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Hydrophobization and Photo-Stabilization of Radiata Pinewood: The Effect of the Esterification on Thermal and Mechanical Properties

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Abstract: Wood protection through chemical modification has received increasing interest over the last decades due to the environmental issues related to conventional biocides or protecting products. Consequently, a wide range of new treatments are developed in laboratories, which are later scaled up in the industrial environment. The main goal of modifying wood for indoor–outdoor application is to change its hydrophilic character, which in turn improves the intrinsic properties of the material and its durability against external factors. Wood can be esterified through its hydroxyl groups to obtain a hydrophobic and photo-stable material. Chemical modifications of *Pinus radiata* D. Don wood using hexanoyl chloride (P6), dodecanoyl chloride (P12), and stearoyl chloride (P18) were carried out at different concentrations. Esterification was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) technique combined with a discriminatory analysis. Weight percent gain was associated with the number of carbons of the aliphatic chain of the fatty acid (P6 > P12 > P18). Moreover, an increase of wood density as a consequence of modification treatments was observed. A substantial improvement of the hydrophobicity of wood was observed by dynamic contact angle measurements. In addition, the effect of ultraviolet (UV) radiation on color changes was reduced with the treatments. Furthermore, the P6 treatment presented acceptable values of modulus of elasticity (MOE) and modulus of rupture (MOR), being suitable for similar mechanical uses as non-treated pinewood. However, only treatments P12 and P18 enhanced thermal resistance of the pinewood in an oxidative atmosphere.

Keywords: wood esterification; fatty acids; hydrophobicity; photo-stability; mechanical properties; thermal oxidation

1. Introduction

Wood is the most widely used bio-based material for indoor–outdoor applications due to its availability, low price, acceptable mechanical properties, ease of processing, renewability, and appearance, among others. The properties of this anisotropic material are derived from the wood cell wall structure and composition. Wood is structurally composed of cellulose, hemicelluloses, and lignin, with a predominant hydrophilic character, which means affinity to water [1,2]. The dimensional stability of this material is correlated with its capacity to interact with the surrounding moisture, attributable to hydrogen bonding created between water and the hydroxyl groups from the

wood cell wall components. Below the fiber saturation point, variations in the moisture content of wood generate swells and shrinkages in the cell wall and, thus, internal stresses in the fibers that could cause cracks or other physical damage. Excessive exposure to water could also accelerate the process of photo-degradation by opening wood cell wall regions to ultraviolet (UV) radiation, which has sufficient energy to chemically degrade wood structural components. A key challenge related to the wood quality and improved working performance during its service life is to reduce the hydrophilic character of the wood. This, in turn, affects the dimensional stability, limits the negative effect of biotic and abiotic factors, and increases the thermal stability of wood. All these aspects have an influence on the mechanical and aesthetic performance. Consequently, several wood modification techniques have been developed during the last decades [3], by means of heat treatments at mild temperatures (up to 220 °C) in different atmospheres [4] or by using chemical reagents that interact with hydroxyl groups of wood. Another way of ensuring long-term durability is coating the wood surface with protective formulations [5]. Thus far, the most prominent chemical modification process and the impregnation method of solid wood are acetylation and furfurylation, which have been extensively studied and are exploited at an industrial-scale level under different patents [1].

Chemical modification of wood is defined as a chemical reaction between a reactive part of the wood and a chemical reagent. Formation of covalent bonds between chemicals and reactive groups of the wood cell wood can be achieved with or without catalyst [6]. The substitution of accessible hydroxyl groups present in the chemical structure of wood components by means of esterification is a common and easy method of chemical modification of wood, leading to the reduction of free sites able to bind water through hydrogen bonds. In addition, the esterification reaction also results in bulking of the wood cell wall generated by the groups grafted onto the matrix [7]. The main advantage of the ester bond in wood is the reduction of its natural hydrophilic character, thus avoiding excessive moisture absorption, which in turn increases the dimensional stability and delays the arrival of decay agents into the wood [8,9]. Moreover, the functionalization of phenolic hydroxyl groups of lignin present in wood prevents the formation of phenoxy radicals and enhances the wood's UV resistance [10].

Previous studies on wood treatments by esterification showed the results of the reaction of hydroxyl groups of wood with an anhydride, carboxylic acid, isocyanate, or ester group of a modifying agent.

Modification leads to improved dimensional stability, increased fire, and weathering resistance, improved hydrophobicity, and mechanical durability. [11–13]. A recent approach by in situ esterification implemented bulk impregnation of the wood cell wall with an anhydride, carboxylic acid, or isocyanate groups from a modifying agent and hydroxyl groups from other modifying agents and wood [14,15]. The natural occurrence of fatty acids in the seeds of palms and trees, and in fat and oils from animals and plants, make them interesting for the synthesis to fatty acid chlorides, possessing a higher reactivity than their parent fatty acids as well as mild treatment conditions that lower the impact on lignocellulosic substrates. Esterification with different acid chlorides has been reported for different materials, such as fillers for polymeric composites with cellulose fibers [7,16], heterogeneous cellulose-fatty acid chlorides-pyridine systems [17], wood flour and sawdust [11,18,19], and spill oils bio-absorbents made from coconut coils [20]. Results of esterification with the fatty acids (e.g., chlorides hexanoyl, decanoyl, and tetradecanoyl) of solid wood were reported for the tropical hardwood species rubber wood [21–23]. However, no data are available for esterification of radiata pine or similar softwoods. After esterification with fatty acid chlorides, materials generally show improved water-repellence and thermal stability, and in the case of wood, better dimensional stability and photostability. A drawback is the generation of acidic by-products like hydrochloric acid, which sometimes causes degradation of wood due to hydrolysis of the holocellulose [11,24]. To solve this issue, triethylamine can be used to trap the hydrogen chloride generated during the synthesis of esters from acyl chlorides [25] and in this way prevents the degradation of the wood, forming hydrochloride salt of triethylamine. In this study, radiata pine samples were modified with three fatty acid chlorides named hexanoyl chloride (C6), dodecanoyl chloride (C12), and stearoyl chloride (C18), at different concentrations. The results of the esterification

treatments were examined in terms of wetting behavior, hygroscopic properties, and physical-chemical changes. In addition, the thermal resistance, photo-stability, and mechanical properties were also studied to provide a comprehensive characterization of the esterified material and demonstrate the performance of the treatments in a hypothetical process improvement scenario.

