Wettability Variation of Unmodified and Thermally Modified Surfaces of Thinned Wood from a Hardwood Plantation

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The study of surface properties—particularly wettability—and how these vary from pith to bark in relation to changes in surface roughness, chemical composition and crystallinity is of importance to improve the use of wood that comes from thinning of a hardwood plantation. In this study, water wettability was assessed by measuring the contact angle using a drop shape analyzer, while surface roughness was evaluated with a confocal microscope. The chemical composition and crystallinity of the surface were analyzed using Fourier Transform Infrared Spectroscopy (FT-IR). To minimize the influence of machining variables on surface properties, a consistent surface quality before and after thermal modification was ensured using computer-controlled cutting. The results revealed that, prior to thermal modification, the contact angle varied significantly from pith to bark. After modification, the contact angle increased, but the differences were no longer statistically significant, due to the homogenization of the chemical-structural characteristics caused by the thermal modification. Relative crystallinity and surface roughness tended to increase towards the bark, with the contact angle tending to decrease, before and after modification.

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INTRODUCTION

It is well known that wettability is a crucial surface property that directly influences the adhesion, penetration, distribution, and bonding strength of adhesives and coatings (Boonstra *et al.* 2006; Nguila Inari *et al.* 2006). It has been observed that an increase in surface roughness reduces the contact angle, thereby improving wettability and the bonding performance of adhesives and coatings (Candan *et al.* 2012, 2021). The wood species directly affects its wettability, as it can be influenced by hydrophilic components such as hemicelluloses, the degree of surface crystallinity, and the level of polymerization, among other factors (Young 1976). It is important to mention that in this study water wettability is being used, as there are other types of wood wettability, such as adhesive wetting (using different kind of adhesives on the wood surface to see how they penetrate (Shi and Gardner 2001)). Thorough the text, when wettability is mentioned, it is referred to water wettability using water drops.

When wood is thermally modified, it changes various properties, such as a decrease in density, and higher fungal resistance and dimensional stability (Sandberg *et al.* 2017; Hill *et al.* 2021; Mai and Militz 2023). However, this treatment often leads to a decrease in

mechanical properties, which may limit its use in certain applications (Kasemsiri *et al.* 2012; Bakar *et al.* 2013; Sandberg *et al.* 2017; Mai and Militz 2023). These changes in physical and mechanical properties are associated with chemical modifications in the main components of wood: cellulose, hemicellulose, and lignin (Hill *et al.* 2021; Mai and Militz 2023), and these changes affect the wood surface properties (Nguila Inari *et al.* 2006; Pelit *et al.* 2015; Chu *et al.* 2016; Pelit *et al.* 2021).

The first analysis of the relationship between the contact angle and roughness was done by Wenzel (1936), where he stated that an increase in roughness will tend to decrease the contact angle on hydrophilic surfaces in a completely flat surface. This model has been questioned by Gao and McCarthy (2007), where they also question the Cassie and Baxter (1944) model. They say that contact angle behavior is determined by interactions of the liquid and the solid at the three-phase contact line alone (in the case of wood, this line would be that the moment the droplet makes contact with its surface), and that the interfacial area within the contact perimeter is irrelevant. Nonetheless, Gao and McCarthy (2007) do not discourage using Wenzel or Cassie-Baxter theories. The complex porous and fibrillary composition of the wood surface, composed mostly of cellulosic components, poses difficulties for the quantification of its contact angle (Hubbe *et al.* 2015). Additionally, the influence of cracks, pores, its chemical constitution, and the water-swellable nature of its cellulosic components (Hubbe *et al.* 2015; Gurău and Irle 2017) will also increase the variability of the surface, affecting the water drop and its contact angle.

