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Titre : *Chemical modification of wood by mixed anhydrides.*

Etude de la modification chimique du bois par des anhydrides mixtes.

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General summary

Foreword

The industrial era, that has begun two centuries ago, participated in the frenetic consumption of fossil and renewable resources. In less than two hundred years of industrial development, about 50% of the fossil resources have been consumed. Renewable resources which the mains fields of applications are energy, food, pharmaceutics, textile and raw material in the construction industry are also concerned due to an increase consumption caused by a multiplication of the population by four in less than one century.

Wood as a raw material is also concerned. A global deforestation of about 13 millions of hectares has been observed in 2005 by the Food and Agriculture Organization of the United Nations (FAO). In the past, naturally durable local wood species were traditionally used in the construction. But the increasing consumption of these species that present slow growth has lead to consider them as non renewable. Durable species have then been imported from the fantastic resources that are the tropical forests leading to an ecological disaster. That is why biocide treatments such as CCA and creosotes have been developed to give to fast growth local species an acceptable durability to be use as lumber. Nevertheless the toxicity of such treatments has lead to restrict or prohibit their uses by application of new legislations such as the biocides directive.

A need for developing new wood treatment has therefore become urgent to replace biocides. Wood modification has been initiated since the 1950's and encounter an increased interest in last decade. The main purposes of wood modification are to increase durability by mean of increasing biological resistance and to enhance wood properties such as dimensional stability and photostability to respect the specifications of the wood industry and particularly the one working on joineries.

The main objective of this dissertation will be to present the investigations made to develop a new wood treatment based on the chemical modification of wood. This work has been realized in collaboration with a French company named LAPEYRE, filial of the SAINT-GOBAIN group. LAPEYRE is a joinery maker which priorities and interest in this work has been to develop a treatment able to give high dimensional stability to wood.

The investigations were carried out in the French Laboratory of Agro-industrial Chemistry (LCA) located in Toulouse under the direction of the manageress of the laboratory, Professor Elisabeth Borredon as well as her colleague, Professor Carlos Vaca-Garcia.

The treatment deals with chemical modification of wood by mixed acetic-fatty anhydrides. The process developed during this research allowed to file three patents, one in 2003 under the number WO2003084723 and two in 2007 under the numbers WO2007141445 and WO2007141444. These applications found an industrial interest and have been commercialized since 2006 under the name of **Wood Protect**[®].

Four chapters compose this manuscript.

In the first one, an overview of the chemistry of wood and its preservation will be presented.

The second chapter is composed of two published peer-reviewed articles; one dealing with the development of an analytical technique to analyze mixed anhydrides and the other one on the kinetic and thermodynamic study of their synthesis.

Chapter three is compiling four articles. The first one describes an analytical method to determine de degree of substitution of cellulose esters, the second and the third one describe the esterification reaction on cellulose and the hydrophobic properties obtained. The fourth paper explains the changes of reactivity occurred when passing from cellulose to a lignocellulosics substrate: wood sawdust.

Finally, chapter four presents the treatment of wood blocks at both laboratory and pilot scales. The dimensional stability, the mechanical properties, as well as weathering and biological protection are discussed.

Each of these chapters will be accompanied by an introduction and a conclusion in order to facilitate the understanding of the running of the investigations.

CHAPTER 1

The characteristics and the durability of wood

CONTENTS

1.1 Introduction

Making an extensive description of wood is a tough and long exercise. Indeed, wood is the main source of cellulose, the most abundant biopolymer on Earth. Many studies have been carried out on its formation, its diversity, its properties, its uses, and its durability. In the framework of this dissertation, we cannot afford to go into deep detail of all these subjects. Consequently, we will voluntarily limit to make an introduction to wood structure and to present the techniques to modify wood to improve its properties. We will start however with an introduction to wood as a renewable resource and the forest production in Europe and France. This bibliographical review can be completed by all the comprehensive books we have consulted to compose this report [1-13].

1.2 Generalities

1.2.1 Wood: a renewable resource

Achieving solutions to environmental problems and limited fossil fuel resources requires long-term potential actions for sustainable development. In this regard, renewable resources appear to be one of the most efficient and effective solutions. A gradual shift from fossil fuels to renewable energy sources seems to be the only alternative. Unlike fossil fuels, a renewable resource can have a sustainable yield.

A natural resource is qualified as renewable if it is replenished by natural processes at a rate equal or faster than its rate of consumption by humans. Resources such as solar radiation, tides, and winds are *perpetual* resources that are not in danger of being used in excess because of their long-term availability [14].

Oxygen, water, and photosynthetic biomass such as wood for instance can become non-renewable resources if they are used at a rate greater than the environment's capacity to form them.

Timber, which can be harvested sustainably at a constant rate without depleting the existing resource pool, is a unique and renewable material that has been and remains an important substance throughout history because of its unique and useful properties. It is not only renewable, but also recyclable and biodegradable.

1.2.2   The European and French forest

The European region is covered with temperate or boreal forests over 37% of its area [14]. The number of species in Europe is estimated at 8 000 from the 50 000 in the world. The E uropean forest is l argely of hum an c reation, t hrough t he important reforestation of the last 150 years that followed the extensive exploitation of forests over previous centuries in this densely populated continent. We grow more trees in Europe t han w e f ell, t hus creating a n i ncrease i n f orest a cross Europe by t he equivalent of 25 ha per hour [15].

The ecological zones of Europe range from subtropical to polar types. Countries with the richest forest in Europe are Finland and Sweden (Figure 1.1). The said *cool temperate moist forest zone* covers much of Europe, and is the most exploited. It is composed mainly of needle-leaved trees (coniferous).
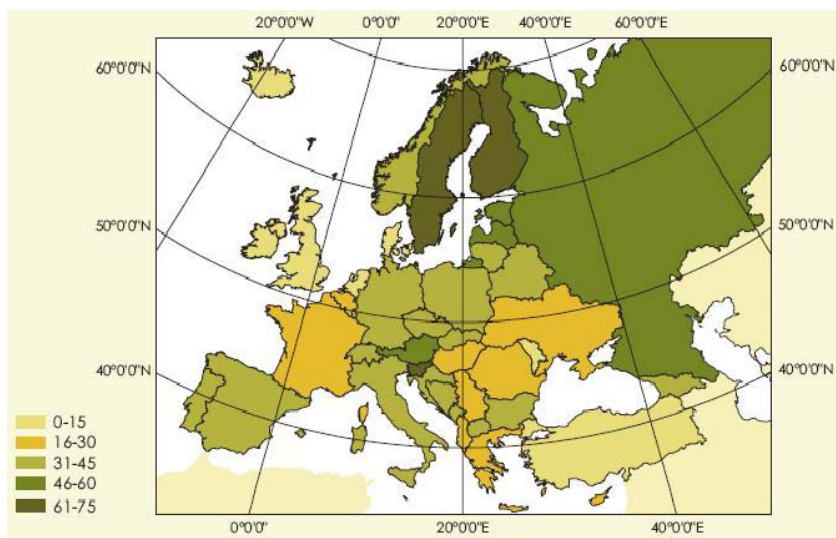
Figure 1.1 Forest cover (%) of European countries in 2005 [16]

In 1830, France wooded surface was between 8.9 and 9.5 millions of hectares [17]. Since then, growth has been constant. The French forests surface reaches now 15.5 millions of he ctares c overing 28 % of t he country's a rea. They m ostly be long t o private ow ners. Since 1980, t he annual expansion r ecorded by t he National F orest Inventory (NFI) is approximately 68 000 ha.

The French forests produce 103 million m^3 of wood per year. They show a wide range of type and tree species composition. The oaks group (*Quercus*) account for 28% of the total volume. The growing-stock is dominated by the broad-leaved tree species but global warming can modify the scenario (Figure 1.2).
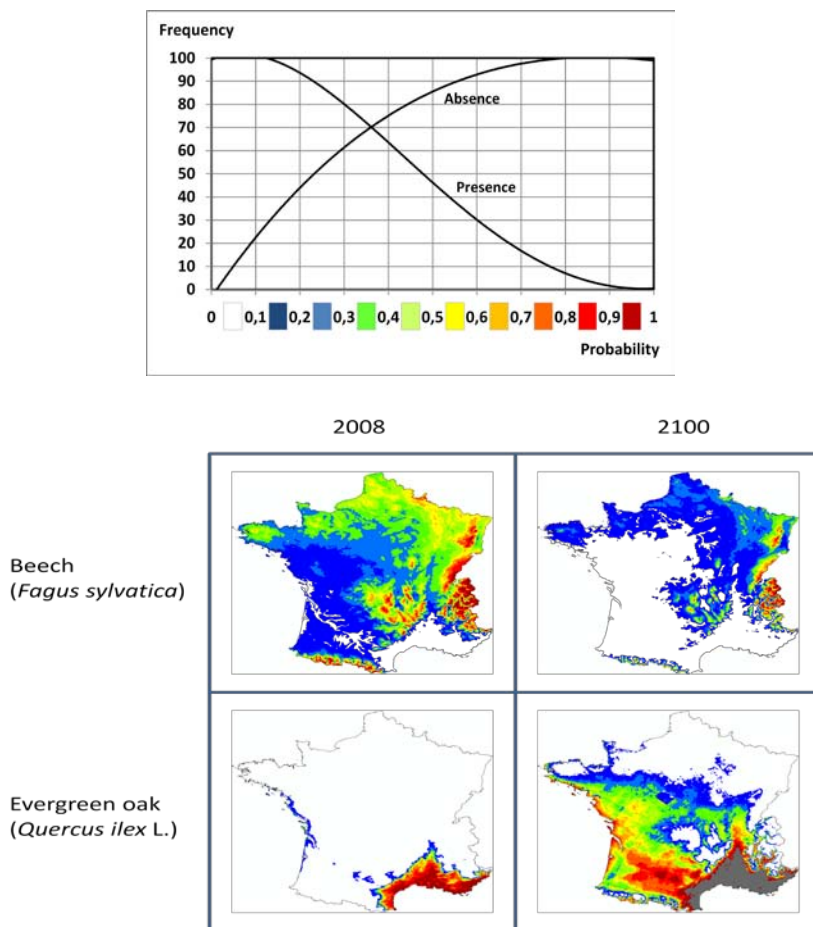
Figure 1.2 Beech and oak forest distribution in France. Present situation and future scenario with a global rise temperature of 2.4°C. (CARBOFOR INRA project; www.pierroton.inra.fr/carbofor)

Due to its climatic, geologic and topographic diversity, France has rich and diversified forests. French forests are composed of about 140 species. The most important coniferous and broad-leaved trees are indicated in Table 1.1.

BROAD-LEAVED		
Pedunculate oak	Hackberry tree	Mulberry tree
Sessile oak	Ash	Hazel
Red oak	Elm	Ostrya
Pubescent oak	Cultivated poplar	Non cultivated poplar
Evergreen oak	Lime tree	Turkey oak
Pyrenean oak	Small maple	Tamaris
Cork oak	Wild cherry	Eucalyptus
Beech	Norway maple	Green alder
Chestnut tree	Aspen	Laburnum
Hornbeam	Willow or sallow	Dogwood
Birch	Plane tree	Strawberry tree
Alder	Walnut tree	Wild service tree
Locust tree	Olive tree	Tulip tree

CONIFEROUS	
Maritime pine	Douglas fir
Scots pine	Atlas cedar
Corsican pine	Cypress
Black pine	Yew
Stone pine	French alpine juniper
Weymouth pine	Mediterranean fir
Aleppo pine	Nordmann's fir
Mountain pine	American fir
Arolla pine	Sitka spruce
Mountain pine	Exotic larch
Silver fir	Lebanon cedar
Norway spruce	Loblolly pine
Common larch	

Table 1.1 Principal tree species composing the French forest [18]

The richness of French forest implies therefore not only a significant wooded surface but also a high diversity of species.

After this general introduction to the French forest, we will now consider the main elements of the wood structure.

1.3 The wood structure

1.3.1 Hierarchical structure of wood

1.3.1.1 Cross section of a tree

The cross section of a tree shows well defined concentric subdivisions. From the outside to the center: bark, vascular cambium, sapwood, heartwood and the pith (Figure 1.3).
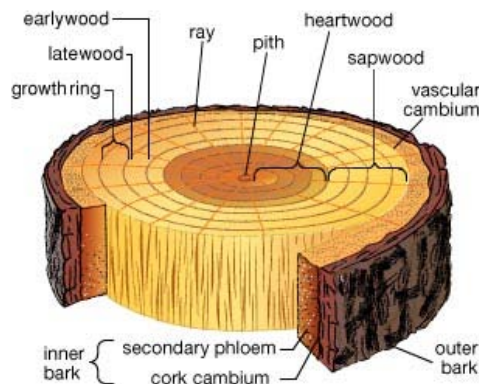
Figure 1.3 Cross-section of a tree trunk (© *Merriam-Webster Inc.*)

Bark comprises the tissues outside the vascular cambium, including secondary phloem (which transports nutriments made in the leaves to the rest of the tree), cork-producing cells (cork cambium), and cork cells. The outer bark, composed of dead tissue, protects the inner bark (phloem) from injury, disease, and desiccation [5,7].

The vascular cambium is the layer between the bark and the wood that is responsible for producing both phloem and xylem. The phloem is the tissue that contains the cells through which sugars produced by photosynthesis are conveyed from the leaves to the roots or to the growing portion of the tree. The xylem is responsible for the transport of water and soluble mineral nutrients from the roots throughout the plant.

The cambium is the only place in a stem where new growth takes place, and its cells are constantly dividing to form new wood and new bark. As a result of the continual division of cells, the cambium layer slowly moves outwards as the tree

grows. The outer bark periodically splits or is shed. It is then replaced by the new outer layer [11].

Wood in most species is clearly differentiated into sapwood and heartwood. The bark is excluded from finished lumber.

- Sapwood is the active living wood where takes place the transportation of water and nutriments. It performs an active role in the life processes of the tree. Sapwoods size varies with species and where the tree is growing.
- Heartwood is older xylem that has been infiltrated by gums and resins and has lost its ability to conduct water once that the life processes of the tree have ceased. In wood industry, heartwood is more valuable than sapwood because of its higher durability. It is usually darker, denser, and more resistant than sapwood. In the center of the heartwood, pith can be distinguished. It is the remnant of the early growth trunk, before wood was formed [7].

In some species, sapwood is present in a limited extent. For instance it is generally accepted that beech is composed only by heartwood.

A tree increases in girth by the formation, between the old wood and the inner bark, of new woody layers that envelop the entire stem, living branches, and roots. In climates where growth virtually ceases for part of the year, such as during cold winter months, the layers can occur in a discrete pattern, leading to what is known as growth rings, as it can be seen on the cross section of a log (Figure 1.4).

**Figure 1.4 A section of a trunk showing the annual growth rings,
pale sapwood and dark heartwood, and pith [10]**

In spring, when trees burst into growth, wood is formed relatively rapidly and earlywood (springwood) cells tend to be large and thin-walled. Later, as tree growth slows down, the cells become smaller and their wall thicker (latewood or summerwood). The larger thin-walled cells tend to be paler in color than the smaller thick-walled cells. An annual ring is made up of these two layers [19].

1.3.1.2   Structural differences between softwoods and hardwoods

Native species of trees are divided into two botanical classes: hardwoods, which have broad leaves, belonging to Angiosperms and softwood, which have needle-like or scale-like leaves, belonging to Gymnosperms. There is no direct correlation between the name and the hardness or softness of the wood. Some hardwoods are softer than certain types of softwood. Nevertheless, hardwoods are generally denser than softwood (specific gravity of 0.8 vs. 0.6 in average) [10].

The bulk of softwood (Figure 1.5) is made of long narrow hollow cells, or tracheids, that fit closely together. Tracheids stand alongside each other and are hold firmly together by lignin, which is deposited between the adjacent cell walls. Conifer tracheids can be up to four millimeters long, and serve both to transport sap and to strengthen the stem of the tree. Pits in the cell walls of the tracheids enable sap to pass from cell to cell as it moves up along the stem [19].
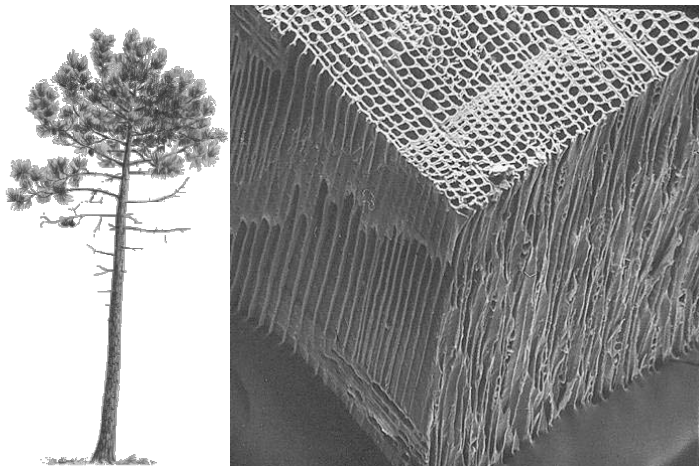
Figure 1.5 A close-up section of a softwood (maritime pine) [20]

Broad-leaved trees, like eu calyptus a nd r ed c edar, a re ha rdwood t rees. T heir wood is made up of two distinct types of cells, vessels and fiber cells (Figure 1.6).
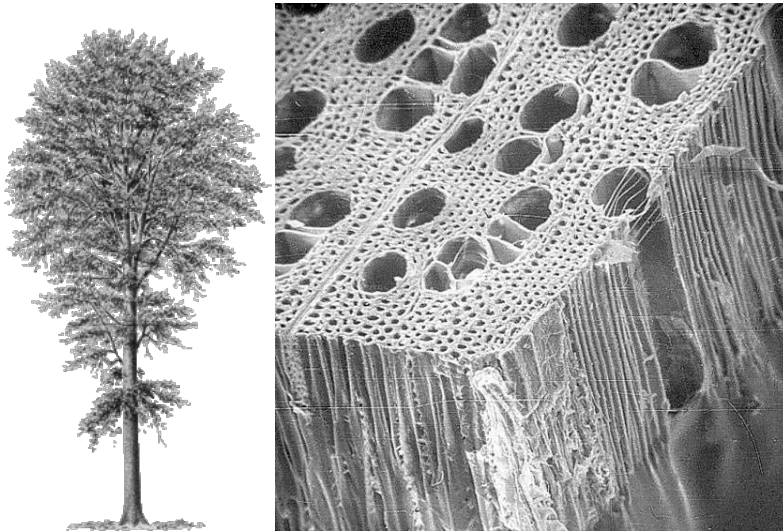
Figure 1.6 A close-up section of hardwood (beech) [20]

Sap is c arried upwards through the vessels. They can usually be s een w ith the naked eye. The a rrangement of t he v essels i n a c ross-section is a us eful ai d to identifying different timbers.

Strength in broad-leaved trees is imparted by the fiber cells. They are shorter in length (commonly about one millimeter long) and usually thicker-walled [5].

Among the other types of cells that occur in wood are ray cells. They store food in the stem and are found in all timbers. Unlike the other cells of sapwood, which are ar ranged vertically, ray cel ls ar e ar ranged horizontally, extending radially outwards towards the bark. Often rays are only one cell wide and several cells high and quite difficult to see without a magnifying lens. However, in some trees the rays are very large and give the wood characteristic patterns, such as the patterns seen in oaks.

1.3.1.3 The cell wall of wood

The cell wall of wood is composed of a number of discernable layers. These are divided into the primary (P) and secondary (S) layers. The secondary layer is further subdivided into the S1, S2 and S3 layers (Figure 1.7).
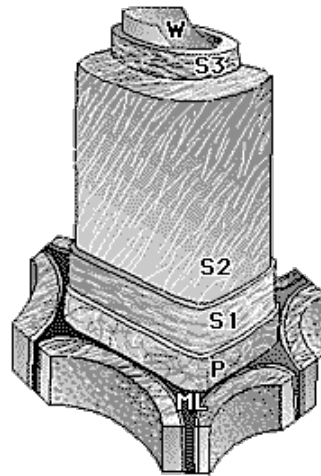
Figure 1.7 Ultrastructure of the wood cell wall [5]

The primary layer is the first to be laid down when the cell is formed and is composed of microfibrils, which have an essentially random orientation that allows expansion as cell growths. The secondary layer is subsequently formed, with each of the sub-layers exhibiting different patterns in the microfibrils orientation. From these, the S2 layer occupies the greatest volume of the wall. Consequently it has the greatest influence on the properties of the cell and hence of the wood. The S2 layer exhibits a definite microfibrillar orientation, and is itself composed of many lamellae consisting of numerous closely associated microfibrils that exhibit a helical winding pattern. The space between the cell fibers is occupied by the middle lamella. But micropores are still present permitting under certain conditions accessibility to the cell wall [21].

1.3.2 The chemical components of wood

Many of the physical, chemical and biological properties of wood can be understood by referring to the polymeric chemical constituents of the cell wall: cellulose, hemicelluloses and lignin. All the other components of wood are part of a general group named, extractives.

1.3.2.1 Cellulose

The cellulose is a polymer of D-glucopyranose units. These monomeric units (anhydroglucose units, AGU) are alternately inverted in the plane of the ring. The

AGU are linked together by β(1→4) glucosidic bonds forming the linear polymer cellulose.
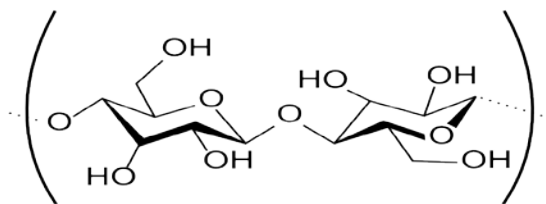
Figure 1.8 Cellulose as a polymer of β-D-glucose

The number of AGU in a cellulose molecule is also called the degree of polymerization (DP). The average DP of cellulose in native wood (before extraction) has been estimated at about 10 000 [11]. After extraction it can be 10 times lower. The cellulose content of wood varies from about 40% to 50% [11].

Cellulose molecules have tendency to form intra- and intermolecular hydrogen bonds. This results in the formation of microfibrils (bundles of about 10 x 10 cellulose molecules), which are the reinforcing element in the cell wall. As the packing density of cellulose increases, crystalline regions are formed. Most wood-derived cellulose contains as much as 65% crystalline regions. Crystalline and amorphous regions can be detected using a variety of methods, such as X-ray [22] diffraction, nuclear magnetic resonance (NMR) [23] and infrared (FTIR) [24] spectroscopy.

Due to its crystallinity, cellulose is relatively unreactive and thermally stable. It is difficult to isolate cellulose from wood in a pure form because it is intimately associated with lignin and hemicelluloses.

1.3.2.2 *Hemicelluloses*

Hemicelluloses are heteropolysaccharides with a lower DP than cellulose of about 100-300. They are also less ordered than cellulose, although some can form crystalline units. Hemicelluloses are referred to by the sugars they contain. The hemicelluloses also may contain carboxyl, acetyl- and methyl-substituted groups.

Galactoglucomannans (about 20%) and arabinoglucuronoxylan (5-10%) are the principal hemicelluloses in softwoods. Glucuronoxylan (15-30%) and glucomannan (2-5%) are the principal hemicelluloses in hardwood [5].

The detailed structures of most wood hemicelluloses have not been determined, only the ratios of sugars that these polysaccharides contain have been determined.

Hemicelluloses appear to act as interfacial coupling agents between the highly polar surface of the microfibrils and the much less polar lignin matrix.

1.3.2.3 Lignin

Lignin is a complex amorphous phenolic polymer of intermediate molecular weight. It is responsible for providing stiffness to the cell wall and also serves to bond individual cells together in the middle lamella region. The precursors of lignin biosynthesis are *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol Figure 1.9.

p-Coumaryl alcohol

Coniferyl alcohol

Sinapyl alcohol
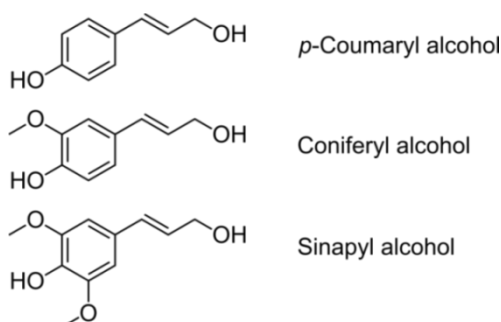
Figure 1.9 Monolignol structures

Due to the random nature of the polymerization reaction, there are several structures of lignin. A representative structure of softwood lignin is shown in Figure 1.10.
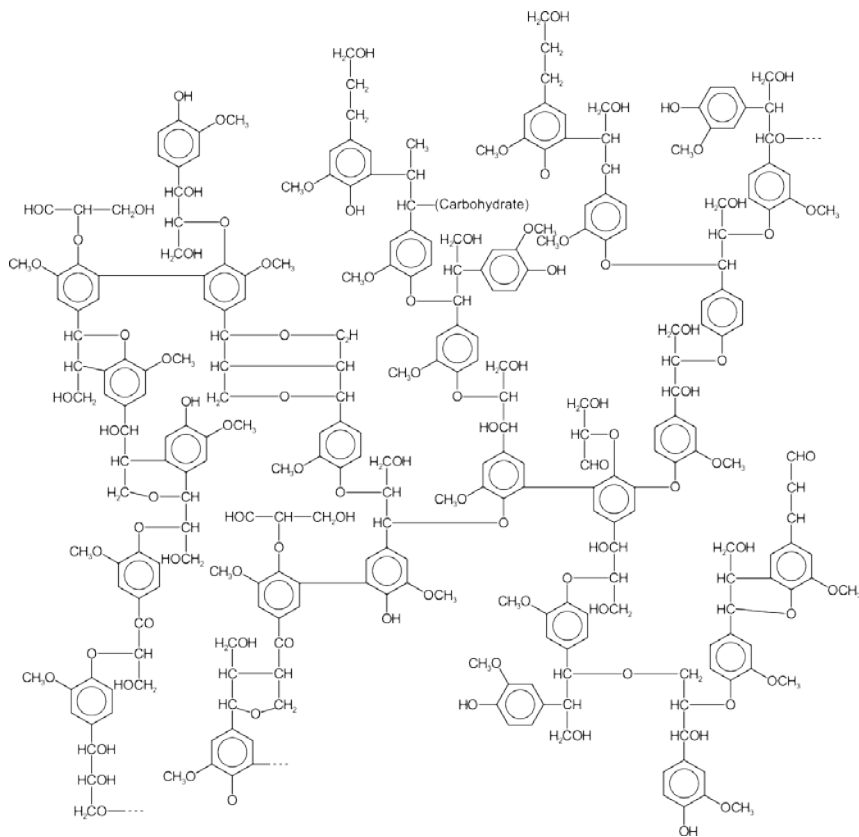
Figure 1.10 Partial structure of a softwood lignin indicating a covalent bond to hemicellulose [5]

There is a wide variation of structures within different wood species. The lignin content of hardwoods is usually in the range of 18-25%, whereas the lignin content of s oftwoods v aries be tween 25 a nd 35% . L ignin f rom s oftwoods i s mainly a polymerization product of coniferyl alcohol and is called guaiacyl lignin. Hardwood lignin is mainly syringyl-guaiacyl lignin, because they are a copolymer of coniferyl and sinapyl alcohols [5].

Lignin is associated by covalent bonding (ester and ether) with hemicelluloses forming lignin-carbohydrate com plexes. T here i s no ev idence that lignin i s associated with cellulose but h ydrogen bonds a re certainly e stablished w ith hemicelluloses (Figure 1.11).
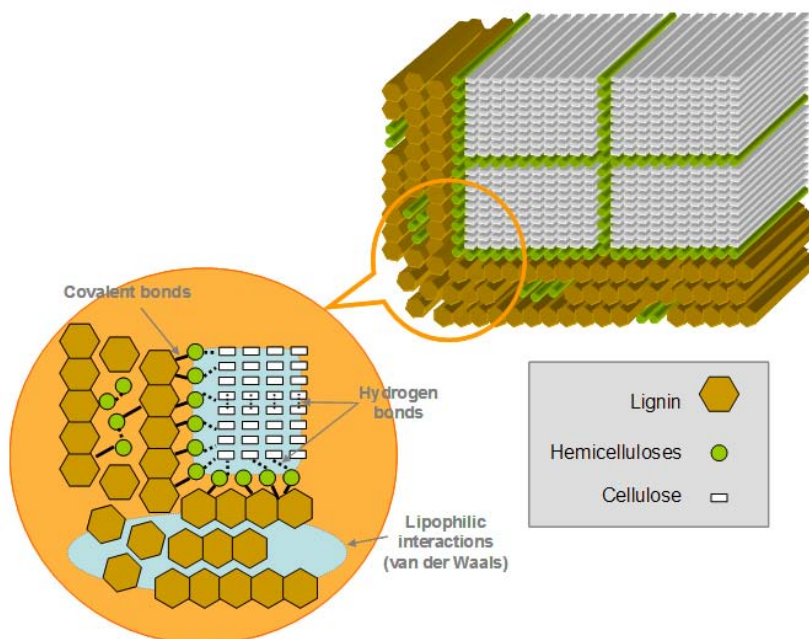
Figure 1.11 Schematic representation of the lignin-carbohydrate complex (LCC) and its interaction with cellulose microfibrils.

1.3.2.4   Other macromolecules

Minor pol ysaccharides a re pr esent a s w ood c omponents. S oftwoods and hardwoods c ontain s mall a mounts of pe ctin, s tarch a nd pr oteins. In t his w ork, w e will consider these molecules as negligible. We will just make a short description of them.

Pectin is a polysaccharide made of D-galacturonic acid units linked in α-(1→4). Pectin is found into the membranes of the bordered pits between wood cells and also in the middle lamella [5].

Starch is the principal reserve of polysaccharides in the plants. Small amount of starch can also be found in the wood cell wall.

Proteins can be found as solid residues in the inner wall of the lumen, especially in dry wood. Their amount is quite low, less than 1% [5].

1.3.2.5 Extractives

Extractives can be considered as chemicals that can be extracted from wood using solvents. They mainly consist of fats, fatty acids, fatty alcohols, phenolics, terpenes, steroids, resin acids, rosin, waxes and many others minor organic compounds. These chemicals exist as monomers, dimers and polymers. Depending on the species, wood can contain levels of extractible material ranging from approximately 0.5% to 20%. The extractives are deposited in the cell cavities or infiltrated into cell wall structure. Most extractives are located in the heartwood and some are responsible for the color, smell and durability of the wood. Fats constitute one of the energy sources of wood cells, whereas lower terpenoids, resin acids and phenolic substances protect the wood against microorganisms or insect attacks [5].

The softwood resins canals are filled with oleoresins, which are mono and diterpenoids. The parenchyma resin of both softwood and hardwood contains triterpenoids and steroids, mainly occurring in the form of fatty acid esters.

Fats and waxes are the predominating constituents of the lipophilic material encapsulated in parenchyma cells. They are different in chemical composition from oleoresin. The fats are triglycerides whereas the waxes are fatty esters of fatty alcohols, terpene alcohols or sterols.

Tannins, which are aromatic extractives, are present especially in heartwood and bark. Most of them are phenolic compounds, and many are derived from the phenylpropanoid structure. Thousands of phenolic compounds have been identified and the most important groups are [5]:

- Stilbenes that are derivatives of 1,2-diphenylethylene,
- Lignans, which are formed by oxidative coupling of two phenylpropane units,
- Hydrolysable tannins, a group of substances upon which hydrolysis yields gallic and ellagic acids and sugars as main products,
- Flavonoids, which have a typical tricyclic $C_6C_3C_6$ carbon skeleton,
- Condensed tannins, which are polymers of flavonoids.

1.4   The properties of wood

Wood i s a he terogeneous material but w ith or iented organized s tructure. It shows a nisotropy, especially in mechanical pr operties. Wood structure is a lso hygroscopic; its di mensions a nd most of its pr operties (thermal, mechanical, and biological) depend on the moisture content [10].

We will first describe the different relations that wood establish with water, then we will present the above cited properties of wood.

1.4.1   Interactions with water

1.4.1.1   Equilibrium moisture content

Wood i s a hy groscopic m aterial due to the f act tha t t he c ell w all pol ymers contain hydroxyl gr oups. Water is pr esent in the c ell v oids or l umens (free w ater) and as bound water in the cell wall. Moisture content of wood is a dynamic property that de pends on the r elative hum idity (RH). When wood i s m aintained i n a n environment with stable R H, it a ttains w hat is c alled the e quilibrium moisture content (EMC). [8] It is calculated on a gravimetric basis:

$$EMC(\%) = \frac{(m_2 - m_1)}{m_1} \times 100$$

where m_1 is the ov en-dry w eight of t he s pecimen a nd m_2 is t he w eight of t he specimen at e quilibrium at a gi ven RH [25,26]. *EMC* can vary c onsiderably w ith t he RH, e.g. S outhern pi ne *EMC* vary from 5.8 t o 21.7% when RH i s r espectively 30 and 90% [7].

In s ome cases, when the wood has been modified by a treatment, a reduced equilibrium moisture content (EMC_R) is used rather than the previous one:

$$EMC_R(\%) = \frac{(m_{M2} - m_{M1})}{m_1} \times 100$$

where m_1 is the ov en-dry weight of t he unm odified w ood, m_{M1} the ov en-dry weight of t he modified specimen a nd m_{M2} the w eight o f t he modified specimen at equilibrium at a given RH [27].

1.4.1.2   The fiber saturation point

During the drying of fresh cut wood, there is no change in the volume of the piece until it reaches the fiber saturation point (FSP). The FSP is defined as the moisture content of the cell wall when there is no free water in the voids and when the cell walls are saturated with bound water. This point ranges from 20 to 50% depending on the wood species, the temperature and the extractives content [28-30].

1.4.1.3   Swelling and shrinking

When the moisture content is below the fiber saturation point, dimensional changes occur. If water is adsorbed, wood swells. Conversely, wood shrinks if water is desorbed. Anisotropy is revealed by the orientation of the cells: wood swells (or shrinks) more significantly in the radial or tangential plane (around 15% variation) than in the axial direction (less than 1%) [7]. The rather low winding angle of the microfibrils in the S2 layer accounts for this (Figure 1.7, page 17).

Swelling (or shrinking) is reported as the swelling coefficient (*S*), calculated as follows:

$$S(\%) = \frac{V_{ws} - V_{od}}{V_{od}} \times 100$$

where V_{ws} is the water-swollen volume of the wood after soaking in water and V_{od} is the oven-dry volume of the wood. Swelling of wood can be studied not only in water but also in organic solvents [31-33].

The **dimensional stability** of the wood is related to the swelling coefficient. It can be better assessed after a certain number of drying-soaking cycles. Woods showing lower *S* values are said to be more dimensionally stable. In the case of non-treated woods, a variation of the S values in the different cycles can put in evidence a leaching phenomenon of natural protective extractives.

Natural wood is subjected to big dimensional changes. They can be as high as 0.5%/Δ%water content under the FSP [34]. This means that in a variation from 0 to 30% water content (usual value for FSP), swelling (or shrinking) of wood can be up to 15% in the transversal section. For most of the applications in joinery, swelling should be less than 2% for a window to be hermetic, for instance.

In the joinery industry, the problem is currently solved by the application of wood coatings (paintings, stains, etc.). They are intended to create a physical barrier

against humidity and to limit the exchange of water between the atmosphere and the cell w alls in wood. A drawback of t his a pproach i s t hat these c oatings c annot completely a void the swelling of wood. The c oating must then be e lastic to follow the m ovements of w ood w ithout c racking. Moreover, paintings a re s ubjected t o intensive ultraviolet radiation. They m ust cont ain effective ant i-UV age nts as pigments (e.g. TiO_2) [35]. This is not the case of inexpensive coatings. This is the reason w hy m ost of t he w ooden w indows s hutters ne ed t o be r epainted r egularly. Dimensional c hanges of na tural w ood c an be also reduced by a pplying more sophisticated treatments (these will be developed in section 0).

In or der to qualify t he ef ficiency of a t reatment, t he i ncrease i n terms of dimensional stability can be evaluated as the **anti-swelling** (or anti-shrink) **efficiency**. Both are the same concept and are denoted by the term ASE:

$$ASE(\%) = \frac{S_u - S_m}{S_u} \times 100$$

where S_u is th e s welling c oefficient of u nmodified w ood a nd S_m is the s welling coefficient of treated wood.

If the treatment confers dimensional s tability to the wood, t he difference between the water-saturated volume and the oven-dry volume of the wood sample is reduced, r esulting i n a l ower v alue f or $S_m(\%)$ a nd therefore a hi gher v alue of $ASE(\%)$ [7,8]. Effective anti-swelling treatments such as wood acetylation can provide ASE values of about 70% [36].

1.4.1.4 *Hydrophobicity and Water repellency*

Hydrophobicity a nd w ater r epellency (WR) are close concepts that will be neatly distinguished in this dissertation:

Hydrophobicity is r elated to the (poor) a ffinity of a material w ith water. As cellulose and wood contain numerous OH groups, they are highly hydrophilic. There is no s cale f or h ydrophobicity or h ydrophilicity. H owever, there ar e quantitative parameters that are directly associated to these concepts. For instance, the equilibrium moisture c ontent de scribed a bove. In t his w ork w e w ill c onsider hydrophobicity as the capa city o f wood to adsorb **vapor water**. This c apacity ha s always to be considered at **equilibrium** state for a defined temperature. Its order of magnitude is low er (30% vs. 100% a pproximately) than the c apacity of a bsorption of liquid water by soaking (which is absorbed water).

Wood hydrophobicity is generally characterized by measuring the EMC of small blocks or sawdust samples at different RH. The gravimetric method, Dynamic Vapor Sorption (DVS) is the most accurate as relative humidity around the sample is controlled by mixing saturated and dry carrier gas streams using mass flow controllers. The DVS measures the uptake and loss of vapor gravimetrically at constant temperature. At each stage, the sample mass is allowed to reach equilibrium before the relative humidity is increased or decreased. From the complete moisture sorption and desorption profile an isotherm is traced. Figure 1.12 shows the isotherm curves obtained at 25°C for Scots pine sawdust [7].
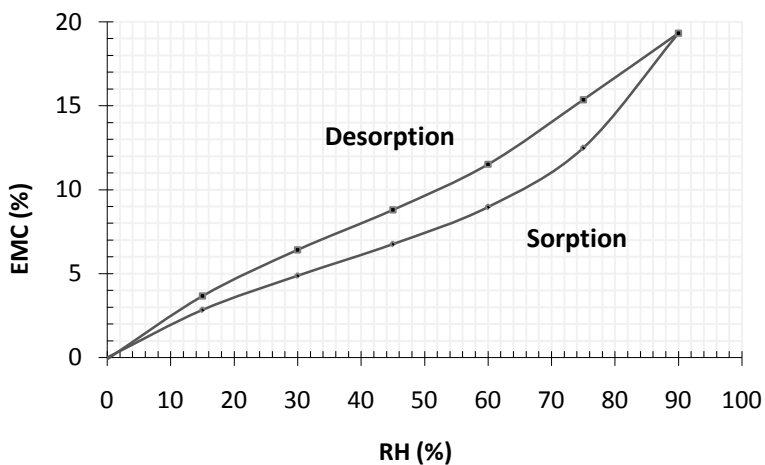
Figure 1.12 Sorption and desorption isotherm of Scots pine sawdust at 25°C

The relationship between EMC and RH in the sorption and desorption modes differs, giving rise to hysteresis. Many models have been developed that deal with the sorption properties in the presence of moisture [28,37-39]. In general, EMC of wood at 95% RH is comprised between 10 and 35% [10].

A reduction in EMC at a fixed RH is synonym of an increase of the hydrophobic character of the wood. It is often accompanied by an augmentation of the time taken to achieve equilibrium principally due to a decrease of wettability (also called water repellency, WR) [8].

The **water repellency** is related to the contact angle between a drop of water and wood under atmospheric pressure at a certain time (Figure 1.13). A water repellent treatment prevents or slows down the rate at which **liquid water** is

absorbed by the w ood. The t heoretical description of contact arises f rom t he consideration of a thermodynamic equilibrium between the three phases: the liquid phase of the droplet (L), the solid phase of the substrate (S), and the gas/vapor phase (V) surrounding the wood sample. It is convenient to analyze this parameter within the frame of the interfacial energies [40].
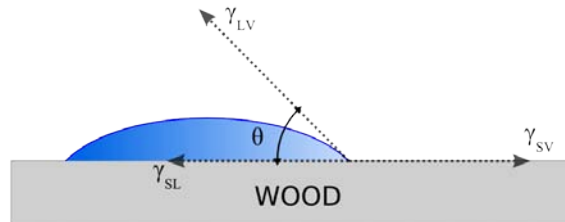
Figure 1.13 Contact angle of a water drop on wood

We denote the solid-vapor interfacial energy as γ_{SV}, the solid-liquid interfacial energy as γ_{SL} and the liquid-vapor energy as γ_{LV}, we can write an equation that must be satisfied in equilibrium known as the Young Equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{SLV} \cos \theta$$

Three methods are commonly used to measure contact angles of solid samples of wood:

- The s tatic s essile drop m ethod t hat c onsists i n a m easure of t he static contact angle (SCA) w ith a goniometer. A high r esolution c amera a nd software are used to capture and analyze the SCA [41].
- The dy namic s essile dr op permits to determine t he l argest cont act angl e possible w ithout i ncreasing i ts s olid/liquid i nterfacial a rea by a dding volume dynamically. This maximum angle is the advancing angle [42].
- The dynamic Wilhelmy method permits to calculate advancing and receding contact angles on s olids of uniform geometry. B oth s ides of the solid must have t he s ame pr operties. Wetting force on t he s olid is m easured as t he solid i s i mmersed i n or withdrawn f rom a liquid of know n s urface tension [43].

In our research, we used only the first method to determine the static contact angles with water and other liquids.

Wood and other materials are generally considered as water repellent when their contact angles with water are superior to 90°. Oppositely, when water is immediately absorbed, the contact angle reported value is 0°; this is the case of most wood species. Water repellency of wood depends on a certain number of factors including surface roughness, porosity, chemical composition and time [44].

1.4.2 Mechanical properties

Beyond anisotropy, wood may be described as an orthotropic material; that is, it has unique and independent mechanical properties in the directions of three perpendicular axes: longitudinal, radial, and tangential. The longitudinal axis L is parallel to the fiber (grain); the radial axis R is normal to the growth rings (perpendicular to the grain in the radial direction); and the tangential axis T is perpendicular to the grain but tangent to the growth rings. These axes are shown in Figure 1.14 [10].
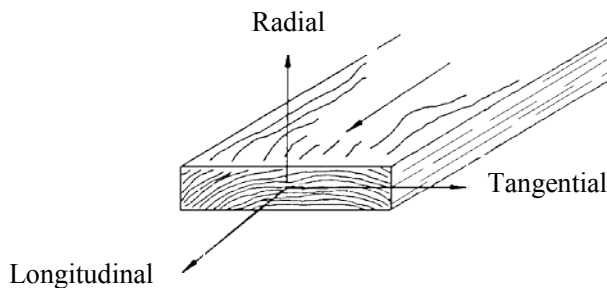
Figure 1.14 Three principal axes of wood with respect to grain direction and growth rings.

The mechanical properties of wood can be divided in three categories [10]:

The **vibration properties** of primary interest in structural materials are speed of sound and internal friction.

The **elastic behavior** of wood can be described thanks to the measurement of three parameters: the Poisson's ratio, the modulus of rigidity and the modulus of elasticity.

The **strength properties** include maximum stress in compression parallel to grain, compressive stress perpendicular to grain, shear strength parallel to grain and modulus of rupture in bending.

The modulus of elasticity and rupture are the most representative modulus used to compare mechanical properties of species. They are usually measured by bending stress (Figure 1.15).
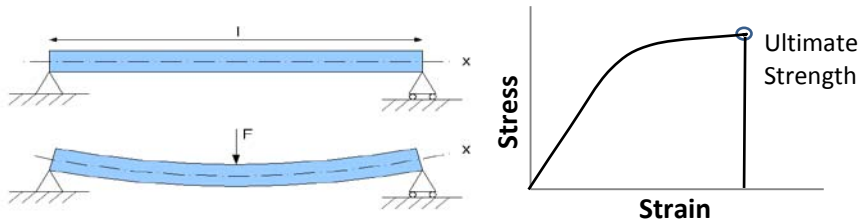
Figure 1.15 Bending stress and typical stress-strain plot of a wood sample

Table 1.2 gives examples of average bending modulus values measured on three common species.

Wood species	Moisture content	Specific gravity	Modulus of rupture (kPa)	Modulus of elasticity (MPa)
Beech, American	Green	0.56	59	9.5
	12%	0.64	103	11.9
Oak, Southern red	Green	0.52	48	7.9
	12%	0.59	75	10.3
Pine, Eastern white	Green	0.34	34	6.8
	12%	0.35	59	8.5

Table 1.2 Strength and elastic properties of some wood species [10]

As any alveolar structure, specific gravity (SG) can be a good indicator of the strength of wood. It is calculated from the mass of a sample of oven-dry wood (m_0) and its volume at certain moisture content (V_α):

$$SG = \frac{m_0}{V_\alpha} \times \frac{1}{\rho_w}$$

where ρ_w is the density of water.

Higher SG indicates generally greater strength (Table 1.2). The strength of wood is also influenced by its moisture content when it fluctuates below the fiber saturation point. Generally, a decrease in moisture content is accompanied by an increase in most strength properties (e.g. Table 1.2).

Temperature and duration of loading also affect strength. In general, strength falls as temperature rises but the most important strength-reducing factors are wood

defects, such as knots, compression and tension wood, and grain deviations. Their adverse effect depends on the kind and extent of the defects, their position, and the manner in which the wood is loaded [10].

1.4.3   Thermal properties and photostability

Although w ood e xpands and c ontracts w ith v arying t emperature, t hese dimensional changes are so small compared with shrinkage and swelling caused by water that the **thermal expansion** coefficient is considered null. Only temperatures below 0 °C ha ve the pot ential t o cause s urface c racks on l iving t rees due t o t he contraction of outer layers.

Wood e xhibits a low **thermal conductivity** (high he at-insulating capacity) compared with materials such as metals, marble, glass, and concrete. For example, the conductivity of the structural softwood lumber at 12% moisture content is in the range of 0.1 to 1.4 W·m^{-1}·K^{-1} compared with 216 for aluminum, 45 for steel and 0.9 for concrete. Thermal conductivity is highest in t he axial direction and increases with density and moisture content; thus, light, dry woods are better insulators [7,10].

Wood bur ns when exposed t o s ufficiently hi gh t emperature i n the pr esence of oxygen. T his pr operty makes w ood suitable for he ating purposes but   is disadvantageous for its technical utilization. The **maximum heating value** of oven-dry wood is about 18 MJ·Kg^{-1} [10].

Wood must be r aised to a temperature of about 250 °C for a spark or flame to ignite i t, but a t a t emperature of a bout 500 °C ignition i s s pontaneous. T he **flammability** of w ood can be r educed by che mical t reatments such a s s odium chloride, ammonium dihydrogen orthophosphate, or halogens (e.g. HBr) [7].

Finally, wood is subjected to photodegradation caused by ultraviolet radiation. The guaiacyl group of lignin is highly chromophore and absorbs in the 250-320 nm range of light wavelength [4]. As we saw in a previous s ection, c oniferous l ignin i s rich in guaiacyl units and softwoods are lighter in color than hardwoods. These are the reasons why the wood from hardwoods is more resistant to UV degradation [45,46].

The free r adicals created under U V at tack make e xtensive oxi dation of ligni n causing its di scoloration [47]. Water accel erates this d egradation because it lixi viates the degraded compounds. The simplest way to limit UV degradation when exposed to s unlight i s t he application of a c olored c oating (painting, w oodstain…). W ood

acetylation can also provide e ffective U V protection, a s it w ill be de tailed in section 1.5.5.11.

1.4.4 Biological properties

1.4.4.1 Biological degradations

Wood i s s ubject t o de gradation b y ba cteria, f ungi, i nsects a nd marine bor ers. Biodegradation c an affect wood of l iving t rees, l ogs, or wooden products, c ausing changes in appearance or structure; these changes range from simple discoloration to mechanical alterations that render wood completely useless. The biodegradability of wood can be considered a positive aspect at the e nd of its life: a wood product can be r eturned t o t he na tural c ycles. B ut during t he service lifetime, t his be comes a problem.

In this dissertation, we will focus on the dimensional stability of wood. The biological pr otection m ight be i ndirectly i ncreased by the proposed treatments. W e considered important to present the main key points concerning the biological attack of wood.

- ▪ **Bacteria** are c onsidered t o be t he c ause of di scolorations i n the for m o f darker-colored heartwood i n l iving t rees. T he color lightens on e xposure t o air, a nd t he pr operties of t he w ood a re not s eriously a ffected. B acteria a lso appear during pr olonged s torage of wood in w ater, i ncluding s eawater. Bacteria can attack the cell wall of wood by tunneling, cavitations or e rosion mechanisms [6,7].
- ▪ **Fungi** that attack wood are responsible f or discoloration (stain) or decay. Blue stain of pines is the most common and serious consequence of attack, by stain fungi. T he s apwood becomes bl uish or bl ackish, us ually i n w edge-shaped pa tches. The de gradation i s mainly esthetic; a mong mechanical properties, only toughness appears to be affected.

    Decay fungi are, by far, the most important cause of wood deterioration. Decay is not an innate property of wood, however; it takes place only if the conditions of e xposure to moisture, a ir, a nd t emperature are suitable for growth and activity of fungi. Moisture content below 20% inhibits growth of fungi, as do temperatures lower than 10°C and higher than 30°C. If wood is kept unde r w ater, i t c annot be a ttacked by f ungi, be cause of i nsufficient oxygen. Extractives contained in wood are toxic to fungi and act as a delaying

factor for biodegradation. Extractives are the main reason for differences in resistance to decay among species, but no wood is immune.

Fungal attack is divided into three classes, which are named according to the appearance of the wood following degradation: brown rot, white rot and soft rot.

Brown rot decay (belonging to Basidiomycetes) is characterized by the removal of the polysaccharide components of the cell wall without altering lignin resulting in high strength losses.

White rot fungi (belonging to Basidiomycetes) selectively attack the lignin component of the cell wall resulting in the bleaching of the wood. Surface of the wood becomes softened with shrinkage occurring in advances stages of decay. Hardwoods are generally more susceptible to white rot than softwoods.

Soft rot (belonging to Ascomycetes and *Fungi imperfecti*) is generally the dominant form of attack where wood is exposed to high levels of moisture or soil contact. High strength losses can be found in wood during early stages of decay by soft rot fungi [6,9].

- **Insects**, can attack the wood of living trees, logs, or wooden products. Once trees are felled, the region between wood and bark (rich in nutrients) is especially vulnerable to insect attack, and for this reason prompt debarking is a protective measure. Insects bore holes and tunnels, and some reduce the interior of wood to dust, leaving only a thin outer layer as they do not like light. Conditions of exposure suitable for insects attack are the same as for fungi: temperature, moisture, and air. Infested wood can be rendered free of insects at temperatures of 50-60°C, by the introduction of insecticides, or by exposure to toxic gases. Surface coatings of paint or varnish also offer some protection, reducing egg-laying sites [6,7].

- **Marine borers** (certain species of mollusks and crustaceans) attack wooden structures in seawater (wharf pilings, boats, and other submerged wood) and cause severe damage. All wood species are vulnerable, but certain woods species presenting a high silica or alkaloid contents provide some temporary protection. Preservative treatment imparts considerable resistance to these organisms [6].

1.4.4.2   Use classes (formerly risk classes)

As c an be a ppreciated f rom the pr evious pa ragraphs, t he a gents c ausing degradation of wood are numerous. Therefore there is a very important correlation between the e nvironment t he installed w ood is i n and the a ttacks of de structive biological agents.

The ENC (European Normalization Committee) through the European standard EN 335 parts 1, 2, and 3 have identified 5 use classes that have been established on the basis of the humidity the wood is exposed to under different conditions of use. The higher the risk, the greater the need to increase the natural resistance level of the wood using impregnation treatment.

Definition of the use classes:

They are defined in the European Standards **EN 599 / EN 355**

- **Use class 1**: situation where wood is used indoors and not exposed to humidity.
- **Use class 2**: s ituation w here w ood is used i ndoors, but w here hi gh environment hu midity may c ause oc casional but not pe rsistent humidity.
- **Use class 3**: situation where wood is used outdoors but is not in contact with the ground. It is continuously exposed to the atmospheric agents or, even though protected from them, is subjected to frequent humidity.
- **Use class 4**: situation where wood is used outdoors and is permanently in contact with the ground or with water.
- **Use class 5**: situation where wood is permanently exposed to sea water.

In every use class, wood is exposed to different biological predators. In outdoor conditions, they are exposed to Basidiomyctes in use class 3 and to Basidiomycetes, Ascomycetes, and *Fungi imperfecti* in use class 4. The laboratory methods used to assess the resistance against this agents are: EN 113 for use class 3, and ENV 807 for use class 4.

Moreover, field testing is the only kind of testing permitting to determine the biological durability in real conditions. These tests can be last up to 5 years to be conclusive. In particular EN 252 for use class 4.

1.5 Current strategies to increase wood stability

We can   conclude f rom t he pr ecedent pa ragraphs t hat under w eathering conditions, lack of dimensional stability, susceptibility to biological attack, and UV discoloration are the main inconveniences of wood.

In t he pa st, t he us e of more e xpensive but durable ha rdwood s pecies s uch a s chestnut or tropical hardwoods was the simplest solution to create durable wood products. As the a vailability of na turally durable s pecies ha s de clined, the i ndustry has t urned t o s oftwoods plantations w ith t he ne ed t o perform w ood t reatments i n order to achieve acceptable longevity under service conditions.