2. Materials and Methods

2.1. Wood Samples

Samples of radiata pine (*Pinus radiata* D. Don) were prepared from a dried heartwood board free of defects and conditioned (25 °C; 65% relative humidity (RH)). For the different tests, specimens with 3 different dimensions were used: 10 mm (rad.) × 10 mm (tang.) × 40 mm (long.) for physical tests; 10 mm (rad.) × 10 mm (tang.) × 170 mm (long.) for mechanical tests; 10 mm (rad.) × 10 mm (tang.) × 20 mm (long.) for other characterizations. After cutting, samples were sanded with silicon carbide (SiC) sandpaper with 280-grit, and control samples were kept at 25 °C and 65% of relative humidity (RH) until further tests. Ten replicates per each dimensional set were used for each modification set.

2.2. Esterification Process

Firstly, the extractives were removed from the wood to increase interaction between the solid wood matrix and the reactive products. For the extraction, the specimens were cyclically exposed to toluene:EtOH (2:1 (*v*/*v*)) solvent mixture and then washed with cycles of ethanol, using for this process a Soxhlet apparatus (Fisher Scientific, Toledo, Spain). Subsequently, samples were oven-dried at (103 ± 2) °C for 24 h, weighed (dry weight), and kept under vacuum atmosphere for 30 min before the esterification reaction. The chemical modification took place in two-necked flasks where specimens were immersed in N,N-dimethylformamide (DMF) (Fisher Scientific, Toledo, Spain); and pyridine (as catalyst 10%) (Fisher Scientific, Toledo, Spain), similar to the standard procedure described by Thiebaud and Borredon, 1995 [11] with some modifications. In this work, triethylamine (TEA) (Fisher Scientific, Toledo, Spain) was added to the reaction as a trapping agent of the hydrogen chloride formed and, thus, avoiding degradation of the solid wood matrix. Three fatty acid chlorides (Sigma-Aldrich, Madrid, Spain), hexanoyl chloride (C6), dodecanoyl chloride (C12), and steaoryl chloride (C18) were added at different concentrations of 0.1 M, 0.5 M, and 1 M. The reaction was conducted for 3 h at 100 °C for C6 and C12 and at 80 °C for C18, according to the conditions established after a preliminary experimental design where the objective was to minimize reaction time and temperature without compromising the reactivity. Table 1 summarizes the procedure used for the esterification process. When the reaction time was completed, the modified samples were washed with dietylether (PANREAC, Barcelona, Spain) for 30 min and then with ethanol for 3 h using a Soxhlet apparatus. Finally, the samples were oven-dried at (103 ± 2) °C for 24 h and then weighed.

Table 1. Procedure and esterification conditions.

Sample Code	Pretreatment	Fatty Acid Chloride	Molar Concentration			Reaction Conditions (°C/h)
PC (*Pinus radiata*)			**Reference**			
P6	Solvent extraction	C:6	[0.1]	[0.5]	[1]	100/3
P12		C:12	[0.1]	[0.5]	[1]	100/3
P18		C:18	[0.1]	[0.5]	[1]	80/3

2.3. Gravimetric Changes

Before measuring their properties, modified specimens were subjected to a leaching test to estimate the values of properties at operating conditions. The leaching test was adapted from the standard EN 84 (1997) with modifications by vacuuming the specimens at 4 kPa for 20 min and then

immersing them in distilled water for 15 days, changing the water 9 times. The weight loss after leaching was calculated and included in the results. The weight percent gain (WPG) and weight loss (WL) was calculated in parallel using Equation (1).

$$\text{WPG (WL) (\%)} = \frac{m_0 - m_i}{m_0} \times 100 \quad (1)$$

where m_0 is the dry mass of the modified/leached sample; m_i is the dry mass before modification/leaching. Moreover, anhydrous density (freeze-dried specimens) and reference density (at 23 °C, 65% RH) were calculated using Equations (2) and (3), respectively:

$$\rho_{anh} = \frac{m_0}{v_0} \quad (\text{Kg/m}^3) \quad (2)$$

$$\rho_r = \frac{m_{est}}{v_{est}} \quad (\text{Kg/m}^3) \quad (3)$$

where m_0 is the anhydrous mass of modified samples; V_0 is the anhydrous volume of modified samples; m_{est} is the stabilized mass of modified samples; V_{est} is the anhydrous volume of modified samples.

2.4. Chemical Changes

The wood esterification process was analyzed by mid-infrared spectroscopy (4000 cm^{-1} to 400 cm^{-1}) using a Spectrum Two FT-IR Spectrometer with Attenuated Total Reflectance (L1050231 Universal ATR, Perkin-Elmer, Waltham, MA, USA). Modified and control specimens were measured (32 scans were accumulated in transmission mode with a resolution of 4 cm^{-1}). Firstly, extended multiplicative scatter correction (EMSC), followed by an average, was applied to the 10 measured spectra on each sample in order to remove the scatter and have more representative processed spectra. Then, the standard normal variate (SNV) and mean centering (MC) were applied.

Near-infrared spectral measurements were performed in a Bruker MPA II spectrophotometer equipped with fiber optics (Bruker, Germany). The near infrared (NIR) spectrum was recorded from an average of 64 scans over the 12,000 to 4000 cm^{-1} range at a spectral resolution of 8 cm^{-1}. Ten measurements were performed on each sample. The spectra were processed with chemometric software Solo+MIA (SOLO Version) (Eigenvector Inc., Manson, WA, USA) to obtain specific information on the chemical differences occurring in the wood.

2.5. Wettability

For determination of changes in the hydrophilic character of wood after chemical modification, dynamic contact angle measurements were carried out by means of a sessile drop technique on the goniometer OCA20 (DataPhysics, Germany). Wood samples were stabilized for one week at 25 °C and 65% relative humidity before wettability measurements. The dynamic contact angle was determined by the placement of a droplet (3 μL) from time 0 s to 120 s (20 calculations per second). Five measurements were taken along the sample to obtain the water contact angle (WCA), expressed as the average value for each sample and for the set of samples. The selected 5 measurements for the surface included particularities of each sample, such as earlywood and latewood or different patterns.

