


Review

Wood Surface Modification—Classic and Modern Approaches in Wood Chemical Treatment by Esterification Reactions

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Abstract: Wood surface modification is a comprehensive concept which, in time, turned out to be as successful as challenging when it comes to improve the resistance of wood during its life cycle in both indoor and outdoor applications. The initial approaches have aimed at simple methods with immediate results. Nowadays, the paradigm has slightly changed due to the scientific and technical advances, and some methods have become intermediate stages in more complex processes, after being used, for long time, as stand-alone procedures. The esterification was employed as a convenient method for wood surface modification due to the high amount of free hydroxyl groups available at the surface of wood and other lignocellulosic materials. Therefore, different esterification approaches were tested: activated condensation with carboxylic acids (monocarboxylic, as well as dicarboxylic acids, fatty acids, etc.) in the presence of condensation activating agents (such as trifluoroacetic anhydride); reaction with β -halogen-substituted carboxylic acids; esterification using carboxylic acids derivatives (acyl chlorides, anhydrides) or even multifunctional carboxylic acids (i.e., tricine). Thus, wood with improved dimensional stability and weathering resilience, higher fire resistance, enhanced hydrophobic character, and mechanical durability was obtained. This paper offers an overview of some of the most recent advances reported in the field, presented in a systematic manner, using the type of reaction as classification criterion. The main improvements will be outlined in a critical assessment in order to provide a useful tool for a wise choice in future applications.

Keywords: wood; surface modification; esterification; classic approaches; modern approaches

1. Introduction

Wood surface modification is a comprehensive concept which, in time, turned out to be as increasingly successful as challenging when it comes to turn wood species into high-value products. Thus, further improvement in the wood resistance during its life cycle in both indoor and outdoor applications can be attained.

Appropriately modified products of wood and wood-based composites are increasingly being applied in housing, the building industry, transport etc.

Many approaches envisaging wood modification [1–8] include treatment processes, defined as chemical, biological (e.g., enzymatic modification for hydrophobicity), mechanical or physical methods. All these methods are applied to modify wood with the scope to acquire enhanced properties for the sustainable service life of the resulted material which should not pose any environmental hazards related to its toxicity during all life cycle period (referring to use, recycling or disposal issues). Other modification methods are suitable for increasing wood properties such as dimensional stability

and durability (resistance to biological degradation, UV radiation, humidity, and harmful chemicals; thermal stability or fire resistance; mechanical properties), among these impregnation and coating treatment approaches being often applied.

Impregnation treatment represents a passive modification strategy which does not change the molecular structure of wood polymer constituents. It involves usually diffusion of bulking chemicals, such as monomers, polymers, resins and waxes, into either cell wall or lumen, and determines increasing wood density and stop water penetration in the cell walls.

Coating modification strategy implies formation of a physical barrier layer consisting of moisture-, bio-, fire- or UV-resistant agents on the wood surfaces, as the final stage of wood processing. It is effective for an improved wood protection against weathering processes under environmental exposure conditions in exterior uses. Nevertheless, implementation of new alternatives through exploiting new agents derived from natural resources (e.g., resins, waxes, biopolymers) for wood treatment may be of real significance when issues such as reducing the cost and environmental risk at the end-of-life of treated wood are considered [9]. The main strategies applied for wood treatment are schematically represented in Figure 1.

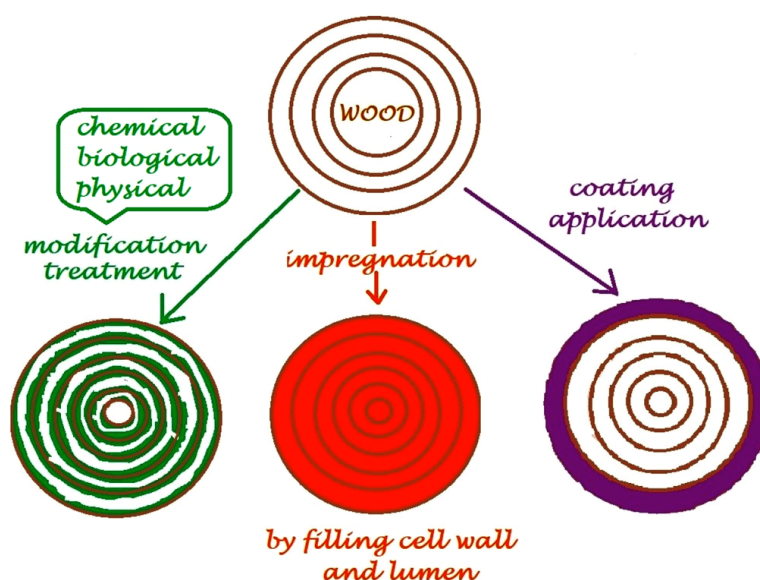


Figure 1. Schematic representation of the methods used for wood modification.

The wood tree chemistry approach [10] may be valuable for investigation of the chemical modification performed both on the wood [2,5] and its major polymer components (cellulose and lignin). Through this process, materials with given and special properties (e.g., thermal stability [11]), resistance to decay under biological organisms' action [12–17] and UV exposure [18–24] may be obtained. Beside all the above-mentioned, the introduction of some reactive functional groups through addition of different chemicals to the hydroxyl groups from wood material can be successfully applied for further grafting synthetic polymers in order to obtain composites [25–29].

Wood fibers surfaces are chemically reactive due to the presence of many hydroxyl groups in the structure of their main polymer constituents, namely lignin and cellulose, thus becoming susceptible for efficient surface modification treatments [30,31]. The inherent reactivity of these hydroxyl groups can be harnessed through modification methods which improve their interfacial interactions with non-polar polymer matrices in composite formulations. In such obtained multi-component polymer systems are consequently noticed improved properties, including wettability, gluing and adhesion of resin type coatings in the case of wood acetylation for example [32], through modifying the surface energy and polarity of wood surfaces [33]. Wood modification strategies include different approaches [34] such as:

- Physical methods: electrical discharge-corona, cold plasma treatments [35–39], thermal treatment [40] and mercerization [41];
- Chemical methods: pre-treatment of wood fibers surface, grafting, use of coupling agents and functionalized polyolefin-coupling agents [42].

Chemical modification of wood is based on the reaction of the wood structural polymer components with chemical reactants that do not have any protective result (e.g., biocides or fire retardants) but which determines the required protective effect and improvement in selected properties directly in the wood substrate. The chemical reactants used for wood modification can act on the surface on which they remain or only partly penetrate wood superficial layers (namely, passive modification strategies such as impregnation), but they also can be present deeper in the wood structure (in the lumens of the cells or inside the cell walls) when they react through chemical bonding with the polysaccharides and lignin from wood (namely, active modification strategies). The new interactions that occur between the wood surfaces and modifying agents are of chemical or only mechanical nature, these contributing to the increased resistance of the modified wood against water, UV radiation and biological pests. Thermosetting polymers (e.g., resins such as phenolic, amino and furfuryl-alcohol type) and thermoplastic polyacrylates are usually preferred for filling the lumens of wood cells during wood modification. Occurrence of reactions with the hydroxyl groups or other chemical groups of the wood when using reactants (e.g., carboxylic acids and their anhydrides, aldehydes, lactones, isocyanates, nitriles, or epoxides) can generate formation of reactive monomers [2,3]. Some usual methods often applied for modification of wood surfaces, through both active and passive ways, can be summarized as presented in Table 1.

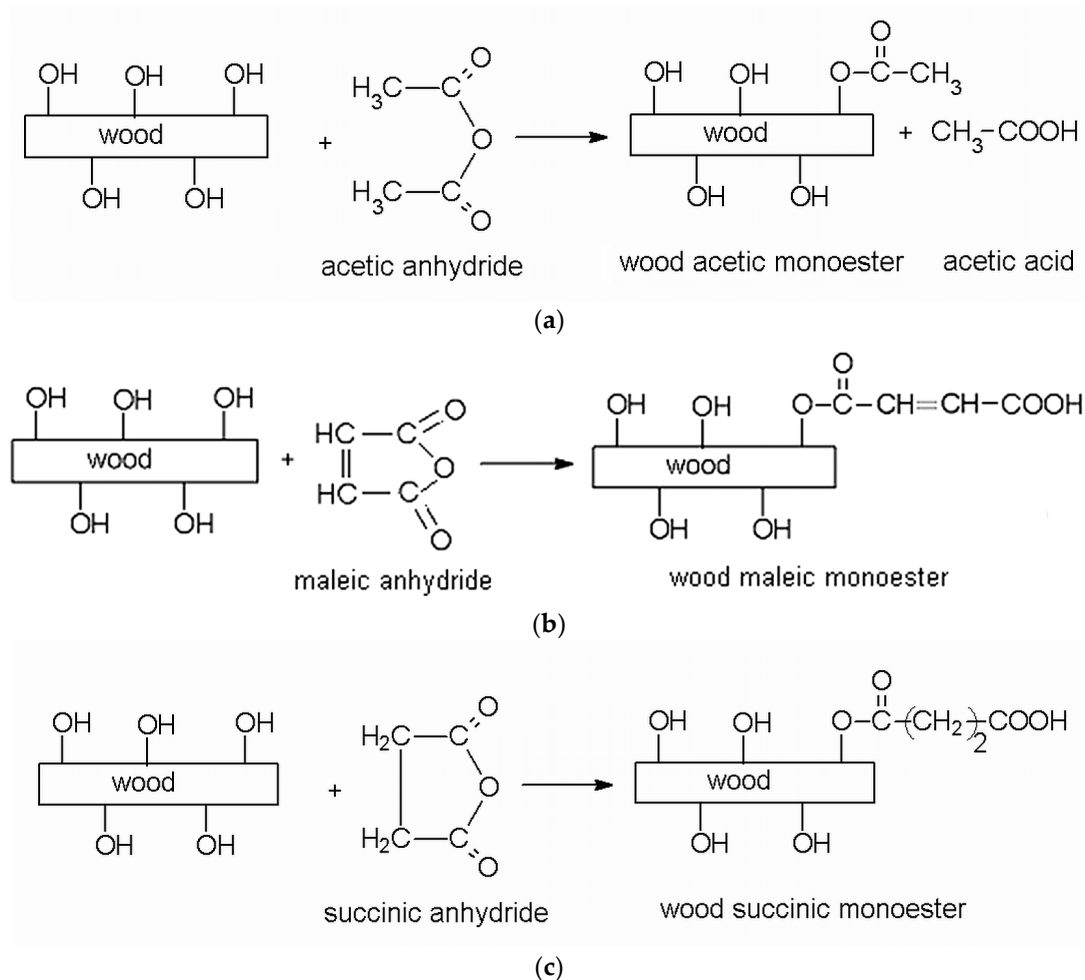
Table 1. Examples of methods used for wood modification.