When the wood is modified, depending on the species and the process configuration, there is a tendency of a relation of increased roughness with an increased measured contact angle, due to the hydrophilic surface of the modified wood. At high modification temperatures, water droplets tend to take on a rounder shape on the surface due to the increased hydrophobicity of the modified wood. In contrast, unmodified wood exhibits a flatter droplet shape, as the liquid is absorbed more quickly, resulting in a smaller contact angle (Bakar *et al*. 2013). An example of this difference was presented by Chu *et al*. (2016), where they reported an increase in contact angle after modification in *P. beijingensis*. Similar results were shown by Lopes *et al*. (2018), utilizing juvenile teak wood (*Tectona grandis*). In jack pine (*Pinus banksiana*), heat treatment reduced surface water absorption compared to untreated wood due to the degradation of wood components (hemicellulose, lignin, and cellulose) during the process (Huang *et al*. 2012). Žigon *et al*. (2023) reported similar results for beech (*F. sylvatica* L.), concluding that the poorer wettability and reduced water and coating sorption in thermally modified wood were also linked to changes in its chemical composition.

Wood natural hydrophilicity is due to the accessible hydroxyls on the surface. The hydroxyl groups are present on cellulose chains, hemicellulose chains, or lignin, thus decreasing the number of accessible hydroxyls on the surface of wood limits its interaction with water. Therefore, the change from hydrophilic to hydrophobic is often linked with the removal of hydroxyls by modifying, chemically or thermally, the wood surface (Wang and Piao 2011). The changes caused by the thermal modification on the water wettability of the surface can be related to the reorganization of the lignocellulosic polymeric components causing plasticization of the lignin (Hakkou *et al*. 2005). The same authors also indicate that high modification temperatures were not necessary to modify the hydrophilic properties of wood, as they seem to start to modify at lower temperatures. Furthermore, Žigon *et al*. (2023) showed that the lower wettability of thermally modified wood was due to its altered chemical properties, where the lower presence of OH groups, C = O groups and C–O (related mainly to changes in hemicelluloses and lignin after the

modification) bonds contributed to a more hydrophobic character of the modified wood. Hakkou *et al*. (2005) indicated that the modifications of the wood polysaccharide components were related to changes in the crystalline and amorphous cellulose. This can be related to the crystallinity changes showed by Pétrissans *et al*. (2003), which influence the wettability of the modified wood.

The evaluation of surface roughness depends on multiple factors, such as the wood species, its structural characteristics, the measuring instrument used, the operating conditions during machining, and the processing of the wood profile. These variables make it challenging to standardize a methodology for measuring this property, as there are both conventional measuring instruments, such as stylus profilometers, and contactless measuring equipment, such as confocal microscopes or autofocus roughness meters (Gurău and Irle 2017; Iglesias *et al*. 2024). Some studies have shown a high linear correlation between measurements obtained with a stylus profilometer and confocal microscopy, confirming that confocal microscopy can be used to assess the surface roughness of wood pieces. Although this method requires a longer processing time, it also offers higher measurement resolution (Magoss *et al*. 2022; Iglesias *et al*. 2024).

To achieve a high-quality surface, for a standardized measurement of roughness and wettability, it is essential to evaluate processing conditions such as cutting speed, tooth pitch, blade sharpness, cutting angle, and cutting direction, as well as wood-related factors like density and moisture content. In the case of thermally modified wood, although roughness generally decreases, it is not the primary influencing factor. It has been observed that as spindle speed increases, roughness values decrease, whereas an increase in feed rate leads to higher roughness values, indicating that these parameters have a greater influence on wood surface roughness (Pelit *et al*. 2021). Furthermore, the surface roughness values of thermally modified wood cut with circular saws with different tooth numbers were higher compared to untreated wood (Budakçı *et al*. 2011). Most likely, the differences in roughness after modification in different species are also related to the surface preparation. Therefore, properly controlling machining parameters not only would allow for better comparison between wood surfaces, but also would help to minimize issues caused by incorrect processing settings during machining.

Fourier-transform infrared spectroscopy (FT-IR) has been used to directly characterize the wood surface, allowing for the evaluation of its chemical composition and crystalline structure (Feng *et al*. 2022; Rolleri *et al*. 2024; Wentzel *et al*. 2024b). This technique provides a spectrum that serves as a unique chemical fingerprint of the analyzed wood samples. Additionally, FT-IR has been employed as a complementary tool to analyze the chemical changes associated with variations in the roughness of solid wood samples (Kubovský *et al*. 2018; Gurău *et al*. 2023).