Several appr oaches ar e capable to i ncrease w ood pr operties of non dur able species. The three main developed and under investigation are:

- ▪ **Impregnation treatments**: they consist for example in impregnating wood with biocides to give biological resistance or in filling cell voids by polymers (Bulk effect) to give dimensional stability.
- ▪ **Thermal treatments**: t he a pplication of he at t o w ood r esults i n degradation as sociated w ith chemical cha nges i n t he m aterial. If carefully c ontrolled, t he pr operty c hanges on w ood due to thermal modification can be interesting for certain applications.
- ▪ **Chemical modifications**: They can be de fined as t he r eaction of a chemical reagent with the cell wall polymer of wood. They involve the formation of c ovalent b onds with O H groups f rom cellulose, hemicelluloses or lignin. The chemical nature of wood is thus changed, which confer to wood enhanced properties.

These wood treatments are intended to improve at least one of the properties of w ood. They c an how ever ha ve a n i mpact on t he ot her w ood properties. Sometimes posi tive, sometimes ne gative. For instance, the i mpregnation of w ood with metal salts to improve resistance against fungi decay has a limited but positive impact on t he dimensional s tability. Conversely, thermal t reatment ha s a ne gative impact on the mechanical properties while they increase the dimensional stability of wood.

We w ill pr esent i n t he ne xt pa ragraphs a s hort de scription of t he pa st technologies t o i mprove the c haracteristics of non -durable w ood a nd t hen w e w ill detail t he new t echnologies t hat are a pplied in industry or a re under current

investigation in research laboratories. Commercially a vailable treatments w ill be clearly indicated.

1.5.1 Biocides

Among t he i mpregnation t reatments, t he i n-depth pe netration of bi ocides i nto wood ha s be en t he m ost e mployed. Biocides us ed i n wood pr eservation w ork by being t oxic t o t he bi ological pr edators. S ome of t hem a re i nsecticides (e.g. pyrethroides), s ome a ttack s pecifically the f ungi (e.g. a zoles), a nd ot hers ha ve a broadband spectrum action (e.g. creosotes and metal salts). Biocides can be further divided i nto non -aqueous a nd w aterborne pr eservatives a ccording t o t he s olvent used.

We will first present the biocides that have been extensively used in the past but that a re now on t heir w ay to be l imited or pr ohibited. T his w ill m ake us be tter understand t he r ecently e stablished l egislation t o protect hum an he alth a nd t he environment a nd t he c urrent t ransition t o a ne w generation of biocides and alternative treatments.

1.5.1.1 Old generation of biocides

a) Non-aqueous preservatives

Copper na phthenate, c hlorothalonil, oxi ne c opper, zinc na phtenate, bi s(tri-*n*-butylin) oxide, 3-iodo-2-propynyl butyl carbamate, alkyl ammonium, propiconazole, 4,5-dichloro-2-*N*-octyl-4-isothiazolin-3-one, tebuconazole and chlorpyrifos are some examples of preservatives that a re a pplied di luted i n a n or ganic s olvent [6]. Nevertheless, creosotes and s olutions of pe ntachlorophenol i n white s pirit are t he principal oilborne pr eservatives that have been t he m ost e mployed a t i ndustrial scale.

- ■ **Creosotes** belong to the most widely spread wood preservatives with a broad spectrum of activity. For more than 150 years, creosotes have been us ed t o pr otect r ailway t ies, masts, pol es, a nd w ood f or c ooling towers a nd for m arine t imbers. They w ere originally d erived from a wood distillate but t hese da ys virtually all of t he creosotes are manufactured f rom t he di stillation of c oal t ar oils. The av erage retention ne cessary t o pr otect w ood w ith c reosotes i s 160 K g/m^3.[7] Once impregnated in wood, they can be effective for 20 to 50 years. A

large number of chemical compounds are responsible for this long-term biological pr otection. T he m ost abundant aromatic h ydrocarbons contained in creosotes are a cenaphthene, fluorene, phe nanthrene, a nd anthracene (Figure 1.16). Advantages of c reosote a re: hi gh t oxicity t o wood-destroying or ganisms, l ow s olubility i n w ater (that li mits leaching) and low volatility. At present the environmental pressure has constrained applicators to use only the he avier f raction of cr eosotes called creosotes t ype C. T he Western E uropean I nstitute f or W ood Preservation (WEI) is in charge of the specification of tar oi ls for t he EC [6].
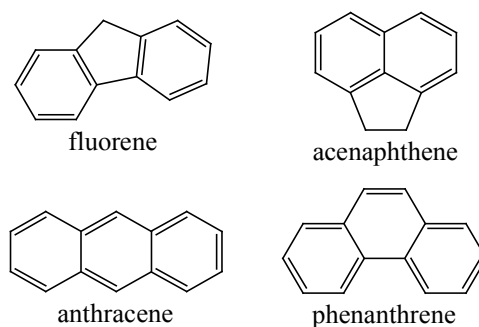

Figure 1.16 Principal aromatic hydrocarbons present in creosotes

- Pentachlorophenol (PCP) was a universally accepted wood preservative for m any years because i t s hows a br oad s pectrum of a ctivity a gainst fungi a nd i nsects, a nd i s r esistant t o bi odegradation l eading t o l ong-term pr otection. T oday, t he us e of PCP i s r estricted o r f orbidden i n many countries not onl y be cause of i ts pe rsistency in the environment but also because of the possible formation of highly toxic dioxins when incinerating PCP-treated wood. In the U SA, PCP is s till a popul ar preservative for ut ility pol es where it is applied dissolved in diesel oi l by pr essure t reatment at r etention levels of 5–8 kg pe r c ubic meter of wood for pine species [48].

pentachlorophenol
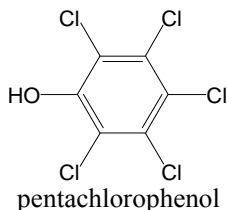
b) *Waterborne preservatives*

Waterborne preservatives must be soluble in water, but once they are into wood, they should resist to leaching. Inorganic salt mixtures employ chromium as fixation agent. Soluble organic compounds are precipitated to form insoluble compounds on the wood fibers. Certain fluorine and boron compounds, which are suitable wood preservatives, are not fixed and can therefore be used only to protect wood that is not exposed to moisture.

The highly popular chromated copper arsenates (known as **CCA**) are represented by three types from A to C depending on their composition (Table 1.3).

Component	Composition (wt. %)		
	Type A	Type B	Type C
Chromium trioxide, Cr_2O_3	65.5	35.3	47.5
Copper oxide, CuO	18.1	19.6	18.5
Arsenic pentoxide, As_2O_5	16.4	45.1	34.0

Table 1.3 Composition of the tree types of chromated copper arsenates [10]

Type C is by far the most common formulation of CCA because it has the best leaching resistance and field efficacy among the three CCA formulations. For a long time CCA were the most widely used wood preservatives due to their broad-spectrum activity, lasting permanence in the wood, and excellent cost efficiency [6,7]. In Europe they are no longer used due to legislative restrictions.

1.5.1.2 Legislation

Concerns about the safety in service and the disposal of preservative-treated wood have pushed legislation to phase out certain classes of biocides. In the EU, wood biocides are regulated by the **Biocide Directive 98/8/EC**. By the time of writing this manuscript, toxic metal containing preservatives are being banned or restrictions placed upon their use are being established. Concerning biocides, the trend goes towards the use of less toxic metal salts (e.g. copper and zinc) and organic chlorine-free biocides.

Legislation is also moving towards the registration of wood preservative chemicals other than biocides. Indeed, **REACH** is a new European Community Regulation on chemicals and their safe use (**EC 1907/2006**). It deals with the Registration, Evaluation, Authorization and Restriction of Chemical substances. The

new law entered into force on 1 June 2007. REACH provisions will be phased-in over 11 years.

The general aim of both directives is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances.

a) **Non-aqueous preservatives**

In particular, due to their industrial importance and wide applications, the use of creosotes is regulated by the Commission Directive 2001/90/EC, which prohibits their use as a wood preservative except in specified products. They should contain less than 50 ppm of benzo-α-pyrenes, and less than 3 wt. % of water extractable phenols. Moreover they must be applied only in industrial installations or by professionals. The treated wood must be for industrial use only (e.g., railroad ties, utility poles, agricultural stakes without food contact) and cannot be used for residential and leisure facilities where skin contact is possible [8].

Pentachlorophenol are today restricted or forbidden in many countries and no longer used in Europe. This was already the case even before the application of the Biocides directive. Germany prohibited them since 1989 [49]. In the USA, PCP is still a popular preservative for utility poles .

b) **Waterborne preservatives**

In February 2002, the US Environmental Protection Agency announced a voluntary decision made by the lumber industry of the United States to replace the sale to consumers of CCA-treated wood with alternative preservative systems by the end of 2003. This voluntary ban affected all residential uses of CCA-treated wood, including decking, picnic equipment, playground equipment, residential fencing and so on.

In Europe, the Commission Directive 2003/02 (6 January 2003) was published, concerned with restrictions on the use and marketing of arsenic. According to this directive, CCA-treated wood will not be allowed for certain end-uses especially where there is potential human contact [8]. To our knowledge, CCA are no longer used in Europe.

1.5.1.3   New generation of biocides

Variations of CCA such as ammoniacal copper arsenate (ACA), am moniacal copper–zinc ar senate (ACZA), copper-chrome-boron (CCB), copper-chrome (CCO or C C) and copper-chrome-fluorine (CCF) are s ome exa mples of a ne w t ype o f biocides that had been developed to comply with national legislations or for specific applications. H owever, none of t hese v ariations have be come universally accept ed because of l ower pe rformances compared t o C CA. Another r eason i s the f act t hat more e nvironmentally-friendly c hromium- and arsenic-free c ompounds have become available in the meantime [7]. The latter are generally effective for at least use class 4. T heir pe rformance de pends o n t he f ormulation a nd s ynergy i s of ten observed. The main molecules in these formulations are:

- Ammoniacal coppe r quaternary (**ACQ**) pr eservatives are at pr esent by far t he m ost popular a fter t he pr ohibition of C CA. T hey c an b e ammoniacal or amine-based and they contain c opper oxide and quaternary a mmonium s alts s uch a s didecyldimethylammonium chloride (DDAC).
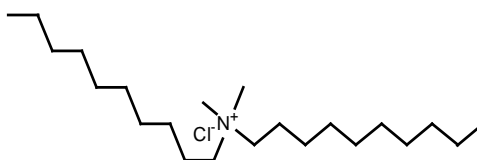
didecyldimethylammonium chloride

- Acid c opper chromate (**ACC**) c ontains 32% c opper o xide a nd 68% chromium trioxide.

- Copper bi s(dimethyldithiocarbamate) (**CDCC**) i s a r eaction pr oduct formed in wood as a result of the dual treatment of two separate treating solutions. T he f irst t reating s olution c ontains a maximum of 5% bivalent copper-ethanolamine and the second treating solution contains a minimum of 2.5% sodium dimethyl-dithiocarbamate.

- Ammoniacal coppe r ci trate (**ACC**) ha s 62% c opper o xide a nd 36% citric acid dissolved in a solution of ammonia water.

- Copper azole-type A (**CBA-A**) has 49% copper, 49% boric acid and 2% tebuconazole dissolved in a solution of ethanolamine in water.

- Sodium tetraborate decahydrate (**Borax**) and other polyborates, such as disodium oc taborate t etrahydrate, are soluble i n water a nd hi ghly leachable. Because of the ir water s olubility a nd their ina bility to be fixed, use of these compounds is limited mainly to wood not exposed to rain. Contrarily t o t he a bove-cited preservatives, the biological protection of borax is limited to use class 3.

* * *

Biocides (old a nd ne w) were de veloped to protect w ood a gainst bi ological predators. The c urrent t endencies aim at increasing wood dur ability i n r egard not only t o bi ological pr otection but a lso to di mensional s tability a nd U V pr otection. The new wood treatments presented in the next paragraphs were developed to cover at least one of the wood insufficiencies. Sometimes the pa rallel improvements have been clearly i dentified. In other cas es, t hey ha ve s imply not be en studied and potential benefits can be expected from them.

1.5.2   Bulk-effect preservatives

Treated wood us ing this t echnology is ge nerally impregnated w ith m onomers that polymerize *in situ*; the main objective being to limit the penetration of water and to reduce the possible development of decay.

Reaction of the bul king a gent may oc cur w ith the cell w all c onstituents, resulting in some cross-linking, but this factor is never predominant in the increase of the properties. The blocking of cell wall micropores, the space within the cell wall occupation, the swelling of the material and so on are the main factors impacting the durability of the treated wood. Here are the most representative techniques using this strategy.

1.5.2.1   Formaldehyde based resins

Much of t he e arly w ork i n r esin i mpregnations was pe rformed dur ing the 1940's [50,51].
They c onsist in i ntroducing und er v acuum a w ater-soluble or m ethanol-soluble

resin: phenol-formaldehyde (PF), melamine-formaldehyde (MF), methylolated melamine-formaldehyde (MMF) and ur ea-formaldehyde (UF). Once t he wood blocks are fully saturated, they are left for 24 h in the treating solution at room temperature to allow the resin molecules to diffuse into the cell wall. The resin then polymerize *in situ* by heating at 105°C during several hours. Anti shrink efficiency (ASE) values between 70 and 90% can thus be obtained.

Recently, treated softwoods with methanolic solutions of P F, M F or U F resins have been investigated [52-54]. The wood samples exhibited volume increases which was nearly equal to the calculated volume of polymer added, showing that most of the resin was located in the cell wall. ASE of 70% with PF and MF was obtained [52]. Several t echniques c an be u sed i n or der t o de termine t he m icrodistribution of t he resin impregnants in the c ell w all: SEM-EDXA [55], fluorescence m icroscopy, autoradiography, transmission e lectron m icroscopy (TEM), e lectron e nergy l oss spectroscopy (EELS) [56], UV microscopy and confocal microscopy [57].

Van Acker *et al.* (1999) determined the decay resistance of MMF-treated Scots pine and beech with EN113 and ENV807 tests. Resin retentions in excess of 50 Kg·m^{-3} were found t o be r equired i n or der t o pr ovide a dequate pr otection t o t he wood [58].

1.5.2.2 *Dimethyloldihydroxyethyleneurea (DMDHEU)*

Dimethylol di hydroxyl e thylene ur ea, better know n a s D MDHEU, is us ed worldwide in textile industry as an anti-wrinkling agent. It has recently been applied to wood treatment.
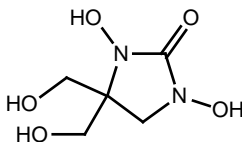
dimethylol dihydroxy ethyleneurea

DMDHEU can react with the phenolic groups of lignin and the hydroxyl groups of polysaccharides, but it can also form complex polymers with itself (cross linking agent). Krause et al (2005) [59] gave an overview of D MDHEU a nd derivatives and their a bility to m odify wood. T ypical A SE v alues are in t he r ange of 3 0 t o 40% when t he w ood s ample w as treated to a le vel in w hich t he a dded DMDHEU represents 40 wt. % of the initial wood weight. This parameter is known as weight

percentage gain (WPG[*]) and is commonly used in literature to evaluate the extent of wood chemical modification.

Strength properties are not or hardly influenced by DMDHEU treatments [60]. The attainable durability class was not reported. Decay resistance of DMDHEU treated-pine and beech was determined in EN113 and ENV807 and significant reductions in weight loss due to decay were found. Results were strongly dependent upon the treatment conditions and on the resin retention [58].

Wood treatments by DMDHEU have not been developed at industrial scale due to the fact that traditional DMDHEU treated wood may release formaldehyde. [61] Novel chemicals based on DMDHEU, which release a lower amount of formaldehyde, or are completely formaldehyde-free, are investigated: for instance the so-called *modified* DMDHEU (mDMDHEU) and dihydroxydimethyl-imidazolidinone (DHDMI). The BASF company has recently introduced on the market the mDMDHEU-modified wood called "Belmadur[®]".

1.5.2.3 *Furfurylation*

Furfuryl alcohol is a renewable chemical derived from furfural, produced from hydrolyzed biomass waste (e.g. molasses).
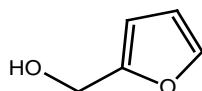
furfuryl alcohol

The acid catalyst reaction chemistry of furfuryl alcohol in wood is very complex. The result is a highly branched and cross-linked furan polymer grafted to wood cell wall polymers [62]. Furfurylation of wood was no longer commercial since the early 1970s in USA. The Norwegian company Wood Polymer Technologies (WPT) developed new processes that have recently become commercial. In Lithuania and in Norway the first plants have been built [8].

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[*] $WPG(\%) = \frac{(m_M - m_U)}{m_U} \times 100$

m_M is the oven dry mass of the modified wood
m_U the oven-dry mass of the unmodified wood

The w ood is f irst im pregnated with the tr eating solution (aqueous s olution of furfuryl a lcohol). T hen a n i ntermediate dr ying s tep i s ne eded a nd t he r eaction curing-step i s c arried out . D uring t he c uring s tep the w ood i s br ought t o temperatures of 80 -140°C by injection of steam. The curing pe riod is 6 -8 h. ASE values range from 30% to 80% and best results are obtained when WPG is around 100%. Durability a gainst f ungi and termites can be v ery good provided t hat the WPG is superior to 60% [62-64]. Most of the applications of such treated wood are flooring and decking. Important darkening of treated wood is nevertheless observed under the most se vere conditions l eading t o a n ASE of 80% . This is e ven commercial under the name of "Kebony Dark" [63].

1.5.2.4 Other treatments

We will briefly present in this section, wood treatment that are not commercial or that are still under investigations at laboratory scale.

**a) <u>Maleic acid with glycerol</u>**

A maleic acid-glycerol (MG) mixture treatment for woods have been developed for improvement of water resistance and durability of woods and particle boards [65].

maleic acid   glycerol
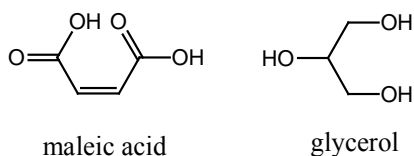
The heating of MG s olutions i n w ood c an l ead t o t he formation of pol yesters with molecular weights higher than 1.0 00 [65]. G ood dimensional s tability c an be obtained, even with low levels of MG treatment. For example, a 10% WPG resulted in an ASE of 80%. [65] Such MG-treated wood exhibited good performance in outdoor weathering t rials. H owever, t he us e of t he hi gh c uring t emperature of 160° C weakened treated wood in terms of mechanical properties with a decrease of 25% of its modulus of elasticity [66,67].

b) __Maleic anhydride with polyglycerol__

Polyglycerol (P G) is s ynthesized f rom gl ycerol, an agricultural b y-product of biodiesel industry. It can be reacted with maleic anhy dride (MA) t o give he at curable c ompounds which a re us eful for i mpregnating w ood t o improve bi ological resistance, dimensional stability and strength.
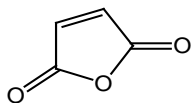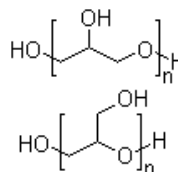
maleic anhydride   Polyglycerol

Roussel *et al* (2001) r eacted pol yglycerol w ith m aleic a nhydride a nd impregnated wood with aqueous solutions thereof. Methyl ethyl ketone peroxide and cobalt naphthalene were also present to promote polymerization. After heating of the treated w ood t o f orm bou nd pol ymer, t here w as a significant w eight change observed due t o l oss of water. Treated blocks e xhibited good di mensional stabilization (around 48% of ASE). I mpregnation of w ood f ollowed by polymerization (WPG of 3 8%) resulted i n a n increase (150%) of t he modulus of elasticity. T he i mpregnation m odification i mproved t he de cay r esistance of t he wood, a s determined in pure culture tests against *Coriolus versicolor* and *Poria placenta*, which are Basidiomycetes (characteristic of use class 3) [68].

Conditions recommended for producing polyglycerol/maleic anhydride PG/MA treated wood are v acuum/pressure (Bethel) impregnation of a queous s olutions of PG/MA a dduct (30%) i n t he pr esence of 2 -butanone pe roxide (2%) a nd cobalt naphthenate (2%) [68].

c) __Silicon-containing preservatives__

Several s tudies on t he a pplication of wood preservatives containing silicon in their f ormulation have be en r eported. T hey act t hrough c hemical m odification by covalent bonding or by hydrogen bonding.

▪ Tetraalkoxysilanes such as t etramethoxysilane (TMS) have be en described for wood treatment.
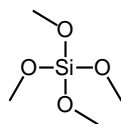
TMS

After impregnation, the TMS present in wood is hydrolyzed and cured to form a SiO_2 sol-gel *in situ*. T he ASE of the t reated w ood increases in pr oportion w ith WPG, r eaching 40% ASE a t 10% W PG [69]. T reated w ood pr esents goo d w ater repellency but m ight be l eached by w ater. T he presence of t he sol-gel reduces the flammability of t he modified w ood. However, the t reatment doe s not of fer significant protection a gainst de cay. For t his r eason, silicon treatment ha s be en combined with fungicides such as quaternary ammonium compounds [69].

▪ Organo-silanes such as for example methacryloxypropyl trimethoxysilane (TMPS) or vinyl trimethoxysilane (V TMS) have be en de scribed a s property enhancers in order to impart a hydrophobic nature to inorganic silicates derived from the sol-gel process [69,70].
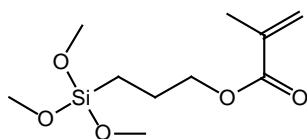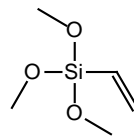
TMPS   VTMS

Hill *et al.* (2004) modified wood with TMPS or VTMS. Maximum ASE values obtained were around 40%. The r esistance aga inst decay w as not demonstrated for the T MPS t reatment e ven a t hi gh W PG up t o 70% . VTMS t reatment a fforded protection against *Trametes versicolor* (soft rot) and *Phanaerochaete chrysosporium* (white rot) at high WPG (50%) but not against *Coniophora puteana* (brown rot) [8].

The pot ential of silicon-based hydrophobation agents for improvement of wood properties is at t he m oment e valuated a nd demonstrated w ithin t he ne w European project "HYDROPHOB" (full na me "Improvement of w ood pr oduct properties by increased hy drophobicity obtained by t he us e of 372 s ilicon c ompounds", coordinated by t he T echnical R esearch C enter of F inland). Some com mercial products are tested at present in the Netherlands.

1.5.3   Pyrolitic treatments

Thermal modification of wood has long been recognized as a potentially useful method t o improve t he di mensional s tability of w ood a nd i ts de cay r esistance. Thermal t reatments ar e based on t he controlled py rolysis of w ood be ing he ated (>180°C) under po or oxygen atmosphere. Significant modifications occur at temperatures between 180°C a nd 260°C, heating a bove 260°C r esults i n extensive degradation of the wood.

As f or a ll m odification treatments, the che mical s tructures of c ell w all components (lignin, c ellulose a nd h emicelluloses) are altered. Hemicelluloses are the most conc erned, their degradation r esults i n the production of methanol, a cetic acid and various heterocyclic compounds (e.g. furans; valerolactone etc.) and leads to an increase of w ood crystallinity. Microstructural and phy sical as pects of thermally treated s oftwood a nd ha rdwood ha ve be en r ecently i nvestigated [71,72]. These changes t end to influence negatively the strength properties of the thermally modified wood leading to a reduction in impact toughness, modulus of rupture and work to fracture [73-75]. Moreover, tendency to form cracks and splits, and darkening of t he wood af ter t reatment ha ve t o be c onsidered. Keeping unde r c ontrol t he strength r eduction a nd t he i ncreasing of t he brittleness a re two of t he bi ggest challenges of thermal treatments.

Nevertheless, thermally treated wood presents an enhancement of its properties: improvement in dimensional s tability, reduced hy groscopicity and improved resistance to microbiological a ttacks. In F inland, France, Germany and the Netherlands, num erous laboratories ha ve be en e xperimenting w ith m odification of wood by he at t reatments. A t pr esent t here ar e f our commercial treatments: Thermowood®, Plato Wood® [76], Retification®, and Perdure®.

a) Thermowood®. This process is operating in Finland with an annual capacity of almost 50 000 m^3 in 20 04. Big i nternational t imber c ompanies like Finnforest a nd S tora E nso 365 a re pr oducing u nder t he T hermowood patents. In the Thermowood pr ocess the wood is heated i n the pr esence of steam. Air contents ar e typically unde r 3.5% . Temperatures r ange f rom 150°C to 240°C, the time of the period is 0.5 to 4 h. In general the bending strength is reduced up to 30%. A reduction in shrinking and swelling up to 50-90% has be en announced by t he c ompany [77]. According t o t he corresponding patent, protection against brown and white rot is attained but the resistance against soft rot is limited [78].

b) Plato[®]. This process consists of three steps. In the first step, wood is heated under wet conditions (hydrothermolysis) for 4 to 5 h. Aldehydes and phenols are released from the hemicelluloses and lignin. The second step is a drying process over 5 days, previous to the last curing steps, carried out under dry conditions for 16 h. The aldehydes and phenols react with each other during the curing and form new polymers around the existing structures in the cell wall. Temperatures are typically between 160°C and 190°C. Biological protection is obtained in some cases for use class 3. Reduction in bending strength varies from 5% to 18%. ASE values vary between 15% and 40% [79].

c) Retification[®] and Perdure[®].

"Retified" wood has been developed in France at the *Ecole des Mines de Saint-Etienne*. The company New Option Wood now operates under the license. The process consists in heating wood with a moisture content of around 12% up to 210°C to 240°C, in a nitrogen atmosphere with less than 2% oxygen content. In 2001 three plants were operating [80].

Another French process, namely Perdure[®], is very similar to retification. The difference consists in the use of fresh wood accompanied of an artificial drying in an oven. Then the wood is heated up to 230°C under steam atmosphere (low O_2). The steam is generated from the water of the fresh timber.

With both processes, the bending strength losses are up to 40%. They are very sensitive to slight temperature changes. This is believed to arise from exudation of the resin from resinous species. Swelling and shrinkage are reduced by half. Equilibrium moisture content is typically 4-5% instead of 10-12% for untreated wood [81,82].

1.5.4 Oleothermal treatments

In France, the company Oléobois[®] exploits a hot oil treatment that includes two phases [83,84]. In the first step, wood is dipped in hot crude vegetable oil at a temperature comprised between 100 and 160°C until wood temperature reaches at least 100°C. At this moment, water contained in the cells evaporates creating an overpressure inside the wood. The vaporization phenomenon advances from the surface to the centre. Vapor is evacuated from the wood mostly through the end grain. In the second step, wood is soaked into an oil bath at a temperature lower than 95°C but preferentially at 60°C. The wood then cools down leading to water

condensation. The created depression causes oil penetration [84]. No chemical reaction is supposed to occur between wood cells and the oil. According to the company, wood is suitable for use class 3 applications.

The Company Menz Holz® in Germany uses a process in which wood is soaked in rapeseed oil, linseed oil or sunflower oil. It is necessary to maintain the temperature at 220°C in the core of the wood for 2 to 4 h. The oil provides good heat transfer and separates the oxygen from the wood. In this sense, this process may be compared to the pyrolitic treatments. For spruce, temperatures up to 220 °C are needed to reach significant biological resistance (use class 3); for pine 200°C is sufficient. With the Menz process no reduction in stiffness has been observed. However, the strength is reduced by 30% when heated at 220 °C. Typical ASE values are of 40% [85].

1.5.5 Chemical modification of wood

The hydroxyl groups of the wood macromolecules can react as any alcohol function. Acylation reactions are the most studied derivatizations. As a consequence of the functionalization of the OH groups, the natural hydrophilicity of wood is reduced. In parallel, an improvement of both the dimensional stability and the biological resistance has been reported in most cases [86]. This increase of properties is due to covalent bonding and is therefore durable and not subject to leaching by water.

Depending on the aim of the study, various properties of the chemically modified wood might be reported but they are seldom exhaustively determined. They are:

- laboratory biological tests to determine the decay and insect resistances,
- dimensional stability,
- mechanical properties,
- water repellency, and more rarely
- fire resistance and photodegradation

We will present in the following paragraphs the mostly frequently reported chemical reactions for wood enhancement. Only few of them have the potential to be conducted to an industrial scale. Reactions presenting the best prospective will be fully detailed whereas those involving toxic reactive or those that are inefficient concerning the increase of wood durability will be briefly presented.

1.5.5.1 Reaction with acid chlorides

Wood can be acylated using acid chlorides. Hydrogen chloride is released as a by-product leading to degradation of the wood fibers if a base such as pyridine is not used (Figure 1.17). Therefore, the use of this technique is limited when treating lumber because of the necessity to remove the by-products present in wood after treatment (HCl or neutralized base).
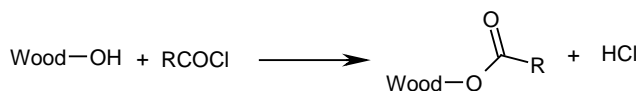

Figure 1.17 Reaction of wood with an acid chloride

It has been reported that reaction of wood with palmitoyl chloride (prepared from palmitic acid and thionyl chloride) permits to obtain a treated wood presenting an ASE of 48% for a WPG of 21% [87].

1.5.5.2 Esterification with carboxylic acids

The reaction between wood and carboxylic acids without a catalyst is very ineffective. A co-reagent is often used to convert in situ the carboxylic acid into a more reactive entity such as an anhydride or an acid chloride (see paragraph above).

The formation of anhydrides is efficiently achieved with trifluoroacetic anhydride [88-90] or with *N,N* –dicyclohexylcarbodiimide (DCC) (Figure 1.18) [91].
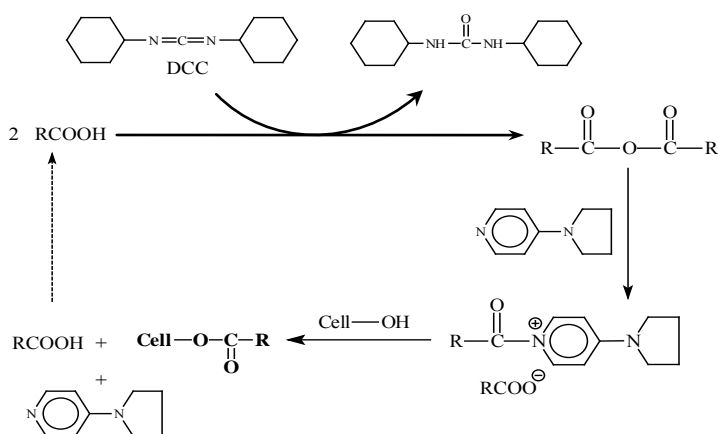

Figure 1.18 Acid-catalyzed reaction of wood with a carboxylic acid and a co-reagent [91]

In our laboratory, reaction systems including a fatty acid and acetic anhydride have been studied [92]. They lead to the formation of a mixed acetic-fatty anhydride. Wood sawdust was acylated with this system to yield mixed esters of wood [93]. No properties were reported. This reaction will be the base of the bulk of the work described in this dissertation. It will be fully described in the subsequent chapters.

1.5.5.3   Reaction with ketene

Ketenes are very toxic and reactive molecules presenting the tendency to polymerize. The particular case of ethenone (also simple called ketene) has been used to acetylate wood (Figure 1.19). This reaction does not create any by-product provided that the wood contains no moisture.

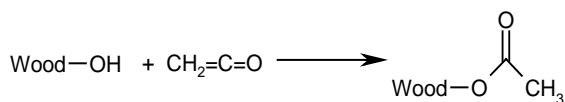$$Wood-OH \ + \ CH_2=C=O \longrightarrow$$

Figure 1.19 Acetylation of wood with ketene

Ketene modification of wood has been found to improve dimensional stability but it is not as effective at improving this property as acetic anhydride. Oven-dry aspen and southern pine wood flakes react with ethenone at 50-60°C leading to WPG of the order of 20% after 10-15 h of reaction [94]. Moreover, wood acetylation with ketene has not been found to be decay resistant at a WPG of 17% [95].

1.5.5.4   Reaction with aldehydes

The addition of an aldehyde to a hydroxyl group forms a hemiacetal. The later can further react with another OH group of the cell wall polymers producing cross-linking while an acetal bond is formed (Figure 1.20). This bonding is susceptible to hydrolysis.
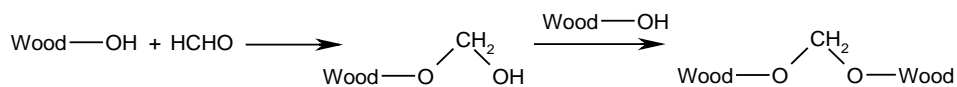
Figure 1.20 Cross-linking of wood cell wall polymers with formaldehyde.

One of the aldehydes used and most frequently reported in literature is formaldehyde [96,97]. The mechanical properties of such treated wood are poor, with

severe embrittlement essentially due to rigidity induced by the cross-linking and the acidic conditions of the treatment [98]. Wood treated by formaldehyde has also been investigated under vapor phase [99] in the presence of SO_2 as a catalyst with a loss of strength minimized compared to other treatments in liquid phases.

Even low levels of formaldehyde modification result in significant reductions in the equilibrium moisture content (EMC) of wood. Yasuda et al. (1995) found that a WPG level of only 3.5% resulted in a 50% reduction of the EMC compared to unmodified wood [100].

Decay resistance of wood treated by formaldehyde showed good results at only 2% of weight gain. Very good resistance to white rot fungi has been reported but resistance to brown rot was poor [101].

Glyoxal, glutaraldehyde and other aldehydes have also been investigated as reagents for wood modification [102-104]. It was concluded that none of them formed stable cross-links in the cell wall.

1.5.5.5 Reaction with isocyanates

Isocyanates [105] and thio-isocyanates [53] react readily with hydroxyl groups of wood to form urethane bonds (Figure 1.21).
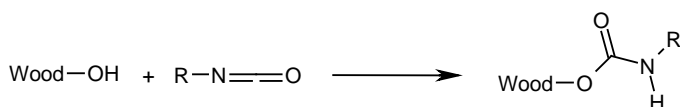

Figure 1.21 Reaction of wood with an isocyanate

A frequently used isocyanate in fiber technology is 4,4'-diphenylmethane diisocyanate (MDI). Isocyanates swell wood and react with it at 100 to 120 °C without catalyst or with a mild alkaline catalyst such as triethylamine (TEA) [106]. The resulting urethane bond is very stable to acid and base hydrolysis. There are no by-products generated from the chemical reaction of isocyanate with dry wood. However, isocyanates react rapidly with water to yield a di-substitued urea. For this reason, it is important that moisture be rigorously excluded during reaction [107].

Wood modified with butyl isocyanate exhibits a threshold for decay protection at around 15% of WPG with all the tested fungi. There is no significant difference in performance related to the chain length of the isocyanate [108].

Unlike mono-isocyanates, a reaction of wood with di- and poly-isocyanates can result in homopolymerization and consequently in bulking effect.

1.5.5.6 Reaction with epoxides

The reaction of wood with an epoxide leads to the formation of an ether linkage and a new OH group. (Figure 1.22) Therefore graft-polymerization reactions are possible [107,109-111].
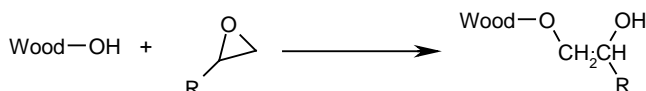

Figure 1.22 Reaction of wood with an epoxide

Several epoxides have been used the past decades for wood modification purposes. They include ethylene oxide, propylene oxide, and butylene oxide [112]. Epoxidation takes place at high temperature and pressure. Usually the reaction is catalyzed under mild basic conditions. In most experiments, triethylamine is used as a catalyst [113].

Decay resistance of wood treated with propylene oxide was ineffective towards *G. trabeum* decay, whereas butylene oxide modification proved to be effective at 23% WPG [114].

Reaction of epichlorohydrin with wood was found to provide decay protection at 31% WPG against *Gloeophyllum trabeum* (brown rot, use class 3), although such modification did not diminish the equilibrium moisture content significantly [115].
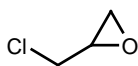
epichlorohydrin

1.5.5.7 Cyanoethylation

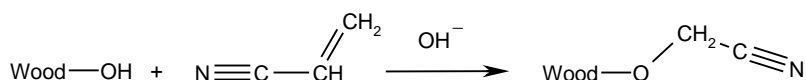Acrylonitrile reacts with wood in the presence of alkaline catalyst (Figure 1.23).

Figure 1.23 Reaction of acrylonitrile with wood

With NaOH treated wood, WPG up to 30% have been reported, giving ASE in the region of 60%. Biological resistance due to bulking, rather than toxicity, of such treated w ood ha ve a lso be en r eported. C yanoethylated wood in gr ound c ontact a t 15% of WP G have an average l ife of al most 8 years, compared with 4 years for untreated samples [116-118].

1.5.5.8 Reaction with alkyl halide

The alkyl ha lides in the pr esence of a s trong ba se can be used for w ood etherification (Figure 1.24).
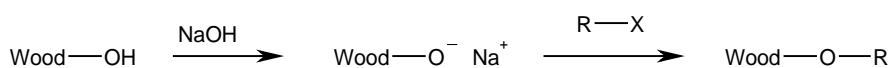
Figure 1.24 Reaction with alkyl halide

Reactions of wood with crotyl chloride, methyl iodide and butyl chloride have led to an improvement in dimensional stability. [8]
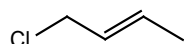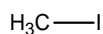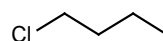
crotyl chloride   methyl iodide   butyl chloride

Decay r esistance ha s al so been investigated for wood treated with fatty dialkyldimethylammonium chlorides a nd br omides. T reated w ood s howed g ood resistance against brown rot (use class 3). [119]

1.5.5.9 Reaction with β-propiolactone

The reaction of β-propiolactone with wood can be catalyzed by acids or bases to yield two different products.
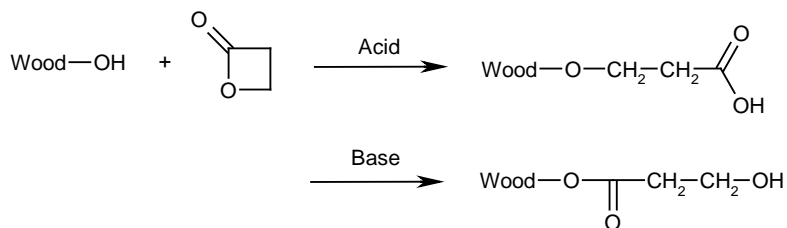
Figure 1 25 Reactions of wood with β-propiolactone

Treated wood in a cidic c onditions with 30% WPG r esulted i n go od decay resistance and ASE of 60%. Nevertheless a s trong de gradation of w ood ha s be en observed [120]. Recently, β-propiolactone has been classified as carcinogenic.

1.5.5.10 Reaction with cyclic anhydrides

Cyclic a nhydrides do not y ield a by-product when r eacting w ith the hydroxyl groups of w ood. The a nhydride c ovalently bonde d on wood by a n e ster f unction yields a free carboxylic group at its end (Figure 1.26). The free carboxylic group can in t heory react w ith another OH group t o cross l ink t he c ell w alls p olymers of wood [121].
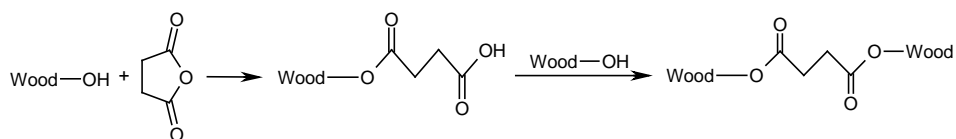
Figure 1.26 Reaction of succinic anhydride with wood

Cyclic anhy drides have be en studied as chemical r eagents f or w ood modification: phtalic a nhydride [122], maleic anh ydride [123], glutaric a nhydride [124], succinic anhydride [125,126], and alkenyl succinic anhydrides (ASA) [125-128].

The research team of Pr. H ill treated samples of S cots pine w ith petrochemical A SAs (octenyl s uccinic anhy drides) dissolved in pyridine tha t a fter treatment did not pr esent e nough r esistance against f ungi de cay [127] but increased dimensional stability [122,123].

Our l aboratory developed in 20 01 a treatment of w ood by t he M ASA (methyl e sters of a lkenyl succinic anhydride) [128]. MASA was defined as a formulation obtained by the maleinization of methyl esters of vegetable oils. MASA can react with w ood t hrough t he a nhydride gr oup and f orm an e ster bond (Figure 1.27).
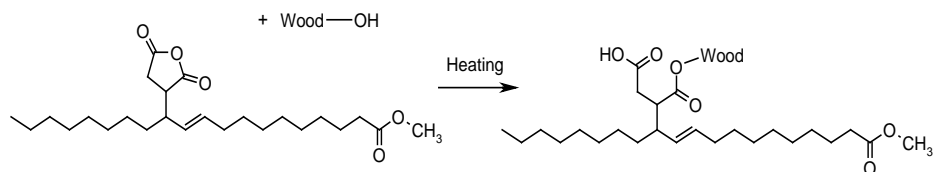

Figure 1.27 Reaction between wood and MASA

The pa tented pr ocess c onsists in a vacuum/pressure (B ethel f or exa mple) impregnation of the wood at 140-170°C for 2 to 4 hours.

Standard tests (fungi: BS 3900, EN 152, EN 113, ENV 807; insects: EN 46 and EN 47, EN 118) were carried out on w ood t reated b y M ASA w ith di fferent formulations. These tests showed a global efficiency for all the predators except for soft rot. Treated wood could then be qualified as use class 3 but not class 4 (exterior use but without ground contact). A recent European project coordinated by the same laboratory ha s developed a ne w A SA m olecule w ith an a lkyl gr oup di fferent from methyl. The use class 4 has thus been reached (www.surfasam.com).

Viitaniemi [129] patented the use of maleic anhydride dissolved in anhydrous alcohol an d crude vegetable oil i n order t o t reat w ood s upposed t o be i n c ontact with soil or water. Treatment is carried out in 3 steps: Wood is impregnated under a vacuum/pressure c ycle, dr ied i n or der t o r emove t he s olvent b y e vaporation a nd finally, s oaked i n the m ixture at hi gh t emperature (150-250°C) dur ing between 1 0 min and 20 h. During the last step, an ASA seems to be synthesized but this has not been demonstrated. A SE o f s uch t reated w ood i s a bout 50% but t he t reatment induces cracks diminishing the interest in the finished product. [8]

Reactive oi l t reatments a t SHR T imber R esearch, modification systems ha ve been de veloped us ing m odified l inseed oi l a s pa rt of EU funded pr ojects [58]. T his linseed oil has be en isomerised t o c onjugate t he dou ble bonds . A Diels-Alder-reaction with maleic a nhydride allowed to cr eate a cy clic anhy dride group in the molecule. T he us e of t his c hemical f or w ood modification ha s be en pa tented by DSM Resins (Dekker 2001). It has lead to high durability, high ASE and no losses in strength in laboratory conditions. At present, the scaling up is being done and the timber treater Foreco in Dalfsen (The Netherlands) is the main industrial partner. [8]

1.5.5.11 Reaction with acyclic anhydrides

This f amily of c ompounds c omprises t he m ain r eaction of L apeyre® Process WoodProtect® [130]. Since thi s is the main subject of the manuscript, it will be discussed in detail in the next chapters.

Of a ll t he w ood chemical m odification r eactions, a cetylation ha s t he l ongest history. Acetylation has b een the s ubject of ext ensive r esearch and industrial products are commercialized (Accoya®).

Reaction of acetic anhydride with OH groups forms an ester bond and acetic acid is formed as a by-product (Figure 1.28). Reaction without catalyst is conducted at 70°C [131,132].
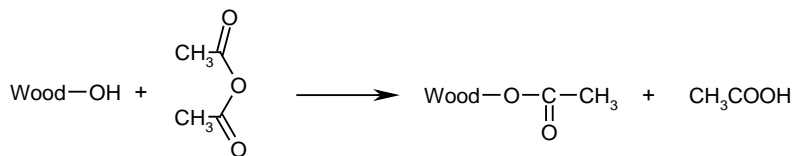

Figure 1.28 Reaction of acetic anhydride with wood

The acetylation reaction depends on the accessibility of the reagent to the bulk of the wood and in the cell wall. It is known that the rate of reaction is promoted by wood-swelling agents such as pyridine that can be used only at laboratory scale [50]. The influence of the moisture content of the wood upon reactivity has to be considered, the water permits a swelling of the cell wall but leads also to hydrolysis of acetic anhydride into acetic acid diminishing the quantity of reactive molecules [133].

The reactivity of acetic anhydride upon cell wall polymers decreases in the following order: lignin>hemicelluloses>cellulose, both within the wood cell wall [134] and with the isolated polymers [135,136].

There have been a number of studies of the reaction kinetics of anhydride reactions within the cell wall. Most studies have shown that the reaction kinetics of acetylation are diffusion limited [137-139]. In general, the level of substitution of whole wood with acetic anhydride rarely exceeds a WPG of 25%.

Anhydride modification is accompanied by a swelling of the wood cell wall due to the volume occupied by the bonded acyl adduct. Since the wood is swollen, exposure to conditions of high relative humidity results in a lower degree of swelling than untreated wood (better ASE).

The Swedish Chalmers University of Technology have developed the use microwave technology for fast heating during the treatment [140,141]. The SHR Timber Research (The Netherlands) has developed a method to overcome the problem of the residual by-product acetic acid, a process now coming in the full scaling-up phase [131]. A pilot plant (2 500 liters with 0.6 m³ wood capacity per batch) was built by Acetyleer Kennis BV (AKBV) in 1999 in the Netherlands. Since the

establishment of the pilot plant, SHR Timber Research has conducted several experiments and results indicate good potential for the commercial acetylation of wood. The construction of a 20 000 m^3 full-scale production plant has started. The company that brought acetylated wood to the market is Titan Wood (now Accoya®). According to the fabricant, the biological resistance is attained at WPG higher than 20%. The ASE is at least 75%. Strength properties are not influenced by the treatment (except a slight increase in hardness), the material is UV-stable and paint tests have shown remarkably good results. Termites do not prefer the material (choice test) but can eat it however.

Although acetylation with acetic anhydride has been widely studied, investigations with other linear or branched chain anhydrides have also been conducted. Longer chain symmetrical anhydrides show much lower reactivity with wood than acetic anhydride, with a constant decrease as the molecular weight of the anhydride increases [139,142-145]. Rate of reaction is however, markedly improved if pyridine is used as swelling solvent and catalyst [146].

Steric hindrance is an important factor explaining the decreasing reactivity with the increase of the fatty chain length. For instance, isobutyric anhydride exhibited lower reactivity than butyric anhydride [144]. The effect of the reaction on the swelling of the cell wall of Scots pine and Corsican pine samples upon the rate of reaction with acetic or propionic anhydride under scrupulously dry conditions has been reported [21]. Oven-dried samples of both species showed no reaction with propionic anhydride in xylene.
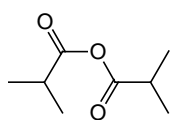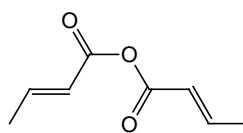
isobutyric anhydride   crotonic anhydride

The improved dimensional stability of wood as a result of anhydride modification has been found to be a function of WPG only, regardless of the anhydride used for modification (Figure 1.29). Improved dimensional stability arises due to bulk effect, caused by the volume occupied by the bonded acyl adducts in the cell wall. Dimensional stability has also been obtained with the unsaturated C_4 crotonic anhydride [147].
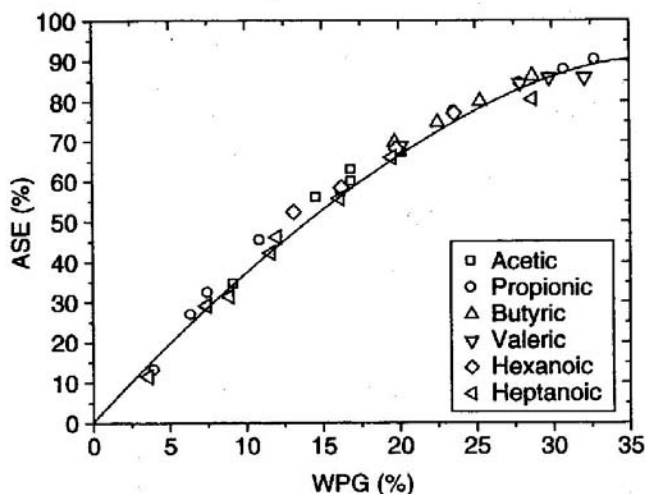
Figure 1.29 Anti shrink efficiency in function of the weigh percentage gain for various linear chain anhydrides [142]

* * *

1.6   Conclusions

Wood is hygroscopic. It tends to absorb water and results in wood swelling, development of fungi decay and insect attacks. Among all the techniques described in this state of the art, chemical modification appears to be a multi-purpose technique that may improve simultaneously the wood durability. The reactions with anhydrides have proved to be efficient in particular to improve the dimensional stability.

In our project with the Lapeyre Company, there is a particular interest to minimize the changes in dimension of wood pieces for joinery. The choice of anhydrides as reagents seems appropriate. Contrarily to most of the works from the literature, we will propose to include a fatty (long aliphatic) chain in the anhydride to obtain improved water repellency. And in order to overcome the disadvantage of steric hindrance of the fatty chain, we will use a mixed acetic-fatty anhydride. This kind of reaction has been developed in previous works of our laboratory.

This molecule can act as a chemical *"Trojan horse"* which makes react the fatty acyl groups provided that we accept to graft acetyl groups in the same reaction. This is not a disadvantage as we have seen in this chapter: acetyl groups are recognized to provide dimensional stability and photostability when grafted to wood.

Other adv antages of m ixed acetic-fatty anh ydrides are t hat t hey can be synthesized from renewable chemicals (roughly speaking, vinegar and vegetable oil) and that neither the raw materials nor the final product are toxic.

From a c hemical poi nt of v iew, mixed a nhydrides a re di ssymmetric a nd therefore m ore r eactive t han symmetric anhy drides. Moreover t heir amphiphilic character s hould f acilitate t he c ontact w ith w ood, w hich s hows bi polarity: pol ar biopolymers s uch a s c ellulose a nd he micelluloses a nd non -polar macromolecules such as lignin.

We w ill ne xt focus i n the s ynthesis of m ixed a nhydrides f rom a f undamental point of view to understand its thermodynamics and kinetics.

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CHAPTER 2

Reaction between acetic anhydride and a fatty acid without a catalyst

CONTENTS

2.1. Introduction

Mixed acetic-fatty anhydrides are not commercial products. Not only because their industrial applications are limited, but the fact is that they are difficult to purify and once they are purified, they tend to dissociate to form symmetric molecules. They have to be synthesized *in situ* prior to utilization.

Thus, complex equilibriums take place during the synthesis of these mixed anhydrides when starting from acetic anhydride and a fatty acid. These equilibriums have been admitted in the past literature but they have never been fully explained. The main reason is a lack of an appropriate analytical technique to separate and quantify all the constituents of the reaction medium.

One of the first steps in our scientific approach was to develop a new HPLC protocol permitting the analysis of reaction mediums obtained after the synthesis of mixed anhydrides. This technique should be able to characterize mixtures of low polar, strongly polar and amphiphilic molecules. The first journal article presented in this chapter has exclusively been dedicated to this problem. It was submitted to the *Chromatographia* journal and is already available on-line. We present here a differently formatted version but with exactly the same text appearing in the journal. It will be the same case for all the papers presented in this manuscript.

The new HPLC technique gave us the tool to study and better understand all the reactions taking place between the fatty acids and the simple and mixed anhydrides. This work was published in the *European Journal of Lipid Science and Technology*. This paper is presented in the second part of this chapter. Although several acetic-fatty anhydrides have been synthesized, we focused in this paper exclusively on the synthesis of acetic-oleic anhydride. Oleic acid has been preferred to other fatty acids because of its availability and lower price, which are of importance when the process becomes industrial. Moreover, it has no unpleasant odor and is obtained from renewable resources.

2.2. Quantitative analysis of mixtures of various linear anhydrides and carboxylic acids

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Abstract

Few quantitative methods have been described to analyze mixtures of symmetric anhydrides, mixed anhydrides and their corresponding carboxylic acids. Reversed-phase HPLC using acetonitrile-water as solvent was optimized for the quantitative determination of such mixtures obtained by reacting acetic or propionic anhydrides with various fatty acids (from C3 to C18). Complex mixtures containing up to three mixed anhydrides, four symmetric anhydrides and four carboxylic acids have been quantitatively analyzed successfully in a single run.

Keywords: Column liquid chromatography; anhydride; mixed anhydride; carboxylic acid; fatty acid; reversed-phase HPLC; flow rate gradient

2.2.1. *Introduction*

Mixed anhydrides, i.e., unsymmetrical anhydrides obtained from 2 different carboxylic acids are molecules finding an increasing interest in the chemical industry due to their high reactivity. They are used for instance in chemical synthesis as co-reagent [1] or in the pharmaceutical chemistry as prodrugs [2]. They are particularly interesting molecules to form ester bonds with hydroxyl groups and are commonly used in the synthesis of cellulose esters [3] as for example acetoformic anhydride often used as a formulating agent or acetic-propionic and acetic-butyric used in the production of acylated cellulose.