Type of Treatment	Reference
Isocyanate treatment (ease reaction in the presence of pyridine or acidic catalysts)	[43,44]
Acrylation	[45]
Benzoylation	[23,46,47]
Acid chlorides treatment (ex. octanoyl chloride and palmitoyl chloride)	[28]
Acid anhydride treatment: -acetic anhydride -maleic anhydride -succinic anhydride	[2,4] [48,49] [21,25,50–52]
Silane treatment	[16,53]
Furfurylation treatment	[54–59]
Ketene treatment (usually applied for wood acetylation in order to avoid formation of acetic acid as by-product)	[60–63]
Other anhydrides: ex. crotonic, propionic or methacrylic anhydride	[64,65]
Polycarboxylic acids treatment: 1,2,3,4-butanetetracarboxylic acid, citric acid (through impregnation)	[29,66–73]
Tricine treatment (tricine is a zwitterionic amino acid)	[74,75]
1,3-Dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) treatment	[76–80]
Fatty acids treatment	[81]
Fatty acid chlorides treatment (induce thermo-plasticity into wood)	[82,83]
Oxalic acid and cetyl alcohol treatment	[84]
Isopropenyl acetate (in the presence of anhydrous aluminum chloride as a catalyst)	[13]

Most of these modification strategies are in fact esterification approaches and some of them will be discussed below.

2. Wood Surface Modification by Esterification Reactions Using Anhydrides

The reaction of wood subjected to anhydride treatment (e.g., acetic anhydride, maleic anhydride, succinic anhydride) can be exemplified as presented in Scheme 1. Through such chemical treatment, the molecular structure of wood polymer constituents is changed with positive effects on the wood properties, mainly the hydrophilic characteristics, thus the wood surface becomes more hydrophobic. Chemical modification of wood fibers is performed to provide a good compatibility by reaction with anhydrides that blocks the hydroxyl groups in the wood chemical structure, mainly for further inclusion in composite formulations with different polymer matrices. All these changes result in an improvement of biological resistance against various pests, and consequently have favorable impact as enhancing the dimensional stability and strength properties [85–87]. Cyclic anhydrides may react partially with wood when results a single ester function and a free carboxylic group.



Scheme 1. Reaction of wood with organic anhydrides: linear (a) and cyclic—(b) and (c).

Acetylation treatment of wood involves the substitution of hydrophilic hydroxyl groups with hydrophobic acetyl groups [2]. At the same time, an increase in the dimensions of the acetylated wood substrates is observed because of swelling of the wood cell wall. In most cases, chemically modified wood presents a lower affinity for water absorption, comparatively with the non-modified wood. By replacing some of the hydroxyl groups on the wood polymers with acid anhydride, the hygroscopic properties of the wood are reduced with positive effects on the resulted properties when combined with other polymer matrices in composite formulations.

Usually, the chemical modification confers wood dimensional stability by deposition of the modifying reactant in the wood cell wall (bulking effect), and/or by cross-linking the wood cell wall

polymers [88,89]. The beneficial effects of using acetylation for wood surface modification include the improvement in the weathering and coating performance [90].

When cyclic anhydrides are used for wood chemical treatment, e.g., succinic anhydride, or maleic anhydride, the carboxylic acid formed through esterification reaction is attached to the wood, as presented in Scheme 1b,c. Nevertheless, an extra cross-linking process can stabilize wood materials even better (e.g., improvement in dimensional stability and increased resistance to biological pests), besides improving the hydrophobic properties [3].

Our previous studies regarding the wood substrates and wood constituent polymers modification by esterification reaction using carboxylic acid anhydrides aimed to investigate the effect of such treatments on the wood thermal stability [11,51], on the structural changes occurred in modified wood [49–51] and on its photo-stability behavior under exposure to the artificial light irradiation [21], as well as on the structural and properties changes induced when modified wood is included in composite formulations comprising thermoplastic polymer matrix such as polyvinyl chloride (PVC) [27].

Fourier transform infrared spectroscopy (FT-IR) is a useful technique for studying the chemical and structural changes that occur in wood and wood polymer components due to esterification treatments [49]. The extent of reaction can be calculated as weight percent gain (WPG) determined by the differences in dry weight of the wood substrate before modification (W_1) and after modification (W_2) according to the equation $[WPG = (W_2 - W_1)/W_1 \times 100\%]$. A reaction parameter, namely time is very significant when consider evaluation of extent of reaction by calculating WPG values, but also it is important the method used for esterification (solvent, anhydride concentration). The amount of water present in the wood substrates is also essential, because a moisture level of around 5% appears to be necessary for an esterification reaction in optimal conditions, while above this value the present water hydrolyses the anhydrides with formation of the corresponding carboxylic acid. It seems that for each 1% of water content in wood sample, a loss of 5.7% of the modifying anhydride can be observed. An inverse correlation exists between the rate of esterification reaction and the moisture content in wood substrates.

Differences in chemical alterations that occurred in wood substrates and their main polymer components (cellulose, lignin) after modification using anhydrides are usually evidenced through analyzing the FTIR spectra, as exemplified in Figure 2, where one can observe the structural units that undergo various changes. These are functional groups located on the glucose monomer in cellulose chains from wood structure, when the carbon atoms occupying various positions in the glucopyranose ring (denoted as C-1, C-2, ... C-6) are losing their identity, gradually being transformed into various carbonyl groups of different degrees of freedom, namely ketonic, aldehydic, and carboxylic groups [49].

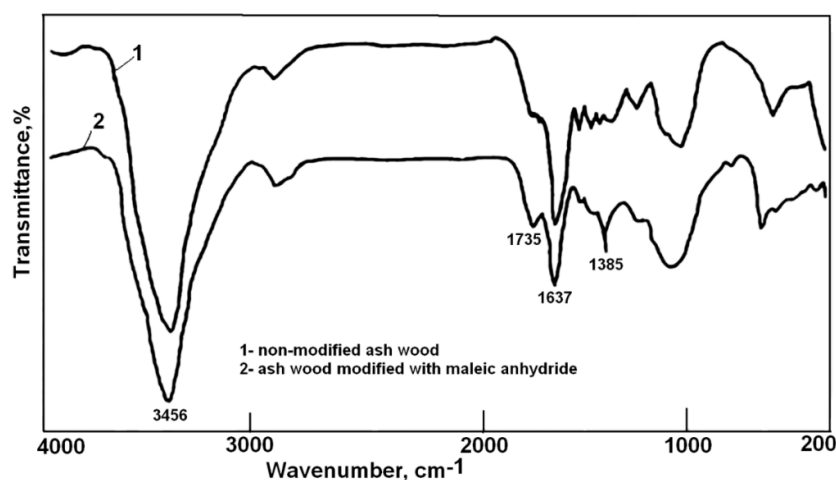


Figure 2. FTIR spectra recorded for wood sample from hardwood tree species (1—non-modified; 2—modified with maleic anhydride)—re-drawn from [49].

As previously presented in one of our first papers dealing with wood modification using anhydrides [49], the decrease in the absorption band for OH groups observed at 3456 cm^{-1} is an indicator of the reduction in hydroxyl group content in the hardwood sample after reaction with anhydride. A strong carbonyl band is noticed at 1735 cm^{-1} (attributed to the formation of C=O ester bonds), this corresponding mainly to the higher xylan content (a hemicellulose-type component) in hardwood sample, as well as an increase in the intensity of OH in plane bending vibration at 1385 cm^{-1} band which is specific to the wood polysaccharide components, namely cellulose and hemicelluloses.

Weak absorption bands between 1500 and 1400 cm^{-1} are specific to the aromatic ring vibrations and ring breathing with C–O groups stretching in lignin polymer from wood substrate. The evidence that modified wood is free both of un-reacted anhydride and of the by-product of carboxylic acid is given by the absence of absorption in the 1800 – 1760 cm^{-1} range, and lack of absorption band at 1700 cm^{-1} , respectively.

Usually, the wood substrates subjected to chemical modification through esterification using anhydrides have to be free of extractives in order to reduce the influence of such compounds on the reaction course and for a better yield. Extractives-free wood is also the supposition for the determination of wood structural constituents like holocellulose (which include all polysaccharides from wood), cellulose, hemicelluloses and lignin accordingly to the Technical Association of the Pulp and Paper Industry (TAPPI) standard methods. The cold water, hot water and organic solvents (toluene-ethanol mixture; xylene) extractions can all greatly improve the permeability of wood cell walls for its further treatments, including esterification with anhydrides [11,25,27,48–51]. Wood fibers esterified, for example, with maleic anhydride and used to prepare composites present reduced water absorption of both of fibers and the resulting composites in comparison to the systems comprising non-modified wood fibers [91–94]. At the same time, properties such as thermal behavior can be affected by the addition of the modified wood and wood constituent polymers resulted by reaction with maleic anhydride in composites with thermoplastic like polyvinyl chloride (PVC) [27]. Modified wood substrates are more prone to degradation with increasing anhydride concentration value. Weight loss values for the main decomposition temperature domain decrease with increasing the modified component (wood, wood polymers) amount in composites. Thermal behavior is improved mainly for the composite samples with modified lignin in composition. As expected, the composites with modified cellulose present a lower thermal stability by comparison with those comprising modified wood and modified lignin, respectively.

3. Wood Surface Modification by Tosylation Reaction

Wood modification, whatever the method, is aiming at altering (especially improving) the properties of the material, either at the surface or in depth. A better level of performance—dimensional stability, mechanical strength, weathering resistance, resilience under biological attack—can be achieved by changing the wood structure at the cell wall level.