Recent studies conducted in Chile, due to a necessity to diversify the forest resources, have evaluated wood from thinning of *Nothofagus alpina* plantations, which is composed of only juvenile wood, as the species approaches maturity, evaluating its properties from pith to bark, to see the potential uses of the whole piece of wood. These investigations have demonstrated that its physical and mechanical properties are comparable to those of *Pinus radiata*, the most widely used plantation species in the country (Wentzel *et al.* 2024a). Additionally, *N. alpina* has been subjected to thermal modification, expanding its potential applications (Wentzel *et al*. 2024b). To the best of our knowledge, there has been only one published study addressing the wettability of Chilean *Nothofagus* species, which was conducted using wood with high moisture content (Rosales *et al*. 2023). However, there are currently no studies that focus on the surface

roughness or wettability of natural or thermally modified wood of plantation-grown *N. alpina* under dry conditions.

The objective of this study was to assess the influence of the surface roughness and surface chemistry variation from pith to bark, both before and after thermal modification, on the wettability of *N. alpina* wood.

The results of this research aimed to optimize the use of this species—both in its natural and thermally modified states—by deepening the understanding of how thermal treatment affects its surface. To ensure consistency across samples and to minimize the influence of machining parameters on surface quality, all specimens were prepared under identical cutting and feed conditions, before and after thermal modification. Surface roughness was measured using a confocal microscope, while wettability was evaluated through contact angle measurements using a drop shape analyzer. Additionally, Fourier Transform Infrared Spectroscopy (FT-IR) was employed to characterize the chemical composition and crystallinity of the wood surface.

EXPERIMENTAL

Thermal Modification Process

Nothofagus alpina wood from the thinning process of a 21-year-old plantation, managed with intensive silviculture at the time of harvesting, was used. The site was selected from among three previously studied sites, as it exhibited the best properties before and after thermal modification (Wentzel *et al.* 2024a,b). For this study, three trees were selected to obtain the samples. Boards were produced and cut at three percentiles of the distance from pith to bark: 25%, 50%, and 75%. Each section was then divided into two pieces, ensuring they followed the same wood ring as closely as possible. Half of the samples remained unmodified, while the other half underwent thermal modification at 190 °C in a prototype chamber (Model Lab3.5e, Neumann, Concepción, Chile). This process was adapted from Herrera-Díaz *et al*. (2019), in which the heating rate was set at 1 °C min^{-1} until reaching 100 °C. Subsequently, the heating rate was adjusted to 0.7 °C min^{-1} until the target modification temperature was reached. The wood was maintained at this temperature for approximately 3 h, followed by a cooling and stabilization process inside the chamber for 9 h. In total, 18 samples were prepared and machined to obtain a consistent surface.

Wood Machining

Figure 1 shows the samples used to obtain a uniform surface were cut to a length of 27 cm and a height of 4 cm. A 4-kW single-spindle wood shaping machine with computer-controlled cutting and feed speed was used (Aguilera *et al*. 2016).

Fig. 1. Sample used in the wood shaping machine to obtain thin strips for measurements. The sample has a length of 27 cm and a height of 4 cm.

The machining process was performed on the radial face of the samples. The cutting head was a 6-knife hydraulic tool with a cutting circle diameter of 177 mm and a cutting geometry featuring a 25° rake angle, a 26° clearance angle, and a 39° sharpness angle. Corrugated high-speed steel (HSS) knives without joints were used for the test. The machining conditions were as follows: conventional cutting mode, cutting width of 40 mm, cutting depth of 2 mm, feed speed of 5.4 m/min, and cutting speed of 50 m/s.

After the machining process, a thin strip of 3 mm was cut from the sample. This process was repeated until three strips per sample were obtained (Fig. 1), for a total of 54 samples with the same surface preparation, in order to minimize differences between them when measuring roughness and wettability.