In order to produce mixed anhydrides industrially, three processes are generally employed: the reaction of a carboxylic acid with a ketene, the reaction between an acyl chloride with a carboxylic acid salt and the reaction of a symmetric anhydride with a carboxylic acid. When synthesizing mixed anhydrides by the latter process, a complex reaction medium is obtained. The mixed anhydride spontaneously reacts again to form the corresponding symmetric anhydrides of the second fatty acid. (Figure 2.1)
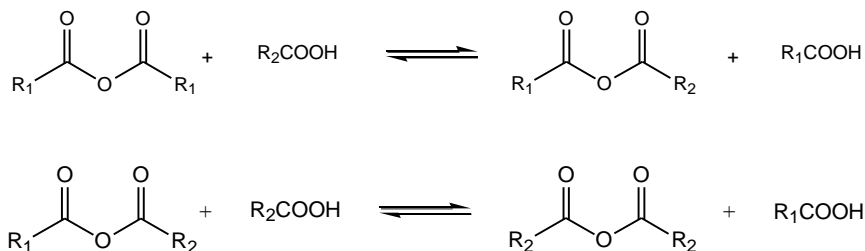
Figure 2.1. Consecutive reactions between carboxylic anhydrides and carboxylic acids.

The separation and quantification of such mixtures, containing several symmetric anhydrides, a mixed anhydride, and the corresponding carboxylic acids, is of importance and few analytical methods have been developed to perform direct determination.

Gas chromatography equipped with a methylphenylsilicone stationary phase [4] is an interesting qualitative method to separate these compounds. Nevertheless, it cannot be use quantitatively. The high temperature of the injector can shift the equilibrium of the reaction increasing the symmetric anhydride content in the mixture.

Reversed-phase HPLC using a mixture of acetonitrile and water as mobile phase [5,6] has been reported for quantitative determination of symmetric and mixed anhydrides and their corresponding acids. Compounds with short aliphatic chains are separated using eluents with a high content of acidified water, usually 90% to 50%. Under these conditions, hydrolysis of anhydrides occurs all along the column. The resulting carboxylic acids are liberated continuously and become part of the baseline. It has been demonstrated that the hydrolysis of anhydrides is a reaction with kinetics of first order [6]. Consequently, this phenomenon does not affect the calibration. Moreover, only low molecular weight aliphatic anhydrides, such as acetic anhydride, are significantly concerned by the hydrolysis.

In the case of mixtures containing long aliphatic chains, the polarity of the involved molecules is lower. The HPLC protocols would require a mobile phase richer in acetonitrile, from 50% to 100%.

But when the need to analyze mixtures with compounds containing short and aliphatic chains comes (as those described in Figure 2.1), it is relatively difficult to obtain the separation of all the molecules in a single run, even with a gradient program. In order to make soluble the fatty molecules, it is necessary to prepare eluents with a high concentration of acetonitrile. As a consequence, 3 problems arise:

- the resolution of short chain compounds is not achieved,

- a loss of resolution between the acetic-fatty mixed anhydride and the fatty acid occurs,

- the solubility of all the compounds with different polarities in the mobile phase may not be complete.

This paper describes a reversed-phase HPLC protocol allowing the analysis in a single run of a complex mixture of compounds as described in Figure 2.1 with R_1 ranging from C2 to C4 and with R_2 from C6 to C18.

We have investigated different conditions to optimize the said method by varying the mobile phase gradient, the flow rate gradient and the column specifications.

2.2.2. *Experimental*

2.2.2.1. *Instrumentation*

The liquid chromatography system used for this work consisted of a Dionex modular system including a P680 pump, an ASI100 automated sample injector equipped with a 20 µL loop condigured at 10 µLs^{-1} for injection and a UVD340U diode-array UV detector (Dionex, Sunnyvale, CA, USA). The temperature of the column was 23°C and the room temperature was 20°C.

Samples (10 µL) in acetonitrile were eluted through a C18 column (VARIAN, Polaris C18-A, 100 A, 5 µm) (250 x 4.6 mm ID).

2.2.2.2. *Chemicals and standards*

Acetic, propionic, butyric, caproic, caprylic, capric, lauric, myristic, palmitic, oleic, linoleic, and linolenic acids and anhydrides 99% (GC) purity where purchased from Sigma-Aldrich (Saint-Quentin Fallavier, France). Phosphoric acid (85% in water) and technical grade oleic acid 90% where purchased from Acros (Halluin, France). Acetonitrile HPLC grade was obtained from Scharlau (Barcelona, Spain), and pure water from a milli-Q water purification system.

2.2.2.3. *Preparation of the model mixtures*

We prepared various model mixtures by making react a short chain symmetric anhydride (acetic or propionic) with a carboxylic acid with R_2 from C3 to C18 without using any catalyst.

Both reagents, with a fatty acid/anhydride molar ratio of 1.5, were introduced in a 100 mL batch reactor equipped with a 350 rpm stirring system and a reflux condenser. Reaction was carried out at 100°C during 1 hour.

2.2.3. *Results and discussion*

The choice of a column permitting the analysis of low molecular weight aliphatic anhydrides and their corresponding acids was our first task. We selected standard conditions used in the analysis of fatty compounds, i.e., with a concentration of acetonitrile in the mobile phase higher than 60%. We selected the

VARIAN Polaris C18-A compared to the reversed-phase columns commonly used for this kind of analysis [1,6] as it resulted to give by far the best resolution factor.

We then optimized the analytical conditions with the selected column in order to achieve the separation of a mixed anhydride and its corresponding carboxylic acids.

We first chose to work on a relatively simple mixture obtained at equilibrium by reaction between acetic anhydride with octanoic acid at 100°C. We worked under a flow rate of 1.5 mLmin^{-1} with an eluent gradient starting at t=0 from 75% acetonitrile/25% water with 0.02 wt% phosphoric acid in water to 100% acetonitrile in 5 min and then keeping at 100% acetonitrile until then of the analysis. 10μL samples were injected. Any wavelength comprised between 205 and 240 nm permits a quantitative analysis of the mixture. Nevertheless, 212 nm seemed to be the best compromise between peak shapes and intensity as shown in Figure 2 2.
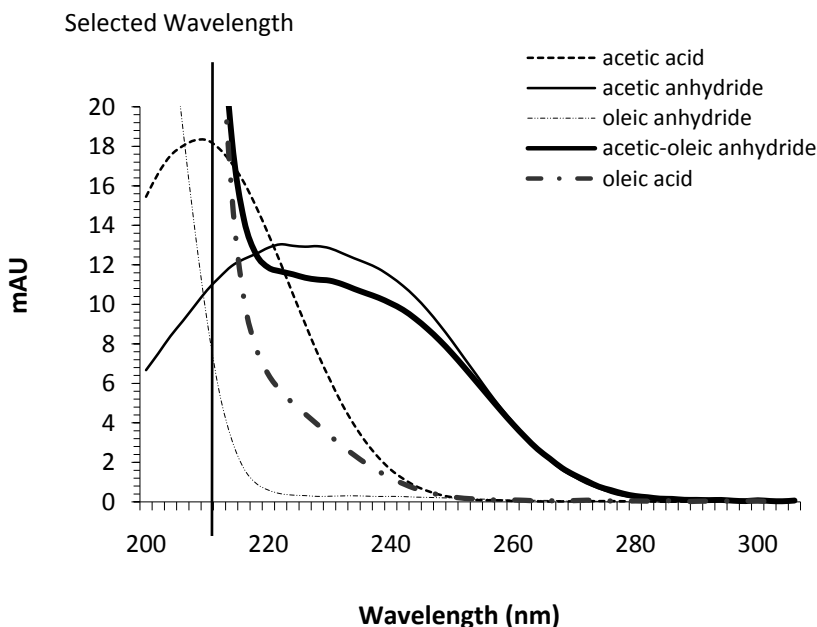

Figure 2 2 UV spectra of carboxylic acids and anhydrides with R$_1$=2 and R$_2$=C18:1

Figure 2.3 shows the chromatogram obtained under the optimized conditions for this mixture. The five compounds described in Figure 2.1 were perfectly separated and identified.
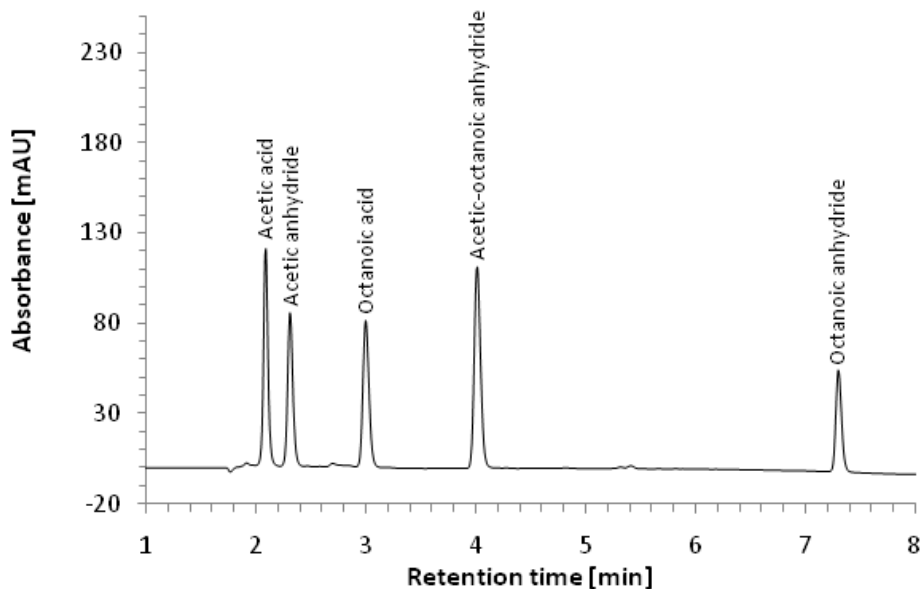
Figure 2.3 HPLC chromatogram of the mixture obtained after reaction between acetic anhydride and octanoic acid. Mobile phase: A=water with 0.2 wt% phosphoric acid, B=acetonitrile. Gradient: 70% A to 100% in 5 min, 1.5 mLmin^{-1}. UV detection at 212 nm

Based on these first results, we then investigated the separation of molecules with a big difference in the length of aliphatic chains. We studied the mixture obtained by reacting acetic anhydride with pure oleic acid. After analyzing this mixture under the previous conditions, we obtained a perfect separation of all the five compounds.

Nevertheless, a relatively important peak asymmetry factor value of 3.2 for the oleic anhydride and a high capacity factor (k) of 25 did not permit an appropriate quantification of this compound. We optimized the analytical conditions by applying a flow rate gradient during the analysis as shown on Figure 2.4.

This permitted to obtain a peak asymmetry factor value of 1.1, which is a satisfactory value, and a capacity factor value of 13.5. This permits the quantitative analysis of all the compounds and diminishes considerably the analysis runtime.
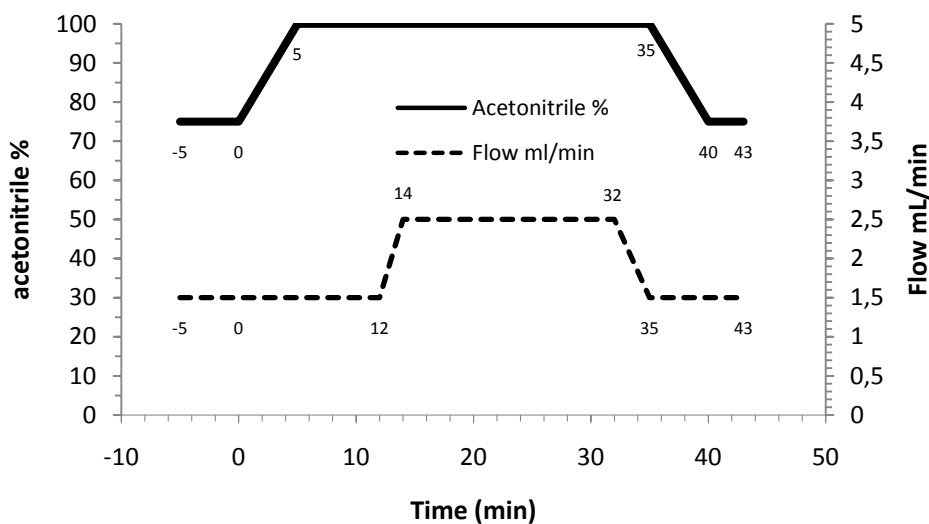
Figure 2.4 Optimized conditions retained for eluent concentration and eluent flow

We proceeded to analyze more complex mixtures. Indeed, when acetic anhydride reacts over technical oleic acid, which contains small but significant amounts linoleic and linolenic acids, it is obtained a mixture with three anhydrides, three carboxylic acids, and three mixed anhydrides. Several analysis conditions were tested, gradients for both eluents and flow. We succeeded to perfectly separate all the compounds (Figure 2.5).
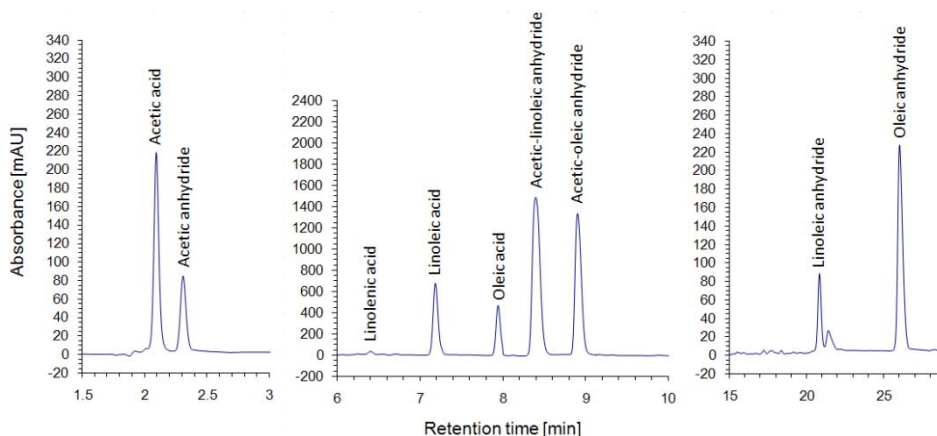
Figure 2.5 Separation of the mixture obtained from acetic anhydride and oleic acid (90% technical grade) under the optimized conditions shown in Figure 2.4

This chromatogram allowed the quantitative analysis of a mixture containing 10 compounds of different polarity and even the resolution of various C18 compounds, which are distinguished only by the number of their unsaturations.

It is important to note that these optimized analysis conditions are very sensitive. A change in only one of the parameters (flow, gradient rate or initial percentage of acetonitrile), will make the accurate separation of acetic-oleic anhydride and their corresponding acids not to occur. For instance, a change of 5% of the initial percentage of acetonitrile (80% or 70%) led to a non selective separation of linoleic, linolenic, oleic acids and their corresponding acetic-fatty mixed anhydrides.

We finally performed analysis under these conditions of various mixtures synthesized with symmetric anhydrides with R_1 ranging from C2 to C3 and carboxylic acids with R_2 from C3 to C18. Results of capacity factors obtained for each compound are indicated in Table 2.1. A perfect separation was obtained in every case.

R_1	R_2	k'				
		(I)	(II)	(III)	(IV)	(V)
2	3	0.30	0.22	0.39	0.48	0.18
2	4	0.30	0.27	0.48	0.78	0.18
2	6	0.30	0.43	0.80	1.84	0.18
2	7	0.30	0.52	0.98	2.48	0.18
2	8	0.30	0.69	1.27	3.12	0.18
2	10	0.30	1.27	2.01	4.41	0.18
2	12	0.30	2.06	2.78	6.60	0.18
2	14	0.30	3.01	3.50	9.75	0.18
2	16	0.30	4.04	4.23	ins.	0.18
2	18:1	0.30	3.73	4.02	13.54	0.18
2	18:2	0.30	3.05	3.48	10.63	0.18
2	18:3	0.30	2.61	n.d.	n.d.	0.18
3	18:1	0.48	3.73	4.55	13.54	0.22
3	18:2	0.48	3.05	4.02	10.63	0.22

Table 2.1. Capacity factors under optimized conditions.
(I) to (V): Molecules shown in Figure 2.1.n.d.: not determined;
ins: insoluble in acetonitrile

As it is shown in Figure 2.4, we forced the mobile phase to come back to 75% acetonitrile and the flow rate to decrease back to 1.5 mL.min^{-1} at the end of the analysis.

Indeed a period of stabilization of the column under 75% acetonitrile is necessary after or before the analysis in order to obtain a flat baseline for a neat quantitative analysis. The required time of stabilization was 5 min at least.

A dysfunction of the pump valves can occur when increasing the acetonitrile concentration in the eluent. It is therefore necessary, after around 100 injections, to clean the valves in a nitric acid aqueous solution (15% in water) assisted with ultrasonic waves. It is also possible to reduce this problem with the use of ceramic valves.

Most of the mixed anhydrides are unstable molecules and particularly difficult to isolate. That is why no standards are commercially available. The quantitative analysis of the studied complex mixtures is possible only by applying the method described in this work. Indeed, it permits to quantify all the other compounds presents in the mixture; it is then possible to determine by calculation the concentration of the mixed anhydride, which depends directly on the concentration of all the other compounds present in the mixture. The only condition to determine the response factor of the mixed anhydride is to know the molar ratio used in the synthesis. Once the response factor known, the mixture itself can be used as a standard, permitting thus the analysis of mixtures prepared with other molar ratios. The composition of useful reaction media for many applications can thus be easily determined.

2.2.4. *Conclusions*

We investigated the analysis of mixtures containing various aliphatic anhydrides, acids and mixed anhydrides and optimized a general reversed-phase HPLC method to quantitatively determine all the compounds. Controlled eluent flow and eluent concentration gradients were required. By this mean, it is possible to perform the analysis of mixtures containing short and long chains of carboxylic acids and anhydrides in a single run.

2.2.5. *References*

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2.3. Consecutive reactions in an oleic acid and acetic anhydride reaction medium

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Abstract

When mixing acetic anhydride and oleic acid, two consecutive reactions take place. The first one yields acetic-oleic anhydride (AOA) and acetic acid. In the second one oleic acid reacts with AOA to form oleic anhydride at 5% in a mixture when the initial molar ratio is 1:1. Therefore the global reaction yields at equilibrium a mixture of AOA, acetic anhydride, oleic acid, acetic acid and oleic anhydride. Based on a new HPLC protocol, all the species of the reaction medium could be separated and quantified. This permitted for the first time to study the kinetics and thermodynamics of the reaction. In the 30-70°C range reactions were of order 2 with partial orders of 1 for each reactant. Equilibrium constants were determined for both reactions. Enthalpy, entropy and activation energies were calculated for the main reaction. The influence of molar ratio on the composition at equilibrium was also investigated. The synthesis of AOA could thus be understood and new data were obtained for this singular molecule scarcely cited in the CAS database.

Keywords: mixed anhydride; consecutive reactions; kinetics; fatty acids; thermodynamics

2.3.1. *Introduction*

Anhydride groups in organic chemistry are acylating agents appreciated for their high reactivity compared to carboxylic acids. Mixed anhydrides, i.e. with two different carboxylic acid radicals, are even more reactive due to the difference of pK values of the two moieties of the asymmetric molecule [7]. Mixed anhydrides found many applications in chemical processes such as key intermediates for the production of carbamates [8], in pharmaceutical prodrugs synthesis [2] and in the esterification of cellulose [3].

Pure mixed anhydrides can be obtained by distillation provided that molecules have low molecular weight and show small differences between the lengths of the acyl moieties. Propionic-acetic anhydride can thus be isolated and seems to be stable enough to be stored at low temperature [9]. When the carboxylic chains are longer, decomposition may occur during distillation.

Another particularity of mixed anhydrides is the fact that they rearrange by reaction with carboxylic acids. If the latter corresponds to one of the moieties of the mixed anhydride, the result is a symmetric anhydride:

$$R_1CO(O)COR_2 + R_1COOH \rightarrow R_1CO(O)COR_1 + R_2COOH.$$
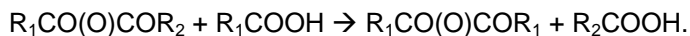
It exists four ways of synthesis of such mixed anhydrides:

– The most recent is the ketene process [10]. Ethenone, the smallest ketene, is the most employed to produce anhydrides by reaction with carboxylic acids. The reaction yields a mixed acetic-carboxylic anhydride [11-14].

– Another method consists in the reaction of an acid chloride with a salt of a carboxylic acid, usually sodium or potassium salts [9,15-17]. The reaction yields NaCl or KCl as by-products, which is very convenient for purification and for shifting the equilibrium.

– A third method consists in the reaction of an acid chloride with a carboxylic acid. This method is not frequently used because it forms HCl as by-product.

– The last synthesis approach is the reaction between a symmetric anhydride, usually acetic anhydride, and a carboxylic acid [12]. This reaction is equilibrated [14] and therefore the remaining carboxylic acids may cause the formation of symmetric anhydrides as explained before. This occurs particularly if the mixed anhydride is not withdrawn by distillation from the reaction medium; which is the most common case unfortunately. Furthermore, in another context this rearrangement feature is exploited when the opposite objective is foreseen: the synthesis of symmetric anhydrides (usually fatty anhydrides). In this case, acetic acid is distilled off from the medium to favor the formation of the desired fatty anhydride [11,13,16].

In parallel, mixed anhydrides are present in industrial processes without being explicit. For instance in the preparation of cellulose acetate-butyrate, the acylating reagents added to the medium are acetic anhydride and butyric anhydride. As they are introduced in the same bath, there is *in situ* formation of the mixed acetic-butyric anhydride [3,12].

There are few studies describing the mixed acetic-fatty anhydrides. On the particular case of AOA, there is only one reference in literature [18] and it does not concern the synthesis. We will consider the synthesis of this molecule by reaction of acetic anhydride and oleic acid, the latter being a common renewable feedstock and this molecule finding an industrial interest in the chemical modification of wood [19].

In general, the reactions leading to acetic-fatty anhydrides are based on assumptions and hypotheses because of three reasons: i) the complexity of the reaction medium, ii) the high reactivity of the mixed anhydride -and therefore its high instability- and iii) the fact that no efficient analytical methods were available so far.

A HPLC method developed in parallel [20] permitted the determination of the composition of such media at different reaction times. We could then study the kinetics and thermodynamics of the equimolar reaction between acetic anhydride and oleic acid in order to determine the order of the reaction, the partial orders, the equilibrium constants, the activation energies, the speed rate constants and other thermodynamic parameters. Finally, we studied the influence of the molar ratio (from 1:2 to 2:1) on the final composition of the reaction medium at equilibrium.

2.3.2. *Materials and methods*

2.3.2.1. *Chemicals and standards*

Acetic anhydride and oleic anhydride (both 99% GC purity) were purchased from Sigma-Aldrich (France) and were used without further purification. Phosphoric acid (85% in water) and other standards for chromatography were bought from Acros (France). Acetonitrile HPLC grade was obtained from Scharlau (Spain), and pure water from a milli-Q water purification system.

2.3.2.2. *HPLC analysis*

Reversed-phase chromatography analysis based on a previous publication of the same authors [20] was performed in a liquid phase chromatograph from Dionex including a P680 pump, a variable 20 µL loop and a UVD340U diode-array UV detector set to 212 nm. The temperature of the column was set at 23°C.

Samples (10 µL) in acetonitrile were eluted through a C18 column (VARIAN, Polaris C18-A, 100 A, 5 µm) (250 x 4.6 mm ID). Concentrations of samples in acetonitrile were between 4 and 6 g.L^{-1}.

An initial flow rate of 1.5 mL.min^{-1} was set. An eluent gradient was used starting at t = 0 from 75/25 acetonitrile/water (with 0.02 wt% phosphoric acid) to 100% acetonitrile in 5 min and then keeping at 100% acetonitrile. After 12 min of analysis the flow rate was increased in 2 min up to 2.5 mL.min^{-1} until the end of the analysis.

2.3.2.3. *Kinetic and thermodynamic study of the reaction*

Equimolar mixtures (ratio = 1 ± 0.001) were prepared with 890 mg of oleic acid and 320 mg of acetic anhydride, i.e. 1.3 mL of mixture in 1.5 mL vials. Samples were prepared in duplicate. During the preparation of all the vials, they were kept at 4°C to prevent the reaction to occur. When all the vials were ready, they were simultaneously introduced in a VorTemp 56 shaking incubator. Precision in temperature was ± 1°C. Shaking agitation was set at 1300 rpm permitting a perfect mixing of the samples.

For sampling, 2 vials were instantly removed and cooled down with liquid nitrogen to stop the reaction. Samples were immediately analyzed by HPLC or

stored at -18°C. It is the average composition of the two vials of each sampling that is reported. At room temperature acetic anhydride and oleic acid are not miscible; the reaction can be considered as heterogeneous during the first minutes of the reaction. In this particular case, acetonitrile was used to dissolve the whole content of the vial to obtain a single phase for HPLC analysis.

2.3.2.4. Results and discussion

The equimolar reaction without catalyst between acetic anhydride and oleic acid was conducted longtime enough to attain the equilibrium (70°C during 5 days). The composition of the reaction medium, continuously monitored by HPLC, showed since the first day constant concentrations of AOA, oleic anhydride and acetic acid. Acetic anhydride and oleic acid were still present in the medium. We cannot say however that the latter are only unreacted chemicals. They are also the by-products of all the reactions taking place (Figure 2.6). The formation of oleic anhydride is the proof of the subsequent reaction (**II**) between the mixed anhydride and the fatty acid. They both co-exist in equilibrium.
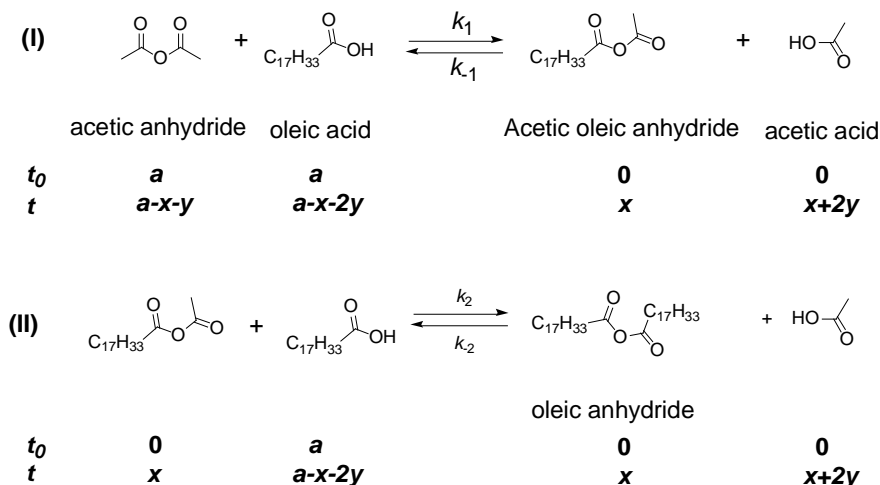
Figure 2.6 Proposed mechanism for the reaction between acetic anhydride and oleic acid

Other syntheses were conducted until the equilibrium in a temperature range of 30 to 70°C. In all the cases the five molecules cited above were present. The final compositions of the media were not identical but were maintained within a narrow range. Regardless of the reaction temperature, the molar fraction of oleic anhydride was always less than 4% for a 1:1 molar ratio.

The example of the slowest reaction, i.e. conducted at 30°C for 5 days, is shown in Figure 2.7.
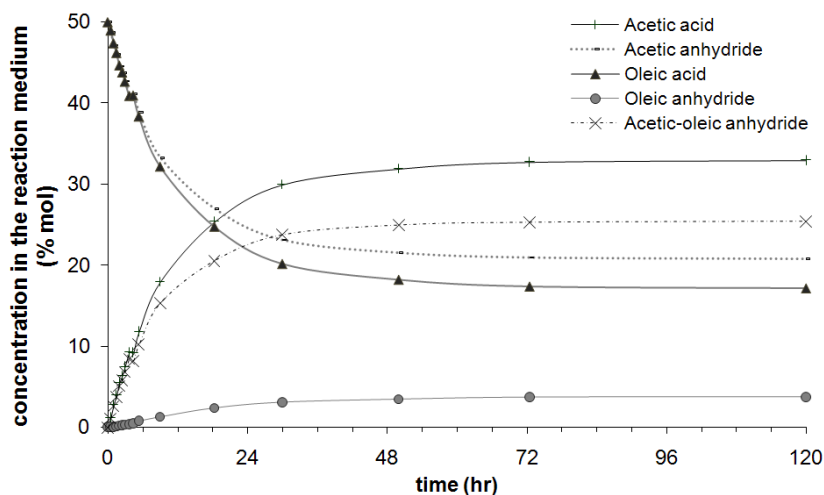

Figure 2.7 Kinetics of the equimolar reaction between oleic acid and acetic anhydride at 30°C

Three parts can be distinguished in the concentration vs. time curves. From 0 to 4 hr, the consumption of the two initial reagents is equimolar. The formation of AOA and acetic acid is also equimolar. From 4 to 40 hr, reaction **II** becomes significant as shown by the formation of oleic anhydride. The consumption of oleic acid is higher than that of acetic anhydride. The former reacts with AOA to yield oleic anhydride. The concentration of acetic acid is particularly high as it is formed from both reactions, **I** and **II**. In the final stage of the reaction, from 40 hr, the concentrations of all the substances reached a plateau. No degradation of the molecules was observed till 120 hr.

The study on the kinetics of reaction **I** involves defining the speed law of the reaction. As it is impossible to integrate the speed law of two consecutive equilibrated reactions, we made the following assumption: reaction **II** is negligible compared to reaction **I**. In this case, $y = 0$ during all the reaction. It is therefore the apparent speed of formation of AOA which will be determined.

In order to determine the speed law, we made the hypothesis that the reaction **I** was of order 2 with partial order of 1 for each reactant.

The speed rate can then be described as $dx/dt = k_1(a-x)^2 - k_{-1}x^2$

After integration, we obtain:

$$\frac{1}{(A-B)a^2} \ln \frac{(1-Bx)}{(1-Ax)} = k_1 t \qquad \begin{aligned} A &= \frac{1}{a} + \frac{1}{a\sqrt{K_1}} \\[2mm] B &= \frac{1}{a} - \frac{1}{a\sqrt{K_1}} \end{aligned} \qquad \textbf{(Eq 1)}$$

where K_1 is the constant of equilibrium for reaction **I** and a is the initial molar fraction of acetic anhydride and oleic acid. (Figure 2.6)

According to our assumption, the formation of AOA depends only on the first equilibrium (reaction **I**). It is important to note that this approximation does not permit to determine the real speed rate constants. Indeed, the formation of oleic anhydride consumes part of the AOA; the rate constant is therefore under-evaluated. The latter has been called <u>apparent</u> speed rate.

The apparent speed law reaction is therefore $dx/dt = k'_1(a-x)^2 - k'_{-1}x^2$ and the integrated law becomes a function of k'_1. It is thus necessary to replace in the integration K_1, which is dependent on k_1 and k_{-1} and not k'_1 and k'_{-1}, by its expression as a function of the concentration at equilibrium x_e.

As $K_1 = x_e^2/(a-x_e)^2$ we obtained the following integrated law:

$$\frac{x_e}{2a^2 - 2ax_e} \ln \frac{(x_e - (\frac{2x_e}{a} - 1)x)}{(x_e - x)} = k'_1 t \qquad \textbf{(Eq 2)}$$

The plot of Eq 2 for experimental results at 30, 40, 50, and 70°C gives a linear correlation (Figure 2.8).

The equation shown at left of the figure:

$$\frac{x_e}{2a^2 - 2ax_e} \ln \frac{(x_e - (\frac{2x_e}{a} - 1)x)}{(x_e - x)}$$
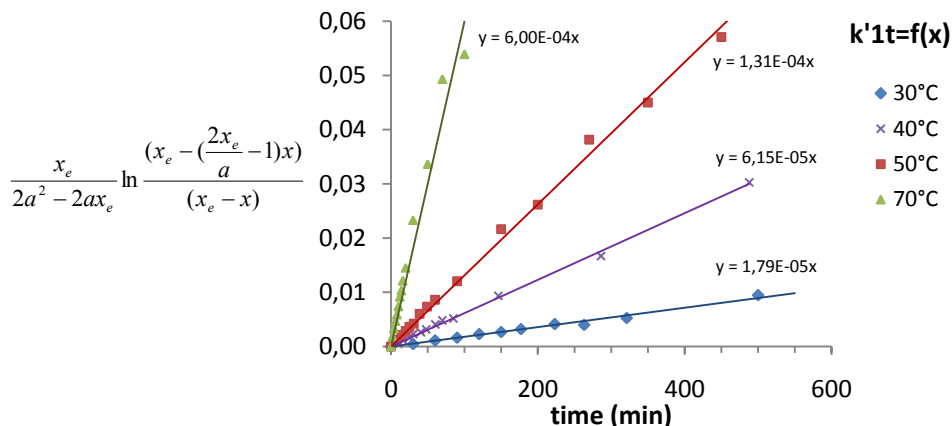
Figure 2.8 Apparent kinetic plots considering x = xe

The slope values correspond to k'_1. We can deduce from these results that reaction **I** behaves as a second order reaction with partial orders of 1 for each reactant. Once this hypothesis has been confirmed, it is now necessary to study and determine the real speed rates of reaction **I** and to determine its thermodynamic parameters.

This time, we can restrict our first assumption: reaction **II** is negligible but only in the first minutes of the reaction; i.e. $y = 0$ as long as y is inferior to 0.5%. This permits to evaluate the underlined real speed rate constants.

The plot of Eq 1, involving K_1, (Figure 2.9) shows linear trends for each temperature followed by a non-linear trend.

The equation shown at left of the figure:

$$\frac{1}{(A - B)a^2} \ln \frac{(1 - Bx)}{(1 - Ax)}$$
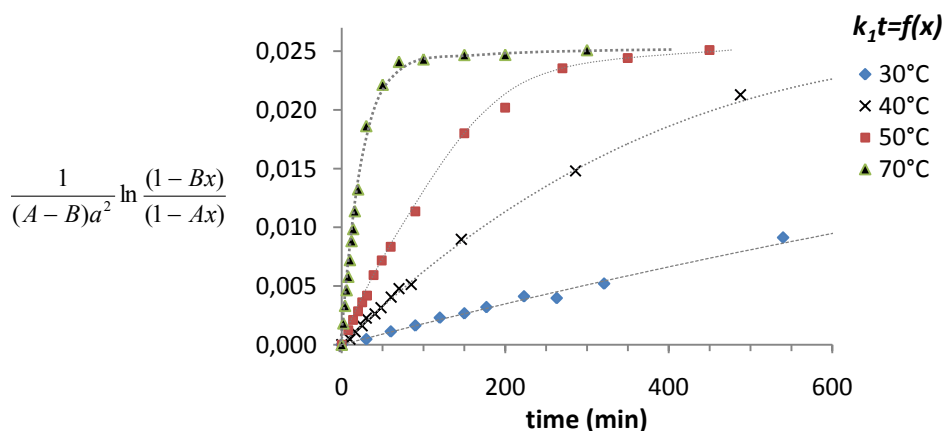
Figure 2.9 Kinetic plots considering K1

On the scale of time, the linear part is maintained only for a few minutes at the highest temperature (70°C) and up to 4 hr at 30°C. During these periods, the formation of oleic anhydride is negligible. When it becomes significant, the general law (Eq 1) is no longer valid. The formation of the AOA depends then on the apparent model (Eq 2). In this case, the concentration of AOA x, instead of following the general model, tends to a plateau x_e, that depends on the two reactions and not only on reaction **I**. For further calculations, we will consider only the linear part of Figure 2.9. The expanded view of this plot and the slope values (corresponding to k_1) are presented in Figure 2.10.
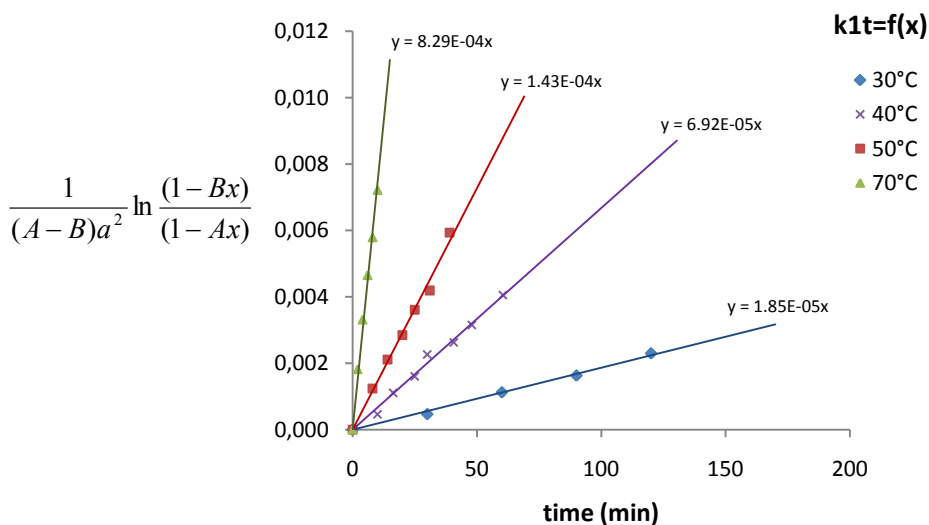
Figure 2.10 Kinetics of reaction I for experiments in which y < 0.5% mol

From these values and the relation $K=k_1/k_{-1}$, where k_{-1} is the speed rate of the inversed reaction **I**, we could calculate the k values presented in Table 2.2.

T(°C)	k_1	k_{-1}	K_1	K_2
30	1.85E-05	7.84E-06	2.36	2.84
40	6.92E-05	3.13E-05	2.21	2.74
50	1.43E-04	5.89E-05	2.43	2.35
70	8.29E-04	3.22E-04	2.57	3.32

Table 2.2 Speed rate constants and equilibrium constants for the equimolar reaction

It is important to precise that the values of K_1 and K_2 were determined experimentally at time equal to 5 days, which can be considered "infinite". The equations used are:

$$K_1 = \frac{[AOA]_e * [Acetic\ acid]_e}{[Acetic\ anhydride]_e * [Oleic\ acid]_e}$$

$$K_2 = \frac{[Oleic\ anhydride]_e * [Acetic\ acid]_e}{[AOA]_e * [Oleic\ acid]_e}$$

We can observe that k_1 is always superior to k'_1. This can easily be explained by the fact that in the apparent model (Eq 2), a part of the consumed AOA is not taken in account as it reacted to form oleic anhydride. Moreover, the speed rate at 70°C is 45 times greater than at 30°C, showing a big dependence on temperature.

Another thermodynamic parameter determined for reaction **I** is the activation energy. Based on the Arrhenius law, we calculated the activation energies by plotting $\ln(k) = E/RT + \ln(A)$ (Figure 2.11).

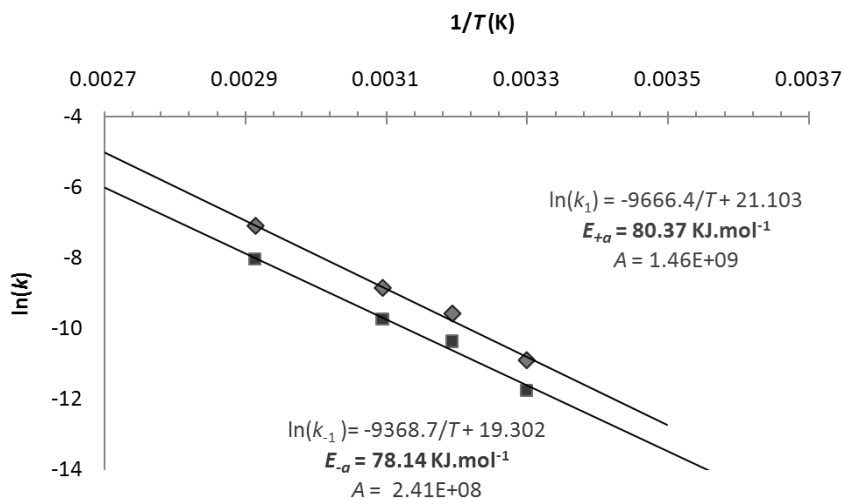**Figure 2.11 Arrhenius-type graph for the determination of the activation energies**

We obtained $E_{+a} = 80.4$ KJ.mol^{-1} and $E_{-a} = 78.4$ KJ.mol^{-1} for the straight and the inversed reactions respectively. These values are very close, indicating that the equilibrium state is barely dependent on the temperature of reaction.

As $\Delta G_0 = \Delta H_0 - T\Delta S_0 = -RT \ln(K)$, plotting $\ln(K_1)$ as a function of $1/T$ permitted to determine other thermodynamic constants of reaction **I** (Figure 2.12): $\Delta H_{01} = 2473.8 \, J.mol^{-1}$ and $\Delta S_{01} = 14.96 \, J.K^{-1}$.
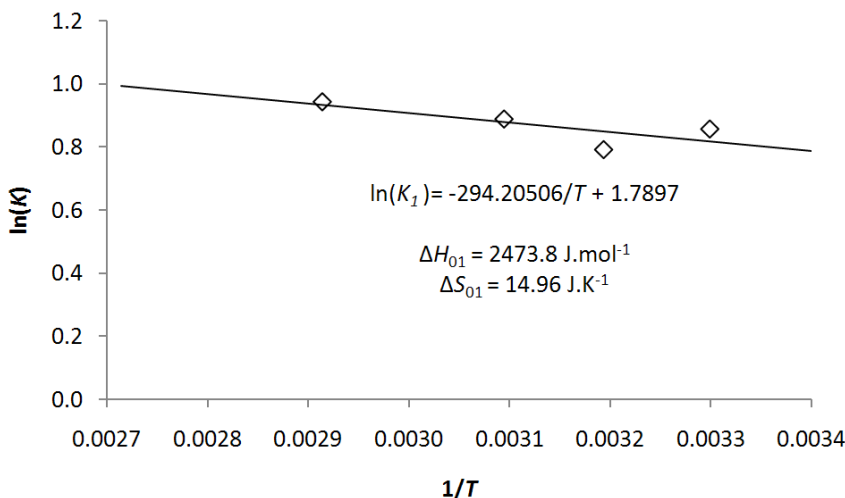

Figure 2.12 Thermodynamic values for reaction I

The reaction is therefore endothermic as these values are both positive. We could have also given ΔH_{02} and ΔS_{02} values. However, the concentration of oleic anhydride, which is the main indicator for reaction **II**, is determined with a relatively high uncertainty due to its low concentration. In order to study the kinetics and thermodynamics for reaction **II**, it would be better to follow the kinetics of an equimolar reaction between oleic anhydride and acetic acid. This was not done because the price of such experiments (about 60 reactors) would be extremely high due to the expensiveness of pure oleic anhydride.

The enthalpy of formation of AOA ($\Delta H_f = -939.9 \, KJ.mol^{-1}$) could be calculated from the ΔH_{01} value and the ΔH_f of the reagents and products of reaction **I**. The latter were obtained from the DIPPR 801 compilation from the AIChE [21].

Finally, we conducted several syntheses with different molar ratios of acetic anhydride and oleic acid.
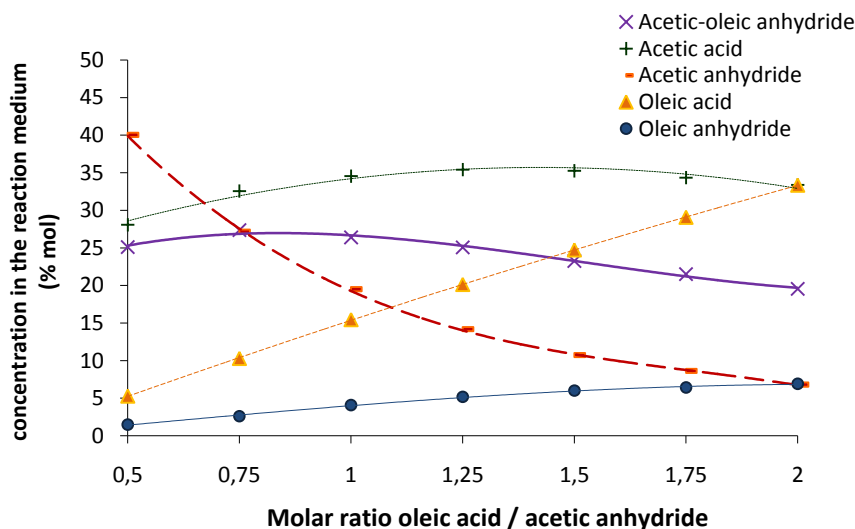
Figure 2.13 Composition of the mixture for different molar ratios oleic acid / acetic anhydride at equilibrium at 70°C

Figure 2.13 shows that the final composition of the mixture at the equilibrium is clearly dependent on the initial ratio of reagents. Nevertheless, AOA is always present in the medium at a molar percentage comprised between 20 and 25% regardless of the molar ratio of the reactants. An optimum seems to be found at around the equimolar mixture.

The present work and the understanding of the reactions involved in the synthesis of mixed anhydrides may also help to understand why they are unstable. Traces of water may hydrolyze the mixed anhydride. The corresponding carboxylic acids act as initiators of a rearrangement conducting to the formation of symmetric anhydrides (reaction II or reaction I inversed). At the end, one molecule of water can be responsible of a great conversion rate of AOA to symmetric anhydrides.

2.3.3. *Conclusions*

The equimolar reaction between acetic anhydride and oleic acid without any catalyst can be described as two consecutive equilibrated reactions. At equilibrium, 5 molecules coexist: acetic acid, AOA, acetic anhydride, oleic acid and oleic anhydride. The speed rate depends largely on the temperature. At 70°C the reaction attains the equilibrium in 90 min. This time can easily be reduced at higher temperatures. Equations allow to predict the equilibrium at less than 10 min at 100°C. The influence of molar ratio is smaller than that of temperature; however the optimum was situated at around 1.

The order of the main reaction (**I**) is 2, and it is expected that the consecutive reaction (**II**) follows the same behavior. Moreover, both reactions are endothermic and the composition at equilibrium is barely dependent on temperature.

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2.4. Conclusions

Thanks to the new reversed-phase HPLC analytical technique developed and described in paper 1, we were able to analyze mixtures containing symmetrical anhydrides, mixed anhydrides and carboxylic acids with any carboxylic chain lengths from C2 to C18:1 in a single run. This has been an extraordinary opportunity to investigate the synthesis of mixed anhydrides obtained by reaction between acetic anhydride and fatty acids.

We could characterize all the 5 compounds implicated in this synthesis and demonstrate that they coexist at the equilibrium of the two involved reactions namely the reaction between acetic anhydride and fatty acid, and the reaction between acetic-fatty anhydride and fatty acid. The 5 compounds are: acetic anhydride, acetic acid, acetic-fatty anhydride, fatty acid and fatty anhydride. Their proportion in the medium was accurately determined.

For the first time the order of the reaction and the kinetic and thermodynamic constants were calculated for the main reaction. However the kinetics of the second equilibrium remains to be studied and can be the object of a future paper. Since oleic anhydride remains a minor compound, we decided with our industrial partner to postpone this study.

Besides, the thermodynamics and kinetics data collected and discussed in paper 2 are indispensable tools to predict the resulting composition at different synthesis conditions. The choice of a particular set of conditions has not to be made at this moment. It will depend on the easiness of reaction with the macromolecules of wood and on the properties conferred to it. However if the aim is to maximize the concentration of mixed anhydride, the molar ratio should be kept in a domain where none of the starting reagents are in huge excess.

Let us remind that our interest in the synthesis of mixed acetic-fatty anhydrides is correlated to the fact that these molecules are amphiphilic, asymmetric and therefore more reactive than symmetrical anhydrides. These characteristics are crucial for the esterification of wood. The ability to determine the composition of the mixtures is primordial in the context where these reaction mediums are employed to treat wood.

Based on these results, we are now able to study the chemical modification of wood by such reaction mediums. The following chapter will present the reactivity of mixed anhydride mixtures toward cellulose, which is a model molecule and the major component of the wood cell wall. We will also study the reaction with sawdust, which is representative of all the wood components with a more homogeneous distribution.

CHAPTER 3

Study of the reactivity of mixed anhydrides toward cellulosics

CONTENTS

3.1 Introduction

Investigating the chemical modification of wood is a complex task. Wood is a natural material, and as such, it exhibits great variability in its composition and properties. Variations exist between species, between trees and within the tree itself.

In the particular case of wood modification with anhydrides, it is the esterification of hydroxyl functions which is considered, and all the major constituents of wood are concerned: cellulose, hemicelluloses, lignin and tannins. Their proportion in wood may vary considerably, even in a small piece of wood. The study of their reactivity can turn out to be complex. Moreover, the wood alveolar structure induces diffusion barriers that make investigations more intricate.

The aim of this chapter is to study the reactivity on wood of mixtures obtained after reaction between acetic anhydride and a fatty acid. As presented in chapter two, we are now able to prepare such mixtures and to control the proportion of each of the five reactants present at equilibrium after the synthesis.

In order to overcome the heterogeneity and diffusion phenomena due to wood structure, we made the choice to study the reactivity of two model substrates, cellulose and Scots pine sawdust:

- Cellulose is the major cell wall polymer constituent of wood but the less reactive due to its crystallinity. Understanding the way this polymer reacts, will help to seize the problem of poor dimensional stability, whose origin is in the wood cell wall.
- Scots pine sawdust presents the advantage to be "homogeneous". Reducing the particle size will help to convert wood pieces into a uniform raw material. At a microscopic level, the constituents keep the same composite-like structure but their accessibility is dramatically increased. In terms of reactivity, extra-polation to wood pieces could be envisaged.

The works described in this chapter have made the object of four more papers. They will be presented as we did in chapter two and their numbering will pursue the previous paper 1 & 2.

The first paper of this chapter, accepted for publication in *Cellulose*, describes a new technique developed to determine the degree of substitution of long chain cellulose esters and mixed cellulose esters adapted to low and very low degree of

substitution. This permitted to characterize cellulose and pine sawdust treated with anhydride mixtures in the following papers.

The second one, submitted to *Cellulose*, presents the chemical modification of cellulose by the anhydrides mixtures described in chapter two. As it is a reaction carried out without any catalyst of solvent, it provides information on the straight reactivity of mixed anhydrides on cellulose.

The third paper, submitted to C*ellulose*, reveals the impact of this chemical modification on the hydrophobicity of the biopolymer and opens new perspectives for the utilization of these new cellulose derivatives. We took in consideration previous unpublished results with high degree of substitution to better establish structure-properties correlations for hydrophobicity and water repellency.

The fourth one, submitted to *Bioresource Technology*, describes in a simplified approach the chemical modification of wood with mixed anhydrides using Scots pine sawdust as a raw material. The relationship between the reaction parameters and the degree of esterification is presented. Moreover, the correlation between the chemical modification and the hydrophobicity of the chemically modified wood sawdust is also investigated.

Contrarily to most of the studies in literature, we decided to use undried cellulose and wood sawdust. Their moisture contents were maintained to be representative of what could be the moisture of wood in the industry after being cut and air-dried. The powdered substrates were therefore conditioned during two weeks at 25°C and 60% relative humidity.

All the treatments performed on cellulose and Scots pine sawdust presented in this chapter were carried out without the use of any catalyst or solvent. These conditions will facilitate the scale-up of the process by reducing the number and the complexity of the involved steps. This approach comes closer to the *Green Chemistry* principles.

3.2 Accurate determination of the degree of substitution (DS) of long chain cellulose esters (LCCE)

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Abstract

The determination of the degree of substitution (DS) of fatty acid cellulose esters with alkyl chain lengths from C8 to C18 was performed by direct transesterification with trimethylsulphonium hydroxide (TMSH) using *tert*-butyl methyl ether (MTBE) as a solvent. Transesterification was demonstrated to be quantitative at 75°C in 60 min. The quantification of the formed fatty acid methyl esters was performed by gas chromatography (GC). After the optimization of the method, long chain cellulose esters (LCCE) could be analyzed in a wide range of DS. The obtained values were compared to those given by other existing protocols. LCCE with DS-values in a range of 5.10^{-5} to 3 were analyzed with high accuracy. Reproducibility is weakened for high DS values if the sample has a compact aspect limiting the accessibility of TMSH to the ester functions. This method can also be suitable for the analysis of mixed cellulose esters.

Keywords: DS determination, TMSH, very low DS, transesterification, methylation, mixed cellulose esters, elemental analysis, titration.

3.2.1 Introduction

Long chain cellulose esters (LCCE) are known for their present and potential applications such as thermoplastics [1], selective lipophilic filters [2], or the preservation of wood [3]. The accurate characterization of LCCE is necessary as their properties depend directly on the length of the grafted acyl chain and on the degree of substitution (DS). High DS-values (> 1.5) are required when working with soluble or thermoplastic biopolymers [4,5], but when the hydrophobic character is the sole property considered, low DS-values are enough to attain this property: 0.10 for lipophilic filters [2], 6.10^{-3} for fluorinated derivatives [6], or as low as 3.10^{-4} for cellulose oleates [7].

Numerous techniques permit to characterize the DS of cellulose esters. Namely: saponification followed by titration of the alkali excess [8,9], elemental analysis [10], NMR [11], NIR [12], alkaline hydrolysis followed by the derivatization of the liquid products to be analyzed by gas chromatography (GC) [13], alkaline hydrolysis followed either by capillary electrophoresis [14] or by reversed-phase liquid chromatography [15], and finally pyrrolidinolysis followed by GC analysis [16].

Elemental (C, H, O) analysis can be used for 1 or 2 different acyl substituents. For 2 or more different substituents, only the cleavage of the ester bonds and subsequent chromatographic analysis is useful. Among them, the pyrrolidinolysis in pyridine method [16] is effective but the standards (1-acylpyrrolidines) are not commercially available. Another method for mixed cellulose esters comprises alkaline hydrolysis, acidification, extraction by an organic solvent of the fatty acids and derivatization prior to GC/MS analysis [13]. Uncertainty is inherently increased due to the numerous steps, in particular the extraction, which needs to be quantitative. This is particularly difficult, especially in the case of LCCE with low DS. Finally, the methods consisting in hydrolysis of the cellulose ester followed by acidification and capillary electrophoresis [14], or by reversed phase HPLC [15] present a limited number of steps but do not permit to analyze carboxylic acids with aliphatic chains superior to C4 because of their insolubility in acidified water. Moreover capillary electrophoresis and reversed phase HPLC may cause significant uncertainties in the case of very low DS due to the detection threshold of classic detectors [14].