The chemical modification remains one of the most used methods as it enables long term improvements through the formation of strong, stable covalent bonds between wood constituents (cellulose, lignin, hemicelluloses) and chemical reagents [95–98], despite its inherent drawbacks (such as: high production costs, use of toxic reagents and solvents, necessity to dispose in a controlled manner of the toxic residues, etc.). The term “wood chemical modification” was used for the first time in 1945 [99], and since then many reagents have been tested for this purpose: anhydrides-acetic, butyric, phthalic, succinic, maleic, propionic; acid chlorides; alkyl chlorides; ketene; β -propiolactone; mono-/dicarboxylic acids; different isocyanates; aldehydes-formaldehyde, acetaldehyde; difunctional aldehydes-trichloroacetaldehyde; o-phthalaldehydic acid; acrylonitrile; dimethyl sulfate; epoxides-ethylene, propylene, and butylene oxide and difunctional epoxides [4,100].

Wood acetylation with acetic anhydride is a classic esterification method that takes place at the available hydroxilic groups in wood. It was carried out, at the beginning, in the presence of zinc chloride (ZnCl_2) and pyridine (Py) as catalytic system [101], and later in liquid phase (homogeneous

system) [96,102], or even without catalysts in more recent approaches [103,104]. Acetylated wood has a high dimensional stability and enhanced decay resistance, despite the residual acetic acid retained that can cause the corrosion of the ferrous elements [105]. Following the same idea, studies have focused also on the use of other esterification agents, such as methane sulfonic acid and p-toluene sulfonic acid, when the resulted esterified materials may be used as such or submitted to further modification reactions.

In a classic approach, the tosylation was carried out in liquid phase (N,N-dimethylacetamide, DMAC, and lithium chloride, LiCl), in the presence of triethylamine (TEA) as acid chloride scavenger and to prevent the occurrence of undesirable side reactions, for 24 h, at 8 °C, where tosyl chloride (TsCl) was employed as reagent [2]. Basically, the wood dried samples are immersed in the reaction medium containing all reagents and solvents. As result, available –OH groups of the wood cell walls were esterified with p-toluene sulfonyl moieties and, by the means of the nuclear magnetic resonance spectroscopy (NMR) study, it was possible to estimate that esterification at the oxygen atom at the C-6 carbon atom evolved with the highest rate as compared to those at C-2 and C-3 of the glucose ring (see Figure 3).

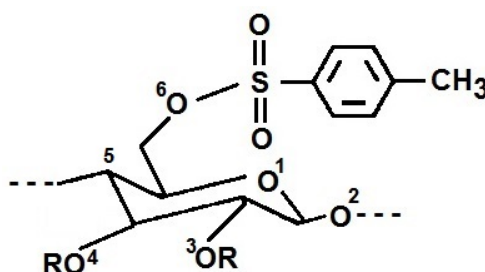


Figure 3. The structure of cellulose tosylate where the ester bond is at the O-6 atom.

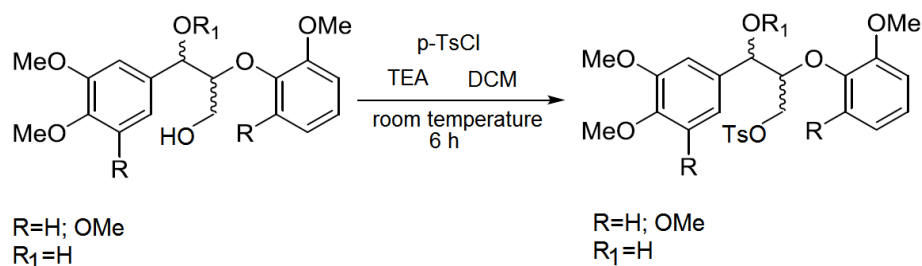
Also, it was proven that the treatment entailed the reduced hydrophilic character of wood and an enhanced dimensional stability as effect of the presence of a bulky substituent in the cell walls [106].

If the sequence of operations is modified, the procedure implies the use of previously dried wood samples which are immersed in pyridine and allowed to swell for 24 h; then, the tosyl chloride solution is added along with other reagents and allowed to react for 24 h at 5 °C [107].

The reaction evolves by bonding each unit of TsCl with one available –OH group, so the amount of TsCl necessary is calculated taking into consideration the anhydrous glucopyranose equivalent (AGU). This procedure allows a higher weight increase, which means a higher amount of tosyl units (15%) were linked to the wood cell walls. Further investigations showed that tosylated wood has an enhanced permeability toward hydrophobic agents under mild conditions which makes it fit for subsequent processing [106].

When pure cellulose was submitted to such chemical modification, the corresponding tosylates are readily soluble in some of the most commonly used organic solvents (dimethyl sulfoxide—DMSO, N,N-dimethylacetamide—DMAC, N,N-dimethylformamide—DMF, acetone, tetrahydrofuran—THF, chloroform, etc.), depending on their degree of substitution [2]. In effect, numerous studies have been focusing on testing various solvents and mixtures able to allow high esterification yields, with or without derivatization, using activation as intermediate stage, either in homogeneous or heterogeneous systems [108].

Apart from –OH groups in cellulose, other available hydroxyl moieties are those from lignin and hemicelluloses. In the case of lignin tosylation, the mechanism has some distinct characteristics due to its aromatic structure and cross-linked supramolecular architecture [109]. Although ether bridges β -O-4 and α -O-4 are susceptible to be thermally and/or chemically broken, it is possible still to perform the tosylation of the primary hydroxyl groups (Scheme 2), especially from guaiacyl and syringyl sequences in lignin, under weak alkaline/neutral conditions, and in time intervals ranging between 5–6 up to 24 h [110–112].



Scheme 2. Tosylation of primary $-\text{OH}$ group at a $\beta\text{-O-4}$ bridge (benzylic position) in lignin (TEA = triethylamine; DCM = dichloromethane).

In a typical case study, lignin was reacted with *p*-toluenesulfonyl chloride in aqueous medium, in the presence of TEA, at 25° , when the tosylation reaction was completed in 24 h [111], without using other solvents or activating agents such as *N,N*-dicyclohexylcarbodiimide (DCC) and 4-pyrrolidinonepyridine (PP) [113], 4-dimethylaminopyridine (DMAP) or *N,N*-diisopropylcarbodiimide (DIC) [114,115]. The degree of substitution can be modulated by setting the TsCl/OH lignin ratio, depending on the final use of the tosylated material. Even more, at higher TsCl content, the tosylated lignin is less thermally stable as there are only a few free $-\text{OH}$ groups available for thermal condensation of lignin fragments [116].

Modern approaches have performed the tosylation in the presence of ionic liquids (ILs). In the past decades, they have been used as highly efficient green solvents for ligno-cellulosic materials: fractionation and biorefinery, dissolution of polysaccharides, processing cellulosic fibers, and, particularly, as reaction medium for the synthesis of substituted polysaccharide derivatives [117,118]. ILs have proven great potential for large scale application due to their structural diversity, recyclability, high dissolution power, their high viscosity and hydrophilicity, and ability to be co-solvents in various systems [117,119–121]. Still, the information on wood surface modification in ILs is scarce, despite the high interest in cellulose functionalization in such medium.

Cellulose tosylation in ILs is usually performed in the presence of 1-allyl-3-methylimidazolium chloride (AMIMCl) or 1-butyl-3-methylimidazolium chloride (BMIMCl), at room temperature or below in order to avoid the tosyl reaction with chloride ions yielding in chlorodeoxycellulose as by-product, or the formation of insoluble cellulose derivatives by the cross-linking reaction between different hydroxyl groups [2,122]. However, cellulose tosylation in ILs at 10°C yielded in a mixture of tosylated derivative (65%) and unmodified cellulose (45%) as result of the ineffective stirring of the reaction medium [117].

1-Butyl- and 1-benzylimidazole have been employed for homogeneous tosylation of cellulose when mixtures of IL and another co-solvent were used [123]. As both ILs have basicity comparable to imidazole and 1-methylimidazole but lower hydrophilic character, they can be easily extracted and recycled due to their high partition coefficient in the non-polar phase [117].

The synthesis of cellulose tosylates in homogeneous phase has been performed in IL/co-solvent mixtures where pyridine was employed, given its ability to act both as a base, by promoting the reaction, and as a co-solvent, reducing the viscosity of the medium during the entire reaction time [124,125].

In the presence of 1-ethyl-3-methylimidazolium acetate (EMIMAc), the cellulose tosylation evolved with the formation of cellulose acetates with high purity as result of the tosyl leaving group substitution by the acetate anions of the IL, evidenced by FTIR spectroscopy. Another possible pathway of the mechanism is the intermediary formation of a mixed anhydride by the reaction between tosyl chloride and EMIMAc, confirmed by NMR data [118,126]. Therefore, it is reasonable to assume that the formation of acetates during cellulose tosylation can be the result of both pathways: nucleophilic substitution of tosyl moiety and the reaction with the mixed toluenesulfonic-acetic anhydride formed in situ.

Special attention must be paid to the influence of the cation as it may affect the viscosity of the reaction mass. Thus, liquid imidazolium dialkyl phosphates cannot be used for the homogeneous

tosylation at room temperature due to the rapid gelation of the reaction mixture upon the addition of the reagent, but the reaction is successful when tetraalkylammonium dialkyl phosphates were used under the same conditions [117,127].

Nevertheless, it is difficult to estimate the opportunity and feasibility of this method for the wood surface treatment, given the high capacity of ILs to dissolve and displace cellulose and, thus, to affect the wood structural integrity in some depth. Extensive research is still needed in this field as to design and test appropriate methodologies in order to apply this reaction to wood with satisfactory results. In addition, some studies evidenced that ILs are solvents not really as “green” as initially asserted, their reduced toxicity strongly depending on the structure, cation type, application, recovery and recycling, disposal etc. [117,128–132].

Aside from the immediate advantages of the tosylated wood, further chemical modification reactions can be performed on the same samples as the tosylation may be considered as a pre-treatment stage. Thus, the tosyl chloride is the activating agent as the tosyl moiety is the leaving group [95] which can be easily substituted by the direct reaction with various nucleophiles. These last mentioned can range from various carboxylic acids (employed in esterification reactions on wood, especially when acids with long aliphatic chains were used) [96] to carbanions or carboxylate anions (used for grafting some “living” polymer anions, such as polystyryl or polyacrylonitrile carbanions, on tosylated wood through an SN2 nucleophilic substitution) [97].