2.6. Moisture Sorption Measurements

Freeze-drying was chosen as the main drying process (about 0% RH) in order to avoid undesired reactions like degradation or evaporation of product or wood components, which could easily occur during kiln drying. The specimens were freeze-dried for 48 h before the sorption–desorption cycle. Then, the wood samples were placed in sealed containers with different hygroscopic conditions until reaching moisture equilibrium. The relative humidities studied were 35% (MgCl2), 75% (NaCl), and 95% (water), and the temperature remained constant during the sorption–desorption cycle (25 °C). The adsorption process of wood started from the lowest RH environment, after equilibrium for several days, then moved to the higher RH conditions, successively. During the desorption process,

the highest RH condition was set as the start with the reverse relative humidity running order to observe the type of adsorption. On each step, the specimens were weighed, and their NIR spectra were collected (see Section 2.4). The collected data were plotted, and their points were interpolated to obtain hysteresis curves (Origin Software, Version 10, Northampton, MA, USA). The equilibrium moisture content (EMC) was calculated based on the average weight at each equilibrium state. Five replicates were used under each condition.

2.7. UV Accelerated Ageing Test

Modified wood surfaces were exposed (240 h) to ultraviolet radiation A (UVA-340 lamps) at 15 cm of distance at 70 °C (temperature on black panel) in a box at controlled conditions (30 °C and 65% RH). Color changes were monitored with a colorimeter PCE-CSM 2 (PCE-Iberica, Albacete, Spain) after UV exposure. The measurements for each sample were performed in 20 selected points on the surface that included particularities of each sample, such as earlywood and latewood or different patterns. The results were expressed according to the CIE-Lab color space coordinate system (Equation (4)):

$$\Delta E* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

where ΔE* is the total color difference between lightness (ΔL*), red-green axis (Δa*), and yellow-blue axis (Δb*). The evaluation criteria for overall color changes was as follows: 0.2 < ΔE* (invisible difference); 0.2 < ΔE* < 2 (small difference); 2 < ΔE* < 3 (color change visible with high-quality filter); 3< ΔE* <6 (color change visible with medium-quality filter); 6 < ΔE* < 12 (high color changes); ΔE* > 12 (different color).

2.8. Mechanical Changes

For the mechanical tests, 10 samples with the dimensions of 10 × 10 × 160 mm were used per treatment plus control. Samples were stored under standard conditions (20 ± 2 °C; 65 ± 3% RH) for 1 week before mechanical testing. The average moisture content of each set of samples before measurements was as follows: PC = 10.5%; P6 = 6.2%; P12 = 8.1%; P18 = 8.3%. The flexural modulus (MOE) and module of rupture (MOR) were experimentally calculated according to the 3-point bending method with a 10 kN load cell and at a crosshead speed of 2.8 mm/min (Instron 4468, Barcelona, Spain). The load was done at the tangential direction of the sample, calculating MOR and MOE as follows:

$$\mathrm{MOE} = \frac{3\mathrm{P_{lim}L}}{2\mathrm{wh^2}} \quad (5)$$

The modulus of rupture or bending strength (σ) at 3 points was calculated as follows:

$$\mathrm{MOR} = \frac{3\mathrm{P_{max}L}}{2\mathrm{wh^2}} \quad (6)$$

where P_{lim} is the load at the limit of rupture; P_{max} is the maximum load supported; L is the free span distance between the centers of the two supports; w is the width and h is the height of the sample

2.9. Oxidative Response of Esterified Wood

To evaluate samples' thermal resistance before and after esterification, dynamic thermo-gravimetric measurements were performed on a TGA Q5000 IR equipment (TA instruments, New Castle, DE, USA). A few milligrams of the sample (5–10 mg) were placed in a platinum crucible and analyzed at a temperature range from 30 to 800 °C with a constant heating rate of 20 °C/min under O_2 atmosphere (airflow rate 60 mL/min).

3. Results and Discussion

3.1. Spectroscopic Analysis of Esterified Wood

The mid-infrared region is well known for showing associations between fundamental vibrations and the rotational-vibrational structure of the analyzed material; in our case, it allows us to verify changes due to the esterification treatment. However, the standard visual verification omits some "hidden" details that could be interpreted by a discriminatory analysis of the spectra. A mathematical model of each band involved in the esterification process was created to estimate the probability of differentiation of treatments with respect to unmodified wood (Figure 1). The models showed differences in the absorbance bands at 2925 cm^{-1}, 2854 cm^{-1}, 1454 cm^{-1}, and 1375 cm^{-1}, related to the stretching and deformation of $-CH_3$ and $-CH_2-$ groups. These signals were attributed to the vibrations of successive methylene groups present in the FA chains attached to the wood structure. Moreover, changes at 1744 cm^{-1}, associated with carbonyl stretching vibrations (C=O), were indicative of the degree of esterification on the wood structure [26]. Unexpectedly, the band at 3400 cm^{-1}(O-H stretching) did not present significant changes between treatments, thus limiting the differentiation of the OH- signals. Moreover, the absence of characteristic bands of dodecanoyl chloride (1800 cm^{-1}, which is related to COCl) and dodecanoyl acid at 1700 cm^{-1} (COOH) [27] showed that the modified wood does not contain traces of free fatty acids. Therefore, the used washing method was suitable for removing impurities from the final product [27,28].