Contact Angle Measurement (Wettability)

To measure the wettability, a Krüss DSA25B drop shape analyzer (Hamburg, Germany) was used, which is equipped with a 25-gauge needle (with an outer diameter of 0.53 mm). Distilled water was used in a 1 mL syringe, with the estimate volume of each individual drop being between 0.008 to 0.014 milliliters (mL). The drop was deposited 10 times across the same wood ring on all test sample strips. Data acquisition starts when the drop meets the wood surface, taking three contact angle readings per recording second, with a maximum recording time of 15 seconds.

Roughness Measurement

Most studies on roughness measurement use stylus profilometers (Kasemsiri *et al*. 2012; Chu *et al*. 2016; Pelit *et al*. 2021), but in recent years, confocal microscopy has been used for non-contact measurement. There is a high linear correlation between the classic measuring method and confocal microscopy (Magoss *et al*. 2022; Iglesias *et al*. 2024). The same methodology used by Iglesias *et al*. (2025) was used in this study.

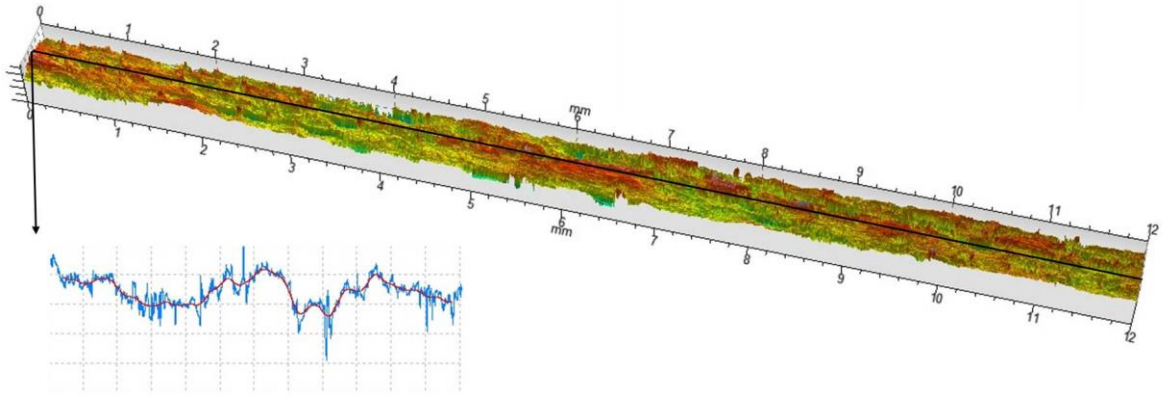

Fig. 2. Confocal microscope roughness profile from Confomap processed image

Surface scanning was performed at two points of the same early wood ring per thin strip, for a total of 108 scans. A Zeiss LSM 700 confocal microscope (Jena, Germany) was used to measure the surface roughness on each sample before and after thermal modification, with the ZEN Black version 8.1 software used to analyze the data. The imaging conditions for surface capture were as follows: Epiplan-Apochromat 10x/0.4 objective, image size x: 638.9 µm, y: 638.9 µm, z: variable between 66 to 132.00 µm, with the z value representing the number of slices acquired in the plane. With a rougher surface,

more slices were obtained after the scan was completed. The scan used a 405 nm laser at 4.0%. To process the scan results for each measured sample, the data were exported to Confomap 6.2 software, where the surface was leveled, data filtered, and roughness parameters extracted using the ISO 21920-2 (2021) standards. The pixel size of the images used for the analysis was 1.25 µm, and each image was 512 x 512 pixels. Surface roughness parameters R_a and R_z were extracted from 10 lines on each sample and position on the sample. An example of this measurement is shown in Fig. 2.