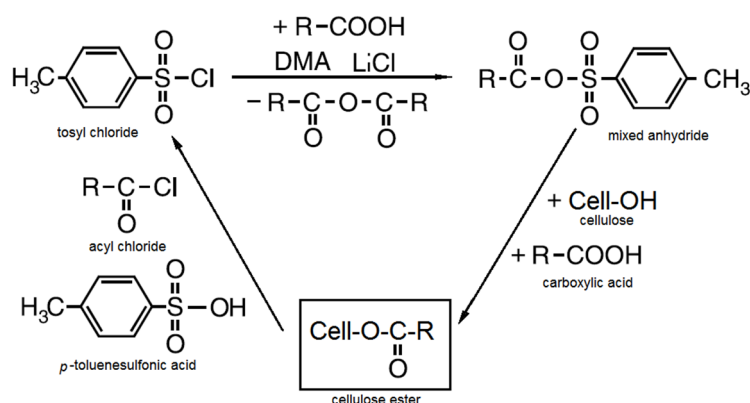
4. Wood Surface Modification by Esterification Reactions Using Carboxylic Acids

The subject has aroused the interest of the scientists for a long time [133] in order to identify methods to improve the properties of wood employed in various applications (mechanical and thermal properties, UV resistance, water uptake, biocide characteristics, etc.). Direct esterification reactions are, typically, difficult to perform due to their equilibrium which often leads to low yields, given the fact that the substrate (hydroxyl groups) is not readily accessible, and carboxylic acids have a lower reactivity as compared to their functional derivatives, such as anhydrides and acyl halides. Thus, the use of activating agents is a common practice even in the case of wood surface functionalization using carboxylic acids, and tosyl chloride was successfully used, as well as other activating agents such as N,N-dimethylacetamide (DMA), 1,1'-carbonyldiimidazole (CDA) or N,N-dicyclohexylcarbodiimide/4-pyrrolidinopyridine (DCC/PP).

4.1. Wood Surface Modification by Esterification Reactions Using Fatty Acids

Fatty acids are preferred for the esterification of wood under mild conditions as they are not aggressive toward the substrate, but, given their low reactivity, activation reagents or systems are required. The in situ activated wood esterification in the presence of TsCl was initially applied for acetylation [134] when a mixed anhydride is formed. The same mechanism occurred when carboxylic acids with long aliphatic chains were employed, ranging from 12 to 20 carbon atoms, yielding in a high degree functionalization of the available hydroxyl groups [96]. This method was further applied to the synthesis of the cellulose oxocarboxylic esters [135], and the resulted materials were stable at high temperature (above 300 °C).

For the case of long chain aliphatic carboxylic acids [116], namely caprylic (C₈), capric (or decanoic, C₁₀), lauric (C₁₂), palmitic (C₁₆) and, respectively, stearic (C₁₈) acid, the reaction medium consisted of DMA and LiCl, where DMA was solvent and base as well. The mechanism evolved through an intermediate stage when a mixed anhydride is formed by the reaction between TsCl and the carboxylic acid, as presented in Scheme 3. This sequence of reactions substantiates the molar ratio of reagents.

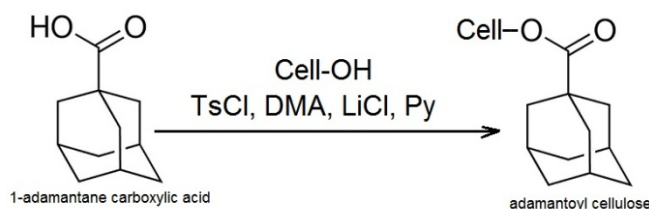


Scheme 3. Direct esterification of cellulose in the presence of TsCl and DMA/LiCl.

FTIR data confirmed the formation of the corresponding esters, and indicated no significant amounts of tosyl moieties as cellulose esters (as result of tosylation without further substitution) or as impurities, which is an indication that TsCl was acting as activating agent only. It was concluded that the degree of substitution as related to the available hydroxilic groups increased along with the number of carbon atoms of the acid when the acid and TsCl are in molar ratios corresponding to the mechanism (see Scheme 3) or higher, or when another base is added to the reaction medium, namely pyridine (Py). The thermal behavior of these esters follows the same pattern: the higher the number of carbon atoms in the aliphatic chain, the higher the degradation temperature, but all values remained in a narrow interval: 290–320 °C.

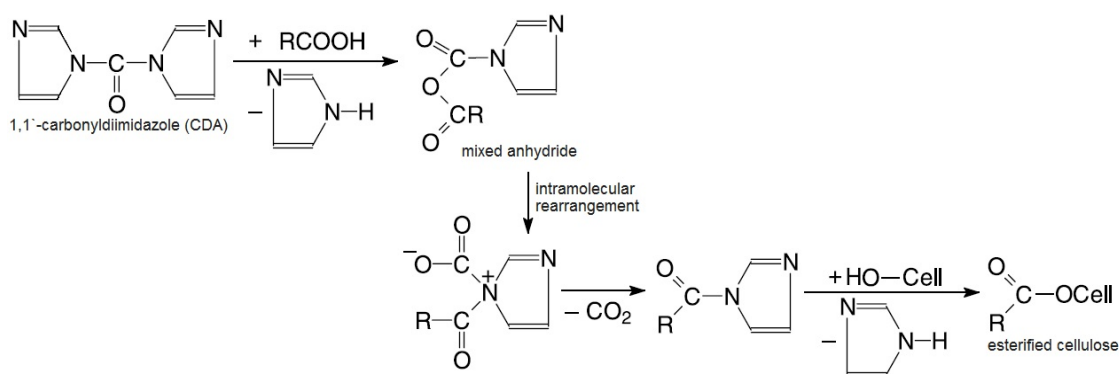
For comparison, the acetylation of cellulose has been performed with acetic anhydride using two different solvent systems: DMA/LiCl (a non-derivatizing solvent) and DMSO/TBAF (dimethyl sulfoxide/tetrabutyl ammonium fluoride trihydrate—a derivatizing solvent), at 40 °C, for 70 h. The results indicated lower values for the degree of substitution due to competing secondary reactions (formation of acetaldehyde as by-product, high rate of hydrolysis of the reagent) [116]. Nevertheless, this approach has proved to be effective for the case of various vinyl carboxylic acids, such as vinyl acetate, butyrate, laurate and, respectively, benzoate, in DMSO/TBAF medium, when high substitution degrees were achieved, but for long reaction time intervals as well (70 h).

A particular study case is the direct synthesis of adamantoyl cellulose by the direct reaction with the 1-adamantane carboxylic acid (Ad-COOH). Ad-COOH is a carboxylic acid with 11 carbon atoms, but it is not a fatty acid as it has a saturated cyclic structure; the presence of an adamantoyl moiety in the structure of various materials grants them biocidal activity [136]. This direct esterification takes place in the presence of TsCl and DMA/LiCl/Py (Scheme 4), at 80 °C, for 24 h, or at room temperature for the same reaction time [7].



Scheme 4. Direct synthesis of adamantoyl cellulose.

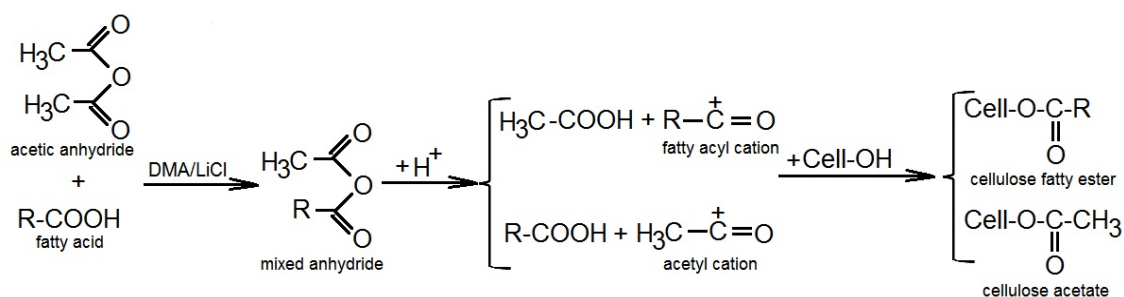
Experimental data indicated this method afforded the highest degree of substitution as compared to the direct esterification in the presence of 1,1'-carbonyldiimidazole (CDA) (Scheme 5) or N,N-dicyclohexyl carbodiimide/4-pyrrolidinopyridine (DCC/PP) as activating agents [137,138].



Scheme 5. Direct esterification of cellulose with carboxylic acids in the presence of CDA as activating agent.

An interesting feature was recorded when CDA was employed: the esterification did not occur at room temperature, even when the molar ratios of Ad-COOH and CDA were higher than required by the mechanism, while at 80 °C the substitution degree was lower than for TsCl/DMA/LiCl. Nevertheless, the esterification using adamantoyl chloride (AdCl) in the presence of DMA/LiCl/Py [116,139] enabled most of the AdCl (85%) to react with the available hydroxylic groups in cellulose, which entailed degrees of substitution slightly higher than in the case of the activating system TsCl/DMA/LiCl.

Another very effective activating system for the esterification of wood using fatty acids was DMAc/LiCl and acetic anhydride as co-reagent [140]. The reaction took place at 130 °C, for 5 h, when -OH available groups were readily modified by the long-chain acyl cations by the means of a mixed anhydride formed in situ (as presented in Scheme 6).



Scheme 6. Mechanism of direct esterification with fatty acids in the presence of DMA/LiCl and acetic anhydride as co-reagent.

In the absence of acetic anhydride, the reaction performed under the same conditions yielded very low amounts of ester. The intermediate mixed anhydride may undergo a dissociation reaction due to the pK_a discrepancy between the acetic acid and fatty acids which all have pK_a values higher than that of acetic acid. Therefore, the formation of the fatty acid cation (the alkanoyl group) is favored, but a significant amount of acetyl groups competes for the esterification as well, hence the mixed esters then resulted from the reaction. It was also possible to assess a correlation between the weight increase and degree of substitution in the fatty acid series n-octanoic-, n-decanoic-, n-dodecanoic-, n-tetradecanoic-, n-hexadecanoic- and n-octadecanoic acid, respectively. Thus, the highest weight increase was recorded for the acids with the highest molecular weight, provided that no significant degradation occurred as in other esterification systems [141].