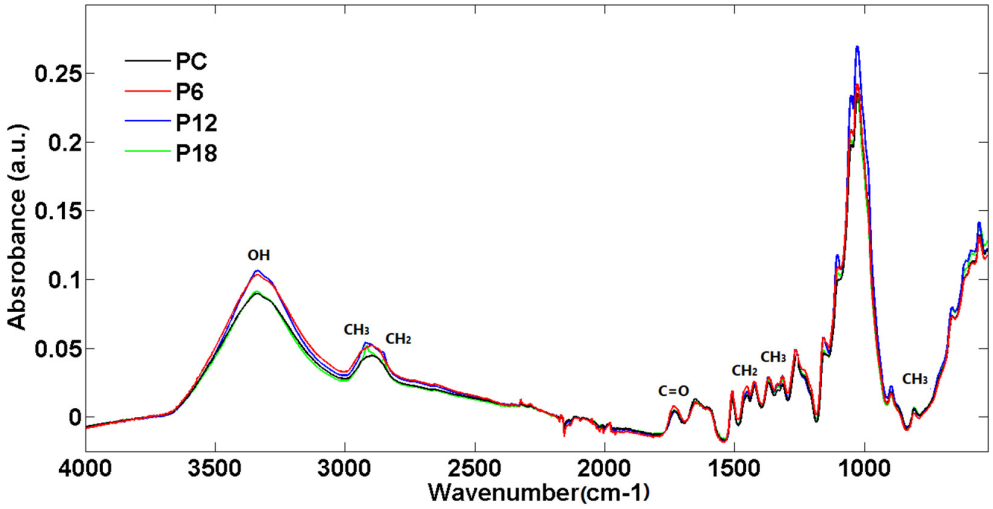

Figure 1. Averaged Infrared spectra of the sample set.

The Support Vector Machine Discriminant Analysis (SVMDA) model contains the spectral information of selected vibrations affected by the esterification. From the model, a confusion matrix showing classification rates of the treatments and the predicted classes was created (Table 2). The estimated probability of differentiation of treatments with respect to control wood was P6 > P12 > P18. This proves that the degree of modification differs from investigated chlorides.

Table 2. Statistics and results of the classification analysis.

Samples	Classif. Analysis	Signal Processing	N	Err	P	Class Err.	N Pred.
PC	SVMDA	EMSC-SNV-MC	15	0.100	0.800	0.261	13
P6			15	0.000	1.000	0.000	15
P12			15	0.015	0.900	0.158	14
P18			15	0.105	0.750	0.363	10

SVMDA = Support Vector Machine Discriminant Analysis; EMSC = Extended Multiplicative Scatter Correction; SNV = Standard Normal Variate; MC = Mean Centering; N = Number of samples belonging to each class; Err = Misclassification error; P = Precision; N Pred = Samples predicted positively.

3.2. Physical Changes

The effect of the esterification on the physical properties of wood was evaluated in terms of density changes (anhydrous and conditioned), weight percent gain (WPG), and product retention after leaching (Table 3). The results show that WPG was not only influenced by the concentration but also by the chain length of the fatty acid chlorides and the moisture content of samples at 65% RH and 25 °C. This connection was evident in treatments at [0.5 M], suggesting the following rate of reaction according to WPG on each treatment: P6 > P12 > P18. One condition that affected physical properties was the number of carbons in the aliphatic chain, which was related to the steric hindrance originating from neighboring substituents in the active sites of wood and could be represented in terms of WPG [7,8.12]. Initially, the number of OH groups available was higher, but once the accessible groups of the surface were modified, the diffusion of the esterification agent in the wood cell wall slows down the reaction rate and, consequently, WPG.

Table 3. Effects of esterification on density and performance.

Chemical Modification	Concentration [M]	Anhydrous Density ρ_A [kg/m³]	Density (65% RH 25°C) ρ_R [kg/m³]	Moisture Content at 65% RH 25°C	WPG [%]	Product Retention After Leaching [%]
Control	-	432.20 (25.26)	471.08 (30.45)	10.50 (1.5)	-	-
P6	[0.1]	439.76 (29.11)	471.95 (22.86)	8.7 (1.4)	1.06 (0.45)	37.45
	[0.5]	481.15 (17.37)	512.81 (16.91)	6.2 (0.5)	5.64 (1.26)	60.57
	[1]	468.32 23.97)	501.05 (28.95)	6.1 (0.5)	4.44 (0.66)	30.88
P12	[0.1]	427.78 (27.68)	458.23 (29.64)	9.8 (1.6)	1.39 (0.27)	58.51
	[0.5]	444.53 (13.70)	474.52 (28.87)	8.1 (0.8)	3.26 (0.49)	57.75
	[1]	441.94 (18.06)	470.72 (20.14)	7.8 (0.7)	6.19 (1.99)	59.09
P18	[0.1]	441.16 (33.60)	474.46 (34.99)	9.8 (1.4)	1.93 (0.30)	48.73
	[0.5]	460.28 (15.65)	494.23 (30.90)	8.3 (0.9)	2.67 (0.45)	50.75
	[1]	436.94 (0.34)	470.32 (41.76)	7.6 (0.9)	2.38 (0.34)	63.49

RH = Relative Humidity; WPG = Weight Percent Gain.

According to the results observed by Fodor et al., 2018 [28], increased wood density after modification treatments could also be due to the bulking of the wood cell wall with the apolar groups of the aliphatic chain, in turn, obtaining a more dimensionally stable material. Potentially, the differences in the performance of P6 and P12–P18 treatments might be related to the reaction duration. For this experiment, all treatments lasted for 3 h; however, it is expected that changes in reaction time will lead to different WPGs and, therefore, influence wood properties. For a better understanding of the effect of reaction time on wood properties, it was necessary to perform extended tests at different reaction times in order to experimentally find with greater precision the optimal point for each of the esterification reagents used [6–8]. Moreover, at lab conditions (65% RH and 25 °C), the moisture content of each esterified sample and concentration was inversely correlated with WPG, where higher MC lowered the physical properties. According to our results, an intermediate moisture content (from about 6% to 8%, depending on the treatment) was optimal to obtain the best results.

An indirect way of contrasting the esterification rate is by quantifying the product retention after the water leaching cycle (Table 3), assuming that the remaining product was chemically attached to the wood cell wall and not leached by the water. In this case, the maximum peak was found at 0.5 M in P6 and at 1 M in P18, while in P12, the rate was steady at all concentrations. According to the overall results, the concentration of 0.5 M could be adequate, since at higher concentrations the product reacts with less intensity, or its increment is irrelevant. The interactions between water vapor and esterified wood were analyzed by measuring the weight increment from anhydrous (0% RH at 25 °C) to the conditioned environment (65% RH at 25 °C). At 0.5 M, PC6 presented the lowest weight increment, whereas the specimens of P18 showed the highest increase. These results showed that the shorter length of FA's alkyl chain was more effective in limiting free radical bonds interacting with water molecules.