In this paper we report a new analytical method for LCCE, which is able to determine DS-values in the whole range. It is accurate and easy to employ with a pre-settled chromatographic analysis. Our endeavor was focused to adapt a known

method of lipids characterization [17,18]. It consists in the transesterification of the esters functions of LCCE with trimethylsulphonium hydroxide (TMSH) using *tert*-butyl methyl ether (MTBE) as a solvent followed by GC analysis of the transesterified acyl compounds.

3.2.2 Experimental

3.2.2.1 Chemicals and standards

Octanoic (C8:0), capric (C10:0), lauric (C12:0), myristic (C14:0), palmitic (C16:0), stearic (C18:0) and oleic acids (C18:1) 99% purity were all purchased from Sigma-Aldrich France. Pentadecanoic acid (C15:0) was used as internal standard (I.S.) and was obtained from Fluka France (99% purity). Alpha-cellulose from Sigma-Aldrich France was the initial biopolymer (degree of polymerization of 960, 4% pentosans). Octanoyl, caproyl, lauroyl, myristoyl, palmitoyl, stearoyl and oleoyl chlorides were purchased from Acros France with a purity of at least 95% (reagent grade). Anhydrous pyridine was purchased from Sigma-Aldrich France and used as received. Trimethylsulphonium hydroxide (TMSH) was obtained from Macherey-Nagel France as a 0.2 mol.L^{-1} solution in methanol. *Tert*-butyl methyl ether (MTBE) HPLC grade was purchased from Scharlau Spain. All the chemicals were stored at 4°C.

3.2.2.2 Synthesis of model LCCE

Long chain cellulose esters with different DS were synthesized by reaction with fatty acid chlorides in a pyridine medium according to a previously described method [19]. Cellulose (10 g) was stirred in excess pyridine (250 mL) at 20°C for 30 min in order to swell cellulose and to increase its reactivity. The desired amount of fatty acid chloride was poured into the reactor and reflux was conducted at 130°C with mechanical stirring. A dry nitrogen bubbling flow was used to withdraw from the reactor the HCl formed during the synthesis. In order to obtain LCCE with different DS-values, the reaction time and the quantity of fatty acid chlorides were varied. After cooling at around 80°C, 250 mL of 50% aqueous ethanol was added to consume the residual acid chloride. The solid product was recovered by filtration over sintered glass and then thoroughly washed with ethanol. Purification was carried out by Soxhlet extraction for 16 h with ethanol. The cellulose ester was dried at 70°C under vacuum to constant weight and stored in a desiccator at room

temperature. Fatty acid chlorides with chain lengths from C8 to C18 where used in order to obtain different kinds of LCCE samples.

3.2.2.3   *Preparation of model standards of LCCE with very low DS*

Standard samples of LCCE with very low DS were prepared by mixing unmodified cellulose and a known cellulose ester as explained below. With this solid/solid dilution procedure, it was possible to calculate *DS'*, the apparent DS-value of the mixture. The principle of this dilution is completely "transparent" to the DS determination. For instance, the method cannot distinguish a sample of cellulose ester with $DS = 0.1$ from a sample consisting in a mixture of p grams of a sample with $DS = 1$ accompanied by q grams of cellulose provided that the total number of ester moles divided by the total number of anhydroglucose units be 0.1.

Cellulose and a LCCE with known DS were oven-dried overnight at 103°C and cooled in a desiccator to ensure the preparation of mixtures on a dry weight basis.

Solid-solid dilution: m_x grams of LCCE and m_o grams of cellulose, precisely weighed, were frozen with direct addition of liquid nitrogen to avoid aggregation. They were mixed in a high speed lab grinder. Calculation of the apparent DS (*DS'*) of the diluted LCCE was done with the formula:

$$DS' = \frac{162.14 \times m_x \times DS_i}{162.14 \times m_x + m_o \times [DS_i \times (M_i - 18.02) + 162.14]}$$

where:
DS_i: DS-value of the known LCCE
m_x: mass of LCCE (in grams)
M_i: molar mass of the RCOOH fatty acid
m_o: mass of cellulose added to the mixture (in grams)

Mixing/grinding was performed during 3 minutes and repeated 5 times with addition of fresh liquid nitrogen between each step. Since condensation of water undoubtedly occurred, the final powder was oven-dried at 103°C. The dilution process was repeated by using the most recently prepared standard as the known LCCE to be diluted with unmodified cellulose. By this manner, we could prepare standard mixtures with *DS'* ranging between 5.10^{-2} and 5.10^{-5}.

3.2.2.4 DS determination by elemental analysis

LCCE were vacuum dried during 48 h at 70°C prior to elemental (C, H) analysis. The equations obtained by Vaca-Garcia et al [10] were applied to convert %C and %H in DS-values. Three replicates of each sample were analyzed and unmodified cellulose sample used as a blank.

3.2.2.5 DS determination by alkaline hydrolysis and titration

0.5 g of LCCE sample was stirred for 30 min in 40 ml of aqueous ethanol (70%). 20 ml of a 0.5 N NaOH aqueous solution was added and the stirring was continued for 48 h at 60°C. The unreacted NaOH was back-titrated with 0.5 N aqueous HCl. The solid was recovered by filtration over 0.45 μ PTFE membrane and thoroughly washed with deionized water and ethanol, then oven-dried at 50°C for 48 h. The absence of ester functions in the saponified solid was confirmed by FTIR spectroscopy. The degree of substitution was then calculated as:

$$DS = \frac{162.14 \times [(VN_S - VN_B) \times N_{NaOH} - (VH_S - VH_B) \times N_{HCl}]}{m - [(VN_S - VN_B) \times N_{NaOH} - (VH_S - VH_B) \times N_{HCl}] \times (M_x - 18.02)}$$

where VN_S and VN_B represent the accurate volumes (mL) of NaOH solution added to the sample and to the blank respectively; N_{NaOH} and N_{HCl} are the normality of NaOH and HCl solutions; VH_S and VH_B are the volumes (mL) of HCl solution added to the sample and to the blank respectively; M_x is the molar mass of the RCO-grafted acyl residue and m is the mass of the dry sample in grams. 162.14 is the molar mass of the anhydroglucose unit and 18.02 the molar mass of water.

3.2.2.6 DS determination by transesterification with TMSH and GC analysis

Sample preparation: For samples with $DS < 0.1$, a precise quantity between 10 and 20 mg of LCCE was introduced into a 2 mL vial. 500 μL of a 0.5 mmol.L^{-1} pentadecanoic acid (internal standard) in MTBE and 200 μL of TMSH were added. For samples with DS-values between 0.1 and 3, a precise quantity of about 10 mg of LCCE was introduced into a 2 mL vial with 1000 μL of a 5 mmol.L^{-1} pentadecanoic acid in MTBE and 400 μL of TMSH.

The vial was hot-stirred during 60 min in a VorTemp 56 shaking incubator set at 1 200 rpm and 75°C. The transesterification protocol yields fatty acid methyl esters

(FAME), cellulose, water, methanol and dimethylsulfide (Figure 3.1). Once the sample was cooled down and the solid decanted, the supernatant reaction mixture was analyzed by GC.
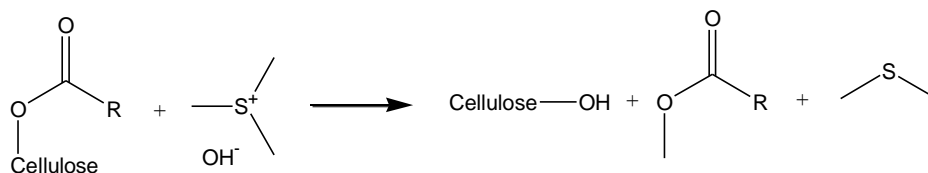
Figure 3.1 Transesterification of cellulose esters by trimethylsulfonium hydroxide

Gas chromatography: The GC analysis was carried out using a Varian 3900 gas chromatograph equipped with a Varian CP 8400 autosampler, a split/splitless injector and a flame ionization detector (FID). Separation was achieved in a CP-Select CB for FAME fused silica capillary column (CP7419, Varian) 50 m, 0.25 mm i.d., 0.25 μm film thickness. Helium was used as carrier gas at a flow rate of 1.2 mL.min^{-1}.
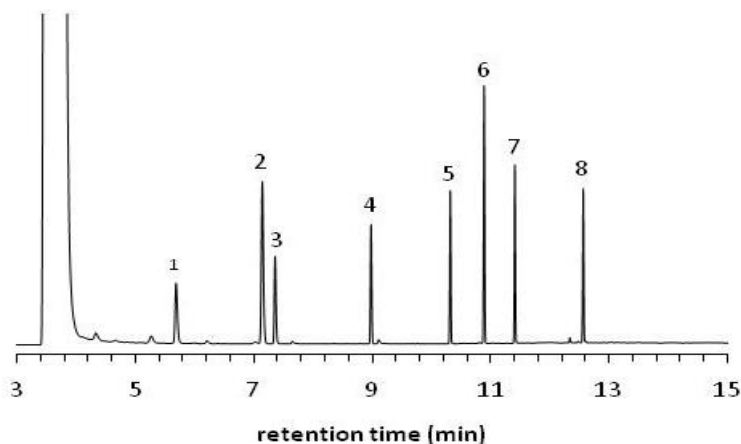
Figure 3.2 GC chromatogram of the analysis of saturated fatty acid standards methylated with TMSH in MTBE: (1) C8:0 (2) dimethylsulfide, (3) C10:0, (4) C12:0, (5) C14:0, (6) C15:0 (internal standard), (7) C16:0, (8) C18:0.

Chromatographic parameters were optimized by using a model mixture of saturated fatty acids that underwent the same reaction protocol and subsequent analysis (Figure 3.2) and resulted in the following conditions: The temperature of the injector used was set at 260°C and the split ratio at 1:20 for samples with DS

inferior to 0.1 and at 1:100 for samples presenting a DS between 0.1 and 3. The oven temperature was programmed as follows: 110°C for 4 min, then rise to 230°C at a rate of 15°C.min^{-1}, then 230°C for 7 min. This enabled the separation of the corresponding FAME within 19 min. Gas flow rates in the detector were set at 25, 30, and 300 mL.min^{-1} respectively for helium, hydrogen and air. The temperature of the FID detector was set at 260°C. A syringe of 10 µL was used for 1 µL injection of each sample and standard solutions.

DS calculation:

$$DS_i \ (TMSH/GC) = \frac{162.14 \times C_i \times V_s}{m - C_i \times V_s \times (M_i - 18.02)}$$

C_i: concentration of the FAME in MTBE after transesterification determined by GC (in mol.L^{-1})
V_s: volume of internal standard solution added to the analyzed sample (in L)
m: mass of the LCCE sample (in g)
M_i: molar mass of the RCOOH fatty acid

3.2.3 Results and discussion

3.2.3.1 Optimization of reaction parameters

Chromatographic conditions were optimized for the separation of FAME presenting aliphatic chain length equal or superior to C8. The protocol given in the experimental section is the result of the optimization (not discussed here). Figure 3.2 shows the optimized chromatogram of the separation of the selected C8-C18 FAME and methyl pentanoate (coming from the internal standard). We also analyzed commercial mixtures of FAME used generally to calibrate GC columns and obtained a perfect separation of all the FAME, from C8 to C22 with or without unsaturations.

Based on state-of-the-art data, experimental conditions were optimized for the DS determination of LCCE. The optimal stoichiometric ratio of TMSH reagent to the total ester functions has been reported to be 2:1 for the analysis of butter and fatty acids [17,18]. We first investigated the effect of the quantity of TMSH added to analyze a fully substituted sample, i.e. cellulose trioctanoate with $DS = 2.9$. We added to 10 mg of LCCE sample 1000 µL of pentadecanoic acid I.S. (5 mmol.L^{-1}) and various quantities of TMSH: 125 µL (molar ratio 1:1), 250 µL (ratio 2:1), and

500 µL (ratio 4:1). An internal standard calibration procedure was performed. Three replicates for each molar ratio and three GC injections for each sample were done to estimate respectively the reproducibility and repeatability. These two concepts will be discussed later. In the following tables, the average and standard deviation of the 9 results will be presented. Transesterification was performed in the incubator set at 1 200 rpm and 75°C during 180 min. For comparison, the DS of the sample was also determined by the elemental analysis, the titrimetry and the NMR methods.

When TMSH was used in excess (2:1), the nine DS-values obtained by the transesterification method (3 samples x 3 analyses) were sensibly identical (2.865 ± 0.128 std deviation, i.e. 4.4%). Similar values were obtained for the 4:1 ratio. This robustness has been reported for the analysis of lipid samples [17]. The mean *DS* obtained for the cellulose trioctanoate was equivalent to the values obtained by elemental analysis and titrimetry (only 1.2% and 3% of relative variation respectively). On the contrary, ^{1}H NMR analysis performed on a 500 MHz Bruker spectrometer did not permit to determine a reproducible (nor valid) DS-value from 3 analyses of one single sample (3.12 ± 0.652). The reason is a big uncertainty in the integration of the 7 hydrogen atoms belonging to the anhydroglucose unit when 70% of the cellulose ester sample is represented by aliphatic side-chains.

For the 1:1 molar ratio of TMSH/cellulose trioctanoate, we observed an under-evaluation of the *DS* of 20% (*DS* = 2.3 instead of 2.9). The ratio of TMSH to acyl groups was therefore an important factor to assure the quantitative transesterification of the ester groups. It is so important to keep its value superior to 2:1. The temperature of the reaction was also fixed at 75°C for all the analyses described in this paper. Higher temperatures would have permitted to accelerate analysis but regular lab vials may not resist the over-pressure caused by the solvent.

The reaction time was also investigated. In the analysis of lipids described in the literature, few minutes are required at room temperature to complete the reaction. However, cellulose esters are not soluble in MTBE, making thus a solid/liquid reaction. We observed that 1 h instead of 3 h gave the same DS results. Lower reaction times may still be possible but we decided to privilege the robustness of the analytical method so that samples with different characteristics can be analyzed.

Finally, the stirring speed was investigated. When the stirring at 1200 rpm was turned off, *DS* was under-estimated by 11% compared to elemental analysis and titration techniques.

In conclusion, an excess of TMSH is recommended (see section 2.6 for exact quantities) reacted during 1 h at 75°C with stirring set at 1 200 rpm. These were the conditions that have been chosen as optimal for the analysis of the LCCE described in this study.

3.2.3.2   Comparison with other techniques

Samples of LCCE with various fatty chain lengths and degrees of substitution were synthesized and analyzed in order to evaluate the accuracy and efficiency of the TMSH/GC method over a wide range of parameters compared to other techniques. As indicated in Table 3.1, we synthesized LCCE with six different fatty chain lengths from C8 to C18:1 and characterized each sample using elemental analysis, titrimetry and TMSH/GC. NMR analysis was not utilized since the samples with medium and low DS are not soluble in classic solvents.

Sample	Aliphatic chain grafted	Synthesis		DS-values[a]		
		RCOCl/OH molar ratio	Time (h)	Titrimetry[b] $\pm$ σ	Elemental analysis[b] $\pm$ σ	TMSH/GC[b,c] $\pm$ σ
A	C8	0.5	2	0.419 ± 0.096	0.490 ± 0.021	**0.468** ± 0.012
B	C8	1	2	1.675 ± 0.053	1.850 ± 0.018	**1.875** ± 0.093
C	C8	2	2	2.782 ± 0.219	2.900 ± 0.011	**2.865** ± 0.128
D	C10	0.5	2	0.482 ± 0.103	0.472 ± 0.021	**0.485** ± 0.014
E	C12	0.5	3	0.689 ± 0.077	0.632 ± 0.016	**0.629** ± 0.019
F	C12	1	3	1.672 ± 0.173	1.862 ± 0.036	**1.879** ± 0.091
G	C14	0.5	3	0.110 ± 0.062	0.235 ± 0.073	**0.207** ± 0.008
H	C16	0.5	2	0.071 ± 0.040	0.099 ±0.057	**0.127** ± 0.002
I	C18:0	0.5	3	0.401 ± 0.076	0.428 ± 0.004	**0.415** ± 0.009
J	C18:0	1	3	1.712 ± 0.098	1.700 ± 0.029	**1.682** ± 0.096
K	C18:1	0.5	3	0.195 ± 0.028	0.267 ± 0.008	**0.289** ± 0.007

Table 3.1 Degrees of substitution determined by transesterification using titrimetry, elemental analysis, and TMSH/GC.

[a] Average and standard deviation values
[b] Samples analyzed in triplicates
[c] GC injections made in triplicates

Titrimetry presented DS-values (Table 3.1) with important standard deviations (e.g. $DS = 2.782 \pm 0.219$) and especially when DS-values were low (e.g. $DS = 0.071 \pm 0.04$, i.e. more than half of the value). The comparison of the results obtained by titrimetry and by TMSH/GC analysis is shown in Figure 3.3.
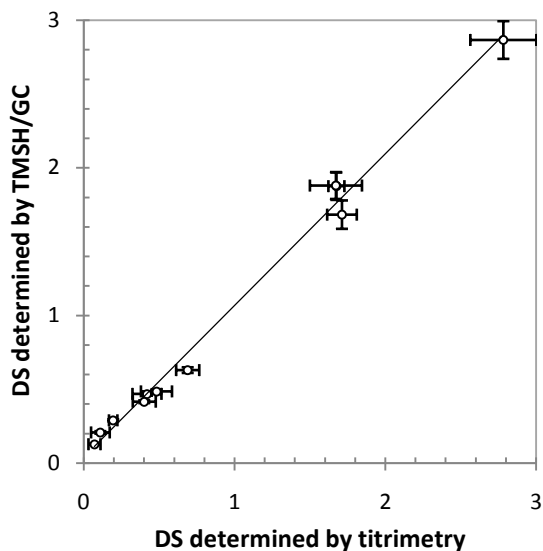
Figure 3.3 Comparison of the DS obtained by TMSH/GC and titrimetry.

The coefficient of correlation (R^2) was 0.9922. We observed that DS-values obtained by titrimetry were often, but not systematically, lower than those obtained with the TMSH/GC method. In contrast, there was no significant difference between the results from TMSH/GC and elemental analysis ($R^2 = 0.9995$) in this range of DS, (Figure 3 4).
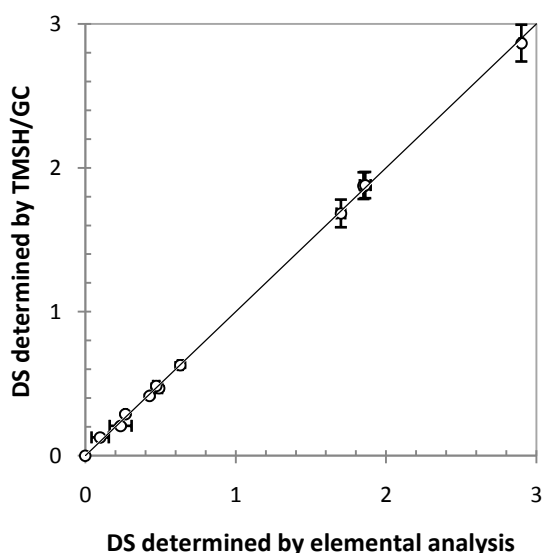
Figure 3 4 Comparison of the DS obtained by TMSH/GC and elemental analysis.

Nevertheless, according to the standard deviation values shown in Table 3.1, the TMSH/GC method was less accurate than elemental analysis for the samples with DS superior to 1. For instance, sample **C** shows $DS = 2.9 \pm 0.128$ with the TMSH/GC method and a standard deviation of only 0.011 when determined by elemental analysis. This could be due to the fact that for high DS-values, the relative proportion of cellulose backbone in the sample is low, for instance in the case of sample **C** it is only 30%. As this value is represented by the denominator in the formula for the DS calculation, the uncertainty in the result of the calculation increases. Nevertheless, in a relative scale (standard deviation / mean value), it does not exceed 5%. We must also consider that in some cases, the aspect of the sample can play an important role in the accessibility of the reagent to the ester groups in the biopolymer. Highly substituted samples have a rather plastic aspect and, in general, analytical techniques based on hydrolysis of the ester groups are not appropriated for this kind of samples. This is the case for example of pyrrolidinolysis [16].

Conversely, for the samples with low DS-values, the TMSH/GC method was more accurate than elemental analysis. For instance, sample **H** shows $DS = 0.127 \pm 0.002$ with the TMSH/GC method and a standard deviation of 0.057 when determined by elemental analysis. The reason is that the calculation of the DS based on elemental analysis is highly sensitive on the accuracy of the elemental analysis results. For very low DS, as indicated by Vaca-Garcia et al., a small divergence of the measure will have a big impact on the DS-value. Furthermore, we could demonstrate that elemental analysis is dependent on the material and the conditions of analysis. We made two series of analyses with one week of interval of one control homogenous sample. The standard deviation of the three replicates of each series was much the same, but the two averages showed a difference of 4.5%. This is probably due to a presumed disparity on the calibration of the apparatus for each series. This clearly indicates that the analyses of the samples by elemental analysis are repeatable but lack of reproducibility. A positive fact for the TMSH/GC determination is that the analysis of the same sample with two different GC calibrations and internal standard solutions showed a global difference of less than 2% for the $0.1 \leq DS \leq 1$ range. The TMSH/GC is therefore repeatable and reproducible.

3.2.3.3   Accuracy for LCCE with very low DS

In order to assess the accuracy of the method on LCCE samples with low and very low DS, we performed the analysis of model mixtures prepared by solid/solid dilution as described in the experimental section. Calculated apparent *DS* from the dilutions (*DS'*) and DS-values determined by TMSH/GC are indicated in Table 3.2.

| Sample | | Mixing | | | DS' | DS TMSH/GC | σ | rv (%) |
		m_x (g)	x	m_o (g)				
E1	C12	0.7654	E	5.7645	$4.54.10^{-2}$	$\mathbf{4.43.10^{-2}}$	$1.2.10^{-3}$	-2.4
E2	C12	0.6397	E1	4.5159	$5.39.10^{-3}$	$\mathbf{5.43.10^{-3}}$	$1.5.10^{-4}$	0.7
E3	C12	0.6408	E2	5.2348	$5.85.10^{-4}$	$\mathbf{5.48.10^{-4}}$	$1.8.10^{-5}$	-6.3
E4	C12	0.5693	E3	5.345	$5.63.10^{-5}$	$\mathbf{4.79.10^{-5}}$	$1.9.10^{-6}$	-14.9
I1	C18:0	0.7783	I	5.6144	$3.17.10^{-2}$	$\mathbf{3.04.10^{-2}}$	$7.6.10^{-4}$	-4.1
I2	C18:0	0.7693	I1	4.9872	$4.05.10^{-3}$	$\mathbf{3.79.10^{-3}}$	$1.7.10^{-4}$	-6.4
I3	C18:0	0.7294	I2	5.2492	$4.92.10^{-4}$	$\mathbf{4.48.10^{-4}}$	$2.0.10^{-5}$	-8.9
I4	C18:0	0.4973	I3	4.9857	$4.46.10^{-5}$	$\mathbf{4.06.10^{-5}}$	$2.7.10^{-6}$	-8.9

Table 3.2 Degrees of substitution determined by transesterification using TMSH and gas chromatography analysis. Samples analyzed in triplicate and injected in triplicate also. σ: standard deviation; *rv*: relative variation.

There was an excellent correlation between the *DS* determined by TMSH/GC and those estimated by dilution ($R^2 = 0.9998$). *DS* as low as 5.10^{-5} could thus been determined accurately.

The comparison could not be done with elemental analysis for LCCE with DS-values lower than 0.1. The sensitivity to error was too high and some elemental analyses gave even negative DS-values. As it can be deducted from Table 3.2, TMSH/GC gave good reproducibility even if for very low DS-values, the relative variation tends to increase (e.g. sample **E4** presented a relative variation of 14.9%). Nevertheless, for all the four samples analyzed, the chromatogram was perfectly defined and the signal levels far from the detection threshold of the chromatograph integrator as it can be seen in Figure 3.5 for the chromatogram obtained from sample **E3** (*DS* = $5.48.10^{-4}$).
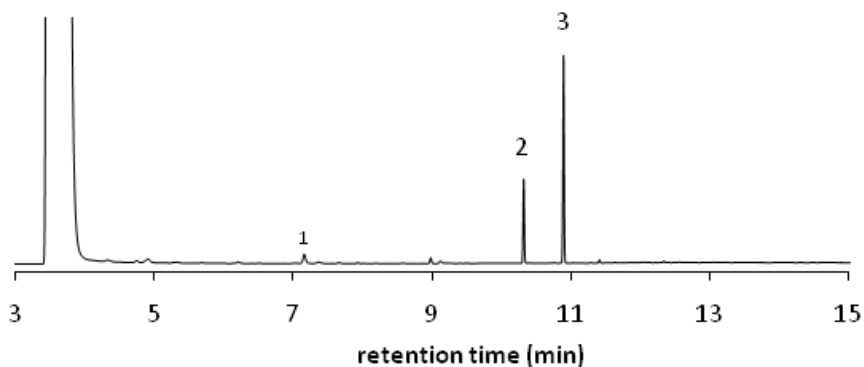
Figure 3.5 GC chromatogram of the analysis of laurate cellulose ester (sample E) (1) dimethylsulfide, (2) methyl myristate, (3) methyl pentadecanoate (internal standard).

Therefore, it is believed that the uncertainty generated during the dilution steps (grinding, mixing…) may create heterogeneity. As this effect increases with the consecutive dilutions, there is an increase in the relative variation of the measured *DS* of the replicates.

Figure 3.6 shows graphically the correlation between the expected results of DS and those determined by TMSH/GC analysis for the **E** and **I** samples ($R^2 = 0.99973$). The high accuracy (low detection threshold) for the method on the analysis of cellulose esters with very low DS is thus demonstrated.

Figure 3.6 Comparison of the DS-values determined by TMSH/GC and those calculated for solid/solid diluted mixtures for the sample E (squares) and I (circles).

The robustness of the TMSH/GC method was finally investigated by repeating the analysis several times taking a different mass of samples **I3** and **I4** for each analysis.
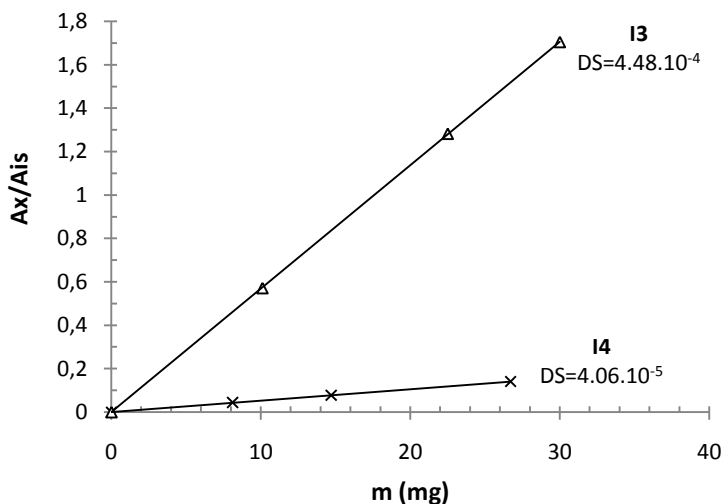
Figure 3.7 Relative area of the analyzed FAME peak in GC for samples I3 and I4 as a function of the mass of LCCE analyzed.

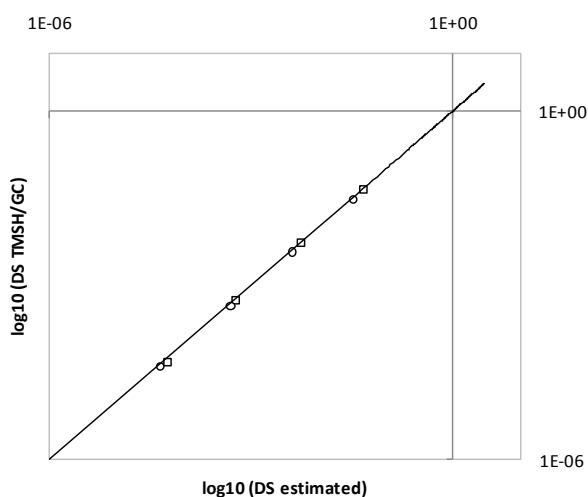Figure 3.7 shows the peak area of the FAME in the chromatogram (normalized to the internal standard) as a function of the mass of the analyzed sample. It is clearly observed that there is no influence of the quantity of the analyzed sample (provided that the molar ratio of TMSH is 2 or higher, as demonstrated above). Therefore, the TMSH/GC method shows a good reproducibility as all the points stand along the line with a coefficient of correlation R^2 of 0.9997 for the sample **I4** with a $DS = 4.06.10^{-5}$ and $R^2 = 0.9999$ for sample **I3** with $DS = 4.48.10^{-4}$.

3.2.3.4   Perspectives

The fact that the chromatographic analysis is able to evaluate the individual concentration of different FAME opens the possibility for the proposed method to analyze mixed cellulose esters of the studied fatty acids. Indeed, Figure 3.2 shows the clear separation of all the chromatographic peaks, therefore any combination of them is possible to analyze. The calculation of the individual DS-values becomes in this case:

$$DS_i \ (TMSH/GC) = \frac{162.14 \times C_i \times V_s}{m - V_s \times \sum_{j=1}^{n} C_j \times (M_j - 18.02)}$$

C_j: concentration of each FAME in MTBE after transesterification determined by GC in $mol.L^{-1}$

n: number of fatty substituents on cellulose

M_j: molar mass of each RCOOH fatty acid

The analysis of other mixed esters (for instance acetic-stearic) is possible provided that the GC separation of the involved methyl fatty acid esters is good, which has not been the case with the present protocol because the chromatographic peak of short aliphatic chains has similar retention time with the solvent peak.

3.2.4   Conclusions

The TMSH/GC method, established in this study, constitute an easy and accurate method for the determination of the degree of substitution of long chain cellulose esters over a range of saturated fatty chain lengths from C8 to C18 and over the whole of DS. LCCE with higher fatty chain lengths can potentially be analyzed by this method, provided that the reaction time and the TMSH:acyl ratio is optimized. This method could also be interesting and efficient in the analysis of cellulose mixed esters presenting more than one acyl substituent. Compared to other methods, TMSH/GC is the only method permitting a complete analysis of a sample multi-substituted in less than 2 hours. For samples with high DS-values (superior to 1), elemental analysis is more precise in terms of repeatability than the TMSH/GC technique but not in term of reproducibility. When *DS* is inferior to 1, the TMSH/GC method is more accurate than elemental analysis. The key point of this method is the fact that LCCE esters with degrees of substitution inferior to 0.1 and up to 10^{-5} are able to be analyzed with high accuracy and reproducibility. This is the first time that such cellulose esters have been analyzed with such precision.

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3.3 Mixed acetic-fatty cellulose esters with extremely low fatty degree of substitution. Part I. Synthesis

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Abstract

The global reaction between acetic anhydride and a fatty acid yields at equilibrium a mixture of five compounds: acetic-fatty anhydride, acetic anhydride, fatty acid, acetic acid and fatty anhydride. Mixed cellulose esters (MCE) with very low total degree of substitution ($DS_{total} < 0.1$) were obtained by reaction of this mixture with cellulose without solvent or catalyst. Based on new analytical protocols, the very low DS for acetyl groups ($DS_2 < 0.1$) and the extremely low DS for fatty acyl groups ($DS_f < 2.10^{-3}$) could be determined with high accuracy. The influence of temperature, molar ratio, reaction time, and length of the fatty chain on the DS and on the ratio of grafted acetyl/fatty acyl was investigated.

Keywords: Very low DS, mixed cellulose esters, acetyl content determination, uncatalyzed reaction, acetic-fatty esters.

3.3.1 Introduction

Cellulose esters are well known polymers that, after many years of research and industrial use, still present a high potential for future applications considering their abundant renewable resource and their physical and chemical properties. Many innovative ways of synthesis are continuously developed [1].

Applications for cellulose esters include pharmaceuticals, tow, textiles, plastics, coatings and photographic products. Cellulose acetates are by far the most studied and developed at industrial scale [2]. They are thermoplastic, soluble in organic solvents, and potentially biodegradable [3].

Mixed cellulose esters (MCE), i.e. substituted by different aliphatic chains, are polymers with interesting properties. Nevertheless, only cellulose acetate-propionate (CAP), and cellulose acetate-butyrate (CAB) are of significant industrial importance, especially for thermoplastic applications since they present lower melting points than cellulose acetate [4]. Cellulose acetate-phtalates are used for coating applications but they are of lesser industrial importance [4]. Research on other mixed acetic-aliphatic cellulose esters have led to discover polyfunctional materials combining good mechanical properties and high hydrophobicity [5].

The preparation of MCE can be made in two steps, usually acetylation first, then the other substituent; e.g.: reaction with butyric or hexanoic anhydrides [6] or maleic anhydride [7]. Some authors have used commercial cellulose acetate as starting material [4]. Occasionally, the order of the reaction is inversed: first an aliphatic ester is prepared and then it is peracetylated with acetic anhydride, but essentially for analysis purposes [8,9].

One-pot reactions for the preparation of MCE are simpler in the process but more complex regarding the multiplication of reactions taking place between the acylating agents [10].

A first method employs mixtures of two anhydrides. This is the case of the industrial preparation of CAP and CAB [4] or the laboratory preparation of acetic-lauric and acetic-caproic cellulose esters [11].

Another procedure uses trifluoroacetic anhydride as co-reagent and a mixture of two different carboxylic acids to form *in situ* mixed anhydrides (trifluoroacetic-aliphatic or aliphatic-aliphatic). The former are able to graft the aliphatic chain without grafting the fluorinated moiety, whereas the latter can graft either of the

aliphatic moieties [12]. The same technique has also been used for the synthesis of various mixed esters of starch (Yang and Montgomery 2008).

Finally, the third procedure consists in the acylation of cellulose with mixed acetic-aliphatic anhydrides fabricated *in situ* by reaction between acetic anhydride and a carboxylic acid [5,13,14]. By this means, either of the moieties of the asymmetric anhydride is grafted to the cellulose. This technique has also been applied for the acylation of lignocellulosics, in particular wood [15,16].

Besides, it is commonly accepted that the modification of the intrinsic properties of cellulose with a single substituent or with multiple acyl groups requires a high DS [17,18]. Nonetheless, we have previously reported that simple lowly substituted (*DS* < 0.15) cellulose esters appear to present interesting properties such as water repellency [19], or selective lipophilic adsorption ability [20]. In addition, the preparation of lowly substituted cellulose esters can be accomplished with reagents that are less reactive and less expensive than those used for the preparation of highly-substituted esters.

The aim of this paper is the preparation of lowly substituted MCE obtained by reaction between cellulose and mixed acetic-aliphatic anhydrides. Contrarily to previous studies, no solvent or catalyst will be used. By this manner, a double objective will be attained: to get information on the straight reactivity of mixed anhydrides towards cellulose and to synthesize directly the desired lowly substituted MCE. Moreover the degree of polymerization of cellulose should be less diminished thanks to the absence of acidic catalysts. The hydrophobic properties of these novel cellulose derivatives are described in the second part of this paper series [21].

3.3.2 Experimental

3.3.2.1 Chemicals

Acetic anhydride and carboxylic acids: propionic (C2:0), octanoic (C8:0), capric (C10:0), lauric (C12:0), myristic (C14:0), palmitic (C16:0), and oleic (C18:1) of 99%+ purity were purchased from Sigma-Aldrich France. Pentadecanoic acid (C15:0) was used as internal standard (I.S.) in gas chromatography and was obtained from Fluka France (99% purity). Alpha-cellulose from Sigma-Aldrich France was the initial biopolymer (degree of polymerization = 960, 4% pentosans, 7% moisture content). Trimethylsulphonium hydroxide (TMSH) was obtained from Macherey-Nagel France as a 0.2 mol.L^{-1} solution in methanol. *Tert*-butyl methyl ether (MTBE)

HPLC grade was purchased from Scharlau Spain. All the chemicals were stored at 4°C prior to use.

3.3.2.2   Preparation of the mixed acetic-fatty anhydrides

The appropriate amounts (molar ratio varying from 1:2 to 2:1) of fatty acid and acetic anhydride were added to a glass reactor equipped with a condenser. Reactions were carried out at 100°C with mechanical stirring at 500 rpm during 1 hour. The reaction mediums were analyzed by reversed-phase HPLC [22] and used without purification for the synthesis of MCE.

3.3.2.3   Synthesis of MCE

Reactions were performed in 50 mL reactors equipped with a condenser. 1 g of undried cellulose (7% moisture) was stirred at 350 rpm in 15 mL of reaction medium without catalyst at the desired temperature and duration time. After cooling down to about 80°C, 20 mL of ethanol were added to precipitate the soluble fraction. Cellulose esters were separated by filtration over fritted glass and purified by Soxhlet extraction with ethanol for 8 h. The purified product was then dried under vacuum at 70°C at least for 24 h and to constant weight.

DS determination

To our knowledge, there is no analytical technique that allows to determine simultaneously and accurately the DS of long and short substituents in MCE when DS is below 0.1. Consequently, we employed two different techniques. The first one was used to determine the fatty acyl content and the second one quantified the acetyl groups. The two analyses are required to evaluate the individual and total DS-values. Let us remember that the DS calculation requires knowing the number of moles of anhydroglucose units. These can only be calculated by substracting the mass of the fatty acyl and acetyl groups from the total mass of the sample.

Determination of the fatty acyl content

We employed the method based on the reaction of cellulose esters with TMSH followed by gas chromatography (GC) analysis. The conditions were those recommended for low DS values according to a recently published work [23]. The MCE sample is reacted in a vial with TMSH during 1 h at 75°C in MTBE as solvent. Once the sample is cooled down and the solid decanted, the fatty acid methyl esters

(FAME) are quantified by GC. From the GC analysis the concentration of fatty acyl groups C_f in solution can be determined.

Determination for the acetyl content

This is an original method based on saponification of the MCE followed by GC analysis.

Sample preparation: A precise amount of about 20 mg of MCE was weighed and introduced into a 2 mL vial. 1000 µL of aqueous sodium hydroxide (0.5 N) and 500 µL of a 0.5 mmol.L^{-1} propionic acid (internal standard) solution in water were added. The vial was stirred during 5 hours in a VorTemp 56™ Shaking incubator set at 1200 rpm and 100°C. The sample was cooled down and 45 µL of H_3PO_4 were added. The vial was stirred again at 1200 rpm during 10 min at room temperature. Once the solid was decanted, a small sample of the supernatant in the reaction mixture was analyzed by GC.

Gas chromatography: The GC analysis was carried out using a chromatograph comparable to those used for the TMSH/GC analysis. Separation was achieved in a CP-Select CB for FFAP fused silica capillary column (CP7845, Varian) 25 m, 0.32 mm i.d., 0.25 µm film thickness. Helium was used as carrier gas, at a flow rate of 2.6 mL.min^{-1}. The temperature of the injector was set at 250°C, the FID detector at 270°C, and the split ratio at 1:100. The oven temperature was programmed as follows: 80°C for 1 min then rise to 145°C at a rate of 20°C.min^{-1}, then 250°C for 2 min. This enabled the separation of the acetic and propionic acids in less than 12 min. From the GC analysis the concentration of acetyl groups C_2 in solution can be determined.

DS calculation

The DS values of the grafted fatty chain (DS_f) and of the acetyl chain (DS_2) are calculated as follows:

$$DS_f = \frac{162.14 \times C_f \times V_f}{m_f - \frac{m_f}{m_2} C_f \times V_f \times (M_f - 18.02) - C_2 \times V_2 \times 42.03}$$

$$DS_2 = \frac{162.14 \times C_2 \times V_2}{m_2 - C_f \times V_f \times (M_f - 18.02) - \frac{m_2}{m_f} C_2 \times V_2 \times 42.03}$$

where:

C_f: concentration of the FAME in MTBE determined by GC (in mol.L^{-1})

V_f: volume of internal standard (pentadecanoic acid) solution added to the analyzed sample (in mL)

m_f: mass of the MCE sample analyzed in MTBE with TMSH (in g)

M_f: molar mass of the RCOOH fatty acid

C_2: concentration of the acetic acid after saponification and acidification determined by GC (in mol.L^{-1})

V_2: volume of internal standard (propionic acid) solution added to the analyzed sample (in mL)

m_2: mass of the MCE sample analyzed in water (in g)

3.3.3   Results and discussion

3.3.3.1   Preparation of the reaction mediums

The reaction between acetic anhydride and a fatty acid consists in two consecutive and equilibrated reactions [10]. The first one yields acetic-fatty mixed anhydride plus acetic acid. The second one is the *in situ* reaction of the mixed anhydride with the carboxylic acids to yield symmetric anhydrides. Therefore, at equilibrium a mixture of acetic acid, acetic anhydride, acetic-fatty anhydride, fatty acid and fatty anhydride is obtained (Figure 3.8). For the sake of simplicity, we will refer simply to the main (first) reaction.
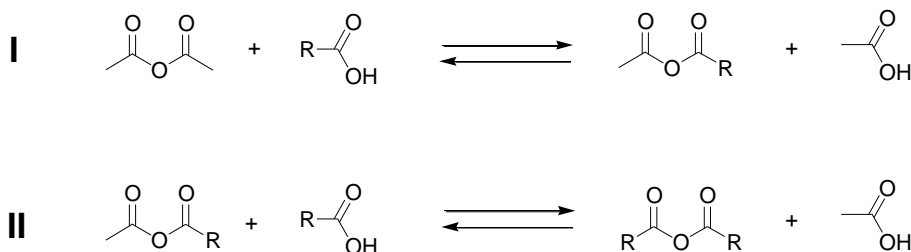
Figure 3.8 Consecutive reactions occurring when making react a fatty acid with acetic anhydride

Thus, the reaction between acetic anhydride and oleic acid was carried out at different ratios, comprised between 1:2 and 2:1. The molar ratio of reagents in this work has been defined as fatty acid/acetic anhydride. From the previous work cited above it is known that the equilibrium state is reached in less than 15 minutes at 100°C. All the mixtures were analyzed after 1 h of reaction to ensure the equilibrium

state. Table 3.3 shows the composition of different reaction mediums prepared from different proportions of reagents.

Molar ratio	% Acetic acid	% Acetic anhydride	% Oleic acid	% Oleic anhydride	% AOA
0.5	28.1	40.05	5.3	1.5	25.1
0.75	32.6	27.17	10.3	2.6	27.4
1	34.6	19.51	15.5	4.1	26.4
1.25	35.4	14.20	20.1	5.2	25.1
1.5	35.3	10.74	24.7	6.0	23.3
1.75	34.4	8.63	29.1	6.4	21.5
2	33.4	6.81	33.3	6.9	19.5

Table 3.3 Reaction mediums compositions (molar percentage) obtained at equilibrium from mixtures of oleic acid and acetic anhydride with molar ratio varying from 0.5 to 2

Among the five entities constituting the reaction medium, the concentration of acetic acid and acetic-oleic anhydride (AOA) were relatively constant: $33.4\% \pm 2.5\%$ and $24\% \pm 2.8\%$ respectively. The concentrations of the three other molecules were dependent on the molar ratio. Oleic acid and oleic anhydride molar concentrations are multiplied by about 6 when the molar ratio increases whereas the acetic anhydride concentration is divided by 6. Despite these differences in trend, the equilibrium constant calculated for every experiment showed little variation ($K = 2.48 \pm 0.17$). This value is perfectly consistent with the equilibrium constant previously reported (2.5) [10].

Oleic anhydride is formed from the consecutive equilibrated reaction (reaction II in Figure 3.8) between acetic-oleic anhydride and oleic acid. As the molar ratio increases, the excess of oleic acid increases and the equilibrium of the second reaction is shifted to the right favoring the formation of oleic anhydride. A part of the mixed anhydride reacts in the same proportion. That is the reason why its concentration is relatively constant in this series of experiments.

3.3.3.2   Synthesis of MCE

Due to the extremely low reactivity of carboxylic acids, especially in the absence of catalyst, only the three anhydrides present in the medium: acetic, acetic-oleic and oleic are expected to react with cellulose in order to form a mixed (acetic-oleic) cellulose ester (Figure 3.9).
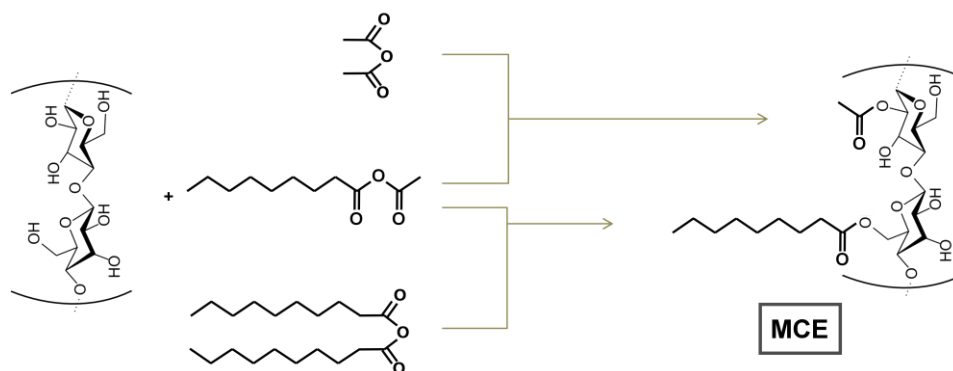
Figure 3.9 Esterification of cellulose treated by a mixture of acetic anhydride and a fatty acid

Figure 3.10 shows the evolution of the grafting yield as a function of the temperature. The reactions were conducted during 1 h and with a molar ratio of 1.5. The values of the degree of substitution of oleates ($DS_{18:1}$) and acetates (DS_2) obtained at 175°C were $3.9.10^{-4}$ and $7.1.10^{-2}$ respectively.
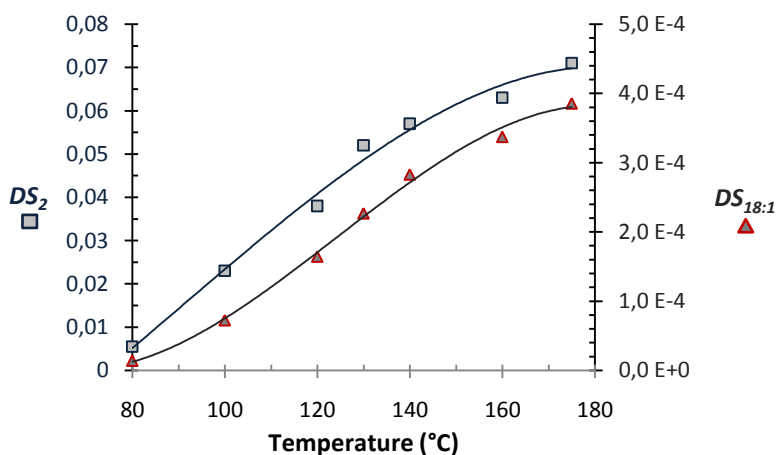
Figure 3.10 Influence of the temperature of the treatment on DS_2 and $DS_{18:1}$.
(treatment during 1 h, R=1.5)

The global DS value is low, especially when compared to the results obtained with the same system but under acidic catalysis [13] for which $DS_{total} > 2$. However, this value is not negligible because a DS_{total} of 0.06 corresponds to the esterification of about 2% of the hydroxyl groups in cellulose. Let us remind that we keep voluntarily the DS into low values. As it will be explained in the following article [21], such low DS_{total} values are able to modify the surface properties of cellulose.

The individual acetyl and oleoyl DS-values obtained at 160°C are around ten times and twenty times bigger than those obtained at 80°C. These results highlight the fact that the esterification reaction is strongly dependent on the temperature.

In order to confirm that these DS-values are not originated from residual reagents trapped in the structure of cellulose, we performed FTIR analysis of the solvent-extracted MCE. No characteristic band of the carboxylic acid was observed. Only the characteristic ester band was clearly seen. Moreover, the purification method was also validated by impregnating a sample of cellulose with the acylation mixture at room temperature followed by the same purification steps. The DS of this sample was null.

Besides, from these spectra, we calculated and plotted the IR index (Figure 3.11), defined as a quotient of transmission intensities: ester band at 1733 cm^{-1} divided by a constant band of cellulose at 1641 cm^{-1}. Intensities were measured from the base of the cellulose band, not from the absolute zero. The trend of this curve followed the same tendency than the DS curve (Figure 3.10). The flat line in Figure 3.11 represents the value of the IR index for untreated cellulose. It is interesting to note that both lines cross at a temperature of about 50°C. This would be the hypothetical temperature at which there is no reactivity between the anhydrides and the cellulose without catalyst. For comparison, let us remind that acetic anhydride reacts with cellulose in the presence of sulfuric acid at temperatures as low as 30°C in the cellulose acetate process.

Figure 3.11 IR index of solvent-extracted MCE after reaction at different temperatures.
(treatment during 1 h, R=1.5)

Even though Figure 3.10 may give the impression that the oleoylation and the acetylation follow parallel trends, in reality, the increase of the temperature causes an augmentation of the global grafting but with amplified proportions of fatty chains as shown in Figure 3.12. The substituents ratio DS_2/DS_f is divided by two passing from 389 at 80°C to 187 at 160°C.
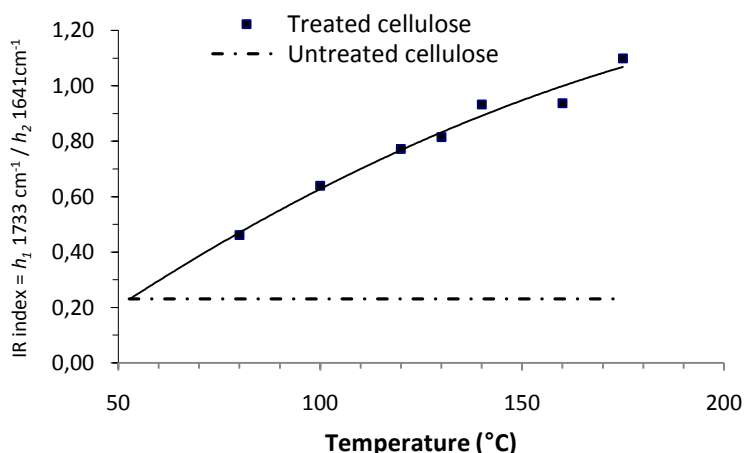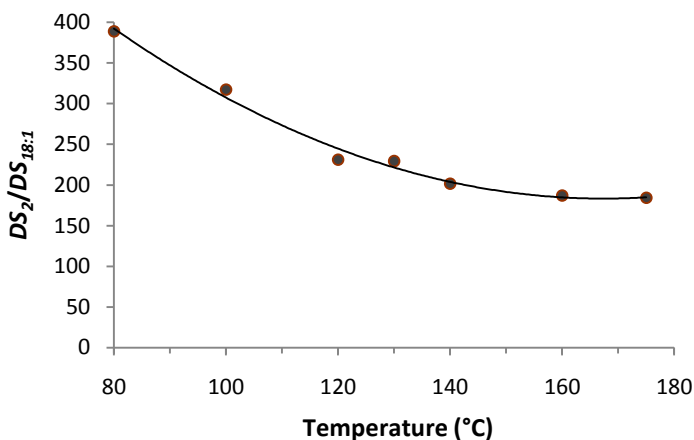

Figure 3.12 Influence of the temperature of the treatment on $DS_2/DS_{18:1}$ (treatment during 1 h, R=1.5)

In order to explain the diminishing of this ratio it would be reasonable to think that the composition of the reaction medium depends on the temperature, becoming richer in fatty anhydride when the temperature increases. Nevertheless, we demonstrated in a previous article [10] that the composition of the medium at equilibrium was practically independent of the temperature. In the present case, for the considered temperatures, the variation of the composition would be of only 3% maximum. In all the cases, this small variation cannot account for a decrease of 50% in the substituents ratio.

Another possible explanation for the diminishing of acetyl proportion with temperature could be that the vaporization of acetic anhydride and acetic acid, whose boiling points are respectively 116°C and 145°C, have also consequences on the reaction medium composition and displace the equilibrium. This does not seem to be the case because the decrease of the grafting ratio is bigger in the range 80-120°C where these compounds are preferably in the liquid phase. In the 120-175°C range, the compounds would be preferably in the vapor phase but it was observed that the ratio $DS_2/DS_{18:1}$ tends to a plateau.