4.2. Wood Surface Modification by Esterification Reactions Using Unsaturated Carboxylic Acids

The use of unsaturated carboxylic acids for the esterification of wood was motivated by the need to improve its dimensional stability which was one of the effects of the newly achieved reduced hygroscopicity. Studies have been conducted on beech wood samples submitted to direct esterification in

the presence of trifluoroacetic anhydride (TFAA) which acted as activating agent [142,143]. The acylating species (RC^+O) resulted from the dissociation of the mixed anhydride obtained by the reaction of TFAA with the acid (acrylic, methacrylic, trans-crotonic, adipic, fumaric, maleic, mesaconic, citraconic, phthalic acid). The rate of this intermediate stage can be increased by using an acid catalyst, such as sulfuric acid, but its use is strongly limited by the degradative side effects on the wood support as it can dislodge lignin, cellobiose and other wood components [142,143]. Thus, the dissociation equilibrium depends on the pKa values of the selected acids as related to TFAA, and on the molecular weight of acids to a lesser extent. The IR data indicated the simultaneous formation of both carboxyl and trifluoroacetyl esters, and the latter are not easy to remove from the surface of modified wood by washing with water as it would be expected [142]. The same conclusions ensued for vinylacetic, tiglic, p-methylcrotonic, sorbic, 10-undecylenic, and elaidic acid, respectively [143]. Most of the selected acids yielded a weight increase after esterification of wood, but the weight decrease recorded after esterification with acrylic, methacrylic and elaidic acid indicated a degradation phenomenon associated with a loss of the structural integrity of wood, in spite of the significant decrease in the value of anti-shrinking efficiency.

The direct esterification of wood in the presence of TFAA was previously employed for the modification of beech (*Fagus sylvatica* L.) sawdust and sapwood from Ponderosa pine (*Pinus ponderosa* D.) samples with various acids [144]. The results were different: the esterification of the beech sawdust caused a discoloration of wood due to the degradation of trifluoroacetic esters in time, at room temperature, while the esterified Ponderosa pine chips acquired, in addition, a decrease in impact strength.

4.3. Wood Surface Modification by Esterification Reactions Using Polycarboxylic Acids

Polycarboxylic acids (PCAs) are reagents of high interest for the esterification of wood as surface treatment due to their structure and to the remarkable improvement in properties recorded for the modified wood, mainly durability and dimensional stability, but hygroscopicity and resistance toward biologic attack as well [145–148]. The most prominent representative of this class is citric acid (CA), but other acids were used as well, such as tartaric acid (TA), 1,2,3,4-butanetetracarboxylic acid (BTCA), and trimellitic acid (as anhydride which is more stable), although to a lower extent (Figure 4).

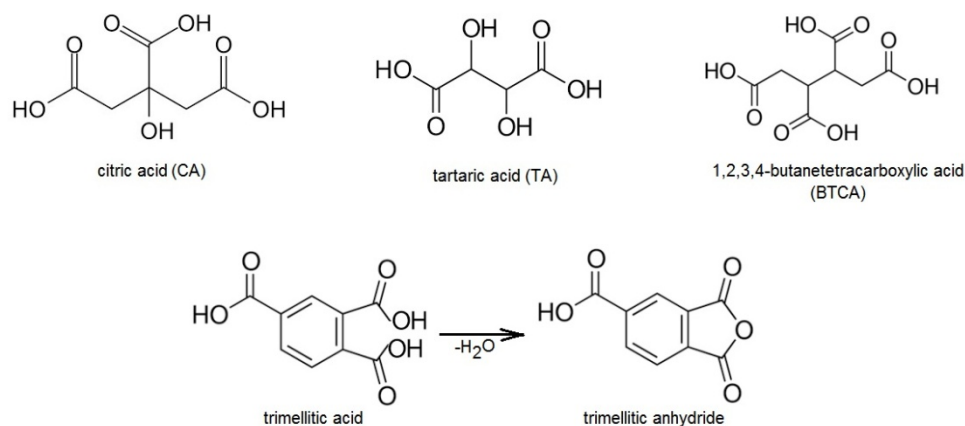
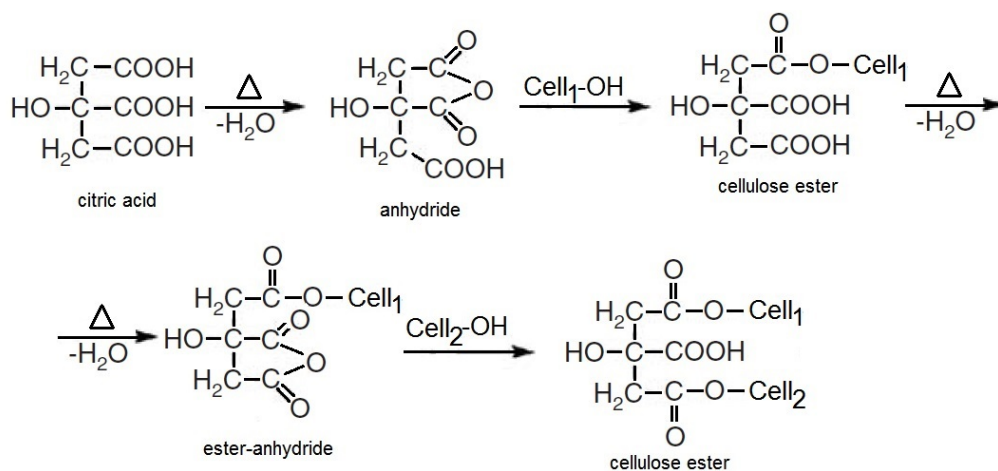


Figure 4. Representative polycarboxylic acids used for wood esterification.

All these multifunctional reagents are able to react with the available active moieties in the cell wall polymers [149]; still, BTCA is more effective in cross-linking than CA as it contains a higher number of $-COOH$ groups, but CA is cheaper and easily accessible (either natural or synthetic) [150], as well as environmentally friendly [145,148]. The main characteristic of this method is the ability of these acids to form multiple ester bonds, which results in a tridimensional cross-linked network.

The mechanism evolves in two stages, as presented schematically in Scheme 7, when internal anhydrides between two adjacent COOH groups are successively formed and each of them reacts with units of cellulose from different sites.



Scheme 7. Mechanism of esterification with citric acid (CA).

The second ester bond is usually formed when the reaction is performed either at high temperatures or at moderate temperatures but for longer time intervals. It is possible for the remaining carboxylic groups to interact with others in the wood structure and form a mixed anhydride which may further yield in another ester bond. In the case of BTCA, its ability to form esters is higher than that of CA, hence, the higher cross-linking density.

In most cases, the direct esterification required the use of a catalyst, such as sodium hypophosphite (NaHP), as well as a thermal treatment. In example, fir (*Abies alba* Mill) and beech (*Fagus sylvatica* L.) samples were treated with BTCA and CA, in the presence of NaHP, at 140 °C for 10 h, or by microwaves at 2.5 GHz, 750 W for 35 min [151]. The concentration of catalyst may also vary: 2.1% [151], or 6.5% [152,153], but the levels of performance of the esterified wood are in the same range. The effect of the concentration of NaHP on the properties of wood esterified with CA was studied over a wide range of concentration values, but at low temperatures in two stages (40 °C for 24 h, then 120 °C for 24 h) [154]. Three series of tests were designed, as follows: (a) 8% CA-1%, 3%, 5%, 10%, 15% NaHP; (b) 4%, 12%, 20%, 30% CA-without NaHP; and (c) 4%, 12%, 20%, 30% CA-5% NaHP. The characteristics used as comparison criteria were dimensional and weight stability of treated wood samples (anti-swelling efficiency—ASE), and mechanical properties (elasticity, impact strength, compression strength). The results were somewhat unexpected: the esterification occurred successfully in the absence of catalyst, but its presence caused slightly different effects on the properties of treated wood samples. Thus, the esterification without catalyst caused a weight increase in wood of 36% (when cell walls acquired a level of saturation), which entailed increased bulking (7%), ASE (50%), and compression strength (48%), but lower modulus of rupture (30%) and impact strength (50%). These effects can be explained by the higher density of the modified wood as compared to raw samples, which resulted in an enhanced stiffness. Therefore, NaHP is not indispensable if the reaction is allowed longer time intervals.

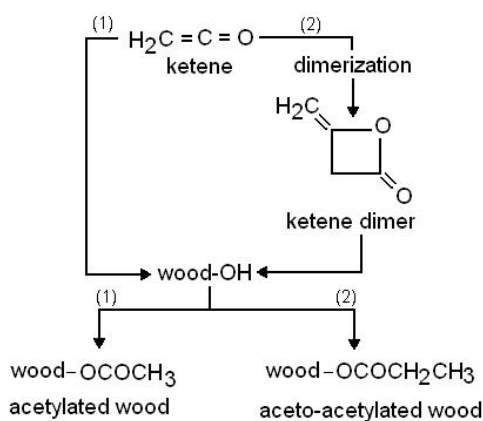
High compression strength values were also registered for fir (*Abies alba* Mill.) and beech (*Fagus sylvatica* L.) samples treated with CA by the microwave method [153], when polar macromolecules in wood (cellulose, lignin, hemicelluloses) underwent activation by polarization under the effect of the high energy field. It is well known that the microwaves treatment causes a rather homogeneous and fast heating in bulk, and the energy and mass flow have the same direction. As result, higher amounts of CA were linked to wood as compared to the typical thermal treatment, evidenced by the weight increase values, with the observation that fir wood retained a larger amount of CA than beech wood, but the values of the compression strength were lower, probably due to an inconsistent distribution of

ester bonds in fir as effect of its low permeability. The same species submitted to the same treatment, but using BTCA instead CA, have showed a higher weight increase after esterification, which entailed reduced water sorption and improved ASE, and a higher cross-linking density due to the presence of 4 carboxylic moieties per each molecule of acid [151].

Remarkable biologic resistance also was achieved by esterification with CA. Thus, beech wood (*Fagus sylvatica* L.) samples were modified with CA/NaHP, for 10 h, at 140 °C, when an increase of 6.1% in wood weight was recorded and the resistance against brown rot fungi *Poria placenta* was over eight times higher than for raw wood [145]. For comparison, the same esterification performed on pine sapwood yielded in a weight increase of 12.4% and biological resistance against some rot fungi of 5.3 times higher biological durability [155].

