly to adhesion problems, as average wood failure decreased from 90% to 76%. As modified *P. taeda* resulted in a water repelling surface with relatively high hydrophobicity, added to the fact that EPI has water on one of the components, the adhesive had difficulties to spread and, mainly, penetrate inside the wood. As the adhesive remained on the surface (Figure 4.48), mechanical anchorage was weaker than on non-modified *P. taeda* causing a decrease on the % of wood failure resulting on a decrease on the resistance of the bond. Decrease on physical resistance of wood -specially shear strength parallel to grain - is also a contributing factor to failure of the bond as wood fail occurred, yet, at a significant percentage.

Figure 4.48 EPI adhesive failure on modified *P. taeda*. Adhesive remained at the surface, evidencing penetration problems

4.9.3.2 E. grandis

Even though, EPI adhesive performed slightly worse on *E. grandis* than polyurethane, an average shear stress at failure of 7.99 MPa and 89% of wood failure is acceptable. EPI could be a viable adhesive for glued products of national *E. grandis.* Nonetheless, thermal modification of *E. grandis* had such impact on the wood, that EPI performance was poor.

Shear stress at failure was reduced on 64%, but the main impact was on % of wood failure. The average was 44%, which is unsatisfactory, evidencing the weakness of the adhesion. ANOVA test rejected the null hypothesis of equality of means of shear stress at failure. Comparison of the samples by Tukey test resulted in a significant statistical difference after thermal modification. As shown on Figure 4.49, the water-based EPI had difficulties on spreading and penetration. The fact that modified *E. grandis* is strongly hydrophobic, added that there was a decrease in pore size, clearly reduced the effectiveness of this adhesive. In this case, surface properties negatively affected adhesion, even in a more important proportion than the deterioration of physical resistance.

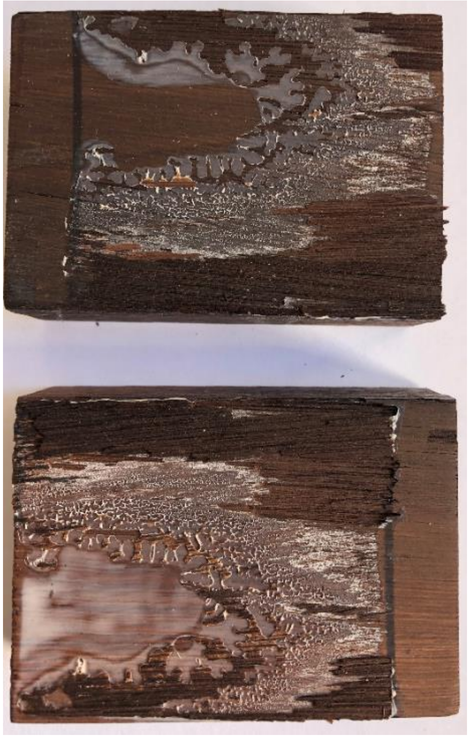

Figure 4.49 EPI adhesive failure on modified *E. grandis*. Adhesive remained at the surface, evidencing penetration problems

5. Conclusions

P. taeda and *E. grandis,* after thermal modification in nitrogen for 3 hours at 200°C*,* suffer from physical and chemical changes that affects interaction with liquids and adhesives. In consequence, bonding performance is reduced, although, in different amount depending on wood specie and the used adhesive.

By cause of their different chemical compositions, *P. taeda* and *E. grandis* responds differently towards thermal modification. Due to the high amount of pentoses in *E. grandis*, mass loss after thermal modification is more important in this specie than in *P. taeda*. Mass losses indicates that chemical reactions occur more extensively in *E. grandis* wood, thus, chemical changes are more relevant than in *P. taeda*. This was reflected in the FTIR spectra, where a significant reduction of OH groups, deacetylation, condensation reactions between lignin and carbohydrates with a reduction of C-O bonds was observed after thermal modification of *E. grandis*. On the other hand, in *P. taeda,* loss of OH group was observed to a lesser extent, however, crosslinking reactions between lignin and higher crystallinity in cellulose was detected.