A third hypothesis, the most probable, would be that the activation energy for the grafting of acetates is lower that for the grafting of oleates. At high temperature (175°C), the substituents ratio tends to reach a plateau and the number of acetyl groups remains about 200 times superior to the number of oleoyl groups. The steric hindrance of the fatty chain can account for such a difference; the acetyl group would present reasonably more ability to reach hydroxyl functions in the cellulose microfibrils.
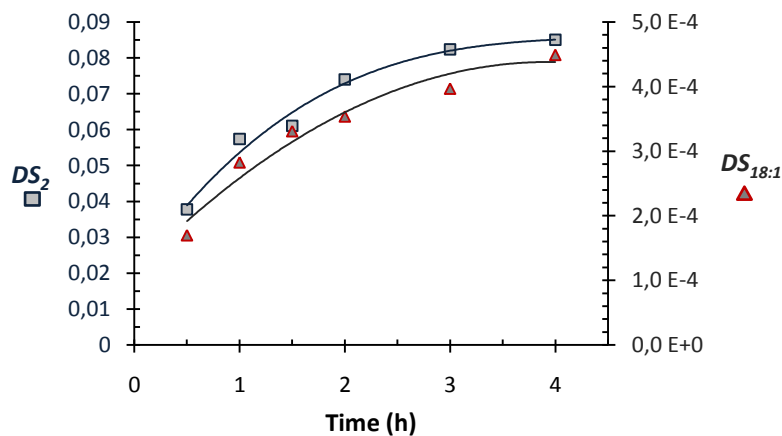

Figure 3.13 Influence of the duration time of the treatment on DS_2 and $DS_{18:1.}$ (treatment at 140°C, R=1.5)

Reaction time is also an important factor (Figure 3.13). In reactions with a mixture at a molar ratio of 1.5 at 140°C, the total DS increases rapidly and levels off after 3 hours. Since reactions involved 1 g of cellulose in 15 mL of equimolar reaction medium (5.9 eq anhydride / eq OH_{cell}), the total consumption of reagents (only the anhydrides) after 3 h is only about 1.3% due to the reaction with cellulose and 10% due to the hydrolysis by the water contained in the substrate (7%). Therefore we cannot attribute this leveling off to a lack of reactants. The weak reactivity of cellulose and the low accessibility of OH groups seem to be more involved. It is significant that the substituents ratio (acetate/oleates) remains constant at a value of about 200 during the whole duration of the reaction (Figure 3.14). This means that acetyl and fatty acyl have different reaction rates but they are not interdependent. The hypothesis formulated above concerning the energies of activation is backed up also by this fact.
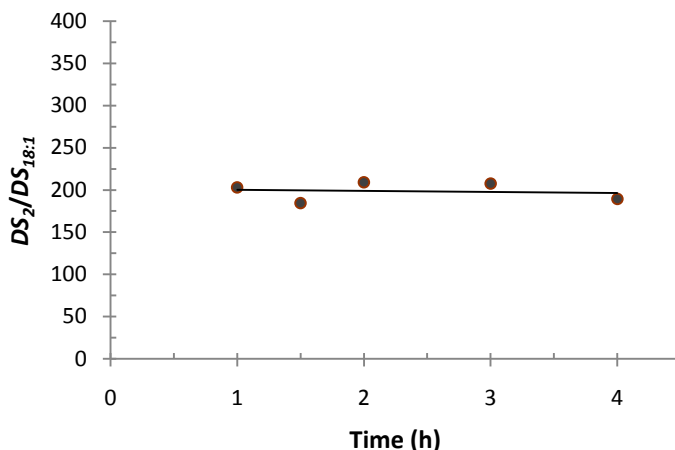
Figure 3.14 Influence of the duration time of the treatment on the ratio $DS_2/DS_{18:1}$ (treatment during1 h, R=1.5)

In the following series of experiments, the temperature and reaction time were kept constant (140°C, 1 h) and we only varied the reagents molar ratio for the synthesis of MCE. The plot of DS_2 and $DS_{18:1}$ as a function of the molar ratio shows an increase of oleates with the molar ratio accompanied by a decrease of acetates (Figure 3.15). In detail, when the molar ratio passes from 0.5 to 1, $DS_{18:1}$ is increased by 107% while DS_2 diminishes only slightly (- 5%). Furthermore, it is important to note that cellulose treated with pure acetic anhydride, i.e. a molar ratio of zero, presents a DS_2 of 0.072. Unsurprisingly, this value is much lower than those obtained under strong acidic catalysts in acetylation literature. The reactions with molar ratios between 0.5 and 1 yield also DS_2-values of the same order of magnitude (respectively 0.07 and 0.066). For the reaction mediums obtained with molar ratios superior to 1, we note an important decrease of DS_2 while $DS_{18:1}$ keeps on increasing. This does not mean that $DS_{18:1}$ will keep increasing with molar ratio because the content of reactive molecules (anhydrides) tends to diminish to reach eventually the value of 0 for an infinite molar ratio (pure oleic acid). The grafting of fatty chains is then null.

Figure 3.15 Influence of the molar ratio oleic acid / acetic anhydride used for the preparation of the mixture on DS_2 and $DS_{18:1}$. Treatment during 1 h at 140°C.

The ratio $DS_2/DS_{18:1}$ decreases when the molar ratio of reagents increases (Figure 3.16). The theoretical value of $DS_2/DS_{18:1}$ for a molar ratio of 0 (pure acetic anhydride) is infinite. This is why the decrease of its value is dramatic for molar ratios comprised between 0 and 1.
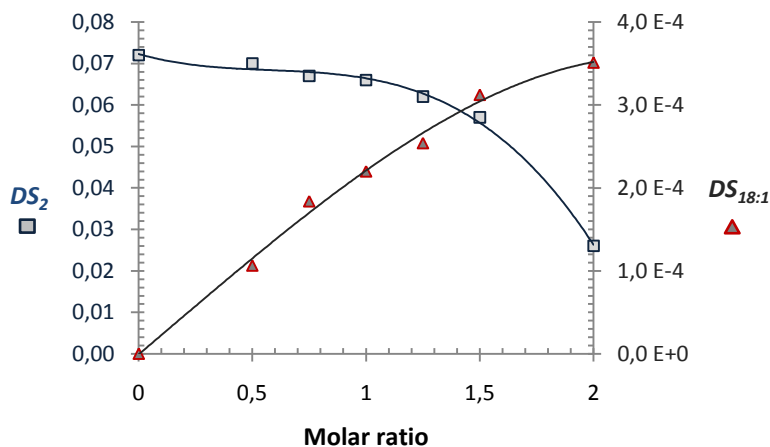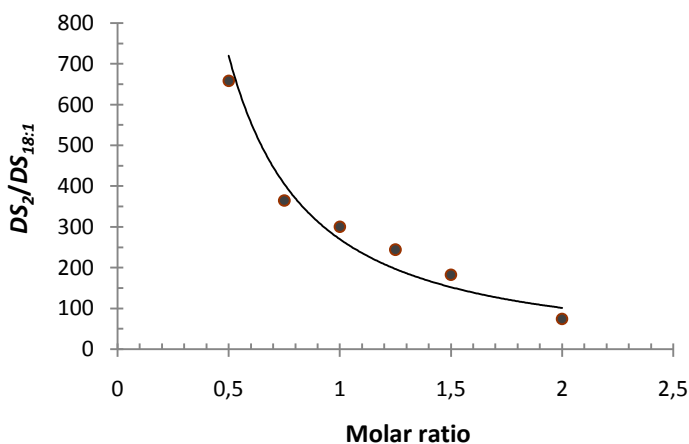

Figure 3.16 Influence of the molar ratio oleic acid / acetic anhydride used for the preparation of the mixture on the ratio $DS_2/DS_{18:1}$. Treatment during 1 h at 140°C.

Finally, we varied the nature of the fatty chain by preparing mixtures form acetic anhydride and different fatty acids bearing saturated aliphatic chains from C8 to C16 at a molar ratio of 1.5 (Table 3.4).

Fatty chain	% Acetic acid	% Acetic anhydride	% Fatty acid	% Fatty anhydride	% AOA
Octanoic (C8 :0)	25.20	17.25	20.18	10.72	23.76
Decanoic (C10 :0)	26.76	14.58	22.23	11.03	25.41
Lauric (C12 :0)	27.87	15.61	22.15	7.73	26.64
Myristic (C14 :0)	29.16	15.79	22.58	6.71	25.75
Palmitic (C16 :0)	29.80	17.48	24.10	5.95	22.67

Table 3.4 reaction mediums compositions (molar percentage) obtained at equilibrium from 1.5 molar ratio mixtures of fatty acids (C8 to C16) and acetic anhydride

The plot of DS as a function of the chain length (Figure 3.17) shows a decrease of the number of grafted fatty chains (DS_f) when the number of carbon atoms of the aliphatic chain increases. This can be explained by the steric hindrance encountered by the bigger molecules and by the presumed higher activation energy for the grafting of longer fatty chains.

Figure 3.17 Influence of the aliphatic chain length of the fatty acid used for the preparation of the mixture on DS_2 and DS_f. (treatment at 140°C during 1 h, R=1.5)

Conversely, DS_2 seems to keep roughly the same value but we can note a slight increase with the fatty chain length. At a first glance, this might be due to the higher reactivity of the mixed anhydride as it becomes more asymmetrical. Hence, it dissociates more readily to form an acyl R_1CO- group (reacting with cellulose) and a R_2COOH carboxylic acid (Figure 3.9). According to Arni et al.[24], R_2COOH is formed preferentially if its pK is lower than that of R_1COOH. They demonstrated this principle with trifluoroacetic- aliphatic (short chain) anhydrides, for which the

difference of pK values is quite big (0.5 vs 4.9). Thus, the cellulose esters prepared by Arni et al. did not show any grafted trifluoroacetic groups. In our case, the difference in pK between acetic acid (4.75) and the oleic acid (9.85) [25] is also big, but the values are much higher. Fatty acyl groups should be formed preferentially. Nevertheless they do not graft readily to cellulose because an important steric hindrance. An increase in the grafting ratio acetyl/fatty acyl is then observed (Figure 3.18).
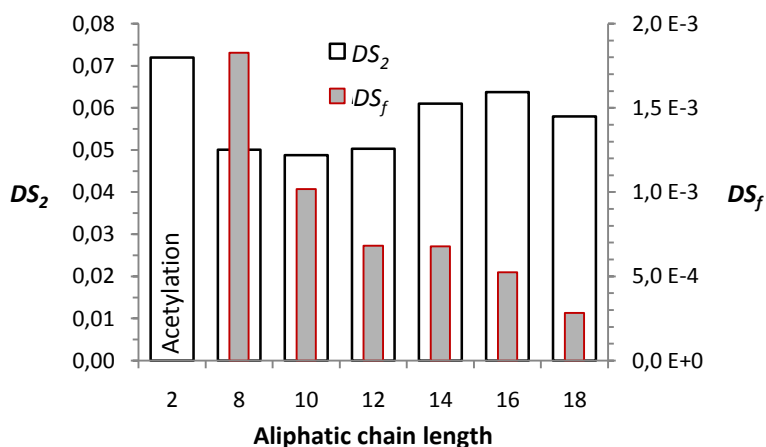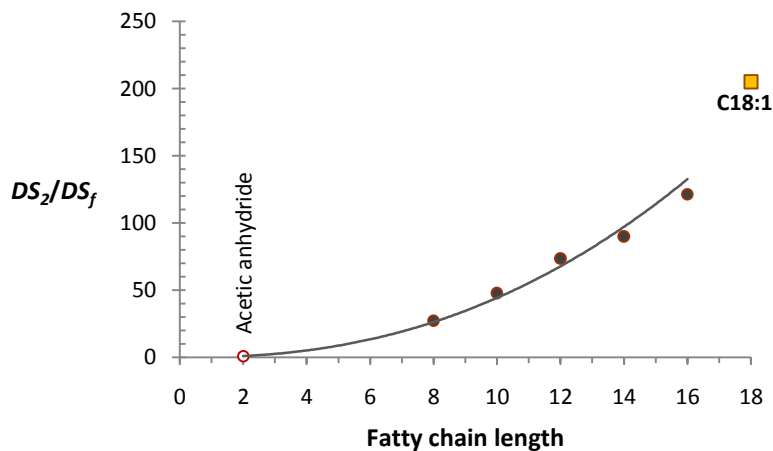

Figure 3.18 Influence of the aliphatic chain length of the fatty acid used for the preparation of the mixture on the ratio DS_2/DS_f . (treatment at 140°C during 1 h, R=1.5)

If the objective was to increase the proportion of fatty groups, the only possibility would be the increase of the reaction temperature. This would compensate the higher activation energy but it would never eliminate the bigger steric hindrance. The hydrophobic properties of these MCE will be presented in the second part of the paper [21].

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3.3.4   Conclusions

These investigations permitted to put in evidence that:

- Mixed cellulose esters bearing acetyl and fatty acyl groups can be synthesized by reaction of cellulose in a reaction medium prepared from acetic anhydride and a fatty acid.
- No catalyst or cellulose solvent is needed. However, the total degree of substitution remains in very low values ($DS_2 \geq 0.072$; $DS_f \geq 1.8.10^{-3}$).
- Thanks to new analytical protocols, the precise DS determination allowed the accurate characterization of the cellulose esters.
- The straight reactivity without catalyst revealed a high relative proportion of the acetyl to fatty acyl groups (from 27 to 659). This ratio can be controlled by an appropriate selection of the molar ratio of the initial reagents, by the nature of the fatty acid used for the preparation of the reaction medium and by the temperature of reaction. On the contrary, it cannot be controlled by the reaction time, this ratio being constant at all moments of the reaction.

The impact of the grafting on the affinity of cellulose with water is developed in the second part of this series of paper.

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3.4 Mixed acetic-fatty cellulose esters. Part II. Hydrophobicity

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Abstract

Cellulose powder was esterified with mixtures containing acetic, fatty and acetic-fatty anhydrides to form acetic-fatty cellulose esters. The total degree of substitution (DS) of the mixed cellulose esters (MCE) ranged between 2.10^{-2} and 2.92. MCE were characterized according to their interactions with water. Pellets were cold-molded to obtain a regular smooth surface and static contact angles (CA) with water were measured over 5 minutes. CA-values were dependent on the fatty acyl content and independent of the acetyl content. The minimum DS of the fatty acyl group required to obtain permanent water repellency was as low as 3.10^{-4} in the case of acetic-oleic cellulose esters. The microporosity of the samples may account for this outstanding hydrophobic character. Water vapor adsorption measurements on powder samples revealed a slight increase in hydrophobicity of the mixed acetic-fatty cellulose esters compared to cellulose acetate bearing the same acetyl content. It was demonstrated that water repellency and vapor water adsorption are not correlated.

Keywords: mixed cellulose esters, contact angle, differential vapor sorption, hydrophobicity, water repellency

3.4.1 Introduction

Mixed cellulose esters (MCE), i.e. bearing at least two types of substituents are renewable based multifunctional polymers. The main representative examples of this family are the cellulose acetate butyrate and acetate propionate, which are industrially produced and exploited for their thermoplastic properties [1,2]. Properties can be modulated according to the type and amount of side chains. For instance, fully substituted long chain cellulose esters show better water barrier properties compared to cellophane [3].

Some properties change sensibly with the introduction of a little amount of substituents. Indeed, we have reported that long chain cellulose esters with low degree of substitution ($DS \leq 0.15$, i.e. acylation of only 5% of the hydroxyl groups) appear to present interesting properties such as water repellency of cotton yarns and fabrics [4] and ability for selective adsorption of oily compounds useful for the decontamination of polluted water [5]. Moreover, in an extension to the chemical wood modification, these esters have recently found an industrial success due to excellent weathering properties [6].

The properties obtained in the works cited above are difficult to correlate with the esterification extent because the DS-values are low and their determination is subjected to high standard deviation values with present techniques. Thanks to the TMSH/GC analytical technique recently developed [7] we are now able to characterize precisely cellulose esters with $DS < 0.1$.

In the first article of this series [8], we synthesized mixed cellulose esters (MCE) with DS comprised between 7.10^{-5} and 7.10^{-2}. In this article we will report the interactions of these MCE towards liquid and vapor water and establish correlations with the DS. The static contact angles and the equilibrium moisture contents were utilized as characterization tools.

Some years ago, the synthesis of mixed acetic-octanoic cellulose esters was reported [9]. The contact angles of the prepared samples measured at that time have not been reported so far. They will be used in this paper for comparison purposes.

3.4.2 Experimental

3.4.2.1 Chemicals

Pure water was obtained from a Milli-Q device from Millipore. Alpha-cellulose from Sigma-Aldrich France (degree of polymerization = 960, 4% pentosans) and conditioned at 7% moisture content was used here as reference in the study of interactions with water.

3.4.2.2 Mixed cellulose esters with DS_{total} < 0.1.

Synthesis

The synthesis of MCE is described in the first article of this series [8]. Cellulose was reacted with an acylation mixture obtained after reaction of acetic anhydride and fatty acids without catalyst. MCE were thoroughly washed with ethanol then purified by Soxhlet extraction with ethanol for 8 hr. The absence of residual reagents was done by FTIR. Moreover, the purification method was also validated by impregnating a sample of cellulose with the acylation mixture at room temperature followed by the same purification steps. The DS of this sample was null. The purified product was then oven-dried under vacuum at 70°C at least for 24 hr and to constant weight. The samples were manipulated in such a way to avoid contact with pollutants that might modify the surface energy.

Contact angle measurements

Pellets (10 mm diam.) of the esterified products were obtained using a laboratory press (10 t) and a conventional pellet mold. Metal surfaces in contact with the sample were carefully cleaned to avoid pollutant sources. A drop of Milli-Q water (3 µL) was placed on the surface of the pellet and the static contact angle was measured with a goniometer (GBX Instruments, France), equipped with an automatic camera registering still images every 0.1 seconds. Contact angles were measured automatically using the triple point calculation method. Three specimens were used for each sample. Two contact angle measurements were done per specimen.

Dynamic vapor sorption (DVS) analysis

All the experiments were performed on a DVS automated gravimetric vapor sorption analyzer (Surface Measurement Systems Ltd., London, UK). The DVS

measures the uptake and loss of vapor gravimetrically using a Cahn D200 recording ultra-microbalance with a mass resolution of ±0.1 μg. The relative humidity around the sample was controlled by mixing saturated and dry carrier gas streams using mass flow controllers. The temperature was maintained constant (±0.1°C) by enclosing the entire system in a temperature-controlled incubator. The samples were stored in a desiccator. For each experiment cellulose ester was immediately placed in the DVS under a continuous stream of dry (< 0.1% relative humidity, RH) air. A sample size between 5 and 10 mg was used. Prior to being exposed to any water vapor the samples were dried at 0% RH to remove superficial water present and establish a dry baseline mass. The samples were exposed to the following relative humidity profile: 0%, 10%, 20%, … 90%, then decreasing 80%, 70%, … 0% RH. At each stage, the sample mass was allowed to reach equilibrium before the relative humidity was increased or decreased. From the complete moisture sorption and desorption profile an isotherm was calculated using the DVS Advanced Analysis Suite v3.6 software. All experiments were performed at 25.0°C.

3.4.2.3   Mixed cellulose esters with DS_{total} > 0.1.

These samples were prepared and characterized (DS and contact angle) nine years ago [9] but the contact angle measurements have never been published. The synthesis protocol was as follows: A mixture composed of octanoic acid (5.6 eq/cellulose OH), acetic anhydride (2 eq/OH) and H_2SO_4 catalyst (3-7 meq/OH) was heated at 90°C for 1 h. Solvent-exchanged cellulose (2.0 g dry basis) was added to the reaction medium. The whole mixture was stirred at 110-130°C for 1-3 h. At the end of the reaction, 150 ml of ethanol were added to precipitate the soluble fraction. The solid was separated by filtration over fritted glass and purified by Soxhlet extraction with ethanol for 8 h. The purified product was then dried at 105°C to constant weight.

3.4.3   Results and discussion

3.4.3.1   Mixed cellulose esters with total DS values superior to 0.1

Mixed acetic-octanoic cellulose esters were synthesized with sulfuric acid as catalyst. This allowed to obtain acetic-octanoic cellulose esters with total DS-values comprised between 0.26 and 2.9 (Table 3.5).

Sample	DS_2	DS_8	DS_{total}	DS_2/DS_8	$\theta°$	DP
A	0.19	0.07	0.26	2.71	103	404
B	0.21	0.08	0.29	2.63	106	450
C	0.22	0.1	0.32	2.20	104	330
D	0.25	0.1	0.35	2.50	104	299
E	0.27	0.1	0.37	2.70	104	287
F	0.66	0.25	0.91	2.64	97	190
G	0.66	0.27	0.93	2.44	96	138
H	0.67	0.29	0.96	2.31	96	183
I	0.76	0.26	1.02	2.92	95	215
J	0.75	0.34	1.09	2.21	94	174
K	0.83	0.31	1.14	2.68	92	238
L	0.80	0.41	1.21	1.95	95	136
M	0.94	0.41	1.35	2.29	91	138
N	1.31	0.69	2.00	1.9	92	100
O	1.42	0.76	2.18	1.87	93	100
P	1.86	1.04	2.90	1.80	89	100

Table 3.5 Acetic-octanoic cellulose esters with DS$_{total}$ comprised between 0.1 and 3

The water repellency of these MCE was evaluated by measuring the contact angle (CA) during 5 min. The CA-values (*Θ*) were practically constant in the whole period. Such a behavior will be qualified in this work as "permanent" water repellency. Thus, all the samples showed permanent water repellency with CA-values of at least 89°C. Conventionally, a material is qualified as hydrophobic if *Θ* is higher than 90°.

The upper line in Figure 3.19 represents the plot of the CA-values obtained at 60 seconds. The CA decreases with the total degree of substitution.
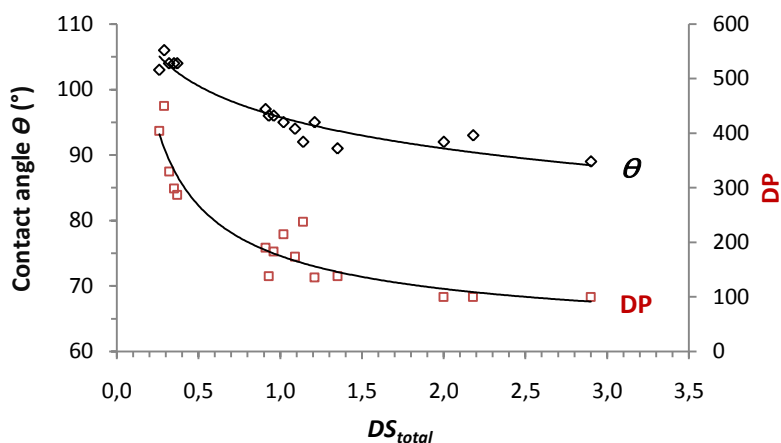

Figure 3.19 Water contact angles and degree of polymerization
of mixed acetic-octanoic cellulose esters with *DS$_{total}$*>0.1

This fact is surprising because of three reasons:

i)   the increase of the total DS means less hydrophilic hydroxyl groups;

ii)   the OH groups are substituted by fatty moieties supposed to increase the hydrophobicity;

iii)   the proportion of octanoyl groups increases with the total DS as shown by the plot of DS_2/DS_8 as a function of the total DS (Figure 3.20).
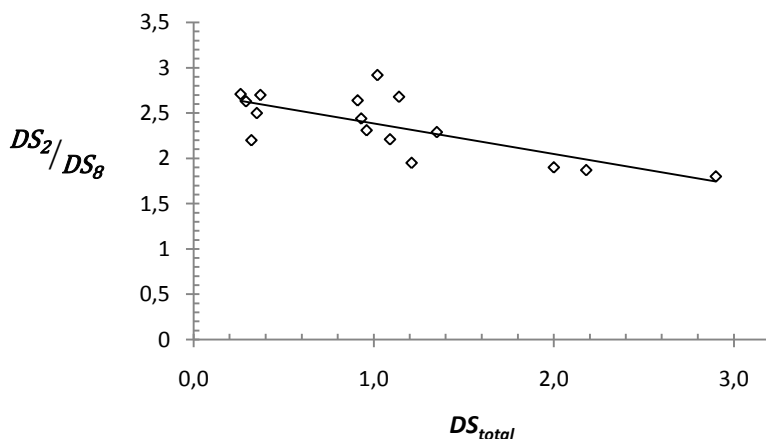

Figure 3.20 Ratio DS_2/DS_8 of mixed acetic-octanoic cellulose esters with $DS_{total}>0.1$

This disagreement can find an explanation in the change of porosity of the samples. In the synthesis of MCE in heterogeneous medium (solid cellulose, liquid acylating agent), the samples with low DS keep their fibrous structure and the chemical modification takes place on the external molecules of the microfibrils. On the contrary, a highly substituted sample loses its fibrous aspect and show a "plastic" appearance. Consequently, when making a pellet at room temperature from all these powders, the ones with lower DS-values should present a higher porosity and irregular surface than those highly substituted. According to the Cassie's law, the apparent contact angle of a porous material is increased compared to a non porous version of the same material [10].

$$cos\theta = x(\cos \theta_0 + 1) - 1$$

where θ_0 *is* the apparent contact angle of a perfect surface without air included and *x* the contact surface fraction of the drop with the material.

Let us remind that the super-hydrophobic materials are constructed based on this principle. Protuberances artificially created at a nanoscale on the surface (nanopins) of a metal or other non-hydrophobic materials create voids filled with air under the drop [11]. The *x* term in the Cassie's law equation tends to zero and *θ* tends to 180°.

In the case of fatty esters with low DS, isolated fatty chains must protuberate when fixed on the cellulose surface because this state requires less energy than forcing themselves to lay on the surface of a hydrophilic substrate. These protuberances reinforce the Cassie's effect.

Moreover we observed a correlation of the degree of polymerization (DP) with the total DS (lower line of Figure 3.19). The trend of this curve is quite similar to that of CA. Indeed, the samples showing the highest DS were synthesized under tougher conditions of temperature, catalyst and time [9] leading to lower DP values (Table 3.5). The decrease of the DP can therefore diminish the entanglement of the cellulose chains leading to more compact configurations. The voids, and thus the porosity, are less important decreasing therefore the CA-values.

Taking in account that cellulose esters with DS values below 0.5 present permanent water repellency with very high contact angles, we decided to investigate the characteristics of cellulose esters in which the chemical modification is very low and without acidic attack of the biopolymer (synthesis without catalyst). The fibrillar structure will be therefore maintained and will be the closest to that of cellulose.

3.4.3.2   *Lowly substituted mixed cellulose esters*

Acetic-fatty cellulose esters, with fatty chains from C8 to C18:1, were prepared under the same conditions of treatment (1 h, 140°C, without catalyst), their DS-values are presented in Table 3.6. A sample of cellulose acetate (Sample n°1) was also prepared by reaction of cellulose with acetic anhydride under the same conditions.

Sample	DS_2	DS_{fatty}	n	DS_{total}	DS_2/DS_f
1	$7.20 \cdot 10^{-2}$	/	/	$7.20 \cdot 10^{-2}$	/
2	$5.01 \cdot 10^{-2}$	$1.83 \cdot 10^{-3}$	8	$5.19 \cdot 10^{-2}$	27
3	$4.88 \cdot 10^{-2}$	$1.02 \cdot 10^{-3}$	10	$4.98 \cdot 10^{-2}$	48
4	$5.03 \cdot 10^{-2}$	$6.82 \cdot 10^{-4}$	12	$5.10 \cdot 10^{-2}$	74
5	$6.10 \cdot 10^{-2}$	$6.78 \cdot 10^{-4}$	14	$6.17 \cdot 10^{-2}$	90
6	$6.37 \cdot 10^{-2}$	$5.25 \cdot 10^{-4}$	16	$6.43 \cdot 10^{-2}$	121
14	$5.74 \cdot 10^{-2}$	$2.83 \cdot 10^{-4}$	18 :1	$5.77 \cdot 10^{-2}$	203

Table 3.6 Acetic-fatty cellulose esters with $DS_{total} < 0.1$. n = number of carbon atoms of the saturated acyl chain

CA measurements with water were measured during 5 min. The MCE samples showed high CA-values even after 5 min. We can observe in Figure 3.21 that there is a slight decrease of Θ. We wondered if it could correspond to a slow absorption of the water drop by the porous material or if a slight evaporation phenomenon was taking place.
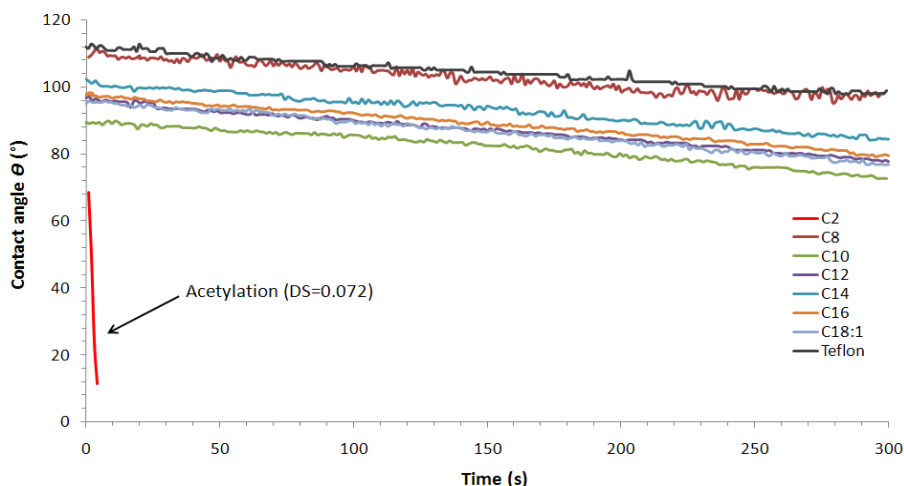

Figure 3.21 Water contact angles of mixed acetic-fatty cellulose esters. n = $n$umber of carbon atoms of the saturated acyl chain. A cellulose acetate and a Teflon samples are also tested.

We therefore made an experiment with a non porous tablet of Teflon. As the slope of the line was identical to those of cellulose esters, we concluded that this decrease was effectively induced by the measurement conditions. All the MCE samples in Figure 3.21 can be defined as exhibiting permanent water repellency as their trends are parallel to the one observed for Teflon. It is worth noting that the

curve of acetic-octanoic cellulose ester outstands from all the others and it comes close to the Teflon curve.

These interesting results demonstrate that mixed cellulose esters with low DS of acetyl groups (DS_2 inferior to 0.1) and with extremely* low DS of fatty acyl groups (DS_f), comprised between $1.83 \cdot 10^{-3}$ and $6.82 \cdot 10^{-4}$, were able to show permanent marked water repellency (Samples 2 to 6 and 14).

The total degree of substitution (DS_{total}) and DS_2 of these samples are practically the same as $DS_f << DS_2$. Moreover, their values are almost constant whereas DS_f varies in one order of magnitude (Table 3.6). The ratio DS_2/DS_f passes from 27 (Sample 2) to 203 (Sample 14). Consequently, the lack of correlation between CA and the length of the fatty chain shown in Figure 3.22 is not surprising.
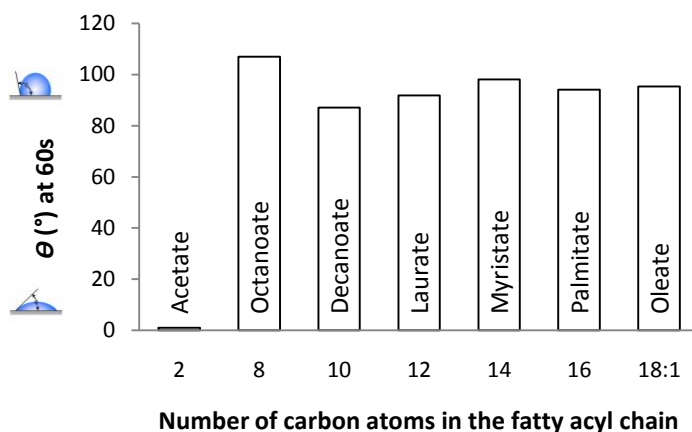

Figure 3.22 Water contact angles of mixed acetic-fatty cellulose esters and cellulose acetate measured at 60 seconds.

Contrarily to MCE, cellulose acetate with DS_2 equal to 0.072 (Sample 1) showed high hydrophilicity as the drop of water was absorbed into the pellet in less than 2 seconds despite the fact that the cellulose acetate sample and any of the MCE samples have practically the same DS_2. This fact illustrates the dramatic impact of the presence of a very few fatty chains on the hydrophobicity of MCE. The lowest DS_f of the MCE in Table 3.6 represents one fatty chain per about 1500 anhydroglucose units.

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* Characterization of MCE with extremely low DS has been possible thanks to a new method recently developed to determine precisely DS of long chain cellulose esters with values as low as 5.10^{-5}. (section 3.2)

Untreated cellulose and the cellulose acetate sample behaved similarly in terms of water repellency. The reference presented an initial contact angle value (at t_0, just after the deposition of the drop) of 59.7° followed by a complete absorption of the drop in less than 3 s and the cellulose acetate sample a θ of 68.6° with a complete absorption in less than 5 s.

If we compare acetic-octanoic cellulose esters obtained with and without catalyst (Tables 1 and 2), we can note that they present CA-values of the same order even if their DS_{total}-values are very different. For example, Sample 2 shows $\theta = 107°$ with $DS_8 = 1.83.10^{-3}$ while Sample A, prepared with sulfuric acid catalyst, shows $\theta = 103°$ with DS_8 40 times higher (7.10^{-2}).

Moreover, all the MCE presented above exhibited the same behavior regardless of the type of fatty chain. The observations made on acetic-oleic MCE and on acetic-octanoic MCE can be globalized in general to that of acetic-fatty cellulose esters.

Table 3.7 shows the characteristics of all the samples synthesized in the first article of this series. They are all acetic-oleic cellulose esters. The DS of the fatty acyl group ($DS_{18:1}$) are as low as $7.25 \cdot 10^{-5}$ but the total DS was of the same order than the previously presented samples (Samples A to P and 1 to 6). The DP-values of the samples presented in Tables 3.6 and 3.7 were practically constant at 745 ± 30.

Sample	DS_2	$DS_{18:1}$	DS_{total}	$DS_2/DS_{18:1}$
7	$2.30.10^{-2}$	$7.25.10^{-5}$	$2.31.10^{-2}$	317
8	$2.60.10^{-2}$	$3.51.10^{-4}$	$2.64.10^{-2}$	74
9	$3.78.10^{-2}$	$1.70.10^{-4}$	$3.80.10^{-2}$	222
10	$3.80.10^{-2}$	$1.64.10^{-4}$	$3.82.10^{-2}$	231
11	$5.20.10^{-2}$	$2.27.10^{-4}$	$5.22.10^{-2}$	229
12	$5.70.10^{-2}$	$2.83.10^{-4}$	$5.73.10^{-2}$	202
13	$5.70.10^{-2}$	$3.12.10^{-4}$	$5.73.10^{-2}$	183
14	$5.74.10^{-2}$	$2.83.10^{-4}$	$5.77.10^{-2}$	203
15	$6.10.10^{-2}$	$3.31.10^{-4}$	$6.14.10^{-2}$	184
16	$6.20.10^{-2}$	$2.54.10^{-4}$	$6.23.10^{-2}$	244
17	$6.30.10^{-2}$	$3.37.10^{-4}$	$6.33.10^{-2}$	187
18	$6.60.10^{-2}$	$2.20.10^{-4}$	$6.62.10^{-2}$	300
19	$6.70.10^{-2}$	$1.84.10^{-4}$	$6.72.10^{-2}$	365
20	$7.00.10^{-2}$	$1.06.10^{-4}$	$7.01.10^{-2}$	659
21	$7.10.10^{-2}$	$3.85.10^{-4}$	$7.14.10^{-2}$	184
22	$7.40.10^{-2}$	$3.54.10^{-4}$	$7.44.10^{-2}$	209
23	$8.24.10^{-2}$	$3.97.10^{-4}$	$8.28.10^{-2}$	207
24	$8.50.10^{-2}$	$4.49.10^{-4}$	$8.55.10^{-2}$	189

Table 3.7 Acetic-oleic cellulose esters with $DS_{total} < 0.1$

The CA-values as a function of time for all the powder samples from Table 3.7 are gathered in Figure 3.23. Even though all the samples show high CA-values (>75°) at initial time, we can notice that some of them are not "permanent". Sample 19 can be considered as a frontier between permanent and temporary water repellency. Moreover, the group of samples 8, 11-18, and 21-24 can be clearly defined as permanent hydrophobic materials (same slope as Teflon and $\theta > 90°$).
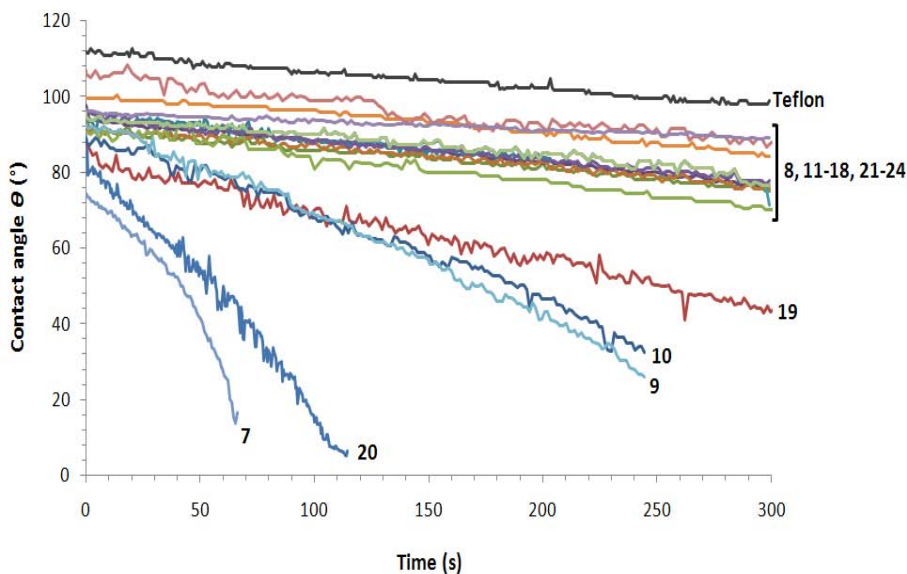

Figure 3.23 Water contact angles of mixed acetic-oleic cellulose esters.
Numbers next to the curves indicate the Sample number.

From these lines, we identified the CA-values obtained at 60 s and tried to correlate them with the DS_{total}-values (Figure 3.24). Surprisingly, no correlation was found between these parameters. Furthermore, as we explained before, $DS_2 >> DS_{18:1}$ (i.e. $DS_{total} \approx DS_2$), we can affirm that there is no correlation between θ and DS_2. In other words, the acetate content has no influence on the water repellency of the considered samples.
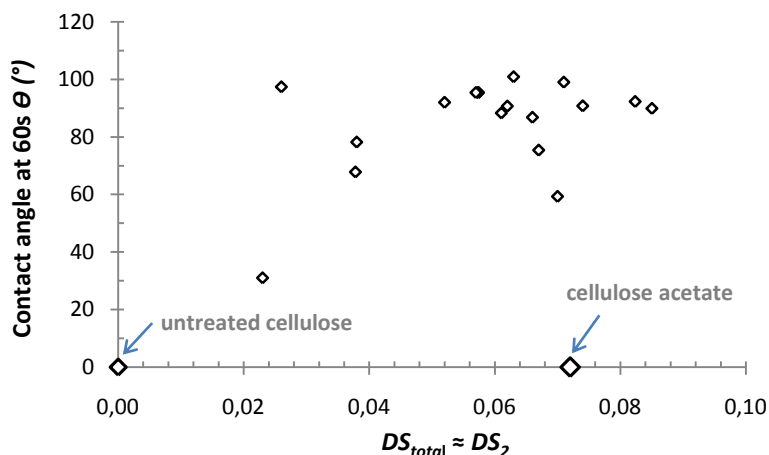
**Figure 3.24 Water contact angles of mixed acetic-oleic cellulose esters
with DS_{total}<0.1 as a function of DS_2**

On the contrary, we found a significant correlation between θ and $DS_{18:1}$ (Figure 3.25). θ increases regularly and levels off at $DS_{18:1}$ value equal to 3.10^{-4}. The CA-value reached at the plateau is of about 95°, which is generally assumed as "hydrophobic". The outstanding fact is that this permanent high hydrophobicity is reached with a substitution equivalent to one fatty chain per 3 000 anhydroglucose units.
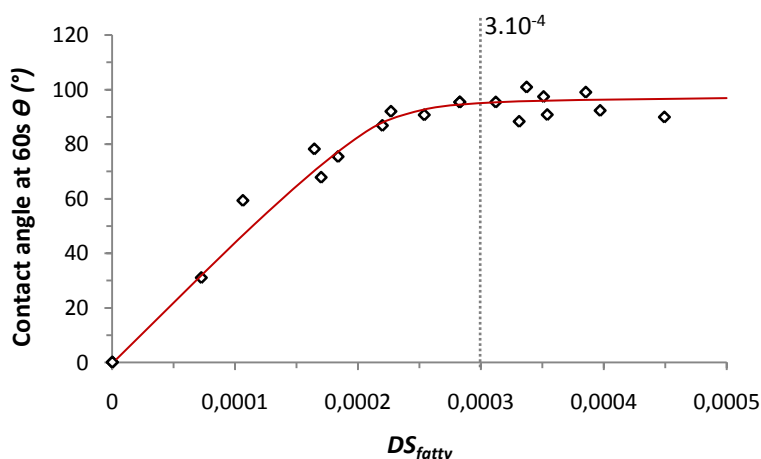

**Figure 3.25 Water contact angles of mixed acetic-oleic cellulose esters
with DS_{total}<0.1 as a function of the oleoyl content**

Even though there is no a solid way to explain this unattended phenomenon, we can formulate two hypotheses. First, when a fatty chain is grafted on the surface of a cellulose microfibril, it would tend to protuberate because its non-polar character is antagonist with the strong polarity of cellulose molecules. It would then spontaneously create a nanopin structure. Second, the protuberating chains would increase the free volume between the cellulose microfibrils of the material. The microporosity is increased and the contact angle is increased due to the Cassie's law.

However, we must keep in mind that the 3.10^{-4} *DS* threshold belongs to acetic-oleic cellulose esters. The value may vary with the length of the grafted fatty chain. It is possible that a relationship exists between the increased apolarity of the aliphatic chain and the hydrophobic character. The number of carbon atoms grafted on the biopolymer would therefore be more relevant than the number of hydroxyl functions substituted. This is the case for many properties such as water vapor permeability [3], glass transition [12] and wood dimensional stability [13].

Therefore we plotted the CA-values of all the samples (regardless of the fatty chain) as a function of the fatty acyl content (Figure 3.26).
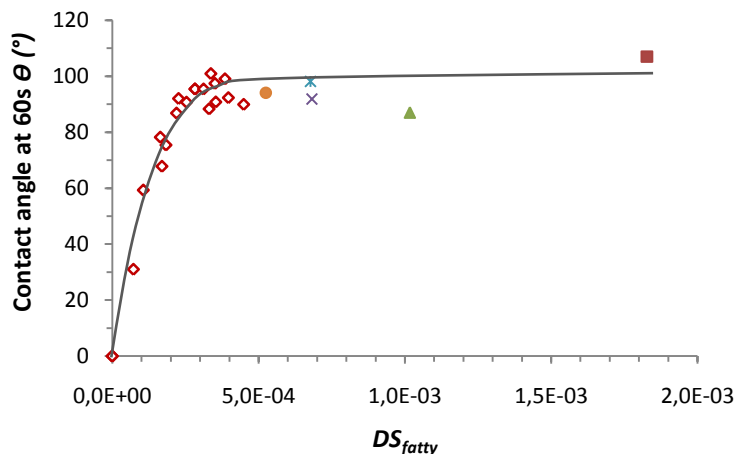

Figure 3.26 Water contact angles of mixed acetic-fatty cellulose esters with $DS_{total}<0.1$ as a function of the fatty acyl content

We can observe that the CA depends on the DS_f for the same type of fatty chain but, in a more general way, it depends on the fatty acyl content. Figure 3.25 is only a particular case in which we consider samples bearing the same type of substituent.
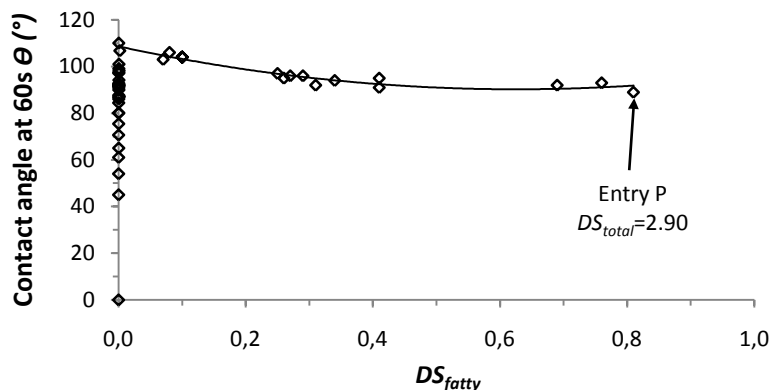
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Figure 3.27 Water contact angles of mixed acetic-fatty cellulose esters
in the whole range of DS_{total} as a function of the fatty acyl content

Figure 3.27 shows the plot of all the samples treated in this paper as a function of the fatty content. The range of DS_{total} of the acetic-fatty cellulose esters goes from 7.10^{-2} to 2.9 and we can clearly observe that considering the hydrophobicity of such material is concerned, there is no need to highly substitute cellulose.

As a final point, we characterized four samples by dynamic vapor sorption with water: untreated cellulose (blank), cellulose acetate (Sample 1), cellulose acetate-octanoate (Sample 2) and cellulose acetate-oleate (Sample 14). Let us remind that the first two samples had not shown water repellency whereas Samples 2 and 14 had shown permanent water repellency. It was therefore surprising to observe that the sorption isotherms of the cellulose derivatives showed practically the same trend regardless of the DS or the type of substituent (Figure 3.28). Moreover, the reduction of the equilibrium moisture content with regard to cellulose was quite small; only one percentage point less than the blank. A sample of Teflon, material recognized to be perfectly hydrophobic shows a water sorption of 0% in the whole range of relative humidity. Therefore, the MCE samples that had contact angles almost as high as that of Teflon show now a behavior of water sorption almost as that of hydrophilic cellulose. Moreover the hysteresis loop between sorption and desorption (not shown) was wider for the mixed cellulose ester. This may be due to an increased free volume created by the fatty lateral chains [3].
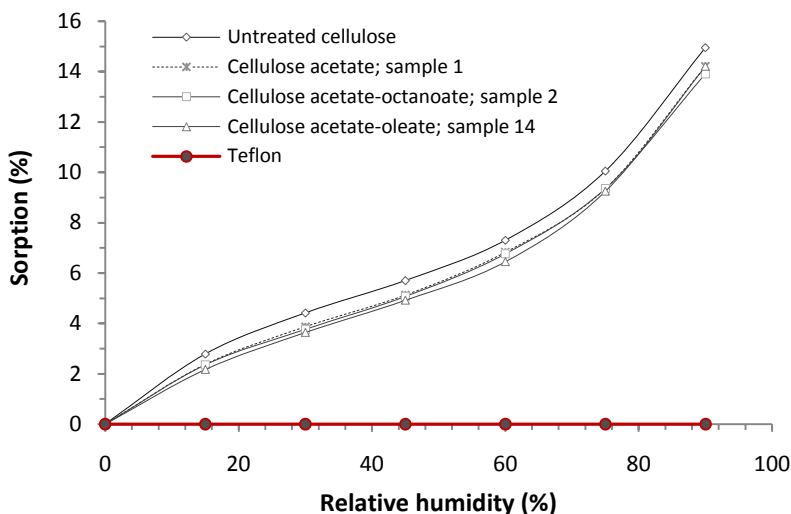
Figure 3.28 Water vapor sorption isotherms for esterified and untreated cellulose at 25°C

We demonstrate clearly that the hydrophobicity of a cellulosic material is manifested in several ways that are not necessarily correlated. MCE with very low DS can be considered as hydrophobic (with regard to their water repellency). But when considering their affinity to vapor water, they are just less hydrophilic than cellulose.

A possible explanation for these differences of behavior towards liquid and vapor water can be drawn when considering the physical state of water. Vapor is constituted of individual molecules able to reach the numerous hydrophilic hydroxyl groups remaining in the cellulose esters. On the contrary, liquid water is a cluster of molecules bonded by hydrogen bonding. A drop of water shows a high surface energy and little wettability on hydrophobic surfaces. Especially if the latter are constituted of fatty nanopins.

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3.4.4   Conclusions

Concerning the mixed acetic-fatty cellulose esters, shaped into pellets, we can affirm that:

- Water repellency is obtained at very low DS_{total} values (< 0.06). Contact angles are comprised between 90° and 100°
- Water repellency depends essentially on the fatty acyl content. The minimum value for permanent water repellency in the case of acetic-oleic cellulose esters is $DS_{fatty} = 3 \cdot 10^{-4}$, which is considered an extremely low DS value.
- The contact angle of cellulose acetate (without fatty acyl groups) with $DS_2 \leq 0.072$ is null.

Concerning the mixed acetic-fatty cellulose esters powders, we can affirm that:

- Equilibrium moisture content of MCE with very low DS is almost as high as that of cellulose acetate with very low DS.
- Both types of samples cannot be considered as hydrophobic according to their affinity to water vapor. Just a little less hydrophilic than cellulose.

In general conclusion we can state that the so-called hydrophobic cellulose esters can present completely different affinities to water depending on its physical form: liquid or vapor. Individual vapor molecules can reach the hydroxyl sites whereas the network that composes a drop of water is confronted to a highly hydrophobic barrier with the fatty chains protuberating on the surface of a porous material. The Cassie's effect results in high hydrophobicity.

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3.5 Mixed acylation of Scots pine sawdust and impact on hydrophobicity

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Abstract

Acetic-fatty esters of Scots pine sawdust (SPS) were obtained by reaction of SPS with mixtures containing acetic-fatty anhydrides and no solvent or catalyst. Such mixtures were synthesized by reaction between a carboxylic acid and acetic anhydride. The global reaction of acetic anhydride and a fatty acid yields at equilibrium a mixture of five compounds: acetic-fatty anhydride, acetic anhydride, fatty acid, acetic acid and fatty anhydride. The influence of temperature, molar ratio, reaction time, and length of the fatty chain on the esterification and on the ratio of grafted acetyl/fatty acyl was investigated. Static contact angles (CA) with water were measured over 5 minutes. CA-values were dependent on the fatty acyl content and independent of the acetyl content. The minimum ester content of the oleoyl group required to obtain permanent water repellency (WR) was 25 mmol.Kg^{-1}. Water vapor adsorption measurements indicated that contrarily to WR, hydrophobicity to water vapor was correlated to the total mass acyl content.

Keywords: Wood esters, mixed anhydrides, hydrophobicity, wettability, acetylation, fatty acylation

Paper 6

3.5.1 Introduction

Wood, even if it is the most important renewable material, presents limiting factors such as: dimensional instability, susceptibility to biological degradation and photo-degradation. When the use of less durable species such as fast-growth softwoods is considered, these limitations are considerably increased. Chemical modification of wood with linear carboxylic anhydrides is one of the potential methods for improving these properties and many reviews have been published on this field [1,2]. Using local non-durable species becomes attractive and the need for importing tropical wood is severely reduced. The ecological benefit is evident.

The treatment of wood by acetic anhydride (acetylation) has been the most investigated and it has been shown that the dimensional stability [3-5], the decay resistance [3,6-8] and the photostability [9-11] of such treated wood was enhanced. Acetylation found recently an industrial interest [12].

Work with other linear chain anhydrides has been relatively limited. Symmetrical carboxylic anhydrides, presenting aliphatic chain lengths from C2 to C7, have been investigated and their reactivity has been revealed to decrease due to steric hindrance with the increase of the aliphatic chain [13-16]. An improved dimensional stability has been highlighted as for acetylation but it has been shown that the length of the fatty chain grafted on wood had no impact on the anti-shrink efficiency (ASE). Instead, ASE has been found to be a function only of the weight percentage gain (WPG, extent of chemical modification in mass) [14,15].

Mixed anhydrides, i.e. with two different carboxylic acid radicals are reactive molecules that have been seldom investigated for reactions with wood constituents [17-19]. These instable molecules are very reactive and present the advantage to permit the grafting of two acyl groups on wood. The acetic-fatty anhydrides permitted obtaining a dimensionally stable treated wood showing better water repellency compared to acetylated wood [20].

Due to their instability, the use of mixed anhydrides must be done in situ. Thus, what is considered is a mixture. Such reactive mediums are obtained by reaction between a symmetrical anhydride (acetic) and a carboxylic acid yielding at equilibrium a mixed anhydride, two symmetrical anhydrides and two fatty acids [21].

The aim of this paper is to study the reactivity of mixed acetic-fatty anhydrides mixtures on wood and to evaluate the impact of the fatty chain grafted on the wettability of the mixed wood ester.

Fatty acids from C8 to C18 were used as the aliphatic long chain. Contrarily to previous studies, no solvent or catalyst was used. The heterogeneity of wood blocks is a handicap to focus on reactivity of the constituents of wood and moreover, the reactivity can be limited by diffusion phenomenon. That is why we investigate the reactivity of wood constituents by using sawdust of the wood specie the most investigated in literature i.e. Scots pine. By this manner, we will get information on the straight reactivity of mixed anhydrides towards wood constituents. Results obtained with Scots pine sawdust will be compared with results obtained in previous works on cellulose [22,23]. The hydrophobic properties of these novel wood derivatives will be described by measuring the wettability of sawdust molded pellets and by measurement of the sorption and desorption isotherms of the treated pine sawdust.

3.5.2 Experimental

3.5.2.1 Chemicals and standards

Acetic anhydride and carboxylic acids: propionic (C2:0), octanoic (C8:0), capric (C10:0), lauric (C12:0), myristic (C14:0), palmitic (C16:0), and oleic (C18:1) of 99%+ purity were purchased from Sigma-Aldrich France. Pentadecanoic acid (C15:0) was used as internal standard (I.S.) in gas chromatography and was obtained from Fluka France (99% purity). Phosphoric acid, 85% solution in water was purchased from Acros France. Trimethylsulphonium hydroxide (TMSH) was obtained from Macherey-Nagel France as a 0.2 mol.L^{-1} solution in methanol. *Tert*-butyl methyl ether (MTBE) HPLC grade was purchased from Scharlau Spain. All the chemicals were stored at 4°C prior to use.

3.5.2.2 Synthesis of the reaction mediums

Reaction mediums were prepared on a 300 mL scale. The appropriate amounts (molar ratio varying from 1:2 to 2:1) of fatty acid and acetic anhydride were added to a 500 mL glass reactor equipped with a condenser. Reactions were carried out at 100°C with mechanical stirring at 500 rpm during 1 hour. The reaction mediums were analyzed by reversed-phase HPLC [24].