For wood used in outdoors applications, it is of utmost importance to resist toward photochemical degradation processes that occur upon UV irradiation and are favored by other associated environmental factors, such as day/night or seasonal temperature variation, humidity, corrosion and exfoliation caused by high speed winds, biological attack [156,157]. This objective can be reached by modification of wood with polycarboxylic acids, namely CA. Experiments performed using 6.5% NaHP as catalyst have indicated that beech wood (*Fagus sylvatica* L.) samples underwent some color modification due to the esterification of cellulose rather than lignin, which is UV-sensitive [152]. During accelerated weathering tests run on both modified and unmodified samples for comparison, it was noticed that all samples showed similar cracking behavior. So, the cross-linking generated by CA was not effective enough to control and limit the degradation effects.

Wood modified by PCAs proved to have a valuable characteristic, namely the ability to retain various chemicals by surface adsorption, such as copper and lead ions upon esterification with CA [158,159], or cadmium, nickel and zinc when TA was employed [160]; aniline [161]; tetracycline [162]. For all cases, the esterification provided supplemental –COOH groups that remained un-reacted and available to retain various solutes from their corresponding aqueous solutions (according to the esterification mechanism presented in Scheme 8). For example, aspen wood samples treated with CA at 130 °C for various intervals (4 and 6 h, respectively) displayed high weight gains (52.55% and 58.43%, respectively) [159], and this enabled them to retain large amounts of Cu^{2+} , but depending on the pH of the medium which influences the acidic groups ionization and the mechanism of the metal ion removal. Better results would be expected in the case of wood modified with BTCA as it potentially introduces more available –COOH groups. In practice, it has been proven that it only caused an increased cross-linking density due to its enhanced ability to react with hydroxylic moieties in wood, and, thus, leaving less available adsorption sites [159]. Considering the pine (*Pinus densiflora* Siebold & Zucc.) sawdust modified with CA or TA, the maximum adsorption capacity was significantly higher than that of raw sawdust (14–57 times higher), and depended on the contact time and pH [160].



Scheme 8. Mechanism of wood esterification with ketene.

In the case of other chemicals, the adsorption mechanism is based on the formation of hydrogen bonds between the CA-modified wood and the adsorbed molecules. Thus, an effective adsorption of tetracycline from wastewater has been performed using wood modified with CA as sorbent [162]. The retention capacity of treated wood increased 8–12 times in comparison with raw wood, and the H-bonding formation massively occurred at pH = 5. When the wood samples were pre-treated with alkaline solutions (2% and 6%, respectively), the esterification was favored due to the fact that more cellulose units became available consequent to the lignin removal during the reaction of wood with NaOH. Thus, a higher number of carboxylic moieties can be active adsorption sites where H-bonds are formed between -COOH groups in esterified wood and O=C link in amide groups from zwitterionic tetracycline. This study exploited the low reactivity of lignin toward CA, so it was partially removed through the alkaline pre-treatment. In contrast, it has been substantiated that esterification reactions with CA took place with both lignin and cellulose, when some internal stabilization re-arrangements may occur in lignin structures [163]. These particular lignin structural rearrangements may contribute to the improved water resistance of the treated wood, as previously evidenced [164].

Other studies on the adsorption mechanism of CA-esterified wood have shown that the retention of aniline on modified wood (pine sawdust) was significantly enhanced when β -cyclodextrin (β -CD) was used along with CA [161] due to a complex mechanism, when the additional hydrophobic interactions and the formation of inclusion complexes with β -CD came to increase the effect of H-bonding.

The ability of PCAs to bridge different wood components macromolecular chains through ester bonds and thus creating tridimensional cross-linked structures, given their multiple functional groups was investigated in order to promote modified wood as binder and/or adhesive. In example, CA-modified wood (poplar) samples were used to study the effect of this surface functionalization as promoter of bonding wood particle boards or other wood joints, or even wood veneer panels [164], as this behavior was already reported for other lignocellulosic materials [165–167]. In the case of PCA-modified wood, the binding effect is granted by the cumulative esterification of cellulose and lignin as well, despite the low reactivity of lignin and some local steric hindering due to the supramolecular architecture of wood components. It has been also concluded that CA used for the esterification of spruce samples [164] may have a strong catalytic effect which may be additionally responsible for the overall improved properties of the functionalized wood and, at the same time, favor the rearrangements of lignin at the modified surface. Thus, it was possible to exploit these findings and obtain flat wood pieces bonded by an active interface made of CA-modified wood (such as veneers, laminated veneer lumber—LVL—panels, plywood), having good mechanical properties in some cases (LVL panels showed increased shear strength as compared to standard, but the veneer-support binding failed upon bending) [163].

The same effect of reactive binding has been demonstrated on small wood particles (powder made of *Acacia mangium* Willd.) [168] processed by molding in the presence of CA, under pressure (4 MPa for 10 min) and at high temperature (140–220 °C). The mechanical characteristics of all samples were satisfactory, but particle boards manufactured at 180 °C showed excellent bending properties. The resistance toward water improved, especially at boiling, while thermal stability of materials enhanced in a direct relation with the processing temperature. These experimental results are due to the increased number of ester bonds formed at the surface of wood particles, confirmed by FTIR spectroscopy data, and this behavior can be explained by a combination of factors and their cumulative effects:

- the small size of wood particles created a significantly increased active surface for functionalization;
- the high amount of CA (20 wt.%) provided a larger number of carboxylic groups;
- the temperature regime favored the reaction rate and degree of substitution;
- the pressure applied during processing enhanced the penetration of CA molecules to reaction sites not easily accessible;
- the short heating time prevented further degradative thermo-chemical processes.

Other reaction systems based on PCAs were studied in relation with wood's functionalization, aiming to maximize the properties improvement in modified wood, limit the formation of by-products and waste (thus reducing the negative environmental impact), or even to employ reagents from renewable resources as measure of sustainable development (such as sorbitol and glycerol). Thus, CA is obtained from biomass, TA results as by-product from grape juice fermentation during wine production [147]. Other chemicals may also come from agro-industrial waste: sorbitol results from starch enzymatic hydrolysis of to dextrose followed by the catalytic hydrogenation of dextrose to sorbitol [169] or can be obtained from biomass by cellulose hydrolysis followed by glucose hydrogenation on mesoporous molecular sieves (porous silica and Ru-functionalized porous silica) [170], while glycerol yielded as by-product from the synthesis of bio-diesel [171].

Comparative studies on beech wood (*Fagus sylvatica* L.) samples were conducted using CA or TA, and mixtures of acids with glycerol (Gly) [147]. The concentration of acid solutions was 33% (TA) and 34% (CA), while the mixtures contained 10% Gly. After impregnation, the pressure (1 MPa, 60 min) and temperature (100–160 °C) regime was applied in order to maximize the treatment effects. However, the impregnation rate had comparable values for CA and CA + Gly, and TA and TA + Gly, respectively, although values for esterification with TA were slightly higher than for TA + Gly. The same conclusion is valid for the anti-swelling efficiency. The weight gain was not as significant as expected, either. It was also noticed that bending strength for samples treated with CA or TA strongly decreased with the increasing processing temperature, while samples treated with CA + Gly or TA + Gly behaved similar to raw samples, but better than acid-modified ones. This may be explained by the formation of the polyester matrix that allowed a high cross-linking density in the wood cell walls. Nevertheless, resistance toward decay [white rot fungi *Trametes* (*Coriolus*) *versicolor*] was improved by using acid-Gly mixtures, with the observation that the best results for TA + Gly were obtained at the highest temperature, so, CA + Gly was more effective for the biological protection.

White pine (*Pinus strobus* L.) and lodgepole pine (*Pinus contorta* D.) specimens were treated with CA + Gly to improve their performance as siding materials in outdoor applications [148]. It was concluded that the treatment enhanced the dimensional stability, biological resistance and hardness as compared to untreated wood, although adhesion and density have not improved as expected, maybe due to a poor penetration of reagents. Further investigations on lodgepole pine (*Pinus contorta* D.) samples treated with CA + Gly from renewable resources, and intended for outdoor sidings [172], evidenced their improved properties (the service life expectancy for modified wood was estimated at 2.8 times longer than raw wood), but the comparative LCA studies on treated and raw samples indicated undesired environmental effects, where the most aggressive stage is the chemical treatment.

An optimization study on CA + Gly reaction system was performed on specimens of white pine (*Pinus strobus* L.) and lodgepole pine (*Pinus contorta* D.) [173] and the FTIR data confirmed a high density of ester bridges. At the same time, the cross-linking length and density caused increased thermal stability. The most effective catalysts were hydrochloric acid (HCl) and p-toluene sulfonic acid (p-TSA), but the amount of CA has also influenced the process. Another observation was that the deeper the reagent penetrated the wood substrate the more stable are the ester bonds and the higher the properties improvement.

Recently, sorbitol (S) has been considered and employed in wood esterification systems based on CA [146,174]. The modification treatment performed on the European beech wood (*Fagus sylvatica* L.) specimens with mixtures of CA and S in various ratios (10%, 20%, 30% and 50% w/w, respectively), and at different temperatures (140 and 160 °C, respectively), yielded materials with improved properties [146]. Thus, optimum results were obtained for the solution with concentration 30% w/w, regardless of the temperature regime, when ASE, modulus of elasticity and decay resistance (tested against white-rot fungi [*Trametes* (*Coriolus*) *versicolor*], brown-rot fungi (*Coniophora puteana*), and soft rotting microfungi) has been increased. Despite these improvements, modulus of rupture and bending strength significantly decreased. Furthermore, studies on samples of pine sapwood (*Pinus sylvestris* L.) submitted to the same treatment [174] indicated that 140 °C is the temperature that allows the highest

weight gain, although an optimization may be of interest. All samples have achieved an enhanced decay resistance to brown-rot fungi (*Postia placenta*) and white-rot fungi [*Trametes (Coriolus) versicolor*], as well as to blue-stain fungi (*Aureobasidium pullulans*; *Sydowia polyspora*; mixed culture of *A. pullulans*, *Cladosporium cladosporioides*, *Ulocladium atrum*, and *Sydowia polyspora*). The main issue of these materials is their leachability even after curing at high temperatures and long time (100–140 °C; 72 h) [147,174], which is an indication that the reagents adsorbed into the wood structure were not entirely linked by ester bonds to the wood cell walls constitutive polymers.