3.3. Wetting Behavior and Hygroscopic Properties

The effectiveness of water repellency was calculated by the water contact angle (WCA) over time (Figure 2). This analysis exhibited important differences between untreated and chemically modified wood. The results showed an expected hydrophilic character of pinewood with initial values of about 80° and around zero after 30 s. On the other hand, the chemical modification changed the wood to a hydrophobic character (values above 110°) with stable values over time in all treatments, except at 0.1 M. In general, the WCA over time was influenced by the length of the acyl substituent in the following order: P6 < P12 < P18. This effect was caused by the decrease of available polar groups [6], especially those capable of hydrogen bonding with water, and in turn, the hydrophobic behavior of modified wood seems to be more pronounced when the aliphatic chain is longer. Thiebaud et al., 1997, also observed a similar trend after the chemical modification of oak sawdust using fatty acid chlorides with a different number of carbons [29]. However, the water contact angle values from chemically modified oak sawdust were not higher than 95°. According to these results, the level of substitution at 0.1 M was not enough to improve the hydrophobic character on wood surfaces, particularly in P6. However, the water contact angle values from chemically modified oak sawdust were not higher than 95°. According to these results, the level of substitution at 0.1 M was not enough to improve the hydrophobic character on wood surfaces, particularly in P6. Moreover, at low concentration [0.1 M], the WPG-WCA has shown a direct correlation, in which P12 and P18 present higher WPG and stable WCA, while P6 presents lower WPG-WCA. One hypothesis was that, at low concentrations, the OH groups on the surface were still available, and the reactant still has space to diffuse into the cell wall. With increasing concentrations, the reactant needs to be diffused into the cell wall. Short aliphatic chains could find more space for diffusion with higher WPG and stable WCA values. Another explanation might be the decrease of porosity during the reaction time of wood-fatty acid chlorides, interfering with the physical accessibility of the reagents, thus varying the WPG and WCA results [7,30].

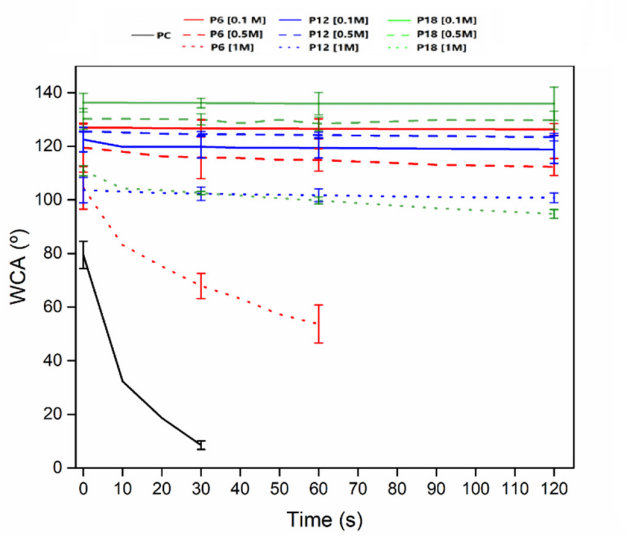

Figure 2. Dynamic contact angle untreated and esterified Pinewood.

In addition, the experimental sorption–desorption isotherms of untreated and esterified wood are presented in Figure 3. According to the International Union of Pure and Applied Chemistry (IUPAC) isotherms classifications [31] and previous reported studies [32,33], both untreated and esterified wood exhibited sigmoid shape isotherms (type II) as a result of monolayer-multilayer adsorption, typical mechanism of lignocellulosic materials. However, the hygroscopic behavior of esterified wood was significantly different to the untreated pinewood. The hysteresis phenomenon of wood was clearly influenced by the chemical modification and by the reagent used for the esterification reaction. The hysteresis is expressed by the difference between the equilibrium moisture content in sorption and desorption at the same relative humidity [34]. The present study revealed a clear trend regarding the hysteresis of evaluated wood samples: P6 < P12 < P18 < control. These results indicated the higher capacity of modified wood, especially P6, to release absorbed water during a desorption process, suggesting a higher dimensional stability in humid environments. Previous research studies demonstrate an improvement of the dimensional stability of rubber wood esterified with octanoyl and palmitoyl fatty acid chlorides [21,22].

Moreover, in order to understand the chemical differences between untreated and chemically modified wood during a water vapor sorption–desorption process, NIR spectra of wood samples at different sorption–desorption points (0%, 35%, 75%, and 95% RH) were collected. The NIR spectra were pre-processed by applying extended multiplicative scatter correction (EMSC) and average. With the aim of analyzing the water vapor-wood interaction during the sorption–desorption cycle, the second derivative and mean center were applied to the spectral region of 6000–7200 cm^{-1}, which was associated with the first overtone of O-H absorption bands of wood [35]. Figure 4 plots the second derivative, scores (PC1 vs. PC2), and loadings of spectra in the range of 7200 to 6000 cm^{-1} at selected RH% points. Principal component analysis (PCA) allowed the effective variable reduction of spectroscopic data into three new sets of variables such as principal components (PCs), scores, and loadings [36]. PCA was used to identify the variables that contribute most to this differentiation. The spectral variance during the sorption–desorption cycle was reduced to three principal components containing <99% of the spectral information. During the sorption (from 0 to 95 RH %), principal PC1 clearly differentiated P6 treatment from the rest of the esterified wood and control, which were grouped together in the score plots. The loadings from principal components can be interpreted by recalling the effect-position of the second derivative peaks/valleys, which are still associated with features in the raw spectra. NIR spectra varied with moisture condition; the loadings at dry state (0% RH) showed only a high positive influence of the bands at 7003 cm^{-1} and 7120 cm^{-1}, which were related to the first OT of O-H stretching in amorphous cellulose and a weak H-bond, probably related to semi-crystalline cellulose [37]. The information contained in PC2 vs. PC3 score plots, which was

associated with the semi-crystalline and crystalline cellulose, did not discriminate between treated and control wood except at high RH%, where esterified wood samples were clearly separated from the control. At saturated state (95% RH), the initial absorbance was negatively influenced and appeared as bands around 6950 cm^{-1} and 7060 cm^{-1}, due to the formation of water–water hydrogen bonds during water sorption [38]. The bands at the saturated state could be related to changes in density, and their evolution could be observed during the desorption steps. As an example, loadings during desorption at 45% RH are shown in Figure 5, and it was possible to observe an increase in those bands that appeared at a saturated state and show positive scores in the P6 treatment. According to these results, aside from hemicellulose and lignin, chemical modification affected the amorphous region of cellulose, with the P6 treatment the one that most affected the original state of the wood. During desorption, it is worth mentioning the clear differentiation not only of P6 treatment from the control but also of P12 and P18 treatments. These results agree with the experimentally obtained isotherms, where the main difference between control and esterified wood was observed during the desorption process.