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3.5.2.3 *Scots pine sawdust esterification*

SPS was Soxhlet extracted with ethanol during 8 h, then dried overnight at 103°C and then conditioned at 25°C and 60% relative humidity (RH) during two weeks in order to reach its equilibrium moisture content: 8.8 %.

Reactions were performed in 50 mL reactors equipped with a condenser. 1 g of conditioned SPS was stirred at 350 rpm in 15 mL of reaction medium without catalyst at the desired temperature and duration time. After cooling down to about 80°C, 20 mL of ethanol were added to recover the soluble fraction. SPS esters were separated by filtration over fritted glass and purified by Soxhlet extraction with ethanol for 8 h. The purified product was then dried under vacuum at 70°C at least for 24 h and to constant weight.

Determination of the fatty acyl content

We employed the method based on the transesterification of ester functions with TMSH followed by gas chromatography (GC) analysis. This technique has been developed for the determination of the ester content on cellulose esters and has been described in a previous paper [25].

We optimized the conditions for wood and determined the ester content as follow:

Sample preparation: A precise quantity of about 20 mg of treated SPS was introduced into a 2 mL vial. 500 µL of a 0.5 mmol.L^{-1} pentadecanoic acid in MTBE and 250 µL of TMSH were added. The vial was hot-stirred during 60 min in a VorTemp 56 shaking incubator at 1200 rpm and 75°C. Once the sample was cooled down and the solid decanted, the formed fatty acid methyl esters (FAME) in MTBE were quantified by GC.

Gas chromatography: The GC analysis was carried out using a Varian 3900 gas device equipped with a Varian 8400 autosampler, a split/splitless injector, a flame ionization detector (FID) and a Varian CP7419 capillary column (50 m, 0.25 mm i.d., 0.25 µm film thickness). Helium was used as carrier gas, at a flow rate of 1.2 mL.min^{-1}. The temperature of the injector used was set at 260°C and the split ratio at 1:20. The oven temperature was programmed as follows, 110°C for 4 min, then rise to 230°C at a rate of 15°C.min^{-1}, then 230°C for 7 min. This enabled the separation of the corresponding FAME within 19 min. The temperature of the FID detector was set at 260°C. From the GC analysis the concentration of fatty acyl groups C_f can be determined.

Calculation of the ester content of fatty acyl groups in mol.g^{-1}:

$$EC_f = \frac{C_f \times V_i}{m_i}$$

C_f: concentration of the FAME in MTBE determined by GC (in mol.L^{-1})

V_i: volume of internal standard (pentadecanoic acid) solution added to the analyzed sample (in L)

m_i: mass of the SPS sample analyzed in MTBE with TMSH (in g)

Determination of the acetyl content

The acetyl content was determined by performing an alkaline hydrolysis followed by acidification and GC analysis of the acetic acid formed. Conditions were performed on commercial cellulose acetates and SPS acetylated and the optimal conditions are the follows:

Sample preparation: A precise amount of about 20 mg of treated SPS was weighed and introduced into a 2 mL vial. 1000 µL of aqueous sodium hydroxide (0.5 N) and 500 µL of a 0.5 mmol.L^{-1} propionic acid solution in water were added. The vial was hot-stirred during 5 hours in a VorTemp 56™ Shaking incubator set at 1200 rpm and 100°C. The sample was cooled down, 45 µL of H$_3$PO$_4$ were added and the vial stirred at 1200 rpm during 10 min. Once the solid was decanted, a small sample of the supernatant in the reaction mixture was analyzed by GC.

Gas chromatography: The GC analysis was carried out using the described above. Separation was achieved in a CP-Select CB for FFAP fused silica capillary column (CP7845) (Varian) 25 m, 0.32 mm i.d., 0.25 µm film thickness. Helium was used as carrier gas, at a flow rate of 2.6 mL.min^{-1}. The temperature of the injector used was set at 250°C and the split ratio at 1:100. The oven temperature was programmed as follows, 80°C for 1 min, then rise to 145°C at a rate of 20°C.min^{-1}, then 250°C for 2 min. This enabled the separation of the acetic and propionic acids within 12 min. The temperature of the FID detector was set at 270°C. From the GC analysis the concentration of acetyl groups C_2 can be determined.

Calculation of the acetyl content in mol.g^{-1}:

$$EC_2 = \frac{C_2 \times V_j}{m_j}$$

C_2: concentration of the acetic acid after saponification and acidification determined by GC (in mol.L^{-1})

V_j: volume of internal standard (propionic acid) solution added to the analyzed sample (in L)

m_j: mass of the treated SPS sample analyzed (in g)

Contact angle measurements

Pellets (10 mm diam.) of the esterified products were obtained using a laboratory press (10 t) and a conventional pellet mold. Metal surfaces in contact with the sample were carefully cleaned to avoid pollutant sources. A drop (3 µL) of Milli-Q water was placed on the surface of the pellet and the static contact angle was measured with a goniometer (GBX Instruments, France), equipped with an automatic camera registering still images every 0.1 seconds. Contact angles were measured automatically using the triple point calculation method. Three specimens were used for each sample. Two contact angle measurements were done per specimen.

Dynamic vapor sorption (DVS) analysis

All experiments were performed on a DVS automated gravimetric vapor sorption analyzer (Surface Measurement Systems Ltd., London, UK). The DVS measures the uptake and loss of vapor gravimetrically using a Cahn D200 recording ultra-microbalance with a mass resolution of ±0.1 µg. The relative humidity around the sample was controlled by mixing saturated and dry carrier gas streams using mass flow controllers. The temperature was maintained constant, ±0.1 °C, by enclosing the entire system in a temperature-controlled incubator. The samples were stored in a desiccator. For each experiment SPS ester was immediately placed in the DVS under a continuous stream of dry (< 0.1% relative humidity) air. A sample size between 5 and 8 mg was used. Prior to being exposed to any water vapor the samples were dried at 0% relative humidity (RH) to remove any surface water present and establish a dry, baseline mass. Next, the samples were exposed to the following relative humidity profile: 0%, 10%, 20% … 90%, 80% … 0% RH. At each stage, the sample mass was allowed to reach equilibrium before the relative humidity was increased or decreased. From the complete moisture sorption and desorption profile an isotherm was calculated using the DVS Advanced Analysis Suite v3.6. All experiments were performed at 25.0 °C.

3.5.3   Results and discussion

3.5.3.1   Synthesis of the reaction mediums

The reaction between acetic anhydride and a fatty acid consists in two consecutive and equilibrated reactions [21] yielding at equilibrium a mixture of acetic acid, acetic anhydride, acetic-fatty anhydride, fatty acid and fatty anhydride (Figure 3.29).

$$RCOOH + CH_3C(O)OC(O)CH_3 \rightleftharpoons CH_3C(O)OC(O)R + CH_3COOH$$

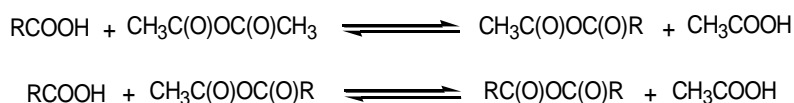$$RCOOH + CH_3C(O)OC(O)R \rightleftharpoons RC(O)OC(O)R + CH_3COOH$$

Figure 3.29 Consecutive reactions occurring when making react a fatty acid with acetic anhydride

Reaction between acetic anhydride and oleic acid at ratios comprised between 1:2 and 2:1 were conducted (fatty acid/acetic anhydride). From a previous work it is known that the equilibrium state is reached in less than 15 minutes at 100°C [21]. Therefore, all the mixtures prepared were then analyzed after 1 hr of reaction. The detailed compositions of all the treated mediums presented in this work have been described in a previous paper [22]. However, for a better understanding of the reactivity of such mediums on SPS, we will remind that among the five entities constituting the reaction medium, the concentration of the most abundant reactive molecules: acetic anhydride and acetic-oleic anhydride were relatively constant: 33.4% ± 2.5% and 24.0% ± 2.8% respectively regardless of the molar ratio.

3.5.3.2   Synthesis and characterization of SPS esters

Due to the low reactivity of carboxylic acids, especially in the absence of catalyst, only the three anhydrides present in the medium: acetic, acetic-fatty and fatty anhydrides are expected to react with SPS in order to form a mixed (acetic-fatty) SPS ester (Figure 3.30).
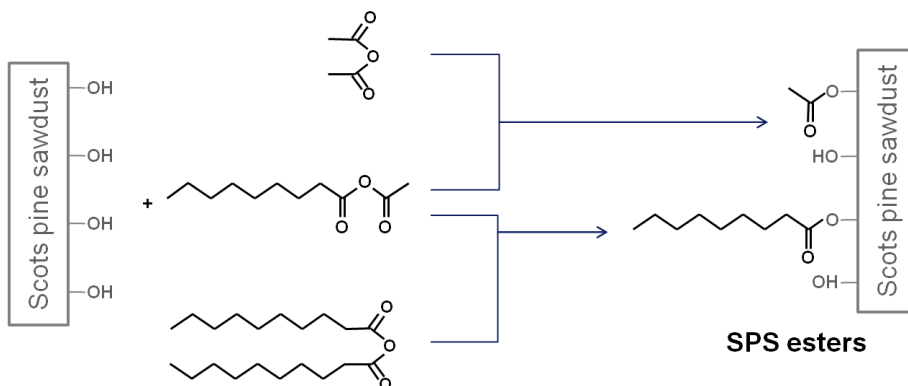
Figure 3.30 Esterification of pine sawdust treated by a mixture of acetic anhydride and a fatty acid

We determined for the treated SPS samples the variations of the acetyl (ΔEC_2) and fatty (ΔEC_f) contents compare to an untreated reference of SPS.

$$\Delta EC = (EC_m - EC_u)$$

where EC_m is the ester content of the chemically modified SPS and EC_u the ester content of the unmodified sample (blank). The blank of untreated SPS was found to contain 917 ± 11 mmol.kg^{-1} of acetyl content principally part of hemicelluloses and 0.21 ± 0.07 mmol.kg^{-1} of oleoyl content from waxes as SPS was not solvent extracted.
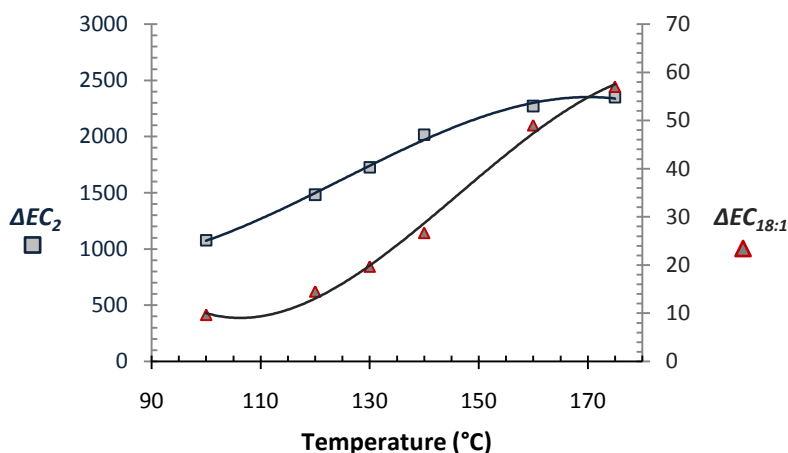

Figure 3.31 Influence of the reaction temperature on the acetyl and the fatty acyl contents. (treatment during 1 h, R=1.5)

Figure 3.31 shows the evolution of the grafting yield as a function of the temperature. The reactions were conducted during 1 h and with a molar ratio of 1.5. The highest increase in ester content of oleates ($\Delta EC_{18:1}$) and acetates (ΔEC_2) was obtained at 175°C with values of 57 and 2350 mmol.Kg^{-1} respectively. These values can be described in terms of WPG as 1.5% for the oleoyl groups and 9.9% for the acetyl content which are consistent values for SPS treated 1 hour without a catalyst or pretreatment. The individual acetyl and oleoyl contents obtained at 160°C are around two times and four times higher than those obtained at 100°C. These results highlight the fact that the esterification reaction is highly dependent on the temperature.

Besides, we performed FTIR analysis of the SPS samples treated at various temperatures. We calculated and plotted the ratio of the transmission intensities of the ester band at 1733 cm^{-1} and of a constant band characteristic of cellulose at 1641 cm^{-1} (Figure 3.32).
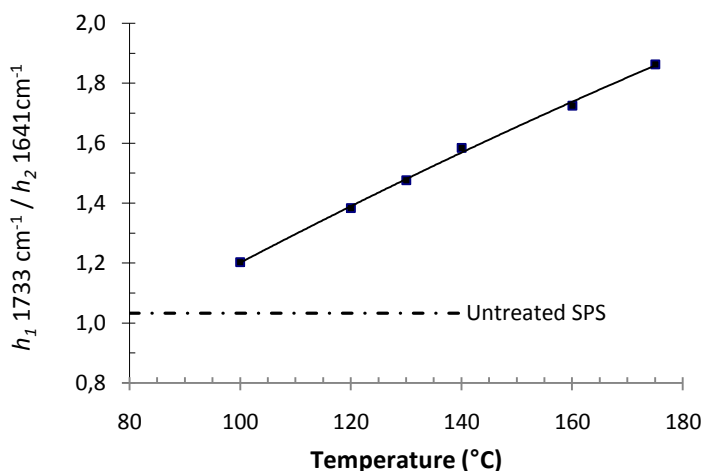

**Figure 3.32 Ratio of 2 FTIR bands transmission intensities
of solvent extracted SPS treated at various temperatures**

The trends for the acetyl and oleoyl ester content follow the same tendency. These FTIR analyses also permitted to confirm that no residual carboxylic acids were present after extraction.

Even though Figure 3.31 may give the impression that the oleoylation and the acetylation follow parallel trends, in reality, the increase of the temperature causes an enhancement of the global grafting but with amplified proportions of fatty chains

as shown in Figure 3.33. The ratio $\Delta EC_2/\Delta EC_f$ is divided by about three passing from 112 at 100°C to 41 at 175°C.
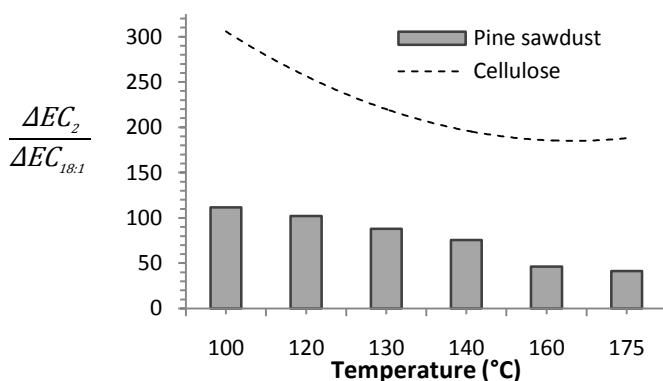

Figure 3.33 Influence of the reaction temperature of the treatment on the grafting ratio acetate/oleate (treatment during 1 h, R=1.5).

One hypothesis that may explain the diminishing of this ratio is that the composition of the reaction medium is dependent on the temperature. Nevertheless, we demonstrated in a previous report [21] that the composition of the medium at equilibrium was little dependent on the temperature. For the considered temperature, the variation of the composition would be of only 3% maximum. This small variation cannot account for a decrease of 50% in the substituents ratio.

Another possible explanation for the diminishing of the ratio could be that the vaporization of acetic anhydride and acetic acid, whose boiling points are respectively 116°C and 145°C, could also have consequences on the reaction medium composition and shift the equilibrium. Nevertheless, this is not the case because the decrease of the ratio is linear in the concerned range of temperature. The third and most likely hypothesis would be that the energy of activation for the grafting of acetates is lower than for the grafting of oleates.

The values of the ratio of grafting tend to reach a plateau at 160°C. More acetyl groups are grafted than oleoyl groups on SPS because the mixture still contains acetic anhydride and that the acetic-oleic anhydride can lead to the formation of both acetates and oleates.

Moreover, the steric hindrance of the fatty chain can account for such a difference; reasonably the acetyl group would present more ability to reach hydroxyl functions in the cellulose microfibrils than the oleoyl group from the acetic-oleic and oleic anhydrides.

If we compare these results with the values of ratio obtained when treating cellulose in the same conditions in a previous work [22], we observe that the ratio of grafting is more important in the case of cellulose. The reactivity of cellulose is lesser compared to SPS; the accessibility of the hydroxyl groups towards oleoyl groups is more difficult because of the crystallinity of cellulose. Hydrogen bonds limit considerably the reactivity of cellulose without a pretreatment or swelling agent. Lignin and hemicelluloses present in SPS, with OH more accessible and therefore more reactive are responsible for the superior reactivity compare to cellulose.
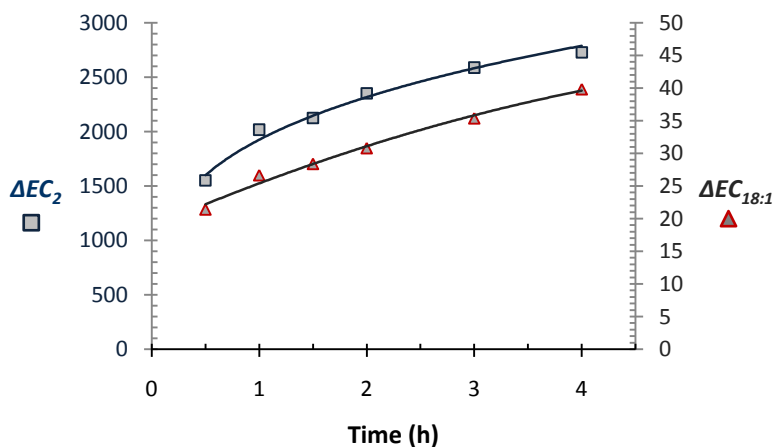

Figure 3.34 Influence of the duration of the treatment on the acetyl and oleoyl content. (treatment at 140°C, R=1.5).

Reaction time is also an important factor (Figure 3.34). When treated at 140°C a mixture with a molar ratio of 1.5, the grafted acetate and oleate contents are multiplied by two when passing from 30 min to 4 hours of reaction. But surprisingly the ratio of grafting (acetate/oleate) remains constant at a value of about 73±3 during the whole duration of the reaction (Figure 3.35).
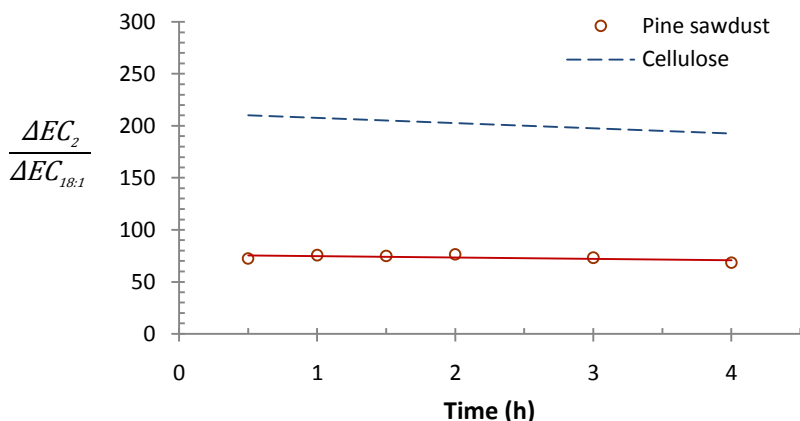
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Figure 3.35 Influence of the reaction time on the grafting ratio acetate/oleate.

Since the grafting is dependent on the temperature only and not on the reaction time, the hypothesis formulated above concerning the energies of activation is confirmed. Fatty acyl groups need more energy to react with hydroxyl groups. A boundary value of this ratio is reached regardless of the temperature. The limitation is due only to the steric hindrance encountered by the fatty compounds.

In Figure 3.36, in the following experiments, the temperature and reaction time were kept constant (140°C, 1 h) and we only varied the reagents molar ratio. The plot of ΔEC_2 and $\Delta EC_{18:1}$ as a function of the molar ratio shows an increase of $\Delta EC_{18:1}$ with the molar ratio accompanied by a decrease of ΔEC_2.
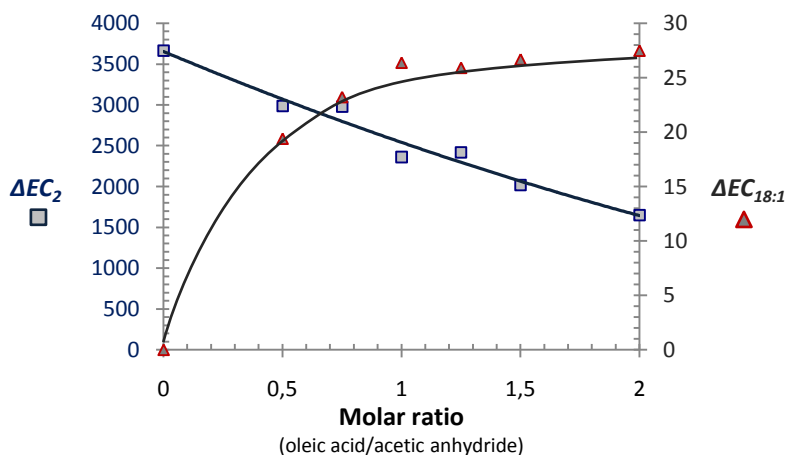

Figure 3.36 Influence of the molar ratio of the mixture on the acetyl and fatty acyl content. (treatment at 140°C during 1 h).

It is important to note that a sample treated with pure acetic anhydride, i.e. a molar ratio of zero, presents a ΔEC_2 of 3664. This is the same order of magnitude than acylation of SPS with a molar ratio of 0.5 (ΔEC_2 = 3005). When the molar ratio increases, the concentration of reactive molecules tends to diminish to reach eventually the value of 0 for an infinite molar ratio (pure oleic acid). $\Delta EC_2/\Delta EC_{18:1}$ decreases when the molar ratio of reagents increases (Figure 3.37).
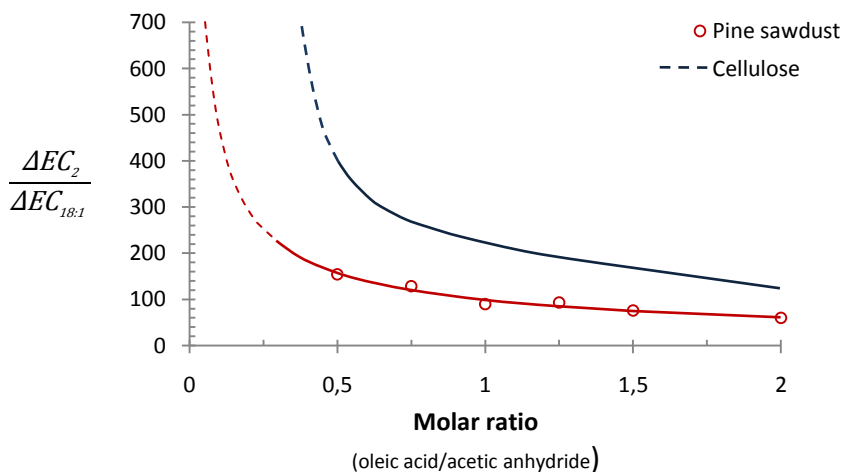

Figure 3.37 Influence of the molar ratio of the mixture on the grafting ratio acetate/oleate.

The theoretical value of $\Delta EC_2/\Delta EC_{18:1}$ for a molar ratio of 0 (pure acetic anhydride) is infinite. This is why ΔEC_2 decreases with the molar ratio as the total concentration of molecules susceptible to acetylate SPS globally decreases. On the contrary, $\Delta EC_{18:1}$ increases despite the diminishing of the total anhydride content in the mixture. This could be explained by the fact that in a mixture of acetic anhydride and oleic acid the concentration of acetic-fatty anhydride remains constant whereas the concentration of acetic anhydride diminishes [21]. The concentration of oleic anhydride also increases, thus increasing in the mixture the concentration of molecules susceptible to form fatty esters of SPS.

Finally, we varied the nature of the fatty chain by preparing different mixtures form acetic anhydride and fatty acids bearing saturated aliphatic chains from C8 to C16 at a molar ratio of 1.5 (Figure 3.38).
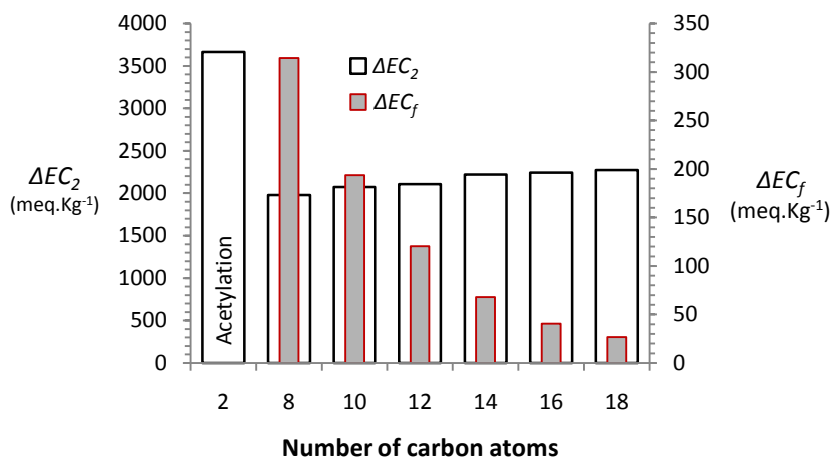
**Figure 3.38 Influence of the aliphatic chain length on the
acetyl and fatty acyl content**

The plot of the ester contents as a function of the chain length shows a decrease of the number of grafted fatty chains (ΔEC_f) when the number of carbon atoms of the aliphatic chain increases.

This can be explained by the steric hindrance encountered by the bigger molecules and by the presumed increase of the activation energies of the reaction of esterification with the length of the fatty chain. ΔEC_2 keeps approximately the same value and seems to be independent from the fatty acid used for the mixture synthesis.

However, we can note a slight increase of its value with the fatty chain length due to the higher reactivity of the mixed anhydride. Indeed, the increase of the fatty chain length makes the mixed anhydride more asymmetrical and therefore more reactive [26].

The ratio of grafting (Figure 3.39) is therefore correlated to the difficulty to graft fatty molecules; the steric hindrance of the fatty chains favors the grafting of acetyl groups. The grafting of fatty acyl groups is however more important on SPS than cellulose as hemicelluloses and lignin are more accessible and therefore more reactive. Cellulose crystallinity is always a handicap when considering its chemical modification.
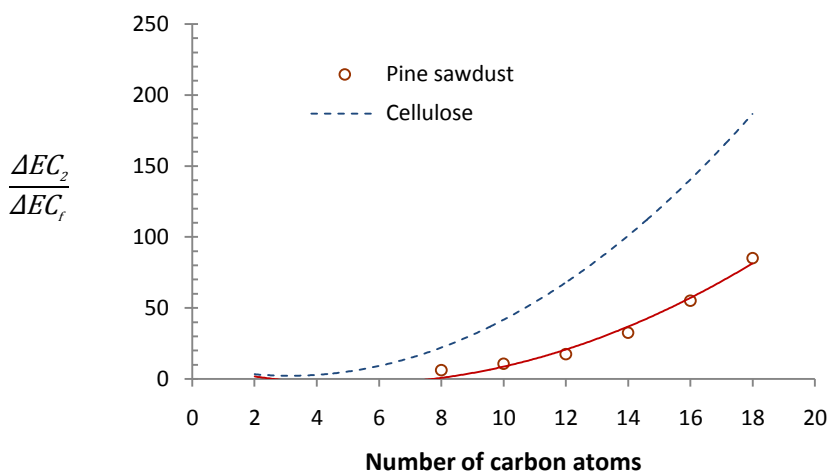
Figure 3.39 Influence of aliphatic chain length on the grafting ratio acetate/oleate

3.5.3.3   *Wettability of mixed SPS esters*

Water repellency (WR) prevents or slows down the rate at which liquid water is absorbed by a material. It may therefore be correlated to the water contact angle measured at a certain time. In the case of pine sawdust, it was necessary to make an object with a regular smooth surface. In this work, static contact angles (CA) with water were measured on pellets molded from the treated SPS samples.

First of all, we determined the CA of untreated SPS samples and found an average value of 39°±4 at initial time (0 s). The drop after deposited was totally absorbed by the material in less than 3 s. Untreated SPS can therefore be considered as highly hydrophilic. We then measured the CA of water drops deposited on the pellets prepared from SPS samples treated at various temperatures with a molar ratio of 1.5 for 1 h. The evolution of the CA as a function of time is shown in Figure 3.40.
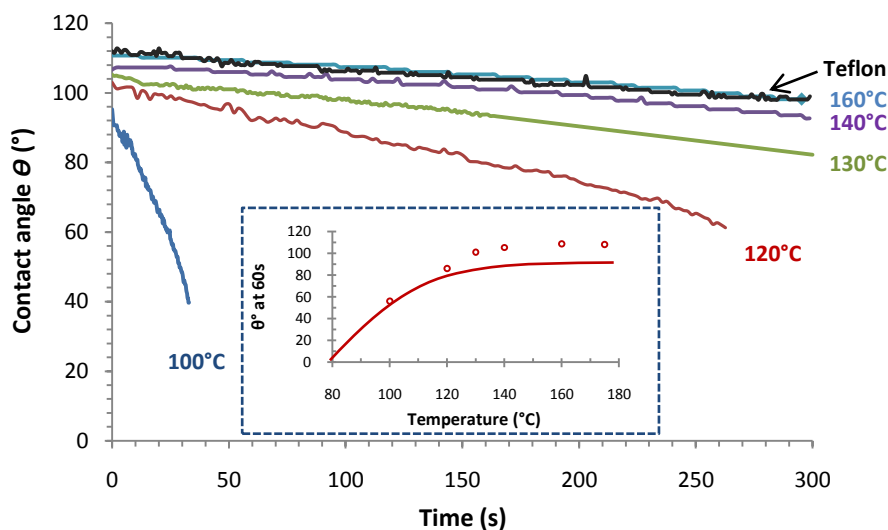
Figure 3.40 Water contact angles of mixed acetic-oleic SPS esters treated at various temperatures. Inside graph: contact angles at 60 seconds for samples obtained at different reaction temperatures.

Although all the samples show high CA values (>95°) at initial time, we can notice that some of them see their CA value decrease after a few seconds. The sample treated at 100°C, for example, can be considered as wettable compared to the samples treated at temperature higher than 120°C. The molded pellets of SPS esters obtained at 140 and 160°C show high water repellency with CA-values of 105 and 109° respectively. We measured the CA-values during 5 minutes and observed for the samples treated at 140°C and 160°C a slight decrease of the contact angle values but no absorption of the water drop. An evaporation of the water drop due to the heat of the light could be at the origin of this decrease. We therefore made an experiment with a non porous tablet of Teflon. Since the slope of the line was identical to those of SPS esters, we concluded that this decrease was effectively induced by the measurement conditions.

A plot of the CA values measured after 1 min of contact with the pellets as a function of the temperature is also indicated in Figure 3.40. If we consider the ester content values of these SPS esters, we can note that their water repellency depends on the grafting. Since the acetyl and fatty contents both increases, it is difficult to define if the increased water repellency depends on the fatty content or on the total grafting. We made exactly the same observation with the samples treated at 140°C

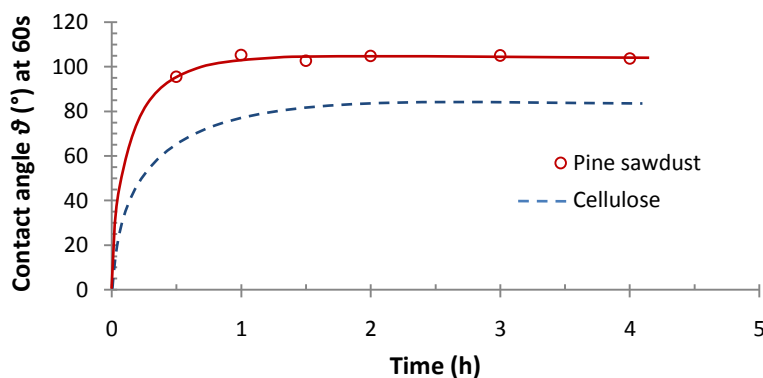with acetic-oleic anhydride mixture (molar ratio of 1.5) during different reaction times (Figure 3.41).

Figure 3.41 Water contact angles measured at 60 seconds of mixed acetic-oleic SPS esters treated at various reaction times.

We studied then the WR of the sample treated with acetic-oleic anhydride mixture at molar ratios comprised between 0 and 2 (at 140°C during 1 h). Let us remind that a molar ratio of 0 corresponds to acetylation.

Figure 3.42 shows the CA of these samples as a function of time. We can note that the acetylated sample (molar ratio = 0) does not present water repellency even if its total ester content is higher than that of all the other samples. Its CA at initial time is 52°±2° and the water drop is absorbed in less than 4 s, as the untreated sample did. The high acetyl content does not give water repellency to the treated SPS. The literature reports acetylated wood blocks presenting contact angle values of 98° [14]. However, these values are measured just after the deposit of the water drop and no information is given on the "permanent" character of this property. Moreover, the reported sample possesses an acetyl content of about 5700 meq.Kg^{-1}, which is higher than our value (3500 meq.Kg^{-1}).

The wettability of the samples decreases with the molar ratio of the mixture used for the treatment. The SPS samples treated with mixtures with molar ratio from 1.25 to 2 can be qualified as highly water repellent. Their initial content angles are comprised between 105 and 110° and no absorption of the water drop by the material is observed in five minutes of measurement. These results are really interesting as there is no correlation between the wettability of the samples and their total ester contents. ΔEC_2 decreases with the molar ratio while $\Delta EC_{18:1}$ increases at the same time.
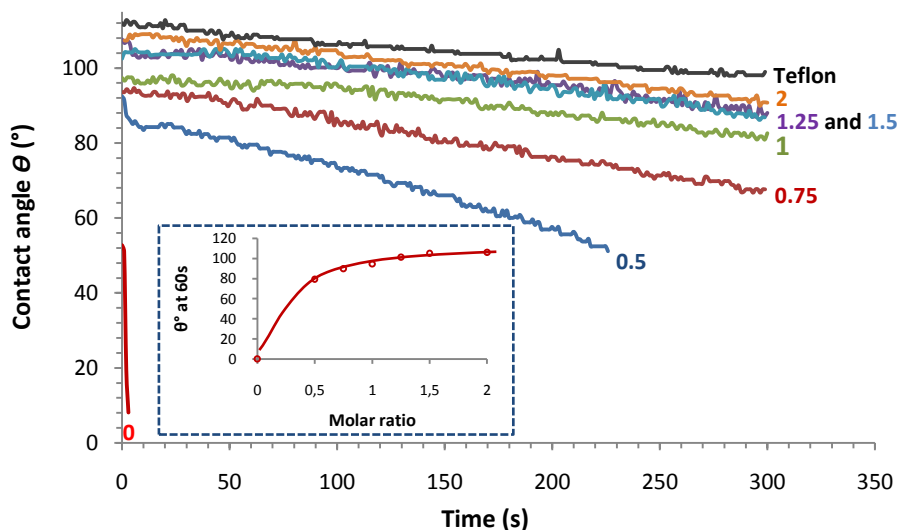
Figure 3.42 Water contact angles of mixed acetic-oleic SPS esters treated at molar ratios comprised between 0 to 2. 0 corresponds to acetylation.

The acetate content seems to have no influence on the water repellency of the pellets. The plot of the CA values after 1 min of measurement as a function of the acetyl content did not show any correlation. This indicates that the water repellency of the treated samples depends mostly on the fatty acyl content. In order to confirm this hypothesis we plotted the CA values after 1 min of measurement as a function of the fatty content added by the treatment (Figure 3.43).
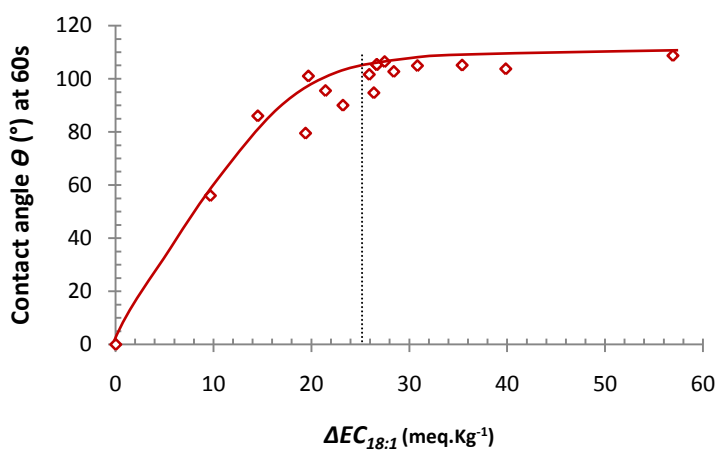

Figure 3.43 Water contact angles of mixed acetic-oleic SPS esters as a function of the *oleoyl content*

A correlation can be clearly observed. On the contrary no correlation was found with the acetyl content. This definitely indicated that by grafting fatty chains in low extent on pine sawdust, an important water repellent character can be given to the material. A threshold at 25 mmol.Kg^{-1} of fatty acyl content for the SPS mixed esters is highlighted in Figure 3.43.

The impact on the aliphatic chain on the water repellency of the treated SPS is shown in Figure 3.44.
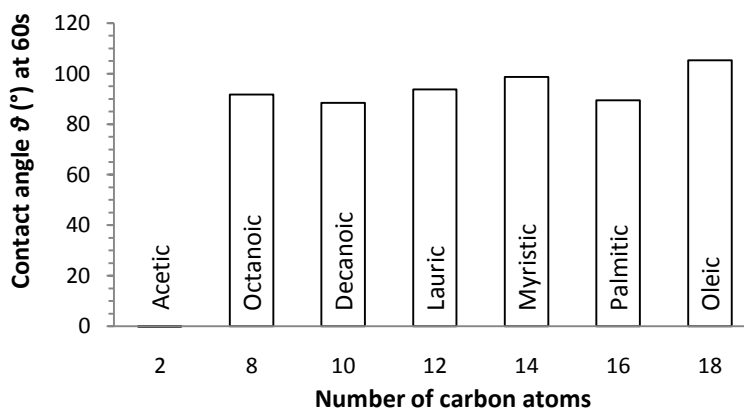
Figure 3.44 Water contact angles of mixed acetic-fatty SPS esters measured at 60 seconds. A synthesized SPS acetate sample is also shown.

Even if the grafting is higher for the short chains, with ratios acetyl/fatty acyl of 6 in the case of C8 and 76 in the case of C18:1, the contact angle values are more or less identical. These results are in accordance with the one observed on mixed cellulose esters. [23]

These results demonstrate clearly that the grafting of fatty chains on SPS has a considerable impact on the water repellency and this with degrees of esterification extremely low. However, the fact that there is no correlation with acetyl content does not necessarily mean that the acetyl groups have no influence. This just means that their contribution is reduced in term of grafting/WR compare to fatty acyl groups.

3.5.3.4 *Water vapor adsorption*

Hydrophobicity is a concept related to the affinity of a material with water. There is no absolute scale for hydrophobicity. However, there are quantitative

parameters directly related to these concepts, e.g., the equilibrium moisture content. In this work we will consider hydrophobicity as the capacity of SPS to adsorb water in vapor form.

Eight of the treated samples were selected to be analyzed by dynamic vapor sorption with water. We aimed to evaluate the influence of the extent of grafting and of the nature of the fatty chain. We selected samples representative of the whole range of variation of these parameters (Table 3.8).

Sample	ΔEC_2	ΔEC_f	ΔEC_{total}	Δ acyl fraction (g/Kg)
SPS1 C_2	3664	-	3664	154.0
SPS2 C_2-C_8	1981	314	2295	166.3
SPS3 C_2-C_{10}	2075	194	2269	138.5
SPS4 C_2-C_{12}	2108	121	2229	120.6
SPS5 C_2-C_{16}	2245	41	2286	105.2
SPS6 C_2-$C_{18:1}$	2018	27	2045	91.9
SPS7 C_2-$C_{18:1}$	1649	28	1677	76.7
SPS8 C_2-$C_{18:1}$	1079	10	1089	48

Table 3.8 Acyl-contents of treated samples selected for DVS analyses

The sorption isotherms of these samples are gathered in Figure 3.45. The values of equilibrium moisture content are spread in a wide range due to the significant differences among all the samples.
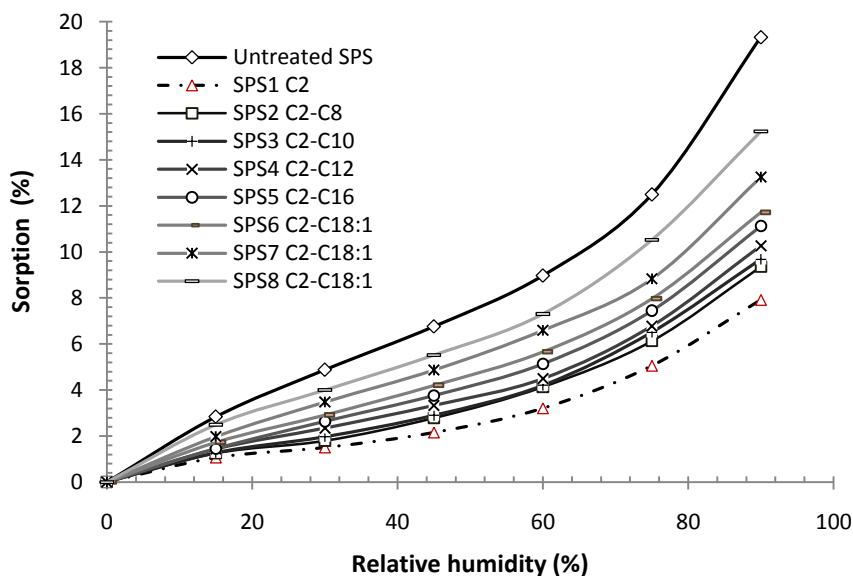

Figure 3.45 Dynamic vapor sorption analysis of samples described in Table 3.8

The sample that shows the highest hydrophobicity is the acetylated sawdust (SPS1). Any of the samples containing grafted fatty chains is less hydrophobic that this sample containing only C2 aliphatic chains. This surprising fact seems to be in contradiction with the values of CA. Indeed, all the acetic-fatty SPS samples exhibited permanent hydrophobicity whereas the acetylated sample did not. Let us remind that the water repellency was dependent on the ΔEC_f. In this case, the hydrophobicity measured with the DVS device does not depend on the fatty acyl content. No correlation when plotting the fatty acyl content with the water sorption (%) was observed. Instead, it depends exclusively on the total acyl content expressed on a mass basis (Figure 3.46).
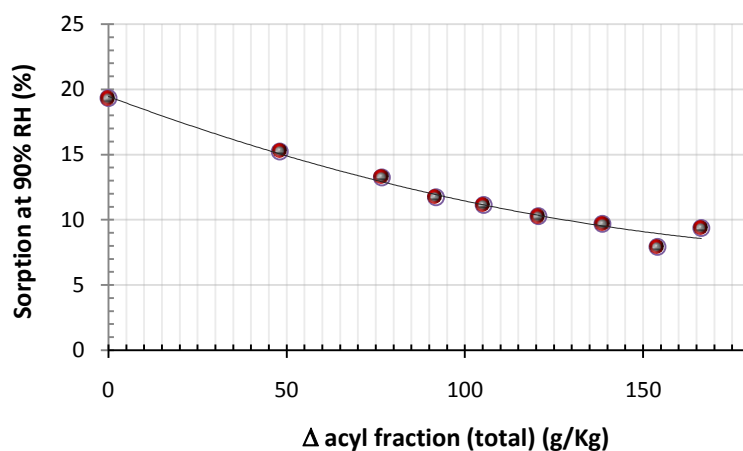

Figure 3.46 Influence of the acyl groups content on the hydrophobicity of esterified sawdust

Other correlations were explored (in function of the molar acetyl content, or the molar fatty acyl content) but none of them was satisfactory. This is not the first time that this type of correlation is expressed. Hill and co-workers [14] demonstrated that the anti-shrink efficiency of Corsican pine was dependent on the weight percentage gain. The latter is a parameter equivalent to the mass acyl content. These interesting results indicate that the water repellency and the ability to adsorb vapor water are two different concepts.

It is difficult to state which are the physical aspects involved in such differences. However, as we suggested in a previous paper [23], liquid water and vapor water present completely different organizations. Liquid water can be considered as a cluster of molecules linked by hydrogen bonding, their interaction with a hydrophobic surface is therefore subjected to high surface energy obstacles. On the

contrary, water vapor is constituted of individual molecules able to reach the numerous hydrophilic hydroxyl groups present in lowly substituted wood esters. The total grafting in terms of weight percentage gain and therefore the occupied volume by the acyl groups is preponderant when considering the water vapor sorption.

Recent works were made on the esterification of guiacol and glucose as lignin and cellulose model compounds by mixed acetic-oleic anhydride mixtures. Lyon *et al* did not find any evidence of the grafting of fatty chains and concluded that the process claimed by Magne *et al* was reduced to a pure acetylation of the substrates [20,27]. The analytical method employed to characterize the chemically modified model compounds (MAS-DEC, ^{13}C NMR) is evidently not adapted to the characterization of low degrees of substitution. In such cases, specific analytical methods are required [25]. The claim by Lyon *et al*, that the water repellency of modified wood observed by Magne *et al* was only due to remaining free fatty acids, is false. We demonstrated in this paper that a small amount of grafted fatty chains compared to acetyl groups, permits to reach permanent water repellency.

3.5.4 Conclusions

- Mixed Scots pine sawdust esters bearing acetyl and fatty acyl groups can be synthesized by reaction in a medium prepared from acetic anhydride and a fatty acid without the use of any solvent or catalyst. The relative proportion of the acetyl and fatty acyl groups grafted on SPS can be controlled by an appropriate selection of the molar ratio of the initial reagents, the nature of the fatty acid, and the conditions of treatment.

- The contact angle of SPS acetate is null indicating that water repellency depends only on the fatty acyl content in the studied range of esterification. Mixed acetic-fatty SPS esters shaped into pellets could exhibit water repellency at low fatty contents. The contact angles values of such mixed SPS esters were comprised between 90° and 110°. In the case of acetic-oleic SPS esters the minimum fatty acyl content to reach water repellency is 25 mmol.Kg^{-1}.

- Equilibrium moisture content of mixed acetic-fatty SPS has been demonstrated to be dependent on the mass acyl proportion, contrarily to the water repellency. The nature of the substituent had no impact in the studied domain.

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3.6 Conclusions

The study of the reactivity of mixed acetic-fatty anhydride mixtures towards cellulose and Scots pine sawdust has permitted to establish a new reaction system without catalyst or solvent. Cellulosics directly treated by mixed acetic-fatty anhydrides are substituted by two acyl groups, acetic and fatty, and the combination of the two substituents influence their properties. The main novelty was the correlation of these properties with very and extremely low degrees of substitution.

The reactivity of pine sawdust was 6 times higher than that of cellulose. Expressed in the same units, the average degree of substitution in the studied domain, were of about 2300 and 380 meq.Kg^{-1} respectively. Such low values were voluntarily achieved by choosing the appropriate reaction conditions. The non-acidic medium preserved the degree of polymerization of the biopolymers.

The widespread idea that a high extent of acyl groups grafted on the material is needed to reach hydrophobicity is subjected to debate. We could observe on samples of cellulose and pine sawdust that extremely low fatty acyl contents could confer good **water repellency**. The threshold of the chemical modification needed to reach such properties ($DS_f = 3.10^{-4}$) could be determined thanks to a new analytical technique able to quantify as little as one side-chain per molecule of cellulose. These results are perfectly innovative. We could not find anything comparable in all the papers of the field. Investigations describing low degrees of substitution do not go below 0.05, which are values one hundred times superior to the threshold. Water repellency from the results obtained on samples of cellulose and SPS can be defined as independent on the degree of esterification. The nature of the acyl group is the principal factor influencing WR. It is therefore important to remind that some of the mixed esters showed water repellency with fatty content 300 times inferior to their acetyl contents where acetylated samples of cellulose or SPS did not show any WR.

Nevertheless, the results of the isotherm sorption analysis permitted to put in evidence that WR and hydrophobicity to water vapor was not correlated. Acyl content of the cellulose esters were quite low and comparable to each over that the differences between their sorption values were not significant. However, the **hydrophobicity** was found on the SPS treated samples to be dependent on the acyl proportion (on a mass basis) independently on the nature of the acyl group grafted. An evident correlation between the mass proportion of acyl groups and the vapor water sorption of the samples was demonstrated.

The concept of hydrophobicity and water repellency seems therefore to be dissociable regarding to these results. The extent of total grafting seems to be correlated to hydrophobicity (tendency not to adsorb water vapor) whereas the fatty nature of the substituent has an importance on water repellency (lack of wettability).

The extrapolation of these results could permit to better understand and to explain the properties observed in the Lapeyre's Wood Protect products. The acetylation of wood is known to contribute to the dimensional stability but the addition of fatty acyl groups onto the wood is the responsible for water repellency. Its durability is undoubtedly increased by limiting its affinity with water.

Finally, the reaction of mixed anhydrides with wood present the following advantages:

- The high reactivity of mixed anhydride: we have seen in this chapter that under non-catalyzed conditions we could obtain acetylated samples with a degree of grafting equal to the one obtained with pure acetic anhydride.
- Mixed anhydride mixtures are less acidic than acetic anhydride; this can limit the degradation of wood properties during treatment.
- The mixtures compositions can be modulated in function of the molar ratio.
- The use of mixtures permits to graft fatty chains and to give water repellency by the grafting of small amounts.

The next step in our scientific approach is the study of this reaction on wood blocks. We will present in chapter four, the changes in properties of wood pieces treated by the mixed anhydride mixtures.

CHAPTER 4

Influence of the treatment conditions on the properties of wood blocks

CONTENTS

4.1 Introduction

There is an apparent inconsistency in the literature [1-15] concerning the chemical modification of wood, in particular with aliphatic anhydrides, about the protocols and the substances utilized.

In most cases, wood samples are solvent-extracted to limit the interactions of the reagent with the wood secondary compounds such as tannins and waxes. The aim of those works is to simplify the wood model and to limit it to an alveolar composite material made of cellulose, hemicelluloses and lignin. Thus, wood samples are usually Soxhlet extracted with mixtures of toluene, acetone, and methanol (4:1:1). They are then dried at high temperature (103°C) to remove the remaining solvent. After that, pyridine, which is well known to be a swelling agent and a catalyst, is used in a mixture with anhydrides to increase the yield of esterification. The problem is that these approaches are not representative of the industrial scale even if they permit to understand certain phenomena. The use of organic toxic compounds, catalysts and solvent extraction is not compatible with the industry constraints especially with the recent legislation concerning chemical products.

Under this consideration, we have chosen to work with a totally different approach. Not only that we avoided the use of toxic substances, but also we have considered that the wood was a complex and heterogeneous material in which **the secondary constituents play a role in the wood properties**. Tannins and extractives participate without any doubt to the natural resistance of wood species such as hardwoods. Moreover, the use of a pretreatment or a catalyst may change considerably the wood properties even without chemical modification. That is why, based on our experience related to the reactivity of anhydride mixtures with cellulose and sawdust, we decided to extrapolate these treatment conditions to wood block samples. The results we have obtained on pine sawdust are a good base permitting to understand the reactivity of the constituents of wood.

We investigated three wood species, Scots pine (sapwood and heartwood), oak (sapwood and heartwood), and beech (heartwood only as beech does not present any significant sapwood). Pine and beech have been selected because they are the two non durable species employed in research to study wood modification. Moreover their use is mandatory in standard biological tests according to European normative. Oak is the species employed presently at industrial scale by our industrial partner.

We must keep in mind that one of the objectives of these investigations was to consider the treatment of wood by mixed anhydrides in such a way it could be extrapolated to industrial scale. Whenever possible, oleic acid was preferred to other fatty acids because of its availability and lower price.

To summarize:

- **Except for few treatments chosen as references, all the other samples presented in this chapter were not solvent-extracted before treatment and have been conditioned during 2 weeks at 25°C and 60% RH in order to reach their equilibrium moisture content (EMC). These samples have the same characteristics as in the wood industry.**

- **The treatment of 3 representative wood species was performed without the use of any solvent or catalyst. The objective was to study the treatment of wood in the simplest conditions to facilitate its scale-up.**
- **Treatment was done at atmospheric pressure without the use of prior vacuum-pressure impregnation.**

4.2 Methodology

In order to study the impact of the treatment conditions on the wood properties, we made systematically vary each parameter as it was performed on cellulose and sawdust (see Chapter 3, paper 6). The temperature, reaction time, molar ratio and nature (aliphatic chain length) of the acetic-fatty anhydride were investigated. The compositions of the reaction medium were studied and presented in chapter 2.

Treatments were carried out on samples of two dimensions, 20x20x5 and 100x20x5 mm (radial x tangential x longitudinal). The first set of samples should permit to evaluate the dimensional stability of the treated samples. Beech heartwood and the sapwood of the other two species were used. The second set of samples was treated to measure the impact of the treatment on the flexural mechanical properties. Both heartwood and softwood were tested.

The three species of wood, **pine**, **beech** and **oak** were treated separately, in a single batch for each species without distinction of sapwood and heartwood.

Ten samples of each were used.

After conditioning the samples during 2 weeks at 25°C and 60% of RH; their average moisture contents were equivalent for the three species (Table 4.1).

	Pine	Beech	Oak
EMC **(25°C and 60% RH)**	9.18 ± 0.41	9.74 ± 0.57	9.19 ± 0.27

Table 4.1 Equilibrium moisture content (in % wet basis) of the considered wood samples before treatment

Samples were then immersed in the hot reaction medium at the desired temperature. The wood pieces were maintained immerged using a block of stainless steel. After treatment, the samples were immediately removed from the reactor and let stand to cool until room temperature. They were then conditioned again during two weeks at 25°C and 60% RH to let them reach their EMC.