A rather recent and interesting experimental approach was the use of nano-sized particulate additives aiming at either an overall improvement in properties [175] or to expand the range of applications [176]. In example, nanoparticulate clay (Cloisite 30B) was employed as catalyst in a CA + Gly reaction system used for functionalization of lodgepole pine wood samples [175], and it proved to be an effective catalyst, yielding in materials with better properties than those obtained in the presence of HCl as catalyst. Dimensional stability and hardness were improved when Cloisite 30B was used and the thermal curing was performed at 180 °C, and the adhesion strength loss was lower. Nevertheless, given the following premises:

- the amount of nanoclay (2%) and its total exfoliation claimed by authors, and supported with XRD and TEM data, and the nanoclay structural features;
- HCl favored the multiple esterification, unlike Cloisite 30B, proved by thermal data;
- for samples prepared with nanoclay, density was not significantly improved compared to HCl samples, and the water vapor sorption was poor (this is an indication of the increased tortuosity of the material, which entailed slow transfer of water vapors in and out of the material), although dimensional stability and hardness increased;
- knowing the reinforcing effect of nanoclays in different types of composite materials, then it is possible to conclude that nanoparticulate clay may have been acting more as a reinforcing agent than a catalyst, even in low amounts. Further studies with nanoclay in various ratios are, though, necessary to elucidate the role of this component and its mechanism of action.

Multi-component systems based on wood sawdust (olive wood sawdust) and CA were designed in order to obtain materials containing magnetite, and with the ability to retain on their surface metal ions from wastewater [176]. Previous studies have confirmed already the ability of sawdust loaded with magnetic nanoparticles and CA-modified cellulose to retain metal ions from aqueous solutions [177,178]. Then, composites where CA was bond to either wood or magnetite particles were thus prepared and their study indicated that the CA-coated magnetite/wood was the material with a remarkable ability to retain metal ions (Cu^{2+} , Co^{2+} and Zn^{2+}) [176], as the process was fast and spontaneous, endothermic, and selective (adsorption of Zn^{2+} and Co^{2+} were significantly affected by the presence of Cu^{2+}) so far it could be used for analytic purposes.

4.4. Wood Surface Modification by Esterification Reactions Using Other Acids

It is not yet known exactly how much lignin and hemicelluloses in wood are able to react under these conditions, but experimental studies have attempted to provide a realistic parallel. Thus, the acetylation of sisal fibers conducted in different solvents has allowed researchers to conclude that the solvent system DMSO/TBAF is able to solubilize the cellulose and promote its functionalization with good results if only the water content of the reaction medium is reduced [135]. On the other hand, hemicelluloses from delignified poplar chips were successfully esterified in homogeneous media (DMF/LiCl and TEA), at temperatures in the range 45–75 °C, but using various acyl chlorides, when over 75% of the available –OH groups were stearylated under optimum conditions [179]. Experiments conducted with other acids concluded that lignin and hemicelluloses from fast-growing poplar species can undergo both esterification and etherification reactions [180]. So, the 4-hydroxycinnamic acid (HCA) esterified most of the available –OH groups in the lignin side chains, but 3-methoxy-4-hydroxycinnamic acid (ferulic acid, FA) was able to bridge lignin fragments by ester or ether bonds formed intra- or

intermolecular. Even more, *p*-hydroxybenzoic, syringic and, respectively, vanillic acids were able to undergo esterification reactions mainly with lignin.

Benzoic acid and some of its derivatives, namely 2-nitro-, 3-nitro-, 4-nitrobenzoic acid, and 4-azidobenzoic acid, were employed for the direct esterification in the presence of pyridine and methane sulfonyl chloride as activating system [181]. A satisfactory degree of substitution (ranging from 0.9 for benzoic acid to 3.0 for 2-nitro- and 3-nitrobenzoic acids) was enabled by using a molar ratio acid:cellulose unit of 3.33:1 (taking into consideration the number of available –OH groups), and maintaining the reaction system at 50 °C for approx. 3–5 h. Still, it was not effective to extend the reaction time for the system with 4-nitrobenzoic and 4-azidobenzoic acid, as the degree of substitution did not exceed the values 2.0 and 1.0, respectively. This confirmed that the reaction rate and degree of substitution are strongly dependent on the acid reactivity, which is influenced by the nature and position on the aromatic ring of the electron attracting substituents.

In the case of esterification with benzoic acid, the formation of a mixed O-benzoyl-O-methane sulfonyl-cellulose ester was evidenced by IR spectroscopy confirming that methane sulfonyl groups were active enough to bind onto the glucopyranose unit. This mesylation of cellulose is a very slow reaction under the afore-mentioned conditions, but even so it could compete with the main esterification reaction.

Benzoylation of wood has been proved to be a very efficient method to protect wood against photochemical degradation caused by weathering and UV exposure. Experimental studies on benzoylated Scots pine wood samples confirmed the beneficial effects of this chemical modification [182]. Thus, the yield of the treatment was high as the weight gain of wood was approx. 70%–72%. It was demonstrated the benzoylation was significantly more effective in the photochemical stabilization of lignin than other chemical treatments (acetylation, alkylation), considering that the main stage in wood photochemical degradation is the absorption of UV radiation by lignin followed by its degradation, when various radicals are formed and, subsequently, they are acting as promoters of the photochemical degradation of cellulose and hemicelluloses [183,184]. It is not yet fully understood if this effect of reducing the amount of free radicals during weathering and UV exposure is due to the capacity of benzoyl moieties to absorb the UV radiation or to their ability to scavenge free radicals. Nevertheless, the study showed that the higher is the amount of benzoylated wood in the sample, the lower are the mass losses during the weathering tests.

Naphtenic acids were also employed for the protection of wood [185–187]. The nomenclature refers to all carboxylic acids present in crude oil. They are alkyl-substituted cycloaliphatic monocarboxylic acids, having the carboxylic group usually attached to the side chain than directly to the cycloalkane ring, and the naphtene moiety consists of cyclopentane and cyclohexane derivatives, although the mixtures of naphtenic acids may also contain low amounts of fatty acids, hydroxy and dibasic acids, phenolic compounds, sulfur compounds and water [188]. Wood modification with naphtenic acids is applied mainly using metal salts (sodium [185] or copper [186]), but organic derivatives (tributyltin naphtenate [187]) were also employed. Due to the chemical reactions that occurred in the wood, this treatment has proved to be effective against insect attack, weathering and UV radiation.

Other carboxylic acids were used too. Thus, cellulose formates were synthesized for analytical purposes by the direct reaction with formic acid for long intervals (4–15 days) or in the presence of an acidic catalyst (sulfuric acid) [189,190]. The one-pot esterification of wood and hydrolysis of modified cellulose was performed by treating softwood samples with molten oxalic acid dihydrate at 110 °C, for various time intervals (15–120 min), under reflux, when cellulose oxalates resulted [191,192]. This procedure allowed the preparation of cellulose nanocrystals in high yields (80%). But esterification of wood with oxalic acid was also employed to improve the moisture and water resistance of wood [193] or to enhance the interfacial interactions between the polymer matrix and wood reinforcements in wood-polymer composites [194].

Rosin is a mixture of extractives compounds originating in pine wood species that primarily consist of acids with various structures (resin acids 90%–95%), fatty acids included, phenolic compounds,

terpenes and terpenoids. Commonly, resin acids are acid derivatives of diterpenes (abietane, labdane) and diterpenoids (pimarane and isopimarane) present in rosin in various amounts [195]. Abietic-type acids (abietic, neoabietic, palustric, levopimaric, and dehydroabietic acid) are predominant in rosin acids in comparison with pimarane-type acids (pimaric, isopimaric, and sandaracopimaric acid), but their ratios vary within large limits depending on the species and origin, time of harvesting, processing and storage, etc.

Wood treatment with rosin acids acquired new importance in recent years as it was employed in the surface modification of fast-growing wood species such as poplar (*Populus tormentosa* Carr. or *Populus* spp.) [196,197] aiming at improving the mechanical properties, dimensional stability, water resistance of wood samples, as well as their surface hardness. Experimental studies reported that wood modification was performed by impregnation followed by a thermal treatment. It is reasonable to assume that esterification reactions took place, given the processing conditions (solvent medium, temperature, pressure, long time intervals), although some specific esterification reactions of resin acids are conducted in industry at 260–300 °C, in the presence of metal oxides as catalysts [195]. This hypothesis is furthermore supported by the significant improvement in wood properties as it appears from the literature. In addition, the sizing process, well-known in paper industry, can be considered as another confirmation since it can be performed using not only rosin [198,199], but alkyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) as well, reagents known to bind –OH groups in cellulose through ester bridges.

An interesting approach for wood modification is the use of amino acid tricine [74] which is N-[tri(hydroxymethyl)methyl] glycine, a zwitterionic amino acid, under the form of a crystalline powder moderately soluble in water. It is suitable for wood impregnation due to its reduced molecular size and its water solubility. Tricine can have beneficial effects after application on wood substrates through deposition of tricine crystals into wood cell walls when it further imparts increased mechanical strength (authors mentioned improved properties such as hardness and tensile strength for the tricine-modified wood), as well as by reaction with wood polymers, mainly polysaccharides, when cause a reduced tendency to retain moisture. As a zwitterion, tricine is involved in strong electrostatic and ionic interactions. For example, it can interact with carboxylate or phenolate moieties from wood polymer components through the presence of its structural amino function and is prone to induce formation of new hydrogen bonds with positive effect upon wood densification process. A previous work of the authors applying tricine for wood impregnation [75] has evidenced an increased wood UV resistance and a reduced degradation of lignin after such treatment.