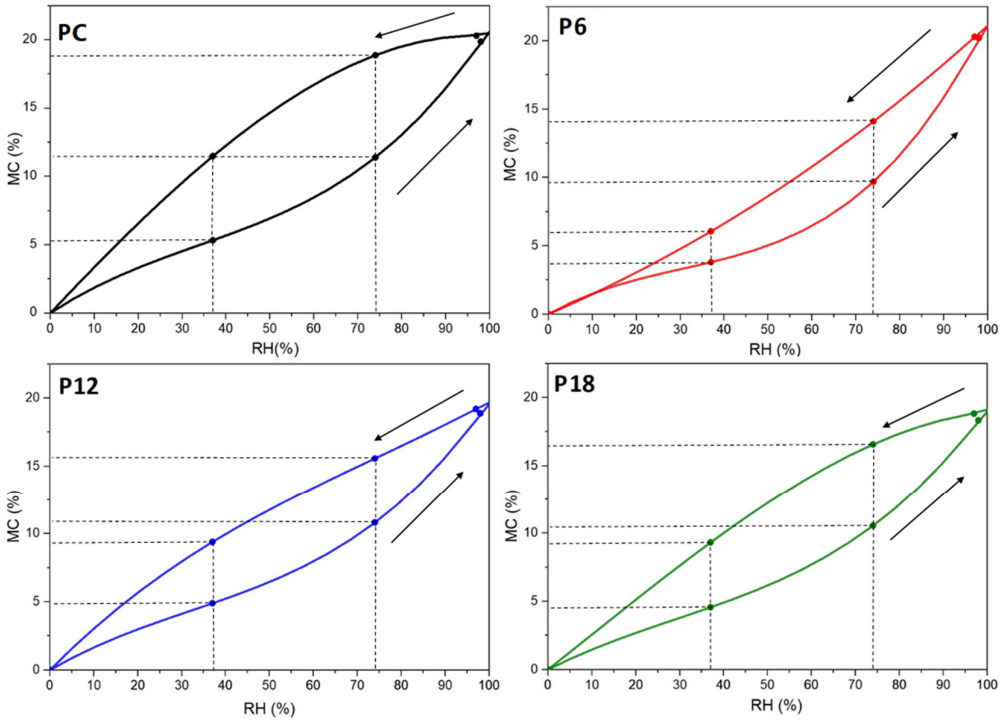

Figure 3. Experimental sorption–desorption isotherms of untreated and esterified pinewood. (RH = Relative Humidity).

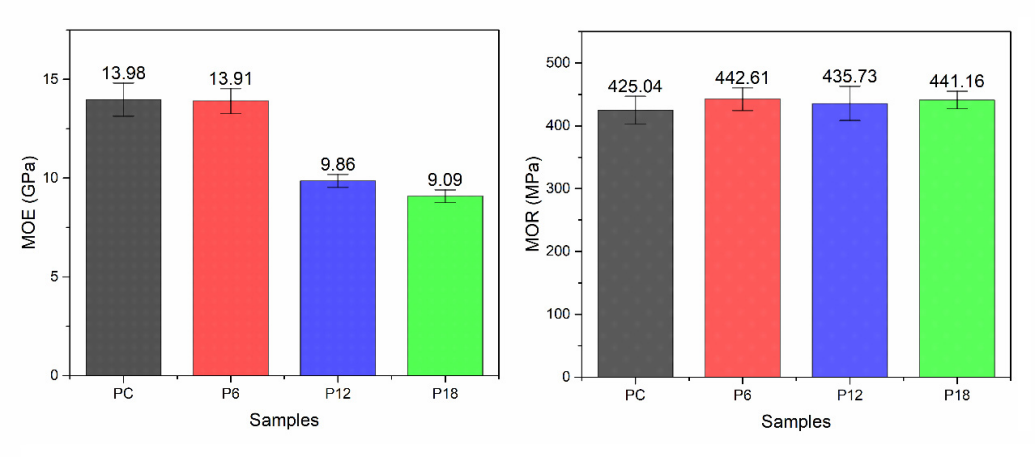

Figure 4. Effect of the esterification treatment on the modulus of elasticity (MOE) and modulus of rupture (MOR) of pinewood.