For the treatment, the **typical** conditions are:

-    A temperature of 140°C
-    A duration of treatment of 1 hour
-    A molar ratio (oleic acid/acetic anhydride) of 1.5

As we have seen in the previous chapter, these conditions would limit the input of acetic anhydride and increase the ratio of grafted fatty chains.

We then made vary systematically one parameter at a time to evaluate its impact on the characteristics of the treated wood.

4.3   Swelling and specific gravity

The treatment of wood can induce changes in terms of volume and therefore of density. These aspects are of importance because treated lumbers are destined to particular applications for which they have to respect specifications. The changes in volume due to the treatment would prevent the treatment of joinery pieces already machined because their assembling could be compromised. The changes in density is also important to preserve the characteristics (weight) of the final product. That is

why we measured the impact of the chemical modification by mixed anhydride mixture on wood blocks of the three selected and representative species.

Samples were then prepared from blocks of dimensions 20x20x5 mm (radial x tangential x longitudinal). Samples were carefully selected so the growth rings were parallel to the tangential direction. All the wood samples were measured (using a micrometer accurate to ±0.01 mm) and weighed before and after modification in order to determine the swelling and the changes in density caused by the treatment.

The swelling (*S*) and specific gravity (*SG*) values for all the conditions of treatment are indicated in Table 4.2. *S* was determined as described in chapter 1.

		Pine		Beech		Oak	
		S(%)	SG*	S(%)	SG*	S(%)	SG*
Untreated (reference)		-	0.50	-	0.75	-	0.67
	80	1.8 ± 0.5	0.64	4.2 ± 0.9	0.83	2.1 ± 0.7	0.72
	100	2.3 ± 0.5	0.70	4.7 ± 0.9	0.87	2.7 ± 0.9	0.74
Temperature (°C)	**120**	2.5 ± 0.4	0.76	5.8 ± 0.6	0.98	3.1 ± 1.0	0.72
	140**	2.9 ± 0.5	0.80	6.5 ± 0.5	0.96	3.6 ± 0.7	0.75
	160	2.6 ± 0.4	0.83	8.4 ± 1.4	1.05	4.1 ± 0.9	0.79
	0.5	2.0 ± 0.7	0.80	5.6 ± 0.8	0.98	2.4 ± 0.6	0.74
	1**	2.9 ± 0.5	0.80	6.5 ± 0.5	0.96	3.6 ± 0.7	0.75
Time (h)	**1.5**	3.1 ± 0.5	0.75	8.3 ± 1.9	0.98	4.1 ± 0.6	0.79
	2	3.0 ± 0.6	0.77	10 ± 1.3	0.93	6.5 ± 1.1	0.79
	3	3.4 ± 0.5	0.81	11.1 ± 1.1	0.96	7.5 ± 1.2	0.76
	0	7.8 ± 0.7	0.50	18.1 ± 0.8	0.65	9.2 ± 1.0	0.78
Molar ratio	**0.5**	6.3 ± 0.8	0.87	14.4 ± 1.1	0.93	7.8 ± 0.0	0.89
(fatty acid / acetic anhydride)	**1**	3.6 ± 0.8	0.85	8.8 ± 0.7	0.91	6.8 ± 1.1	0.80
	1.5**	2.9 ± 0.5	0.80	6.5 ± 0.5	0.96	3.6 ± 0.7	0.75
	2	2.1 ± 0.8	0.79	6.3 ± 0.8	0.95	4.3 ± 1.2	0.70
	C2	7.8 ± 0.7	0.50	18.1 ± 0.8	0.65	9.2 ± 1.0	0.78
	C8	5.3 ± 0.6	0.50	13.5 ± 0.7	0.63	7.1 ± 0.3	0.72
	C10	5.0 ± 0.4	0.52	12.8 ± 0.4	0.71	6.0 ± 0.4	0.72
Aliphatic chain length	**C12**	3.0 ± 0.4	0.61	9.0 ± 0.4	0.75	4.6 ± 0.6	0.69
	C14	3.1 ± 1.0	0.70	8.1 ± 1.1	0.74	3.2 ± 1.0	0.72
	C16	2.7 ± 0.3	0.70	7.6 ± 0.5	0.79	3.9 ± 0.9	0.75
	C18:1**	2.9 ± 0.5	0.80	6.5 ± 0.5	0.96	3.6 ± 0.7	0.75

* Specific gravity based on oven-dry weight and volume of samples conditioned at 25°C and 60% RH.

** Typical conditions

Table 4.2 Swelling (*S*) due to the treatment and specific gravity (*SG*) of the treated samples.

We can notice considerable differences between the treated wood species. Beech is the most sensitive to swelling when treated with mixed anhydrides with values up to 18% whereas pine and oak remain under 10%. The highest values of S are obtained with low molar ratio mixtures as it appears in Figure 4.1.
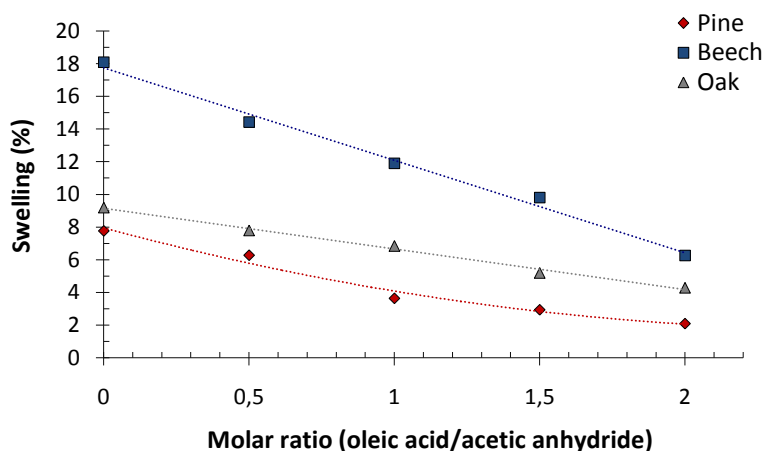

Figure 4.1 Increase of the treated samples volumes as a function of the molar ratio. Temperature = 140°C and 1 h of reaction.

Swelling tends to diminish as the proportion of reactive molecules (i.e. anhydrides) in the mixture decreases. As we have seen in chapter 2 (about the treatment of cellulose and pine sawdust by mixed anhydrides), the total grafting decreases with the increase of the molar ratio, even if the proportion of fatty chains tends to increase. **This could indicate that the swelling is correlated to the esterification of hydroxyl groups.**

In order to verify this hypothesis, it is necessary to quantify the chemical modification. The determination of the ester content that we performed on cellulose and pine sawdust is not adapted to wood blocks. Cellulose and sawdust can be considered as "homogeneous" materials; wood blocks, on the contrary, present considerable differences in their chemical constituent distribution. The natural acetyl content of wood is variable even in a single piece of wood. It is consequently impossible to quantify by difference between a treated and an unmodified block, the acetyl and fatty acyl contents brought by the treatment. So, the heterogeneity of the chemical composition of wood does not allow to evaluate the amount of grafting by classical analytical techniques.

The gravimetric method that consists in weighing the solvent-extracted wood sample before and after treatment is a common method used in literature to evaluate the extent of the chemical modification (weight percentage gain, WPG). Nevertheless, this method is only convenient for highly modified samples; at least when they show changes higher than the standard deviation of such measurements.

The WPG was evaluated on samples treated during 1 hour at 140°C at a molar ratio (oleic acid/acetic anhydride) comprised between 0 and 2. We carried out solvent extractions with a Soxhlet apparatus to remove unreacted chemicals and extractives from wood. Ethanol was used as a solvent and extraction was performed for 10 hours on 10 samples (20x20x5 mm) for each condition of treatment. Results are shown in Figure 4.2.
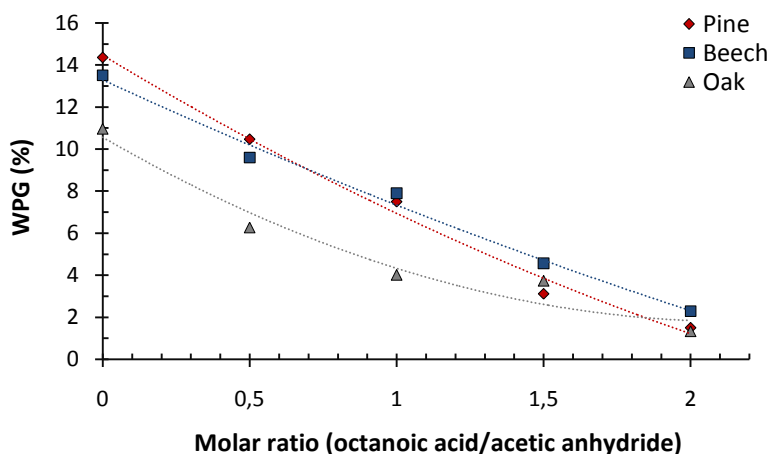

Figure 4.2 Weight percentage gain of wood samples after treatment.
Temperature = 140°C and 1 h of reaction.

We can observe that the trend is similar to that of the swelling (Figure 4.1). This seems to confirm that the grafting is responsible for the increase in volume of the samples.

Differences in reactivity can be observed between the species. Pine and beech are the most reactive under these conditions of treatment. Nevertheless, it is important to consider that the treated samples are extracted after treatment and that the reactivity of the extractives present in wood is not taken in account in this figure. Hardwoods, oak in particular, contain a high concentration of tannins that are undoubtedly implicated in the reaction of esterification by the anhydrides. The esterification of the extractives could compete with that of the cell wall biopolymers,

leading to a decrease of the WPG when considering extracted samples. Moreover, the differences in the chemical compositions of the pine, beech and oak are important factors when evaluating the wood reactivity. We have seen in Chapter 2, and this is well described in the literature, that cellulose, hemicelluloses, lignin and extractives do not present the same order of reactivity with anhydrides. Haque and Hill [16] have shown that lignin limits the access of the reagent to the cell wall and modifies the reactivity with cellulose. Nevertheless, this conclusion should be considered under the light of the structural modification occurred in cellulose during the delignification process that was applied to wood in their work.

If we plot the swelling as a function of the WPG (Figure 4.3), we can note that the swelling is linearly dependent on the WPG. This is in agreement with the results presented in the literature. [17-20]
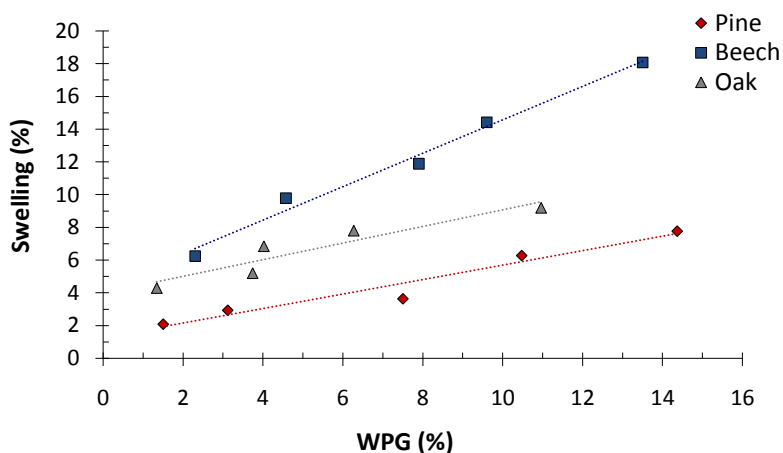

**Figure 4.3 Linear correlations between the swelling due to treatment
and the weight gain of the treated wood.**

The swelling after treatment with anhydrides can thus be interpreted as a swelling of the cell wall occupied by the bonded acyl groups [21]. Moreover, the increase in volume of the treated wood blocks depends on the wood species. Hardwoods seem to be more subjected to swelling when treated with mixed anhydride mixtures. Beech swells three times more than pine for the same WPG. These differences can be correlated to the composition of the species and to the differences in accessibility to cell wall, potentially due to the lignin content. [16]

When making vary the aliphatic chain length of the mixed anhydride (Figure 4.4), we observe first a decrease of the swelling with the number of carbon atoms of the chain.
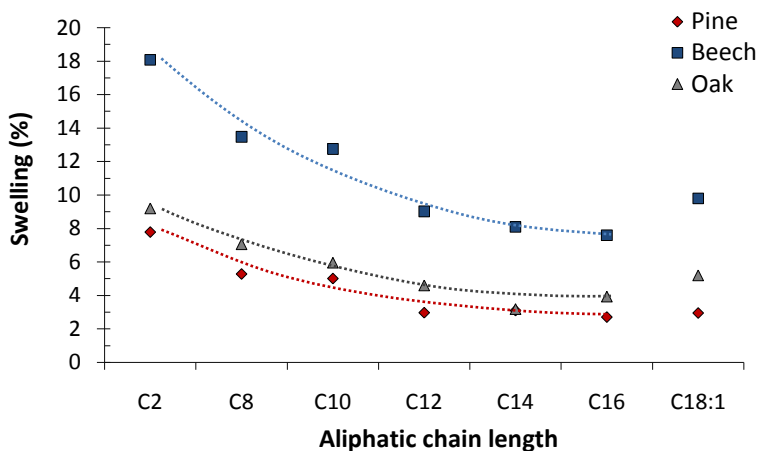

Figure 4.4 Effect of the nature of the grafted chains on the increase of volume of treated wood.

The oleic C18:1 chain contains a *cis* double bond, which makes a bulkier molecule than the saturated aliphatic chains. The observed swelling is therefore bigger than the expected one of the stearic C18:0 substituent.

In chapter 3 (paper 6), we saw that no matter what fatty chain is employed, the total ester content of treated sawdust was practically constant. If swelling depends on grafting as demonstrated in Figure 4.3, the swelling of the samples in Figure 4.4 should be constant. The only explanation about the difference between sawdust and wood blocks is the phenomenon of reagents diffusion in the cell wall. As the aliphatic chain length becomes bulkier, the steric hindrance increases, limiting the accessibility of the mixed anhydride to the hydroxyl groups.

The *cis* conformation of oleic acid makes the molecule bulkier and less reactive but it increases the gained free volume with even lower grafting rates than linear fatty acids.

We can also note that a swelling of the samples occurs even for treatment conditions inducing limited chemical modification. This can be a consequence of the presence of acetic acid (recognized as swelling agent), which is produced during the

synthesis of mixed anhydride and also from the hydrolysis of the reaction medium by action of wood moisture.

Concerning the specific gravity of the treated samples, we can note small differences concerning the treatment conditions. On the contrary, the nature and the quantity of the fatty chains have an important impact on the specific gravity. The bulking of chemicals and the swelling due to the treatment are responsible for this increase or decrease. The bulking may vary with the nature of the reagent, able or not to get into the cell wall. That is why the samples showing a huge swelling (e.g. low values of molar ratio) have a lower SG after treatment. These changes in specific gravity have often an impact on the strength (mechanical properties) of the wood species.

4.4   Mechanical properties

The mechanical properties of wood are of major importance for most of its applications. In the case of joinery makers as Lapeyre, the preservation of the initial properties after treatment is primordial. A final product made from chemically modified wood has to be, in terms of resistance and consistency, comparable to joineries made from natural wood. The potential degradation of wood induced by the treatment can be redhibitory at industrial scale.

Some treatments able to give dimensional stability to wood are in some cases not adapted to applications that need a final product with good mechanical properties. The thermal treatments are a perfect example of the limit in terms of industrial application that can encounter a treated wood presenting diminished mechanical resistance [22,23]

In order to determine if the chemical modification of wood by mixed anhydrides had an incidence on the structural properties, we evaluated systematically the impact of the treatment conditions and the nature of the reaction medium on the mechanical properties, we determined the flexural loading properties with stress-strain testing.

The heterogeneity of wood can cause important standard deviations. For this reason, we carefully selected small, clear specimens (100x10x5 mm), which did not have any knots or splits. Since the moisture content has a big impact on the mechanical properties of wood, all the samples were conditioned as explained previously. These tests at laboratory scale are not representative of the mechanical

properties of industrial-size pieces but give some information about the impact of each treatment parameter.

We evaluated the modulus of elasticity and the modulus of rupture of 10 treated samples. In some cases, we could estimate the differences between sapwood and heartwood (oak and pine).

4.4.1   Influence of temperature and reaction time

All the measurements were performed on samples treated with mixtures of oleic acid and acetic anhydride at a molar ratio of 1.5.

Figure 4.5 indicates the impact of the reaction time and the temperature of treatment on the modulus of elasticity (MOE). We made vary each parameter starting from the typical conditions defined in page 181: 140°C, 1 h of treatment.
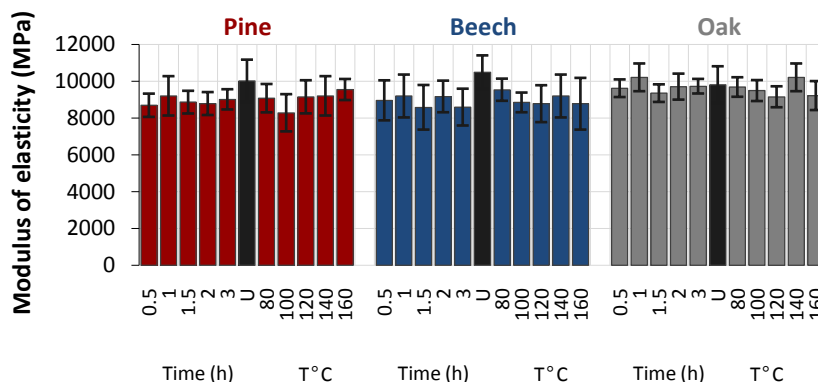

Figure 4.5 Modulus of elasticity of heartwood treated samples compared to unmodified reference (U) for different treatments.

Considering the standard deviations of the measurements, we can see clearly that these two parameters have a low impact on the MOE. We notice a decrease not bigger than 10% of the MOE values for pine and beech but no tendency appears. It seems that the wood structure was preserved at temperature lower than 160°C, especially in the case of oak. These conclusions are confirmed by the modulus of rupture (MOR), which showed constant and sometimes higher values than the control (Figure 4.6).
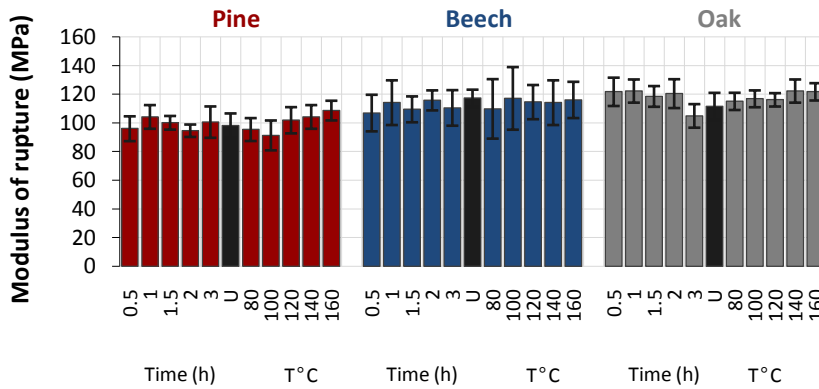
Figure 4.6 Modulus of rupture of treated samples compared to unmodified reference (U) for different treatments. (Molar ratio 1.5)

What should be retained from these results is the fact that the treatment, even carried out at high temperature and for over a long time, does not induce any significant degradation of the wood samples. This has been observed in the case of the three considered species.

4.4.2 Influence of the molar ratio

Samples were treated by acetic anhydride and oleic mixtures made at various molar ratios (oleic acid / acetic anhydride). Treatment conditions were 1 h at 140°C.

Figure 4.7 shows the values of MOE measured on 10 samples for each reaction medium. The variation in percentage compared to an untreated sample is also indicated.
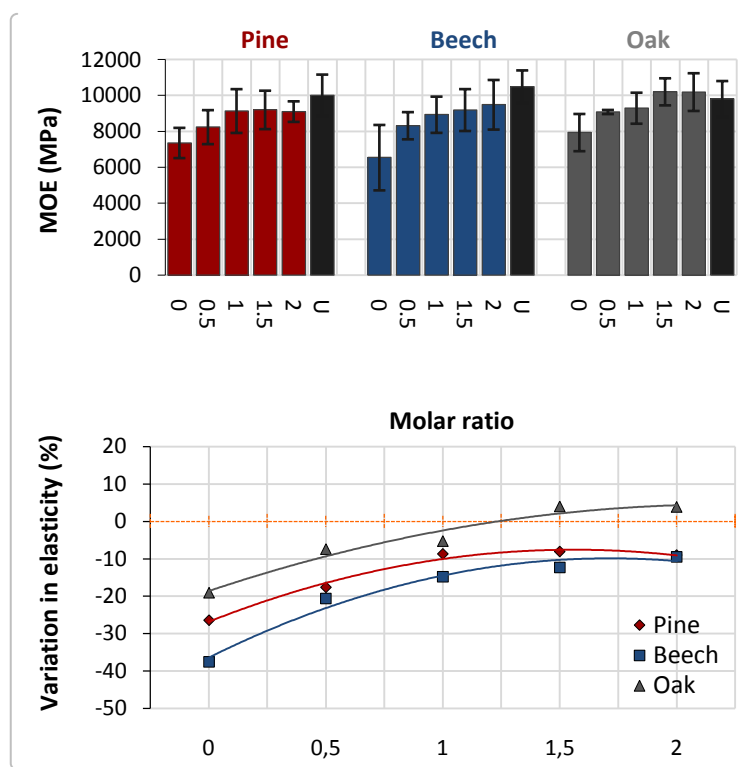
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Figure 4.7 Modulus of elasticity (and its percent variation) of treated samples compared to unmodified reference (U) for different molar ratios. Temperature 140°C and 1 h of reaction.

The composition of the reaction medium has a considerable impact on the MOE of the treated wood. The modulus decreases as the molar ratio diminishes. The most important loss (-40%) was observed for the batch samples treated with pure acetic anhydride (molar ratio = 0). Oak was the less sensitive species to degradation as its MOE did not vary in experiments with molar ratios of 1.5 and 2. Its rigidity decreases however of about 20% in the case of treatment with pure acetic anhydride. Acidic conditions caused by the acetic acid certainly produce degradation to wood. In the case of reaction mediums rich in oleic acid, the pK is higher and therefore they are less aggressive towards the wood.

The same trend is observed concerning the modulus of rupture (MOR) of the treated samples as shown in Figure 4.8.
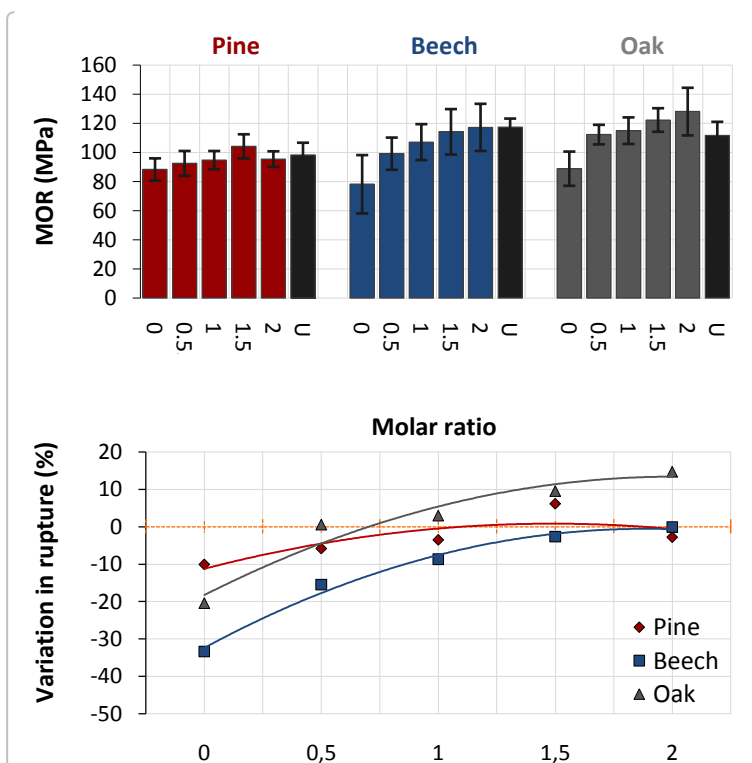
Figure 4.8 Modulus of rupture (absolute and relative values) of treated samples compared to unmodified reference (U) for different molar ratios. Temperature 140°C and 1 h of reaction.

In experiments with molar ratio superior to 1, we can notice that no degradation is observed for the three species. Oak seems even to show an important increase of its MOR (15% at a molar ratio of 2). The improvement is not correlated to the change in specific gravity as the latter decreases when high molar ratios are used. Usually, the strength properties increase with specific gravity because internal stress is distributed in more molecular material [24]. Although we cannot explain the reasons of this increase in the module of rupture, this observation is a quite positive characteristic of treated wood with our method.

4.4.3   Influence of the grafted aliphatic chain length

Mechanical tests were performed on samples treated with mixtures of acetic anhydride with various fatty acids presenting different fatty acid chain lengths. The treatment conditions were kept unchanged, (140°C, 1 h and a molar ratio of 1.5). Results for the modulus of elasticity are indicated in Figure 4.9.
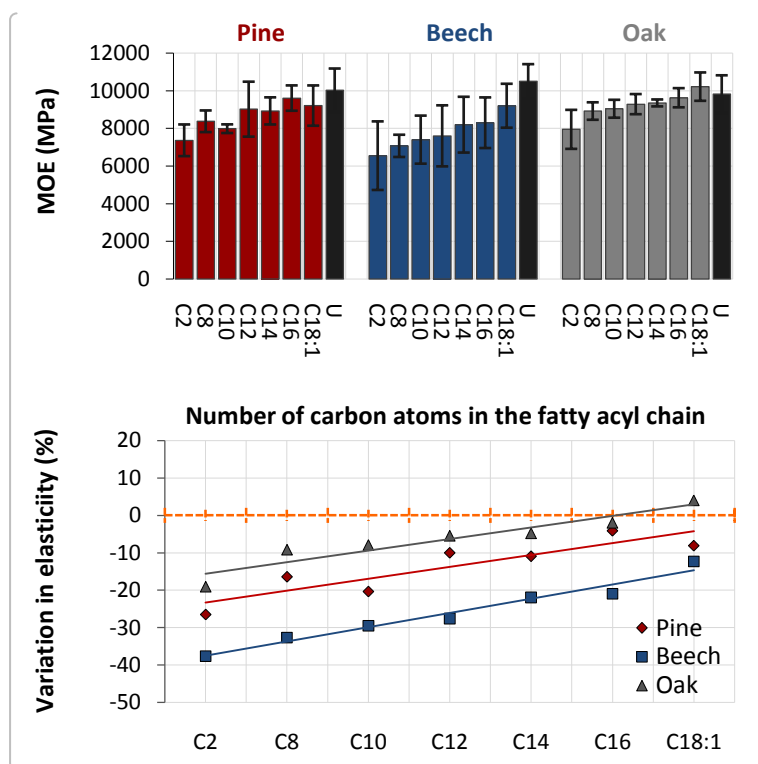
Figure 4.9 Modulus of elasticity and its percent variation of samples treated with acetic-fatty anhydrides. Temperature 140°C, 1 h and R=1.5.

The modulus of elasticity decreases significantly when the aliphatic chain length of the fatty acid used to make the reaction medium decreases. Let us remind that the pKa-values of the carboxylic acids decrease when the number of carbon atoms increases; the reaction medium is therefore less acidic. This demonstrates again that wood is sensitive to acidic conditions at high temperature. We can observe a similar behavior concerning the modulus of rupture (Figure 4.10).
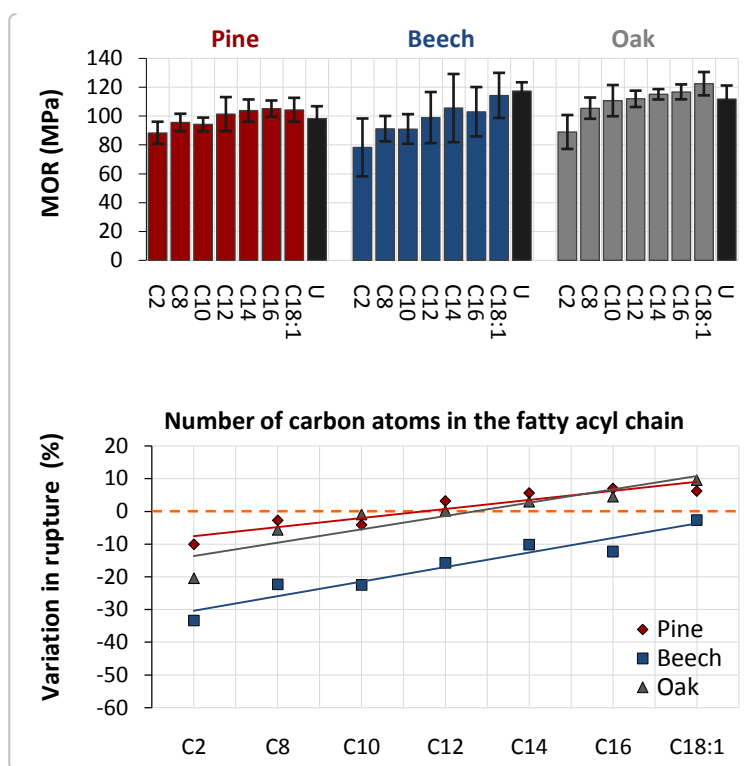
Figure 4.10 Modulus of rupture and its variation in % of samples treated with acetic-fatty anhydrides. Temperature 140°C, 1 h

Pine and oak do not show any loss of their strength when treated with mixtures made from fatty acids from C12:0 to C18:1. In the case of beech, only the reaction with the acetic-oleic is capable to keep the MOR fairly constant. In the other cases, there is a significant loss of its MOR, from 10 to 35%.

4.4.4 Mechanical properties of heartwood and sapwood

For the conditions tested above (140°C, 1 h), we also performed the treatment of sapwood samples of Scots pine and oak. When molar ratios comprised between 0 and 2 were used, we obtained different values for heartwood and sapwood, but they showed the same trends. The MOE and MOR measured on Scots pine are shown in Figure 4.11 and Figure 4.12.

Figure 4.11 Modulus of elasticity of heartwood and sapwood of untreated Scots pine and treated with different oleic acid/acetic anhydride ratios. 140°C and 1 h of reaction.

Unsurprisingly, we can note that sapwood presents modulus values (elastic and rupture) at least 15% inferior to that of heartwood. Moreover, we noted higher values of standard deviations on sapwood samples revealing a higher heterogeneity. The degradation for both types of wood is of the same order of magnitude when varying the molar ratio.
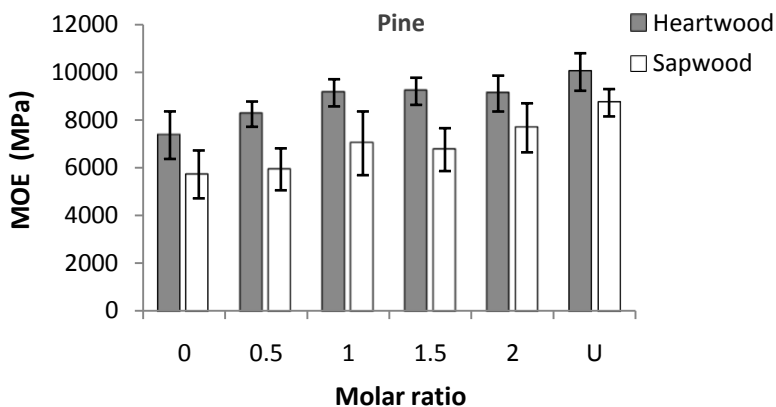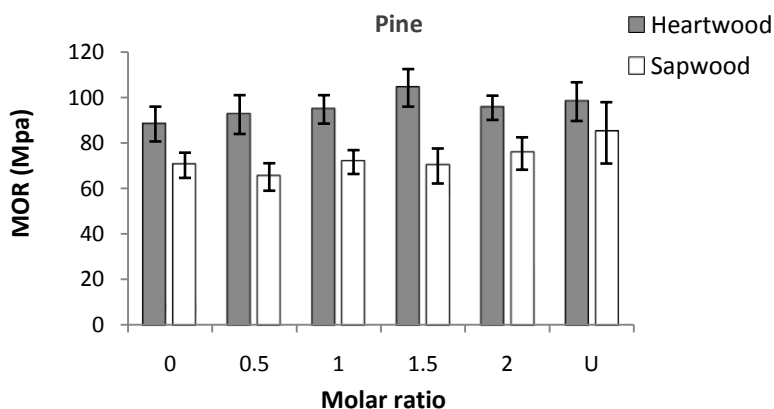

Figure 4.12 Modulus of rupture of heartwood and sapwood of untreated Scots pine and treated with different oleic acid/acetic anhydride ratios. 140°C and 1 h of reaction.

Finally, let us note that untreated sapwood presents the same mechanical properties than heartwood treated with a mixture at a molar ratio of 2 during 1h at 140°C.

Wood chemically modified with mixed acetic-fatty anhydride mixtures does not seem to be sensitive to the treatment conditions such as temperature and reaction time. These outstanding results have been observed in particular with acetic-oleic anhydride mixtures. On the contrary, the nature of the reaction medium has a considerable impact on both modulus of elasticity and rupture. For example, in the case of treatment with pure acetic anhydride, the acidic conditions can lead to a decrease of about 40% of the modulus in the case of treatment with pure acetic anhydride.

4.5   Dimensional stability

Let us remind that this is one of the main objectives of this research work.

At present, in joinery industry, there is not any efficient treatment for dimensional stability based on the simple impregnation of a chemical. As we explained in chapter 1, only more elaborated treatments allow to reach the dimensional stability.

We have demonstrated in the previous chapters that the treatment with mixed anhydride mixtures reduce water vapor adsorption and confer water repellency to powdered samples of cellulose and sawdust. The moment has come to determine if this treatment is able to stabilize the dimensions of a piece of wood. We will determine the influence of all the parameters implied in the treatment process on the anti-swelling efficiency (ASE). We will obtain both, the best parameters for technological improvement and scientific information to better understand the behavior of dimensional variations.

We possess already a first statement inspired by works in the literature: the treatment with anhydride mixtures causes a swelling of the wood whose consequence is that the exposure to humid atmospheres would cause *a priori* a lower extent of water swelling [21]. The reason is simple: the difference between the water-saturated and the oven-dry volumes of the wood is reduced because wood is already swollen (due to chemical modification) and does not tend to shrink because the grafted acyl groups responsible for this swelling are not removed by the drying step.

In literature, the dimensional stability is described as not being due to the extent of the chemical modification. It is therefore not related to the blocking of OH groups. It has been demonstrated, by chemical modification with symmetric

anhydrides from C2 to C7, that dimensional stabilization is related solely to the WPG or bulking of the cell wall [25,26].

In order to verify if mixed wood esters follow the same rule, we developed two approaches:

- Firstly, we have treated wood samples and extracted them after treatment. By this way the samples would present only covalent bonds with the reagent and would not have any free reagent. The determined ASE will be the consequence only of the chemical modification.
- Secondly, we have treated wood samples without extraction, neither before nor after treatment. The ASE-value is therefore the result of the contribution of:
  - the chemical modification,
  - the extractives naturally present (chemically modified or not),
  - the remaining reactants and by-products.

Sapwood samples from oak and pine were investigated altogether with beech heartwood. Treatments of the samples are indicated in sections 1 and 2 of this chapter (pages 179 and 180). Once conditioned after treatment (2 weeks at 25°C and 60% RH) and measured to evaluate the swelling due to treatment, they were oven-dried at 103°C during 24 hours. After they cooled down in a desiccator in order to avoid water uptake, they were measured and weighed with accuracies of 0.01 mm and 0.0001 g. Ten replicates were used for each tested conditions.

Blocks were then soaked in deionized water for 48 hours before determination of the water saturated volume. Following measurement, blocks were oven-dry during 12 hours. This procedure was repeated for a total of 5 oven-drying/water soaking cycles. The volumetric swelling coefficients and the ASE-values were calculated as indicated in chapter 1 for each cycle (page 25). As leaching can occur during water soaking, all the ASE-values presented will be calculated from the 5th cycle. This cycle is more representative of the dimensional stability in the long term.

4.5.1 *Dimensional stability of solvent-extracted samples*

Figure 4.13 shows the ASE of samples extracted with acetone then treated with mixed acetic-oleic anhydride mediums prepared at various molar ratios from 0 to 2. They were solvent-extracted again after treatment.
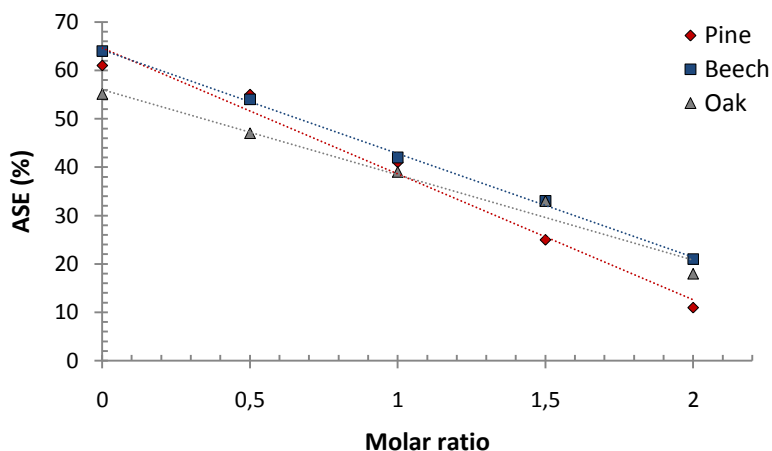
Figure 4.13 Anti-swelling efficiency of solvent-extracted samples, before and after treatment. Reaction at 140°C for 1 h with acetic-oleic mixtures at various molar ratios

We can observe that the three species present the same trend. Also, the ASE of the solvent-extracted samples seems to depend on the extent of grafting. Indeed, the reaction mediums at low molar ratios contain more anhydride functions and the obtained ASE-values are higher. The WPG of these treated blocks has already been shown in Figure 4.2. But if we now plot the ASE obtained for these samples as a function of their WPG, we can confirm that the anti-swelling efficiency of the solvent-extracted samples is indeed correlated to the extent of grafting (Figure 4.14).

Figure 4.14 Anti-swelling efficiency after 5 cycles as a function of WPG (%) for solvent-extracted samples.

The novelty is that all the points are practically on the same curve despite the fact that they include three species treated with different reaction mediums. This fact is really surprising as their macromolecular structures are different a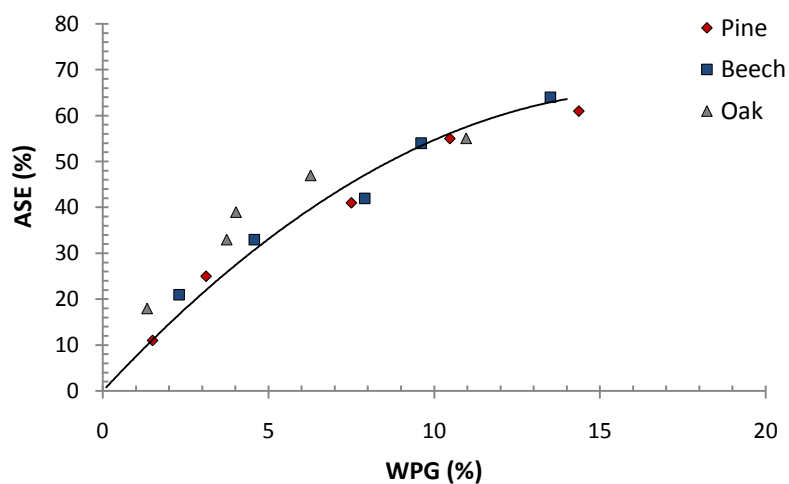s well as their chemical composition. Hill *et al* [26] had reported a similar behavior but only with a single species, namely Scots pine.

Let us remember on the one hand that the grafting ratio (acetate/oleate) varies significantly with the molar ratio (see chapter 3, results on SPS). On the other hand, we have seen that the acetylated pine sawdust did not show water repellency contrarily to the one treated with mixed anhydrides and presenting few fatty chains grafted. These two facts demonstrate that the ASE conferred by the chemical modification depends essentially on the number of methylene units ($-CH_2-$) grafted on it. No matter what type of chain they come from. On the contrary, water repellency depends only on the fatty acyl content.

If we compare the results that we obtained during these investigations to the trend that Hill *et al* [26] discovered for Scots pine with symmetric anhydrides (Figure 4.15), we can notice that our ASE-values are superior even if the trend is similar.

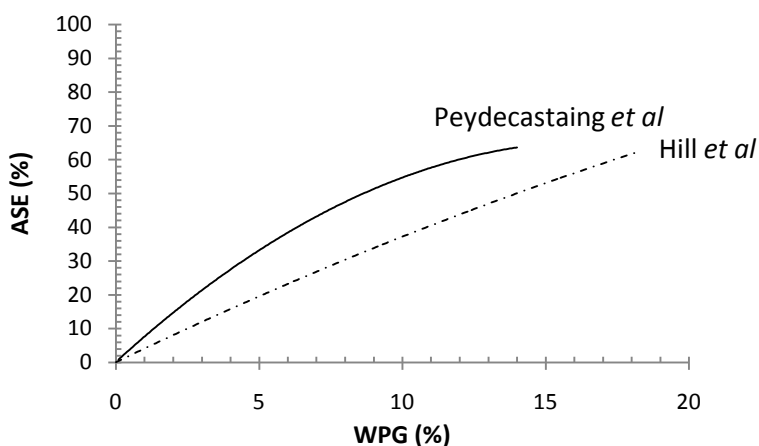**Figure 4.15 Comparison of least-squares (or polynomial) correlation models of the ASE as a function of the WPG**

These differences cannot be attributed to the fact that we treated wood with mixed anhydrides because our samples treated with pure acetic anhydride (molar ratio = 0) are also on the same curve and not on the one described by Hill *et al*. The differences could be due to the fact that protocols employed to

perform the treatments were not the same indeed. Hill *et al* treated their samples using pyridine as swelling agent and catalyst. This could considerably modify the properties of the wood and explain that ASE obtained without using pyridine are higher.

4.5.2 Dimensional stability of samples without washing after treatment

We have performed five cycles of oven-drying/water-soaking; ASE values have been determined for each cycle. The results detailed below correspond to the 5th cycle.

The temperature and duration of the treatment have an impact on the rate of acylation as it has been demonstrated on cellulose and pine sawdust in chapter 3. This has an impact on the dimensional stability of the treated wood as we can observe in Figure 4.16 and Figure 4.17.
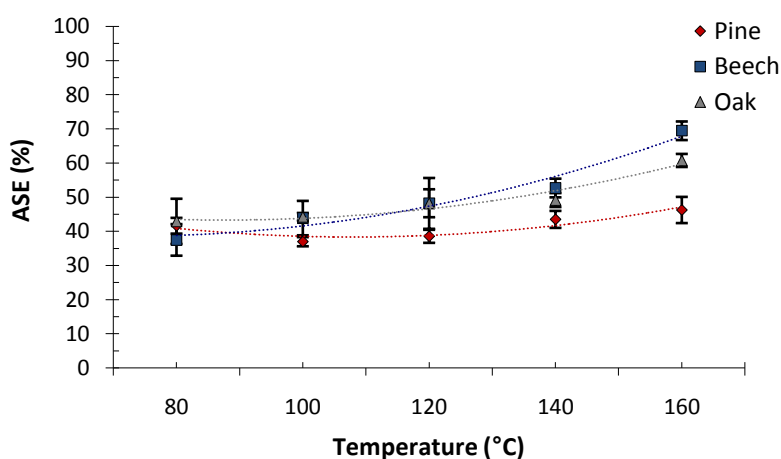
Figure 4.16 Anti-swelling efficiency of treated samples with acetic-oleic mixtures (R=1.5) during 1 h as a function of the temperature. No extraction was done.

Beech and oak show exactly the same swelling when treated with acetic-oleic mixture: their ASE increase considerably as temperature or reaction time increase. On the contrary, when pine is treated at low temperature or for less than 2 hours, there is a slight decrease: the ASE values obtained at 100 and 120°C after 1 h of treatment are about 5% lower than the one obtained at 80°C.
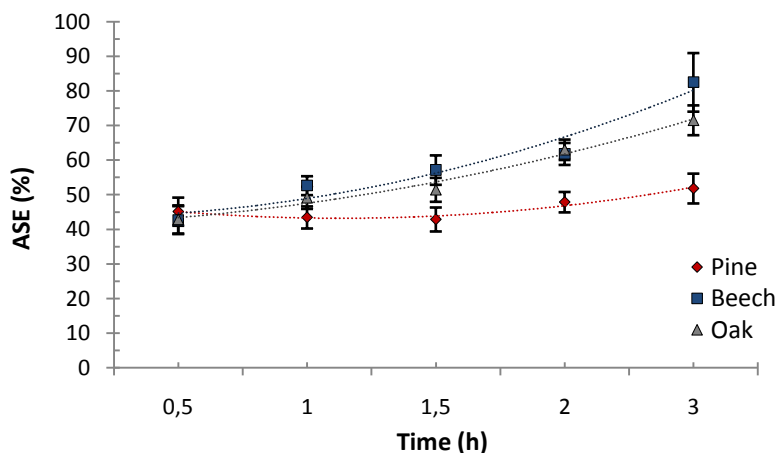
**Figure 4.17 ASE of treated samples with acetic-oleic mixtures (R=1.5) as a
function of the duration of the treatment at 140°C. No extraction was done.**

However, pine does not show an important increase of its ASE values with the
duration of treatment at 140°C. These results are surprising and we do not have any
pertinent explanation. We first thought that the anti-swelling efficiency could have
been caused by the impregnation of the reaction medium playing the role of a
bulking agent. But the results obtained on pine samples solvent-extracted after the
treatment showed ASE-values of 25% in the case of pine (Figure 4.13). This would
indicate that the remaining chemicals in wood after treatment would contribute with
15% of ASE to reach 40%, which is the value for pine treated in such conditions.
Nonetheless, these comments have to be taken with precaution as we are comparing
two different supports. Wood after extraction does not present the same
characteristics; the extractives have been removed and the surface energy of the
support has been changed. Consequently, ASE-values measured on extracted
samples permit only to corroborate the fact that the chemical modification permits to
increase the dimensional stability.

4.5.2.1 Influence of the molar ratio

Sapwood of pine, beech and oak were treated with acetic-oleic mixtures
presenting molar ratios comprised between 0.5 and 2 in order to evaluate the impact
of the rate of grafting on the ASE of non-extracted samples. Results are presented in
Figure 4.18.

Figure 4.18 ASE of treated samples with acetic-oleic mixtures at various molar ratios. Temperature 140°C and 1 h of treatment.

We can observe that as the molar ratio increases the anti-swelling efficiency diminishes as expected. We have concluded from Figure 4.2 that the WPG, correlated to the chemical modification, depends on the concentration of reactive molecules that are in the reaction medium. Also, the ASE depends on the WPG as it has been demonstrated with the treated solvent-extracted blocks (Figure 4.13). However, we can note that the results obtained with the treated blocks without any extraction present higher values of ASE. A comparison of both is present in Figure 4.19.

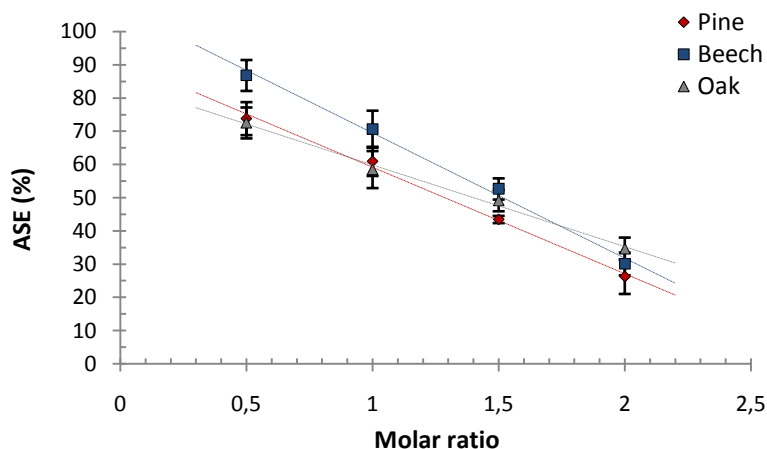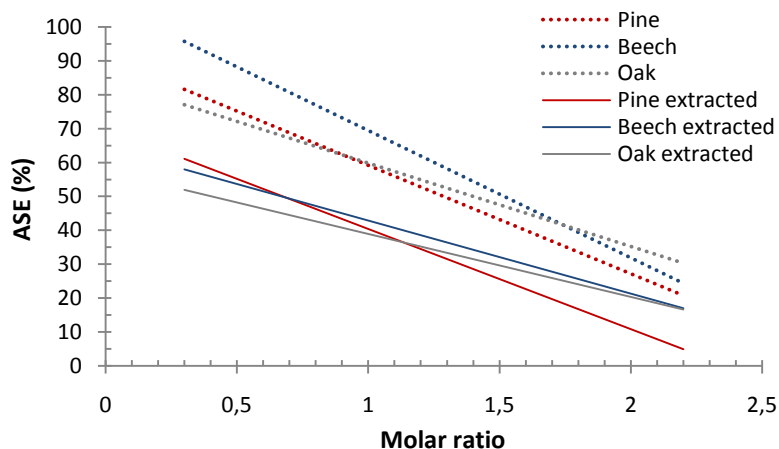**Figure 4.19 ASE of treated samples with acetic-oleic mixtures at various molar ratios. Temperature 140°C and 1 h of treatment.**

The tendencies are the same but ASE values of non-extracted samples are between 10 and 30% higher. A part of this increase is probably due to remaining fatty compounds present in the wood block after treatment which plays the role of bulking agent in the cell voids. Thus, samples of Scots pine, beech and oak were impregnated with the reaction medium obtained at a molar ratio of 1.5 without heating to prevent the reaction of esterification. Table 4.3 recapitulates the ASE-values obtained after five cycles, for the samples impregnated and treated 1 h at 140°C (extracted or not after treatment).

ASE	Scots pine	Beech	Oak
Treated (ASE_t)	43	53	49
Treated and extracted (ASE_{te})	25	33	33
Impregnated only	12	14	8
$ASE_t - ASE_{te}$	18	20	16

Table 4.3 Impact of the remaining reaction medium on the ASE

The ASE-values of the impregnated samples are comprised between 8 and 12% whereas the difference between chemically modified samples extracted or not after treatment are comprised between 16 and 20%. The remaining fatty reagent is therefore not the only explaination for the difference between the ASE-values of the samples extracted or not after treatment.

Another interpretation could be that the non-extracted samples still contain their extractives and these extractives react with anhydrides. These esterified extractives could therefore play the role of water repellent coating agents on the cell wall due to their hydrophobicity.

Finally, we can also consider that the fatty compounds still present after the treatment in wood could form networks by van der Waals interactions. Indeed, the ASE-values commented above were obtained after five cycles and are stable. The fatty chains grafted on wood that interact with the unreacted fatty acids can be at the origin of the stability of the impregnation. For this reason we are going to investigate next the leaching of the treated samples along the cycles of ASE.

4.5.2.2 Influence of leaching

The results previously presented showed ASE values after 5 cylces of oven-drying : water-soaking. It is however interesting to see the evolution of the ASE values all along the cycles. Figure 4.20 shows the evolution of the ASE values

of samples of beech sapwood treated with reaction mediums synthesized at different molar ratio from oleic acid and acetic anhydride. Conditions of treatment correspond to the typical conditions defined in page 180, namely a temperature of 140°C and a treatment of 1 hour.
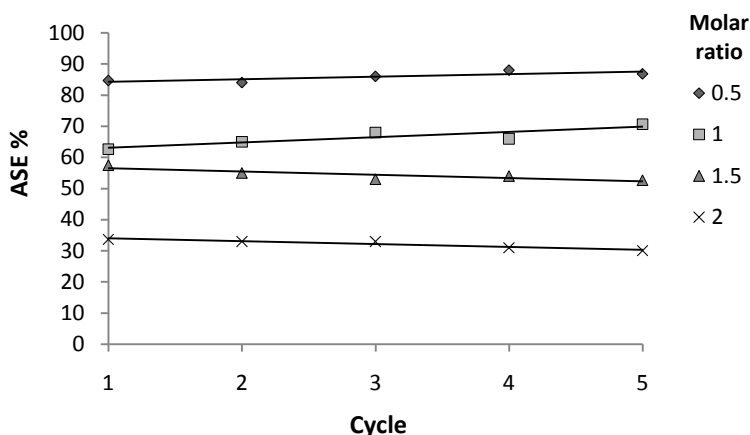
Figure 4.20 ASE-values obtained on treated beech at each soaking-drying cycle. Temperature 140°C and 1 h of treatment.

We can note for samples treated with molar ratios inferior to 1 show a slight increase of the ASE along the cycles. On the contrary, samples treated with reaction mediums at higher molar ratios show a slight decrease of the ASE. The leaching of hydrophobic agents that play the role of bulking agent results in a decrease of the ASE values. Nevertheless, the diminution is limited to 5% only. In any case we can conclude that the most esterified the sample is, the higher the ASE-values are.

The increase of ASE along the cycles is often explained in the literature by a cross-linking reducing the shrinking when drying, and thus inducing a lower swelling. In our case, it seems difficult to consider this possibility because non-cyclic anhydrides do not present any possibility to produce a cross-linking. A rearrangement of the hydrogen bonds is more likely.