4.5. Wood Surface Modification by Miscellaneous Procedures

4.5.1. Wood Esterification with Ketene

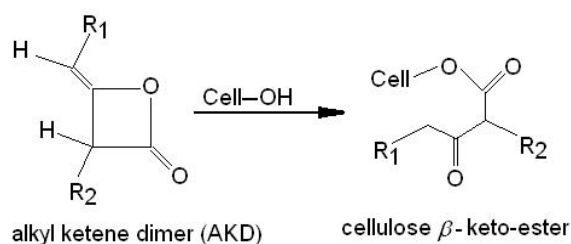
Esterification with ketene gas is an interesting approach due to the fact that it evolves without generating by-products (acetic acid). Basically, ketenes are simple organic compounds with the formula $R_1R_2C=C=O$ (where substituents R_1 and R_2 may be identical or different), highly reactive due to their particular chemical structure, and, therefore, are considered valuable reagents or intermediates in various organic syntheses. Since most of them are unstable, they are prepared *in situ* and used as they are formed [200]. Unfortunately, in the case of surface esterification of wood, the ketene gas has a poor ability to penetrate the wood in order to react with the hydroxyl groups in the cell walls [2,201]. Despite this drawback, it was possible to obtain southern pine and aspen wood flakes modified with ketene gas in a solvent-less procedure, when the reaction mixtures were maintained at 55 °C, for long reaction time intervals (10–15 h, as it was found that this esterification occurs with very low rates), in order to achieve weight gains of approx. 20% [202]. The surface reactions evolve through two mechanisms: (1) the direct reaction of ketene with –OH groups, when acetylated wood resulted, and (2) the dimerization of ketene under the reaction conditions, followed by the reaction of the dimer with

the –OH moieties in the cell walls, yielding in aceto-acetylated wood. The mechanism is schematically presented in Scheme 8.

Some authors reported on the morphological changes occurred during the esterification with ketene gas and evidenced by scanning electron microscopy (SEM) [203,204]. Thus, cellulose I α in wood transformed into cellulose II β which entailed the decrease of the fiber cross-section dimensions, and an enhanced smoothness of the fibers surface was noticeable.

At the same time, a remarkable reduction in water uptake (24.5%) was recorded for acetylated wood as compared to untreated samples. Furthermore, this treatment was also used for wood in order to obtain acetylated cellulose fibers after the removal of lignin and hemicelluloses [203] or dry and hydrophobic microfibrils of cellulose [205].

A more convenient variant of this method is using a stable compound, namely the alkyl ketene dimer (AKD) which is, basically, a 4-membered ring system of 2-oxetanone, having long alkyl chains (C_{12} – C_{22}) pendant to C3 and C4 [206]. By esterification of wood with AKD, β -keto-ester bridges are formed, and the alkyl moieties are transferred to the wood surface thus contributing to the hydrophobization of the treated wood samples (see Scheme 9). The mechanism may also include a concurrent side reaction when AKD reacts with water in the reaction system leading to the formation of the corresponding β -keto acid, which can spontaneously decompose to the corresponding ketone and carbon dioxide [207].



Scheme 9. Esterification of wood with alkyl ketene dimer (AKD).

The method was successfully applied to wood intended for further use in various composite formulations, such as: PP-wood fibers [28], plywood made of alder (*Alnus glutinosa* L. Gaertn.) and beech (*Fagus orientalis* Lipsky) wood logs [60], and particleboards bonded with urea-formaldehyde resin [62]. It can be concluded that AKD acted in the composites not only as an esterification reagent, but as a compatibilizing agent as well, due to its structure. The alkyl chains interpenetrated the polymer matrix macromolecules creating thus an inter-phase with increased thickness and well defined properties, given the fact that the adhesion and cohesion at the interface were provided by both physical and chemical bonding.

In addition to the remarkable decreased water absorption [62], the use of wood treated with AKD in composites caused a significant increase in the mechanical properties of composites. For samples of PP containing high amounts of poplar wood (70 wt.% wood), the tensile strength increased with 41%, modulus-45%, and the impact strength-38% [61]. Reduced water uptake of alder and beech plywoods was also associated with a considerably improved biologic resistance against white [*Trametes* (*Coriolus*) *versicolor*] and brown (*Coniophora puteana*) rot fungi [206].

4.5.2. Direct Esterification of Wood with ϵ -Caprolactone

A particular esterification applied for wood is the reaction with ϵ -caprolactone, in the presence of tin octanoate [$\text{Sn}(\text{Oct})_2$] as initiator. The grafting onto wood cell walls takes place through ester bridges and the ring-opening polymerization of lactone (PCL) occurs under the processing conditions [208,209]. The impregnation of wood samples [Norway spruce *Picea abies* (L.) H. Karst.] with ϵ -caprolactone solution in DMF or toluene for 24 h prior to polymerization reaction (95 °C, 18 h) [208] is a key step in order to maximize the treatment effect. SEM micrographs evidenced a homogeneous distribution of the grafted PCL, although small amounts of unbound PCL remained inside cells after the filtration

stage, and filled the micropores. The modified wood showed significantly improved mechanical properties, resistance toward water and dimensional stability: water repellence and dimensional stability increased by 50% and 45% respectively, when spruce, pine or poplar and other wood species were submitted to this particular esterification [208,210].

4.5.3. Transesterification Reactions for Wood Modification

Another method used for wood esterification is the transesterification in solvent medium (DMF, toluene), at temperature (90–120 °C), in the presence of catalyst (potassium carbonate), and using vinyl esters with various substituents, such as: vinyl ester of carboxyphenyl boronic acid [211], vinyl propionate, butyrate, pivalate, decanoate, stearate, crotonate, methacrylate, cinnamate, benzoate, and vinyl 4-tert-butylbenzoate [212,213]. The main feature of this approach is the continuous exchange of alkoxy-groups at the surface of wood cell walls, and the continuous removal of the alcohol (or aldehyde) resulted as by-product allows the reaction equilibrium to be shifted toward satisfactory yields, knowing that esterification reactions typically evolve with low yields. It was noticed that the number of esterified –OH groups in wood decreased along with the increasing molecular weight of the reagent, which was confirmed by Fourier-transform infrared spectroscopy (FTIR) and ¹³C cross-polarization with magic-angle spinning nuclear magnetic resonance spectroscopy (¹³C CP-MAS NMR), probably due to a limited diffusion within the wood cell walls.

It was reported that poplar wood fibers modified by transesterification with vinyl acetate, propionate and benzoate [213] show increased thermal stability and attenuated hydrophilic character. The corresponding composite formulations with HDPE proved to be more stable under UV exposure, displayed improved mechanical properties and the weight losses caused by biological attack (brown rot and white rot fungi) were considerably reduced.

Another variant is the transesterification of acetylated wood (maritime pine sapwood *Pinus pinaster* Soland) with methyl benzoate, in the presence of dibutyltin oxide (DBTO) as a catalyst, and ethyl trimethylsilylacetate (ETMSA) [214], when it was evidenced that acetyl/benzoyl exchange rate increased along with the increasing amount of catalyst, temperature and reaction time, although a concurrent degradation reaction was also pointed out. Benzoylated wood proved to have an enhanced weathering and photochemical stability [215].

Silane derivatives were employed for wood transesterification, as well, in order for wood samples to acquire significantly pronounced hydrophobic character, and experimental data confirmed the replacement of acetyloxy groups and bonding of the silane moieties to wood [216–218]. Optimization studies indicated the yield of the transesterification depends on the reaction temperature and the presence of the catalyst (dibutyltin oxide).

Depending on the procedure, the properties of the treated wood were different. Thus, tetraethoxysilane (TEOS), methyl triethoxysilane (MTES) and propyl triethoxysilane (PTEO) were employed to modify wood samples of hinoki (*Chamaecyparis obtuse* Endl.), and two different experimental protocols were considered: (i) impregnation of wood with solutions of silane monomers (silane procedure), and (ii) impregnation with pre-hydrolysed oligomeric silanes (sol-gel process) [219]. It was therefore found that dimensional stability, moisture uptake and durability were significantly improved in wood treated with silane monomers (i), despite the fact that the weight gain was lower in comparison with the wood treated with silane oligomers (ii). On the other hand, for the wood samples esterified with silanes having larger alkyl groups, the improvement in properties was more pronounced.

An inexpensive and ecologically benign alternative is wood solvent-less transesterification with a water-based emulsion based on vegetable oil and resol [220], when the vegetable oil (consisting of fatty acids triglycerides) is the transesterification reagent, while the resol (a phenolic resin based on resorcinol-tannin-cashew nut shell liquid) was employed to increase the process effectiveness. After transesterification, the samples have displayed enhanced hydrophobicity and durability, but the improvement in their tensile strength depended on the type and time of treatment, as well as on the pH of the environment where composting experiments were conducted.

5. Conclusions

Wood represents a very complex and versatile natural material that can be modified in many ways to prepare it for direct use or even to activate its surface for further treatments. Modern treatments are physical (mainly plasma and densification procedures), chemical, and enzyme assisted or enzymatic grafting of different functional molecules to the wood surface, and application of thin films (coatings) and deposition of nano-sized particles by sol-gel techniques. Some of the surface modification methods have been introduced a long time ago and are still in use, other strategies of modification have been developed in the recent years.

All these pathways have the main goal to improve or even enlarge the range of properties of wood, such as good adhesion of glues and surface finishes, hydrophobic behavior and/or better hygroscopicity toward water and waterborne formulations. An improved resistance of wood surface against weathering processes when exposed to outdoor conditions is attained by grafting functional molecules onto cell walls and treatment with nanoparticles. Environmental benefits conferred by many wood surface modification technologies recently developed include reduced toxicity of the process, increased wood products life, and reduced maintenance cycles, lower negative impact on the environment and carbon footprint of the products. The resistance against wood decay microorganisms remains a significant topic for such investigations.

Nowadays, an interdisciplinary approach to increase the life of modified wood products used in outdoor and indoor applications (claddings or structural applications) is known as the “four Ds” rules of design and these are: deflection (shedding of water as defense way), drainage (fast removal of water as essential hazard), drying (restoring the optimal conditions as a prerequisite reaction) and durability (improved properties, mainly decay resistance, fire resistance).

As related to the wood surface modification strategies using esterification reactions, the use of natural compounds and their derivatives may represent a feasible trend that can be successfully implemented without major alterations of present technologies. Polysaccharides (such as starch, cellulose, hemicelluloses and lignin-carbohydrate complexes, maltodextrin), caffeine, propolis and other bee products derivatives, etc. are of high interest. The wise choice of treatments will remain a key step as more methods under development are progressing from laboratory scale to industrial scale production. Even combinations of different suitable methods (for example, applying a physical treatment prior to the esterification that would subsequently occur under mild conditions) are under research as they have the potential to maximize the overall effects.

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