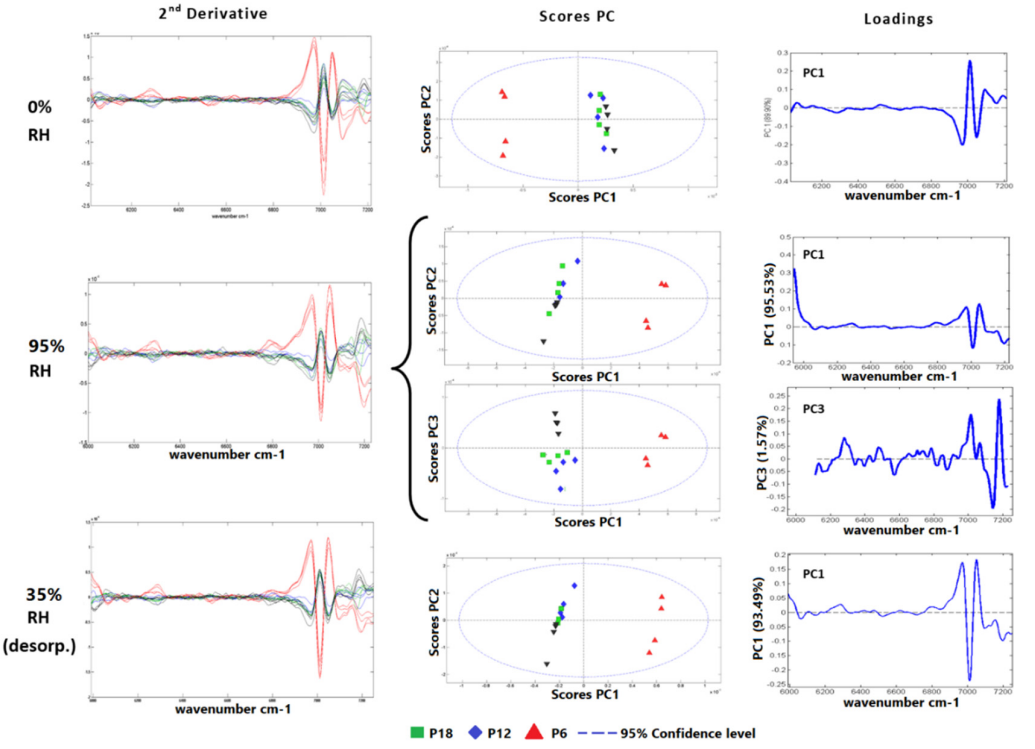

Figure 5. Plots of the second derivative spectra, scores, and loadings in the range of 7200 to 6000 cm^{-1} at 0% RH, 95% RH, and 35% RH desorption. (PC = Principal Component).

3.4. Photostability of Modified Wood

Color changes after wood esterification were analyzed after 240 h of irradiation. The L-a-b parameters were similar, especially lightness, which was statistically equal. On the other hand, parameters a-b, referred to as color tones, showed changes in values, shifting slightly to more yellowish tones (Table 4). After a short radiation time, the unmodified wood surfaces rapidly changed from light to dark as was expected. Moreover, the esterified samples were more stable after 240 h of irradiation, especially with P6 treatment. Esterification of wood using fatty acids was presented as a suitable option to prevent the photo-degradation of wood. Changes in color were

related to chemical changes induced by UV exposure, where lignin was the more susceptible wood constituent to absorb light and form radicals [10,23]. However, esterified treatments reduced the formation of radicals, preventing chemical changes and, as a result, avoiding color changes in wood, particularly in P6 treatment where a-b parameters did not present changes (Δ below 1). During esterification, lignin presented in wood had also been modified, and the -OH groups of its structure were substituted by aliphatic chains of different lengths. Other authors also observed an improvement of the ultraviolet resistance of wood after esterification using palmitoyl chloride [22] and acetic acid anhydrides [2,39].

Table 4. The color change of untreated and esterified wood after 240 h of UV irradiation.

Time	0 h			240 h			
Sample	**L**	**a**	**b**	**ΔL**	**Δa**	**Δb**	**ΔE**
PC	84.95 (1.05)	3.98 (0.40)	9.51 (0.53)	12.11	3.03	13.69	8.37
P6	85.80 (0.96)	4.36 (0.45)	12.96 (0.89)	7.39	0.03	0.27	2.78
P12	84.98 (0.60)	4.02 (0.36)	12.04 (0.55)	8.24	1.02	2.19	4.41
P18	84.64 (0.58)	3.55 (0.22)	10.75 (0.47)	9.61	1.64	6.35	4.20

L = Lightness; a = red-green axis; b = yellow-blue axis; ΔL, Δa, Δb = differences in the parameter L, a, b; ΔE = differences in overall parameters.

3.5. Mechanical Properties

Changes in modulus of elasticity and modulus of rupture were studied to observe the effect of esterification treatment on selected mechanical properties influencing its potential applications as constructive elements [40]. The mechanical properties of control and esterified wood are presented in Figure 6. The results showed that, during the maximum load in bending, deformations were similar between unmodified wood and P6 treatment; however, in P12 and P18 treatments, the stiffness decreased between 29% and 35%, respectively. The decrease in MOE of P12 and P18 treatments could be due to a slight degradation of hemicelluloses and to an increment of the semi-crystalline proportion of cellulose provoked by the acid generated during the modification process [12,41], which was not efficiently trapped by the triethylamine (TEA) added to these reactions. It should also be pointed out that the strength properties of wood are very dependent on the moisture content of the wood cell wall, therefore, the higher MC in P12 and P18 (about 8% at 65% RH) possibly affected the MOE of those treatments.

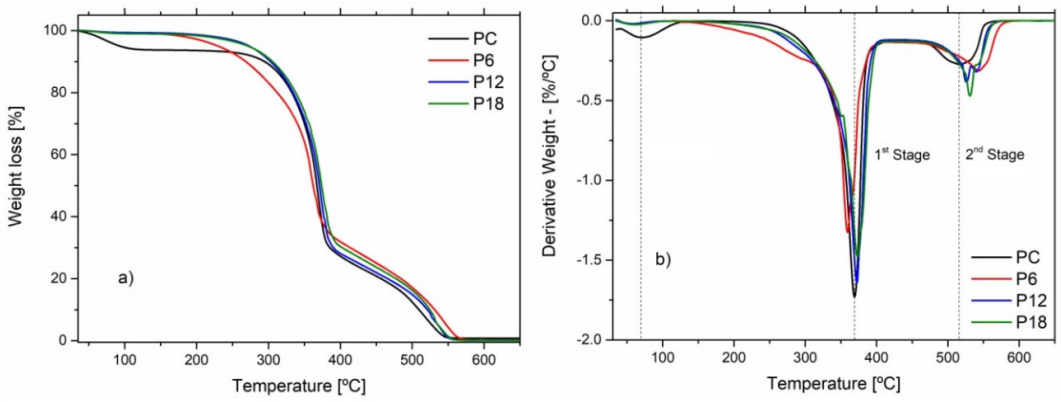

Figure 6. Curves obtained from the thermal analysis for the different samples: (**a**) Thermogravimetric curves pinewood samples, (**b**) derivative thermogravimetric curves pinewood samples.

Furthermore, although the density after treatment increased in all cases, no correlation was found between density and MOE, without any particular trend. Esterification of wood by acetylation

had no significant impact on the modulus of elasticity, as was reported previously [41]. In addition, the bending strength (MOR) was an important criterion for the use of wood as a structural material, where high values were expected to reach specific requirements. After treatments, MOR increased slightly (up to 4%) compared to control wood, which could be positively influenced by the increased density after the esterification treatments. In comparison with recent studies of analogous treatment, MOE of wood esterified in situ with sorbitol and citric acid [9], or by polycarboxylic acids [7], was slightly increased. MOR was lower than in unmodified wood, but while using alkyl ketene dimer, both MOE and MOR significantly increased compared to control. Although all performed treatments have a slightly positive influence on the resistance to failure, only the P6 treatment maintained the initial stiffness of wood and presented acceptable values of MOE and MOR, being suitable for the same mechanical uses as pinewood.