It is also interesting to trace the weight of the treated samples after each drying step (Figure 4.21). We noted for the samples treated at various molar ratios, an impressive stability of the weight. We did not observe any significant variation of the weight after drying of the samples along the cycles. A loose of the reagents was predictable but did not occur for the samples chemically modified. On the contrary

for the samples impregnated at room temperature with the reaction medium (molar ratio 1.5) we noted a decrease of the weights of the samples. The case of the beech samples was the more representative and is presented in Figure 4.21.
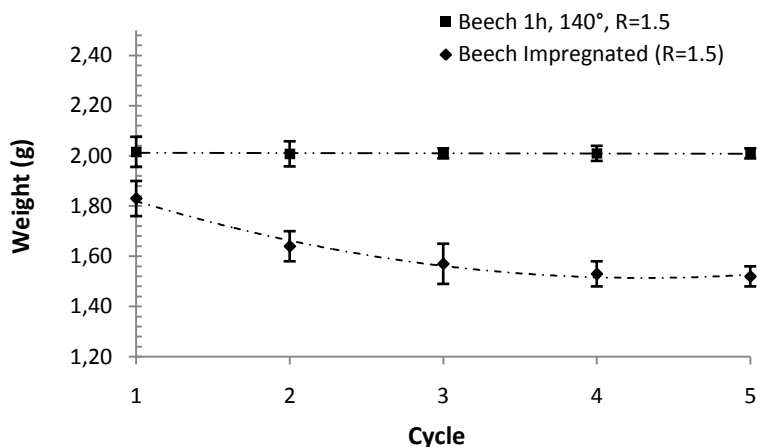
Figure 4.21 Mass of beech treated samples after drying along the cycles

These results are outstanding and could be explained as indicated above by the fact that unreacted fatty compounds of the reaction medium are able to interact with the fatty chains grafted on the biopolymer through hydrogen bonds and hydrophobic interactions. This network could therefore be at the origin of the stability of the mass of the samples all along the cycles.

Moreover, if the wood is stable thanks to the chemical modification, the dimension variations are strongly reduced and the "pumping" phenomena able to make the wood bleed are severely reduced. The consequence is a limited leaching.

Concerning the impregnated samples, we observed that the decrease of the weight was not linear; the weight after 4 cycles reached a plateau. The lost of impregnated products tended to be stabilized after 4 cycles.

4.5.2.3   *Influence of the aliphatic chain length*

The dimensional stability of sapwood samples treated with reaction medium obtained from mixtures of fatty acids with acetic anhydride at a molar ratio of 1.5 is presented by means of ASE values plotted as a function of the aliphatic chain length (Figure 4.22). We could have chosen to study the influence of the fatty chain on sample with molar ratios inferior to 1.5 but the difference observed between the

treatments would have been less significant. We also deliberately chose to fix the ratio at 1.5 as it is a good compromise between reactivity of the medium and ratio of grafting of the fatty chains (see chapter 3).
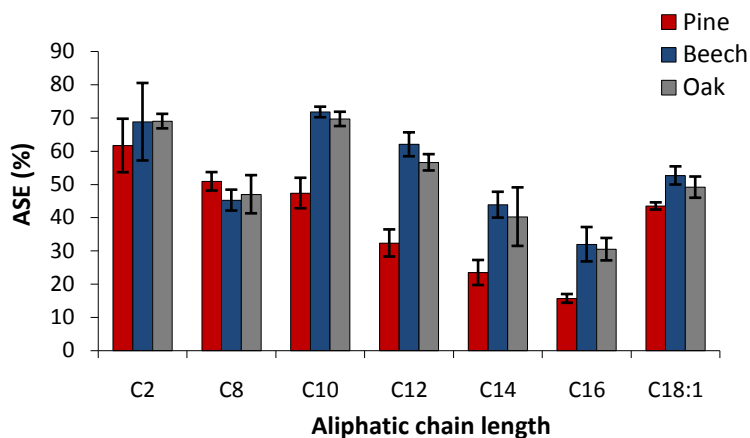
Figure 4.22 Influence of the nature of the fatty chain grafted on the dimensional stability

Studies on cellulose and Scots pine sawdust showed that the increase of the number of carbon atoms of the fatty acid caused a decrease of the fatty grafting but not of the acetyl content. The total ester content was therefore practically constant as well. Consequently, the ASE values should be constant regardless of the fatty acid involved. This is not the case. If we consider acetic-fatty mixtures with fatty chains from C10 to C16, we can observe that as the fatty chains increases, the ASE values diminish. The explanation could be that the steric hindrance limits the access of the fatty molecules to the hydroxyl functions of the cell wall. A decrease of the total grafting could be then observed leading to a decrease of the ASE values.

Nevertheless, we can see that this trend is not respected in two particular cases. The use of a mixture made from octanoic acid and from oleic acid. In the case of octanoic acid, only beech and oak are concerned, their ASE values are 30% inferior to what could be expected if the tendency was respected. We do not have explanation at the moment to justify this phenomenon. In the case of oleic acid, the particularity of its structure could be at the origin of higher results than expected. Indeed, contrarily to the other fatty used in this study, oleic acid is the only one presenting a double bond in the aliphatic chain. It is liquid at room temperature with a melting point of 13.5°C and its conformation is angular due to the unsaturation.
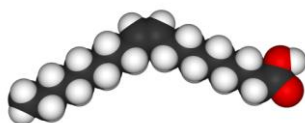
To finish, it is important to note that pine always shows ASE-values inferior to those obtained with beech and oak. This has to be confirmed but it seems that the dimensional stability of softwoods is more difficult to reach with mixtures prepared at a molar ratio of 1.5. Assays with other mixtures are under investigation.

4.6   Scanning electron microscopy

We performed SEM observations on beech samples treated with pure acetic anhydride and an acetic-oleic mixture obtained at a molar ratio of 0.5. Observations were performed on solvent-extracted samples during 8 h with acetone then ethanol.

We did not note on acetylated beech any visible changes of the cell wall surface compared to untreated samples (having been extracted as well). (Figure 4.23)
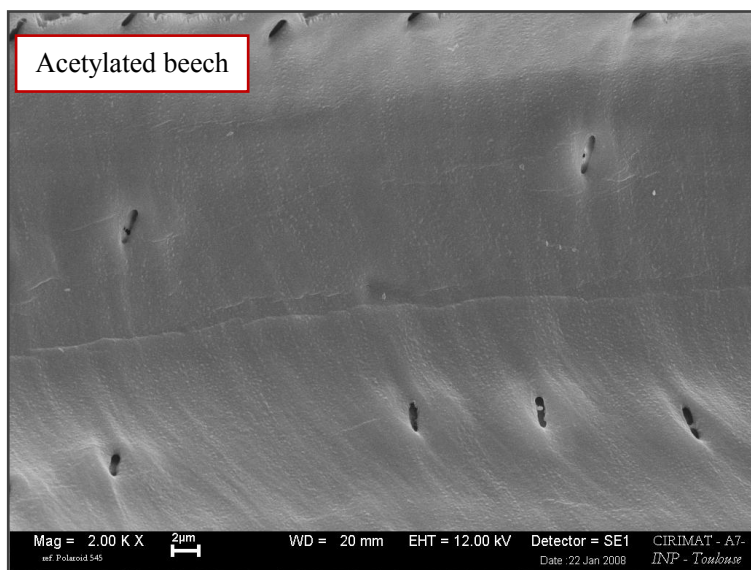
Figure 4.23 SEM observation on beech treated with acetic anhydride (2000X)

But, if we compare with pictures taken on samples of beech treated with mixed anhydrides (acetic-oleic molar ratio R=0.5), we can note that some aggregates are present on the cell wall surface of the treated sample (Figure 4.24 and Figure 4.25).
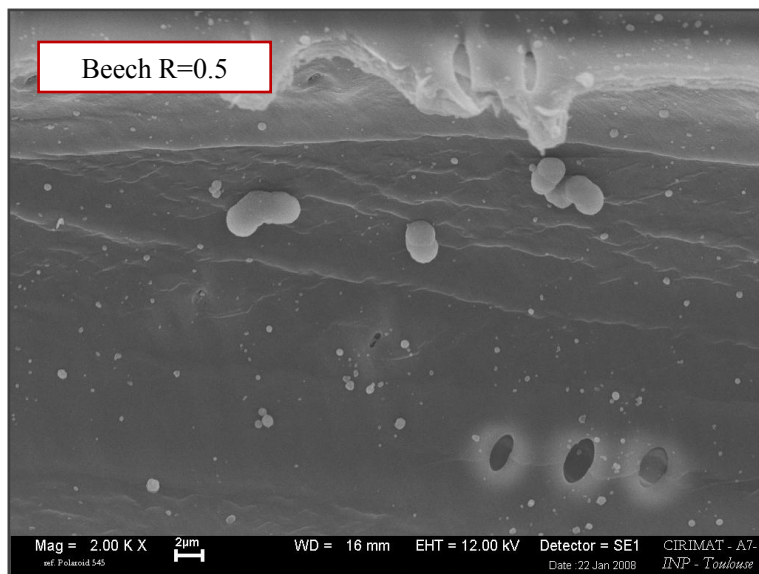
Figure 4.24 SEM observation on beech treated with acetic-oleic anhydride (2000X)
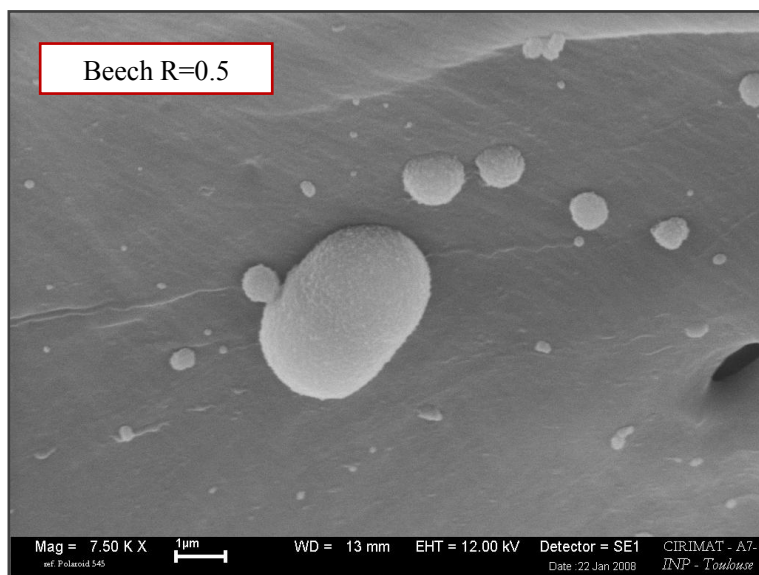
Figure 4.25 SEM observation on beech treated with acetic-oleic anhydride (7500X)

The same aggregates were present on the pine and oak treated samples with the same reaction medium. It seems that fatty molecules can cluster by van der Waals interactions with the grafted fatty chains. This could explain why the samples treated

with mixed anhydride mixtures did not loose mass during the ASE cycles. When we first saw these aggregates, we thought that they were the consequence of the vacuum necessary to perform SEM observations and that remaining reactant present in the cell wall migrated to the surface. However, after a second solvent extraction with acetone, we still observed aggregates on the treated wood. No definitive conclusions can be made at the moment concerning the nature of such clusters.

It is however evident that a strong interaction between the reactant and the wood structure is present.

4.7   *Surface color characteristics*

The color of wood can change after treatment. For instance, Retification[®] turns wood gray, furfurylation turns it black, etc. [22,27] In general the new color depends on the surface, its homogeneity, the species used, and essentially on the treatment conditions. We proceeded to evaluate quantitatively not only these changes but also the evolution of this color with ageing.

CIELAB is the most common color reference used to study changes in color on wood. The three coordinates of CIELAB represent the lightness of the color L^*, its position between red/magenta and green a^* and its position between yellow and blue b^*. The tridimensional model can be represented as indicated in Figure 4.26.
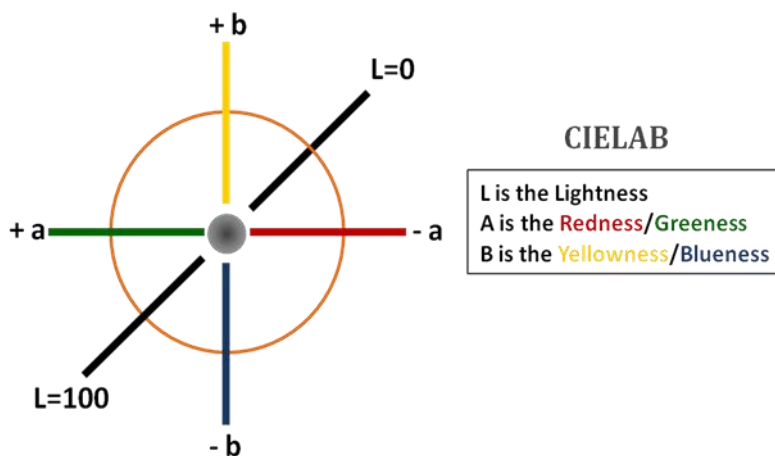
Figure 4.26 L*a*b* parameters

Generally, the CIELAB parameters are used to define a color but also to evaluate the changes in color to make comparisons with the parameter ΔE. The latter can be defined as an interaction between the $L*a*b*$ parameters:

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

ΔE is a relative parameter that indicates only a change between two points but it never implies the direction of a vector. In other words, ΔE does not give the information if a darkening or a yellowing is occuring, for instance.

The samples characterized before and after treatment and after ageing were those used to measure mechanical properties. After mechanical testing, the broken samples were cut to obtain samples of dimensions 40x10x5 mm.

4.7.1 Changes in color due to treatment

The changes in color observed on wood after treatment are of importance when is considered the esthetical aspect of a final product as joineries.

We measured the $L*a*b*$ parameters for 5 specimens of every beech sample. Measures were performed with a colorimeter SE-2000 (Nippon Denshoku Industries Co., Ltd., Tokyo, Japan) (Figure 4.27)
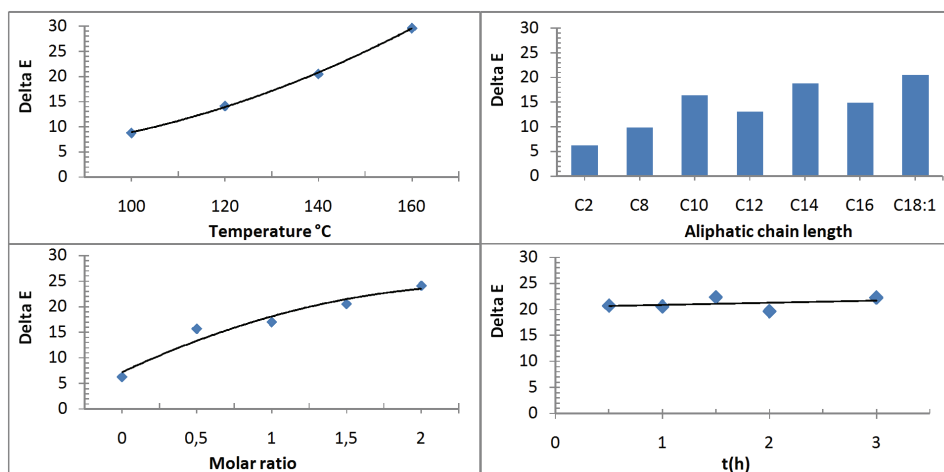
Figure 4.27 Changes in color due to the treatment

The temperature of treatment does have an impact on the color of the samples of beech, a lightening of the samples is visually observed with the increase of the temperature. The degradation of lignin could be involved. The extraction of pigmented extractives such as tannins could also be at the origin of such lightening. On the contrary, the duration of the treatment performed at 140°C with a mixture obtained with oleic acid and acetic anhydride at a molar ratio of 1.5 had no influence.

The molar ratio and the length of the aliphatic chain length had also an impact on the color of the treated samples. The darkening of the beech samples increased with both of these parameters. A darkening of the reagent mixture has also been observed when heated without any contact with wood. Complementary assays have to be done to get more information.

As these results are from preliminary experiments, we do not have enough data to propose full explanations for the observed changes. The origin of the latter are indeed very complex. These aspects will be developed in further research work in collaboration with a Japanese team.

4.7.2 Photostability of the treated samples

Generally, the wood turns yellow by exposure to light, and its color difference increases with irradiation time [28]. Chemical modification with anhydrides in general and acetylation in particular are well known to increase the photostability of wood [29-34]. In order to evaluate the impact of the treatment of wood with mixed anhydride mixtures we performed assays of photodegradation on samples of pine, beech and oak.

The comparison of a treated sample and an unmodified reference has been made by measuring ΔE. A small delta indicates photostability of the sample.

Sapwood samples specimens were irradiated for 50 hours with artificial sunlight from a xenon lamp in a commercial chamber (SX-75: Suga Test Instruments Co. Ltd., Tokyo, Japan) configured to provide an irradiance of 180 W.m^{-2}. After exposition to UV light, the changes in color of the treated samples were measured by determining $L*a*b*$ (CIELAB) parameters with a colorimeter (SE-2000: Nippon Denshoku Industries Co., Ltd., Tokyo, Japan).

The ΔE measured on the treated samples is presented in Figure 4.28.
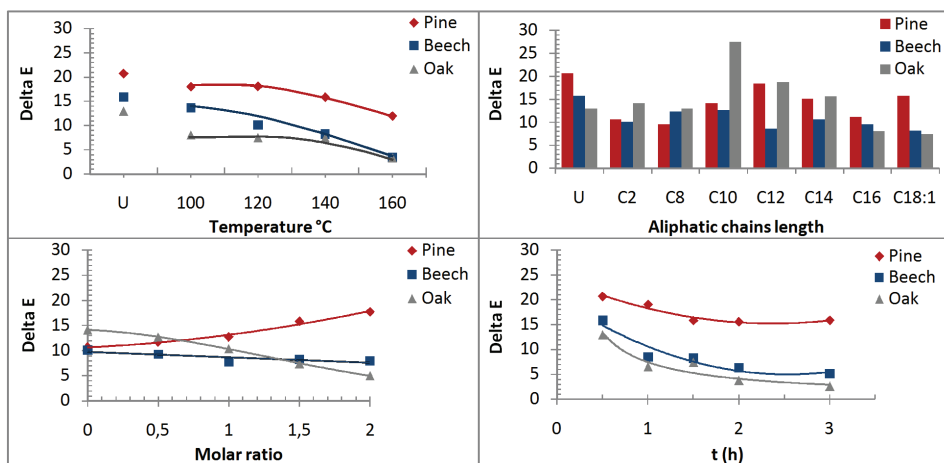
Figure 4.28 Photostability of the treated samples as a function of the treatment conditions

First of all, it is important to indicate that these results are from preliminary tests and were performed on only 5 treated samples of sapwood, that is why standard deviation are not indicated. However, a better accuracy is obtained because; in this case, we measured the variations on each sample before and after irradiation.

The influence of the temperature and reaction time are correlated to a diminishing of the photodegradability of the wood blocks treated with a mixture of acetic anhydride and oleic acid at a molar ratio of 1.5. The chemical modification tends therefore to give photostability to the treated wood. The two hardwoods are the most concerned with values of ΔE inferior to 5% in the best conditions (1 h at 160°C or more than 2 h of treatment at 140°C). Scots pine on the contrary still present a change in color superior to 10% even under the best conditions. The temperature seems however to be the factor influencing the most the efficiency of the treatment in term of photostability.

The impact of the nature of the reaction medium (molar ratio and aliphatic chain length) is difficult to explain. Investigations made on the chemical modification of the surface have to be leaded. The use of FTIR, NIR spectroscopy and TOF-SIMS microscopy is envisaged.

4.8   The Wood Protect® pilot treatment

We are now going to present the results obtained on wood treated at pilot scale. All the data in this section have been provided by our partner, the Lapeyre Company. The parameters of the industrial process are filed as confidential. They are however within the range of conditions described in the previous chapters.

It is relevant to precise that the optimal conditions at laboratory scale are different from those used for industrial production. Moreover, every wood species requires particular conditions leading to optimal performances. The nature of the fatty acid, the impregnation parameters, and the duration and the temperature of the treatment have been optimized in each case.

We will report some significant results from our partner on artificial aging, mechanical properties and wettability of representative wood species treated under optimized industrial conditions.

4.8.1   Weathering resistance

All the measures of weathering on the treated wood that will be presented here were performed on wood blocks of relatively large cross section. We carried out accelerated weathering tests by using two different devices as well as natural ageing tests in real conditions.

4.8.1.1   Gardner wheel test

The Gardner artificial ageing device is shown in Figure 4.29. It consists in a wheel making a rotation of 360° in 90 min. The complete cycle can be divided in 4 steps: a soaking of 12 min in water, 27 min of draining, 24 min of exposure to UV-light and finally 27 min of normal conditions before plunging again into water. Three weeks of artificial ageing are known to be equivalent to 1 year of natural weathering.

Figure 4.29 Gardner ageing wheel

Table 4.4 presents some examples of measurements made on five Wood Protect®
treated species. Acetylation tests with pure acetic anhydride (molar ratio = 0) were
made on fir and Scots pine. Two replicates were done.

	Treatment	Weeks	Years [a]	Sorption (%)	Swelling (%)	ASE (%)
Fir	Untreated	27	11	9	13	/
	Wood Protect	82	27	3	1.4	89
	Acetylation	32	10	7.9	7.4	43
Pine	Untreated	18	6	14	u	/
	Wood Protect	72	24	3	1.8	89
	Acetylation	50	13	4	2.9	64
Oak	Untreated	36	12	11	8	/
	Wood Protect	104	34	2	1.8	78
Beech	Untreated	6	2	u	u	/
	Wood Protect	12	4	-	-	-
Curupixa	Untreated	61	20	10	11	/
	Wood Protect	61	20	2	1.4	87

a: equivalent years calculated on a base of comparison with natural ageing
u: undetermined, deformation too important

Table 4.4 Impact of the Gardner accelerated weathering on volume and weight of the samples.

All the samples treated with mixed anhydride mixtures presented swelling
values of less than 2% compared to up to 15% for untreated samples. We calculated
the ASE-values on the base of these results. The values obtained for fir, pine and oak
treated samples are as high as 78% (Figure 4.33).
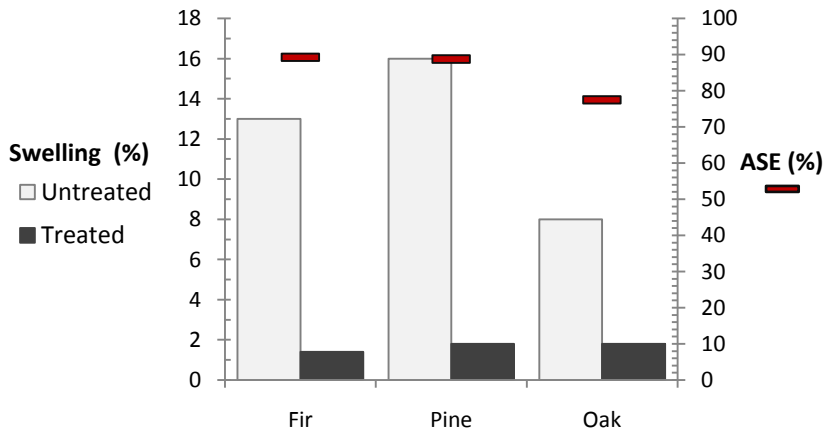
Figure 4.30 Impact of the weathering on the swelling of wood.

However, it is important to precise that the Gardner tests are much more representative of the changes occurring on joineries than the cycles of soaking and drying at laboratory scale (ASE cycles).

Wood treated with mixed anhydrides under optimized conditions are still suitable for joinery applications after 20 years (equivalent) of natural ageing in the case of curupixa and more than 30 years for oak. Testing for beech is still under progress. An example of the changes produced after 60 weeks of Garner artificial ageing (20 years equivalent) on treated and untreated samples of curupixa are presented in Figure 4.31. The aspect of treated samples is the same than in the beginning of the test.
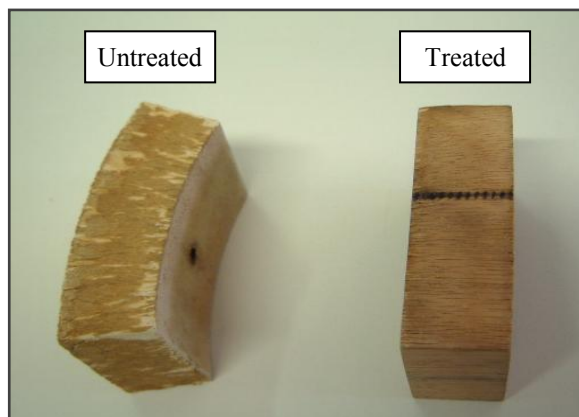
Figure 4.31 Samples of curupixa after 60 weeks of Gardner artificial ageing (20 years eq)

After few cycles, untreated wood was so deformed due to cracks and bending, that the measurement of its dimensions was unnecessary. The degradation of the sample surfaces was also important (Figure 4.33). Delignification of the biomaterial was evident. The development of molds was also observed on the untreated samples whereas fungi development did not occur on acetylated samples and Wood Protect[®].

In the case of acetylated samples (samples treated at pilot scale by Lapeyre), different behaviors were observed depending on the wood species. Scots pine samples were less stable than Wood Protect[®] but with still a high ASE-value (64 and 89%). On the contrary, fir showed first a similar performance in the first 18 weeks (6 years) but then it lost efficiency and after 32 weeks (10 years) it showed an ASE-value of 43% while the Wood Protect[®] sample still showed 89%.

While at laboratory scale an acetylated sample showed better ASE-values, in the case of samples treated at pilot scale and undergoing accelerated Gardner ageing, the difference in terms of dimensional and color resistance is clearly at the advantage of the treatment by mixed anhydrides. The combination of the dimensional stability due to the total grafting and the water repellency confered by the grafting of fatty chains have an important impact on the durability of wood. These really interesting results have been the starter of the industrial process development.

4.8.1.2   Weathering chamber tests

Lapeyre developed a weathering chamber able to reproduce in 24 h, the hardest conditions that can encounter wood in exterior conditions during one year over the different seasons. This weathering chamber is presented in Figure 4.32

Figure 4.32 Weathering device developed by Lapeyre

The test consists in a cycle of 24 h divided in four steps: 8 h of rain simulation, 4 h at -20°C, 4 h at 60°C and 95% of relative humidity and finally 8 h at 60°C (30% relative humidity) and UV exposure. One cycle of 10 days corresponds to 2 years and 6 months of natural ageing.

The size of such device allows carrying out many ageing tests at the same time and we characterized 8 different species of wood treated under each of their optimized conditions. These tests were performed on 10 replicates and the average values are presented in Table 4.5.

The reported values correspond to different ageing periods due to the fact that wood resistances to these tests are different according to the species. The ageing was stopped in the case of untreated samples when the degradation was so important that the measurement of the sample sizes was senseless. In the case of treated samples, assays were stopped after 20 to 30 years equivalent.

	Treatment	Cycles	Years [a]	Sorption (%)	Swelling (%)	ASE (%)
Fir	Untreated	2	5	7	9	/
	Wood Protect	10	25	0.7	0.9	90
	Acetylation	4	10	5.9	8.4	7
Pine	Untreated	2	5	9	U	/
	Wood Protect	11	27	1.5	1.7	92
	Acetylation	7	18	1.9	1.7	88
Oak	Untreated	4	10	15	8	/
	Wood Protect	13	32	1	0.9	89
Beech	Untreated	2	5	u	U	/
	Wood Protect	6	15	1.5	1.7	90
Meranti	Untreated	1	2.5	12	7	/
	Wood Protect	1	2.5	2	1.2	83
Jacaranda	Untreated	1	2.5	17	13	/
	Wood Protect	1	2.5	0.9	1.4	89
Poplar	Untreated	1	2.5	19	11	/
	Wood Protect	1	2.5	0.8	0.9	92
Eucalyptus	Untreated	1	2.5	12	10	/
	Wood Protect	1	2.5	1.7	1.5	85

a: equivalent years calculated on a base of comparison with natural ageing

u: undetermined, deformation too important

Table 4.5 Impact of the weathering chamber tests on dimensions and weight of the samples.

We can observe that all the samples treated with mixed anhydrides present high dimensional stability with swelling values comprised between 0.9 and 1.7 after more than 20 years of accelerated weathering Figure 4.33.
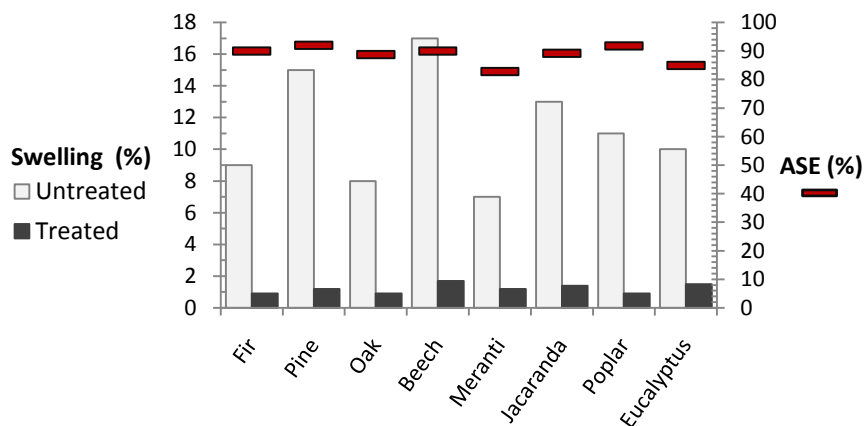
Figure 4.33 Impact of the weathering chamber ageing on the swelling of wood.

ASE values are high and all superior to 83%. These results are in agreement with the Gardner ageing tests described above. An example of aged samples of oak after 2 cycles is presented in Figure 4.34.

Figure 4.34 Samples of oak after ageing in weathering chamber

In the case of acetylated samples, we can observe that the values of ASE obtained are lower than those obtained with the Gardner ageing tests. Moreover, they are always inferior to Wood Protect® samples. Acetylated samples, especially in the case of fir, present high ASE-values during the first cycles but after about 10 years, their characteristics are rapidly altered. Even the sample of pine that shows an ASE-value of 88% is in fact degraded in terms of appearance as its surface tends to fluff and small cracks can be observed after only 5 years equivalent.

> The grafting of fatty chains does have an impact in long term weathering. The water repellency of wood treated with mixed anhydrides that is originated at extremely low fatty grafting seems to preserve the final product from these alterations.

Accelerated ageing systems are interesting tools that permit to evaluate the efficiency of a treatment compared with other modifications but they do not take in account the slow chemical changes occurring along the years in wood when exposed to stress of weather and to biological predators. The natural ageing is the only way to really evaluate the behavior of a treated wood in real conditions of use.

4.8.1.3   Natural ageing

In complement to accelerated ageing, weathering tests in real conditions are being performed since five years in the north of France (Châlons-en-Champagne) on treated windows and window shutters. The device is oriented to the South and with an inclination of 45° (Figure 4.35).

Figure 4.35 Natural ageing device with Wood Protect® window shutters

The changes in volume and mass after 5 years of natural ageing on window shutters made of three different species are presented in Table 4.6.

	Water sorption (%)	Swelling (%)	ASE (%)
Untreated pine	16.8	8.0	/
Treated pine	3.5	1.5	81
Untreated oak	17.6	9.6	/
Treated oak	1.5	2.8	71
Untreated curupixa	9.9	7.9	/
Treated curupixa	0.8	1.9	76

Table 4.6 Influence of the treatment on natural ageing

The results are very close to the one obtained with accelerated ageing; we must however consider that these tests were carried out on a single window shutter for each wood species studied. Besides, the most important in the observations made during these tests is that the surface appearance (even the color) did not change after several years of exposure and that no application of coating is necessary.

4.8.2 Water repellency

The total grafting resulting from the treatment, as we have seen on SPS and wood blocks, confers hydrophobicity and therefore dimensional stability. However when we compare the results obtained at pilot scale concerning the weathering of the Wood Protect® samples with acetylation, we must consider the water repellency to explain the stability along the years. The grafting of fatty chains permits to give water repellency (WR) to the chemically modified wood. Examples of contact angle values measured on three wood species after treatment under the best conditions optimized at pilot scale are presented in Figure 4.36.
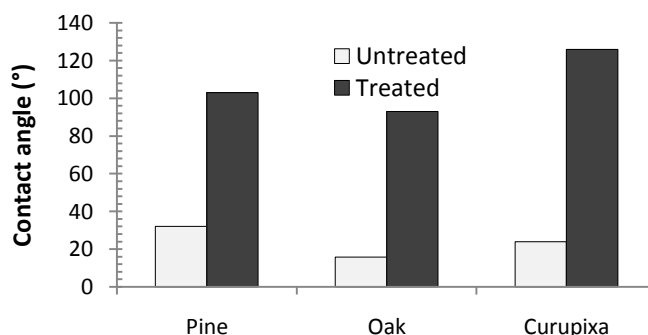
Figure 4.36 Water repellency of the treated wood with mixed anhydrides

These values were measured by our partner on samples treated at pilot scale and therefore without being solvent-extracted. Measures were performed after 2 cycles of accelerated ageing in a weathering chamber, just after the last step of the second cycle. All the static contact angle values were measured just after deposit (t=0 s). They were superior to 90° for treated wood and attested of established water repellency.

Untreated samples showed an initial contact angle that disappeared rapidly after absorption of the drop into wood.

The WR considerably changes the interaction between wood and liquid water. The presence of liquid water on wood surface is incontestably reduced thus the phenomenon of degradation becomes lower. The benefits of the water repellency are difficult to quantify without making observations on modified wood after many years of weathering.

4.8.3   Mechanical properties

The measures of MOE made on 4 representative species treated at pilot scale under optimized conditions are presented in Figure 4.37.

Figure 4.37 Modulus of elasticity of Wood Protect® samples.

The measurements were performed on wood blocks with dimensions used by Lapeyre at industrial scale in the joinery making. **We can observe that the mechanical properties of such treated wood are not altered by the treatment**. This is considerably important at industrial scale to preserve the characteristics of

the joineries produced from the treated wood. These results are in agreement with those obtained at laboratory scale.
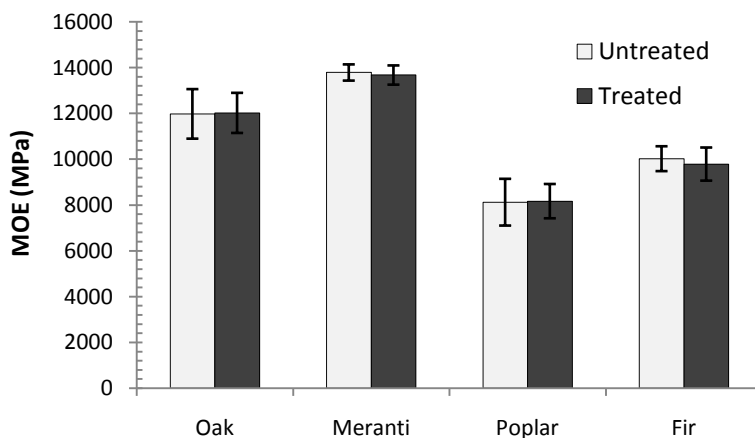
4.9 Conclusions

The chemical modification of wood blocks by mixed anhydride mixtures synthesized from acetic anhydride and a fatty acid have been demonstrated to be possible without the use of a catalyst or pretreatment of the material.

The correlation between the swelling of the sample and the esterification of wood components has been demonstrated on samples extracted after treatment. The weight percentage gain due to chemical modification and the swelling are thus a good indicator of the chemical modification. The heterogeneity of wood does not permit to characterize accurately the final treated product as it was performed on cellulose and Scots pine sawdust but the data collected on these two materials permitted to evaluate the impact of the conditions of treatment on the modification of the properties.

The mechanical properties of wood after treatment are little dependent on the treatment conditions; but they are considerably affected by the nature of the reaction medium used (molar ratio). The acidity of the mixture decreases with the length of the fatty acid and with the molar ratio. Samples of Scots pine, beech and oak did not show any degradation of their modulus of elasticity and rupture when treated with mixtures of acetic anhydride and oleic acid at molar ratio superior to 1. On the contrary, the treatment with pure acetic anhydride led to a degradation of 40% of the mechanical properties of the treated wood, even without acidic catalyst.

The treatment improves the dimensional stability of wood and this increase was correlated to the weight percentage gain due to grafting. No correlation between the degree of esterification by the fatty acyl groups and the anti shrink efficiency was observed. The dimensional stability of wood depends on the total grafting regardless of the considered wood species. The dimensional stability of wood depends therefore on the hydrophobicity but not on the water repellency of the material.

The leaching of samples treated with mixed anhydride mixture was surprisingly quasi-inexistent contrarily to samples impregnated with the reaction medium at room temperature but non chemically modified. Van der Waals interactions between the fatty reagent in excess present in the cell voids and the fatty chains grafted on the cell wall are presumed to be at the origin of this phenomenon. Observations of

treated samples made after solvent extraction by scanning electron microscopy showed aggregates on the cell wall that are possibly formed by hydrophobic interactions. These interactions and aggregations could explain the absence of leaching during the ASE cycles.

The scale-up of the treatment has been a fantastic opportunity to evaluate its efficiency on treated joineries. The more fundamental aspects investigated at laboratory scale have been corroborated by the measured properties on the industrial products. The benefit of the grafting of fatty chains has been reinforced by the natural and accelerated weathering tests. After 30 years of accelerated ageing and 5 years of natural weathering, the benefits conferred by the grafted acyl groups have not been significantly altered.

Finally, our industrial partner, Lapeyre has investigated the biological resistance in collaboration with the FCBA (Institut Technologique Forêt Cellulose Bois-Construction Ameublement). The use class 3 has been assessed and validated and the class 4 is under investigation at the moment. The Lapeyre Company did not wish to communicate on the investigations carried out by the time of writing this document in order to avoid the dissemination of incomplete data.

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General conclusion

Wood modification has become in the last decade a topic of great interest and it is intended to be a response to the increasing legislative pressure on environment protection considerations. A strategy from industrial companies such as LAPEYRE was to invest in the development of a new wood treatment process and to make it as environmentally friendly as possible. From this postulate, collaboration started between LAPEYRE and the Laboratory of Agro-Industrial Chemistry to investigate new ways of wood chemical modification. The idea was to confer dimensional stability and water repellency to wood in order to increase the competitiveness of wood joineries compared with aluminum and PVC.

Since acetylation of wood was known to give dimensional stability, and fatty compounds are supposed to confer hydrophobic properties, our idea was to graft both acetyl and fatty acyl groups to the wood in order to make it dimensionally stable and water repellent. Our innovative protocol uses mixed acetic-fatty anhydrides, which are able to graft both acetyl and fatty groups in a one-pot reaction.

Synthesizing mixed acetic-fatty anhydrides by making react acetic anhydride and a fatty acid without any solvent or catalyst appeared to be the easiest way compared to the ketene process. The capability to synthesize and analyze mixed anhydrides was our first challenge. An optimized reversed-phase HPLC technique was developed for the analysis of mixed anhydrides. Thanks to it, we could characterize the complex reaction medium obtained at equilibrium composed of 3 types of anhydrides and 2 carboxylic acids. The high reactivity of acetic-fatty anhydrides and their instability in the presence of water prevented their isolation. Therefore, the use of mixed anhydrides in a mixture context appeared evident. We then studied the two consecutive reactions involved in the synthesis of the mixed anhydride and that yielded at equilibrium a mixture of 5 compounds: acetic acid, acetic anhydride, acetic-oleic anhydride, oleic acid and oleic anhydride. We were able to control the composition of the mixtures for the reaction with the hydroxyl groups of the wood constituents. We proceeded then to investigate the treatment of lignocellulosics and to correlate their properties to their chemical structure, in particular the degree of chemical modification.

Since wood is highly heterogeneous, we studied the reactivity of mixed anhydride mixtures with homogeneous model compounds, representative of the

reactivity of wood chemical components: cellulose, as it is the major constituent of wood and the less reactive due to its crystallinity, and sawdust, as all the chemical components of wood are present in a more homogeneous way avoiding the diffusion phenomena.

Investigations made on these two substrates permitted to better understand the factors involved in the esterification of wood components by mixed anhydride mixtures. The grafting of acetyl and fatty acyl groups and their proportion depended on the reaction temperature, the initial molar ratio, and on the length of the fatty acid chain but not on the reaction time. The maximum obtained values were $DS_8 = 2.10^{-3}$ and $DS_2 = 0.07$ for cellulose and 314 meq C_8/kg and 2350 meq C_2/kg for sawdust. We developed a **new analytical technique** permitting the characterization of lignocellulosics esters presenting extremely low ester content with a threshold of detection of 5.10^{-5} in terms of DS, in the case of cellulose. This efficient tool permitted to put in evidence that the temperature, the duration of the treatment and the molar ratio between acetic anhydride and the fatty acid highly impacted the yield of grafting. The ratio of grafted acetyl/fatty acyl groups varied between 6 and 659 depending on the molar ratio of the mixture, the aliphatic chain length of the fatty acid and the temperature of treatment.

The characterization of the hydrophobicity and water repellency of the mixed esters of cellulose and Scots pine sawdust (SPS) permitted to put in evidence for the first time two important facts:

- The hydrophobicity of the mixed cellulose esters and SPS esters, measured by water vapor sorption, depend only on the total grafting (in terms of weight percentage gain, WPG) and not in the nature of the grafted chain nor the number of substituted hydroxyl groups.
- On the contrary, the water repellency (WR) depends on the nature of the aliphatic chain grafted onto the biopolymer. There is no need to reach a high yield of esterification to confer WR. A DS of 3.10^{-4} of cellulose oleate was found to be sufficient to give permanent WR to molded pellets.

These results obtained by treating homogeneous cellulose and Scots pine sawdust were extrapolated to the treatment of wood blocks at laboratory and at industrial scales. The results confirmed that the dimensional stability of wood

depends only on the total grafting in terms of WPG. The anti-swelling efficiency (ASE) obtained was as high as 74% in the case of pine or oak and, 87% in the case of beech for WPG-values comprised between 6 and 10%. Let us remind that Hill *et al* obtained in acetylation of pine an ASE of 35% for a 10% WPG. The remaining fatty reagent (fatty acid) in the cell voids after treatment gives to wood supplementary dimensional stability.

Despite the fact that these samples did not undergo solvent extraction, they did not show any significant leaching. On the contrary, the samples that were only impregnated by the reaction medium without heating showed lixiviation.

Scanning electron microscopy permitted to observe that aggregation of fatty compounds occurred even after solvent extraction. Based on these results, we presumed that interactions were created between the fatty reagents of the reaction medium and the fatty chains grafted on the cell wall.

Considering the structural aspect, the mechanical properties of the treated wood were found to be considerably dependent on the nature of the reaction medium. The acidity of the mixed anhydride mixtures was responsible for diminutions of the modulus of elasticity and rupture. Depending on the number of carbon atoms of the fatty acid chain and on the molar ratio of the mixture, a decrease up to 32% can be observed. Nevertheless, when the appropriate conditions are chosen there is no loss of mechanical properties. This positive result was quite surprising because the reported chemical modifications in literature lead systematically to a decrease in the mechanical properties of wood. The limited diminution of hydrogen bonding accounts for this.

Weathering assays on samples treated at industrial scale permitted to confirm that the increased dimensional stability combined to water repellency were able to confer to wood an outstanding increased durability. The water repellency and the dimensional stability were not lost even after many cycles of accelerated weathering. The dimensional stability of wood after mixed esterification was better than for acetylation, especially after many equivalent years of accelerated weathering. As expected, the esterification of wood constituents led to a better photostability of the samples treated with mixed anhydrides. This was demonstrated by the tests of photodegradation performed at laboratory scale and by the weathering assays in real conditions.

The advantages of the chemical modification of wood with mixed anhydrides can be summarized as follow:

- The remaining reagent participates to the dimensional stability of the chemically modified wood. Therefore, it does not need to be removed.
- Compared to acetylation, the excess of anhydride mixture is less odorant due to the fact that it is very concentrated in fatty compounds. Indeed, the acetylation is favored and the fatty acid is obtained as a by-product when the mixed anhydride reacts.
- Compared to acetylation, less acetic anhydride is needed to reach the same, and sometimes better, dimensional stability. This is important in terms of cost and energy consumption because the industrial production of acetic anhydride is more energetic and expensive than the production of fatty acids obtained from vegetable oils.
- The presence of mixed and fatty anhydrides permits to graft fatty chains on wood components in small but significant proportion. This chemical modification is enough to confer to wood water repellency, which is important for the durability observed during the weathering assays.
- The reaction medium is very easy to prepare, and by adding acetic anhydride, it can be regenerated even at room temperature without any catalyst or complicated process. The new equilibrium is reached very quickly.
- The mechanical properties are preserved in most of the conditions, which is primordial for the joinery industry.
- Lapeyre announces a biological resistance of the treated wood corresponding to use class 3.

However, this treatment has some inconvenients:

- It needs energy during the step of chemical modification at high temperature. This tends to make it costly compared to impregnations at room temperature.
- A smell of acetic acid can be detected when using mixtures poor in fatty acid.
- The conditions of treatment and the nature of the reaction medium have to be optimized for each species of wood.
- The processes of regeneration of acetic anhydride such as the ketene process are not accessible to wood companies that lack of experience in organic

chemistry. Moreover, sites of production of acetic anhydride are in France classified as SEVESO.

- Chemically modified wood is not so easy to introduce to the market. Communication campaigns are necessary to explain such treatments to costumers.
- The low energy surface of the treated wood decreases its wettability and thus its compatibility with commercial paints, varnishes, and glues. However the need of a coating is not necessary considering its high resistance to weathering.

Many investigations have been carried out during this research work. However, some scientific aspects of the treatment can further be investigated:

- The phenomena involved in the photostability have not been deeply explained at the moment in our investigations. Spectroscopic analyses of treated samples before and after photodegradation will be performed.
- The measurements of surface energies of wood esters have to be performed by the measurement of contact angles values with polar and non polar solvents using inversed gas chromatography in order to determine the exact impact of the grafting of an acyl group on wood as a function of its aliphatic chain length.
- Environmental scanning electron microscopy tests will be performed in order to confirm if the aggregates observed by SEM are produced by the vacuum (which would transfer the fatty compounds from inside the cell wall to its surface) or if they are the result of a network formation between the fatty compounds and the fatty acyl groups grafted on the cell wall.
- Atomic force microscopy could be performed to verify if the fatty chains grafted on the cellulose microfibrils surface lead to the formation of nanopins conferring an extraordinary hydrophobicity.

Scientific production

Jerome Peydecastaing

Papers in peer-reviewed international scientific journals

Papers accepted and published:

PEYDECASTAING J., GIRARDEAU S., VACA-GARCIA C., BORREDON E. (2006) Long chain cellulose esters with very low DS obtained with non-acidic catalysts. *Cellulose 13*, 95-103.
DOI : http://dx.doi.org/10.1007/s10570-005-9012-5

PEYDECASTAING J., BRAS J., VACA-GARCIA C., BORREDON E., IFTIMIE N.*, GIURGINCA M.*, MEGHEA A.* (2006) NIR study of chemically modified cellulosic biopolymers. *Mol. Cryst. Liq. Cryst. 448*, 717-724.
DOI : http://dx.doi.org/10.1080/15421400500385027
*University POLITEHNICA of Bucharest, Romania.

PEYDECASTAING J., VACA-GARCIA C., BORREDON E. (2008) Quantitative analysis of mixtures of various linear anhydrides and carboxylic acids. *Chromatographia*. In press.
DOI : http://dx.doi.org/10.1365/s10337-008-0765-5

PEYDECASTAING J., VACA-GARCIA C., BORREDON E. (2008) Rapid and accurate determination of the degree of substitution (DS) of long chain cellulose esters (LCCE). *Cellulose*. In press.

PEYDECASTAING J., VACA-GARCIA C., BORREDON E. (2008) Kinetic study of the synthesis of acetic-oleic anhydride obtained by reaction between oleic acid and acetic anhydride. *Eur. J. Lipid Sci. Technol.* In press.

Papers submitted:

PEYDECASTAING J., VACA-GARCIA C., BORREDON E. (2008) Mixed acetic-fatty cellulose esters with extremely low fatty degree of substitution. Part I. Synthesis. *Cellulose*. Under review.

PEYDECASTAING J., VACA-GARCIA C., BORREDON E. (2008) Mixed acetic-fatty cellulose esters. Part II. Hydrophobicity. *Cellulose*. Under review.

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Patents

(LAPEYRE) MAGNE M., EL KASMI S., DUPIRE M., MORARD M., VACA-GARCIA C., THIEBAUD S., **PEYDECASTAING J.**, BORREDON M.E., GASET A. Procédé de traitement de matières ligno-cellulosiques, notamment du bois ainsi qu'un matériau obtenu par ce procédé. Brevet FR 2838369 (17 octobre 2003). Publication demande internationale : WO 03/084723

(LAPEYRE) MAGNE M., EL KASMI S., DUPIRE M., MORARD M., VACA-GARCIA C., THIEBAUD S., **PEYDECASTAING J.**, BORREDON M.E., GASET A. Procédé de fabrication d'un anhydride mixte. Brevet EP 1657231 (17 mai 2006).

(LAPEYRE) EL KASMI S., **PEYDECASTAING J.**, VACA-GARCIA C. Utilisation d'un matériau résistant aux attaques des insectes xylophages. Brevet mondial WO2007141444. (13 déc 2007).

(LAPEYRE) EL KASMI S., **PEYDECASTAING J.**, VACA-GARCIA C. Utilisation d'un matériau résistant au développement des micro-organismes. Brevet mondial WO2007141445 (13 déc 2007).

Invited conferences

GIRARDEAU S., **PEYDECASTAING J.,** VACA-GARCIA C., BORREDON M.E., TONIN C. Water repellent yarns and fabrics obtained by microwave-assisted fatty acylation of cotton. 6th Health and Textile International Meeting, Biella Italy (May 4-5, 2006).

Proceedings of oral presentations

PEYDECASTAING J., VACA-GARCIA C., BORREDON E. Aumento de la durabilidad de la madera mediante reacciones de acilación que utilizan productos naturales. 1er Congreso Iberoamericano de Protección de la Madera. Mérida Venezuela (Dec. 4-7, 2006).

PEYDECASTAING J., VACA-GARCIA C., BORREDON E. Acetic-fatty anhydrides to increase wood stability. 2nd Renewable Resources & Biorefineries conference. York UK (Sept. 6-8, 2006).

PEYDECASTAING J., VACA-GARCIA C., BORREDON E. Mise au point d'un procédé de modification chimique du bois en vue d'augmenter sa stabilité dimensionelle. IX Colloque Sciences et Industrie du Bois. Bordeaux France (Nov. 20-21, 2008).

PEYDECASTAING J., VACA-GARCIA C., BORREDON E. Mecanismo de hidrofobación de la pared cellular de la madera. IRG Americas Meeting. Santa Cruz, Costa Rica (Nov. 30 - Dec 2, 2008).

Proceedings of poster presentations

PEYDECASTAING J., BRAS J., VACA-GARCIA C., BORREDON E., IFTIMIE N.*, GIURGINCA M.*, MEGHEA A.* NIR study of chemically modified cellulosic biopolymers. 8th International Conference on Frontiers of Polymers and Advanced Materials (ICFPAM). Cancun Mexico (April 22-28, 2005).
*University POLITEHNICA Bucarest, Romania.

Awards

- The second prize of the « **26ème Concours Innovation Midi-Pyrénées 2006 »** in the category « Laboratories and research teams » and an award of 1500 € for the researchers.
- The **Pierre POTIER** award in **2007**. Equivalent of the *Green Awards*, this prize was created by the French Minister for Industry. This prize was given to Lapeyre Company for the development of the **Wood Protect**® treatment.

Abstract

The chemical modification of wood with mixed anhydrides with aim to improve its pr operties has been investigated. U nsymmetrical ace tic-fatty anhydrides w ere obtained afte r reacti on between ac etic anhydride a nd a fatty a cid and tw o consecutive equilibrated reactions were put in evidence, yielding at equilibrium also a fatty anhydride in low proportion. Cellulose and Scots pine sawdust were treated by mixed anhydride m ixtures a nd y ielded l owly su bstituted mixed es ters w ith different ace tyl/fatty acy l ratios. T he hydrophobicity of the es ters, measured b y water va por sorption, was correla ted to the t otal DS whereas th e con tact an gle depended onl y on the fa tty acyl substi tution a nd wa s reache d eve n at very low degree of s ubstitution (D S=3.10^{-4}). Th e tr eatment of w ood b locks re sulted in high dimensional s tability (A nti-swelling efficiency A SE of 90 %) a nd depended on the total grafti ng whate ver was the acyl group grafted. Mechanical p roperties of t he treated wood were found to be preserved.

Résumé

La modification chimique du bois par des anhydrides mixtes en vue d'améliorer ses propriét és intr insèques a ét é l'obj et principal de cette é tude. Ces m olécules asymétriques ont é té sy nthétisées en fai sant réagir un acide carboxylique ave c de l'anhydride a cétique. A l'issue de deux r éactions consécutives et équili brées un anhydride gras a été aussi obtenu en faible proportion. Des esters mixtes de cellulose et de sc iure faiblement substi tués fure nt ob tenus a près trait ement avec de t els milieux réac tionnels. Leur caractère hy drophobe, é valué p ar m esure d'iso thermes d'adsorption, dép end du taux de m odification ch imique glo bal a lors que l' angle de contact dépend uniquement du greffage des chaînes grasses et ce même pour de très faibles de grés de su bstitution (D S=3.10^{-4}). L' e xtrapolation d e ce s résulta ts a u traitement d'échantillons de bois a permis d'augmenter leur stabilité dimensionnelle (efficacité a nti-gonflement ASE de 90%)   tout en   préservant l eurs propri étés mécaniques.