Regarding wood-water relations, the difference between thermally modified and non-modified *P. taeda* and *E. grandis* was clear and significant. Modified *E. grandis* was the most hydrophobic and water repelling surface. Even though *P. taeda* is more hydrophilic and absorbs water faster than *E. grandis*, after thermal modification both types of wood presented similar behaviour towards water. It can be concluded that mass loss does not correlates, comparing species, with wood-water relations. Not all chemical changes associated with thermal modification, contributes to the water repelling properties of modified wood. In particular, it seems that hemicellulose degradation does not contributes to hydrophobicity as lignification, crosslinking, and migration of extractives (specially fats and resins in *P. taeda*) does. These results were confirmed through the estimation of the surface free energy of wood: reduction of total energy and an important turnaround of the components of it, predominating the dispersive one, indicates the affinity of thermally modified wood to apolar liquids. Considering these results, the use of water-borne adhesives (such as PvAc and EPI) or coatings are not recommended for *P. taeda* and *E. grandis* thermally modified wood, as they would not wet and penetrate properly, thus, negatively affecting mechanical anchorage.

Shear test determined that polyurethane adhesives performed correctly in thermally modified *P. taeda*, although the addition of water to the surface was necessary. Bonding strength achieved, with pressing of 10 kg/cm^2 for

1 hour and 200 g/cm^2 of adhesive, was superior to the minimum requirements (6 MPa) established by the European Standards for bondline in GLULAM, as well as minimum wood failure percentage (90%) (EN 2001). Although further test on delamination of glueline and physical properties of the beam are necessary, there is potential to develop GLULAM or structural products with thermally modified *P. taeda.* Regarding thermally modified *E. grandis,* adhesion with polyurethane was not as successful as *P. taeda*. Shear strength did not reach the admissible minimum of European Standards for bondline in GLULAM. The limiting factors in this case, as percentage of wood failure is high, are the mechanical properties of thermally modified wood, specially, shear strength parallel to grain. It can be concluded, then, that *E. grandis* thermally modified wood is not suitable to develop GLULAM with polyurethane adhesive.

For the EPI adhesive, results confirmed that despite its good performance on non-modified *P. taeda* and *E. grandis,* it developed a poor-quality bond with thermally modified wood. As one component of the EPI adhesive has a considerable amount of water on its formulation, the adhesive had difficulties to penetrate the surface of the water repelling wood. This led to poor mechanical anchorage and an unsatisfactory performance of EPI adhesive on thermally modified wood. Furthermore, the loss of mechanical resistance of thermally modified wood, and specially the brittle surface of modified *E. grandis*, also contributed to poor performance of EPI adhesive.

It is possible to achieve a good quality bond between thermally modified wood (specially *P. taeda*) with non-water-based adhesives. However, the loss of mechanical strength of thermally modified wood could limit the potential of thermally modified wood to develop glued products; more than surface modifications do.

5.1 Future work

Further investigation is needed to fully understand and optimize adhesion and thermal modification.

In first place, as thermal modification conditions are related to the extension physical and chemical changes in wood, surface characterization and adhesive shear test should be carried out at different conditions of thermal modification. The objective of this could be to optimize and balance the biological resistance, dimensional stability, physical properties, and adhesive performance. Temperature of treatment is reported as the main factor of modification. As thermally modified *E. grandis* in the present investigation showed a poor performance towards polyurethane and EPI, further investigation should reduce the temperature of treatment in order to gain acceptable biological resistance and dimensional stability, and at the same time improve adhesive performance.

Thermally modified *P. taeda* could be correctly bonded with polyurethane and EPI adhesive and have potential to develop glued products. However, further tests should be carried out in order to confirm this potential. Delamination test are usually required to confirm correct performance of the adhesives as it simulates weather and aging conditions. Furthermore, *P. taeda* non-modified and thermally modified glulam beams should be manufactured to properly confirm the possibility of their production by performing shear test, delamination test and physical resistance measurements of the beams.

Urea formaldehyde and phenol formaldehyde adhesives are widely used in the wood industry. Due to the unavailability of laboratory hot press this type of adhesives were not tested. Some installed sawmills in Uruguay uses this kind of adhesives so, testing these adhesives on thermally modified *P. taeda* and *E. grandis* should also be important to develop glued laminated wood products with thermally modified wood.

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