3.6. Thermal Properties

Thermogravimetric analysis was carried out in an oxidative environment to emulate the typical conditions of fire combustion. Thereby, the thermal performance of the samples was assessed, and the influence of the esterification was studied. Thermogravimetric (TG) and first derivative thermogravimetric (DTG) curves are presented in Figure 6, and the most significant parameters are summarized in Table 5. The first mass loss located below 100 °C was associated with the release of the moisture contained in the wood. In this respect, it was seen that the esterification significantly influenced this stage by reducing the mass loss from 6% (untreated wood) to 1% (esterified wood) due to the esterification treatment. Moreover, it was observed that thermal degradation occurred in two different steps.

The main degradation step was observed between 300–400 °C with a maximum degradation around 370 °C. DTG peaks corresponded to the inflection points of the TG profiles and represented the maximum weight loss rates. Below this temperature, where the degradation or fragmentation of hemicelluloses occurred [29,42,43], P6 showed the least stability among studied treatments. It could be remarked that esterification of wood with the shortest aliphatic chain (P6) led to the lowest T50% of all modifications, indicating lower oxidative stability, but P12 and P18 treatments slightly enhanced the thermal stability compared to control wood.

However, the degradation rate of P6 during the main decomposition stage was observed to be slower than other treatments and control samples. Above this temperature, cellulose was almost fully decomposed within a small range of temperature [42–44], and accordingly, this stage was attributed to cellulose degradation. The second step of decomposition was observed within the 450 to 550 °C range. According to the maximum temperature of degradation for the control samples (≈520 °C), this stage was associated with lignin decomposition, which normally occurred over a broad interval of temperatures until high values [45].

Table 5. Parameters determined from the thermogravimetric analysis.

Sample	$T^{10\%}$ (°C)	$T^{50\%}$ (°C)	Temperatures of Degradation (°C)	
			1st Stage	2nd Stage
PC	279.9	367.0	369.1	517.6
P6	263.3	363.1	361.8	538.1
P12	295.6	370.6	372.7	536.7
P18	297.6	373.4	373.3	530.9

$T^{10\%}$ = temperature at 10% of sample degradation; $T^{50\%}$ = temperature at 50% of sample degradation.

Concerning the relationship between the results and fireproofing properties, it has been previously reported that the weight loss obtained in TGA analysis of wood was directly related to its flammability and the efficiency of a fire-retardant compound or treatment [42–44]. Thus, through the obtained results, it could be elucidated that a reduction in the weight loss of the esterified wood (P6 > P12 > P18), compared to PC, would result in a decrease of its combustion capacity. The employment of fatty acids with longer aliphatic chains proved to be convenient regarding the thermal stability of the esterified

pinewood samples. Another work dealing with esterification of lignocellulosic materials shows, by TGA technique, that octanoyl chloride enhanced the thermostability of sawdust by increasing the temperature of maximum weight loss by about 30 °C [45]. Moreover, TG and DTG of esterified beech sawdust shifted to higher temperatures, meaning an improvement in thermal stability [46].

General comparison of the esterification treatments is presented in Table 6. Overall results meet the expectations of the improvements of the selected properties. An outstanding transition to water repellent substrate with higher dimensional stability and photostability was achieved; thermal stability was improved or maintained, and modulus of rupture was slightly increased, while the modulus of elasticity was not satisfactory. Overview of the wood characteristics proves that proposed modification might be successfully applied for wood used in outdoor applications or in wet environments.

Table 6. Summary table of all tests and results compared to radiata pine.

Properties	Treatment		
	P6	**P12**	**P18**
WPG	++	++	+
Product retention	+	++	++
Hydrophobicity	+	++	++
Dimensional stability	++	+	+
Photostability	++	+	+
Modulus of elasticity/Modulus of rupture	=/+	-/+	-/+
Thermal performance	=	+	+

- Deteriorate; = No improvements; + Improvements; ++ Remarkable improvements.

4. Conclusions

In this work, solid Radiata pinewood was chemically modified with three different fatty acid chlorides in order to study the effect of the esterification on the physical-chemical, mechanical, and thermal properties of wood. FT-IR spectroscopy confirmed the esterification by showing spectral differences between control and esterified wood, especially in the treatment with shorter chain (P6), followed by P12 and P18, regardless of product concentration. Results indicated that the number of carbons in the aliphatic chain was a key factor during chemical modification due to the steric hindrance of the molecule to the reactive active sites of wood. Physical properties and product retention were also affected by the number of carbons of the aliphatic chain as follows: P6 > P12 > P18. WPG was not only influenced by the chain length but also by the product concentration, concluding that the product concentration at 0.5 M could be the most adequate, since at higher concentrations, the increment in almost all treatments was irrelevant, and product retention after a water leaching cycle was more accurate at such concentration limit. The effectiveness of water repellency (WCA) was influenced by the length of the acyl substituent in the following order: P6 < P12 < P18, but in general, all the treated surfaces were considered as highly hydrophobic. In addition, the hysteresis phenomenon was clearly influenced by the chain length. The chemical differences during a water vapor sorption–desorption process were studied by NIR spectroscopy and PCA, and the results showed that the esterification affected the amorphous region of cellulose by contrasting the spectral differences of wood at dry state. Moreover, the main chemical differences between control and esterified wood were observed during the desorption process, agreeing with the trends of the obtained isotherms. The effect of UV radiation on color changes was reduced with the esterification process, which was interpreted as an effective substitution of the -OH groups during the treatments. Moreover, the P6 treatment presented acceptable values of MOE and MOR, being suitable for similar mechanical uses as pinewood. However, the P6 treatment provided less thermal stability to the wood, as only treatments P12 and P18 enhanced the thermal resistance of the pine wood. Summarizing proposed treatments might be considered as an alternative modification process for wood, especially in outdoor applications, due to their positive effect on dimensional stability, hydrophobicity, and photostability.

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