The parameter R_a is used to represent deviations in profile height from the mean line. Rougher surfaces are considered to be those with higher R_a. The parameter R_z is the characteristic parameter for the wood surface roughness, as it is defined as the average of the distance per section between the maximum peak height (z_{ph}) and pit depth (z_{vd}), as presented by the ISO 21920-2 (2021). The following equations for arithmetic mean height (R_a) (Eq.1) and maximum height (R_z) (Eq.2) were used to obtain the studied roughness parameters,

$$R_a = \frac{1}{n}\sum_{i=1}^{n}|z_i|, \quad (1)$$

$$R_z = \frac{1}{n_{sc}}\sum_{i=1}^{n_{sc}}\left(\max_{j\in N_{p,i}}\left(z_{ph,j}\right) + \max_{j\in N_{v,i}}\left(z_{vd,k}\right)\right), \quad (2)$$

where n is the number of points of the roughness profile and z_i is the 176 height of the i-th point of the profile, n_{sc} is the number of profile sections, N_p, = j = 1,2,…, $n_p|(i-1)l\text{sc} \le xj < i \cdot l_{sc}$, Nv, = k = 1,2,…, $n_v|(i-1)l\text{sc} \le xk < i \cdot l\text{sc}$, n_p is the number of the profile peaks, n_v is the number of the profile pits, x_j is the position of the j-th peak on the X-axis, and x_k is the position of the k-th peak on the Y-axis.

Chemical Analysis

An FT-IR chemical imaging system (PerkinElmer, Waltham, Massachusetts, United States) was used to obtain spectra from the same strips and both position that were used in the roughness measurements. The system includes a Frontier spectrophotometer with two detectors, DTGS NIR and MIR, covering a spectral range of 14700 to 350 cm^{-1} and a resolution of 4 cm^{-1}. The Spotlight 400 imager, equipped with an MCT MIR detector (7800 to 720 cm^{-1}, resolution > 2 cm^{-1}), was also used. This system generates chemical spectra directly on the wood surface through chemical images. For this study, diffuse reflectance was employed to capture spectra at a resolution of 4 cm^{-1} and 16 scans, with a pixel resolution of 50 µm. Spectra baselines were corrected using interactive baseline correction and then normalized based on the maximum ordinate value in the spectrum (3500 cm^{-1}). The obtained spectra were processed with interactive baseline correction, normalization, and deconvolution. The crystallinity was measured as the relative crystalline ratio, measured between spectra bands 1317 and 1336 cm^{-1}, which represent the ratio between crystalline cellulose and amorphous cellulose (Colom and Carrillo 2002; Colom *et al*. 2003).

Statistical Analysis

A Shapiro-Wilk test was performed to determine the data distribution of the contact angle and surface roughness measurements as parametric or non-parametric, to facilitate the use of either ANOVA or Kruskal-Wallis tests, to determine any significant differences between positions and the effect of thermal modification The significance level was tested at p = 0.05. For the FT-IR chemical composition analysis, the peak intensities of selected

bands were used to compare from pith to bark and before and after thermal modification. The data sets before and after the thermal modification process were compared using a Student's t-test for parametric data and a Mann-Whitney test for non-parametric data, with significance tested at $p = 0.05$. Pearson's correlation analysis was used to estimate the degree of linear correlation among wettability, and the chemical composition and surface roughness.

RESULTS AND DISCUSSION

The wettability of the samples, shown in Table 1 as the contact angle of the water drop against the surface of wood, presents a significant difference between the sample closer to the pith and the ones closer to the bark when unmodified. After the modification, that difference was not significant anymore. The contact angle increased in the modified sample, similar to what other authors showed in their wood species (Huang *et al*. 2012; Chu *et al*. 2016; Lopes *et al*. 2018), showing a deterioration of wetting in the thermally modified samples. The highest contact angle values were observed closer to the pith, with the differences being more pronounced prior to thermal modification. Statistically significant differences between radial positions were found only in the unmodified samples.

Figure 3 shows how the contact angle changed during 45 seconds before and after the modification. There is a fast-decreasing trend in the change of the contact angle until around 5 seconds, and then in follows a stable value in the modified sample in all positions. This trend looks similar to what Lopes *et al*. (2018) obtained with juvenile teak wood.

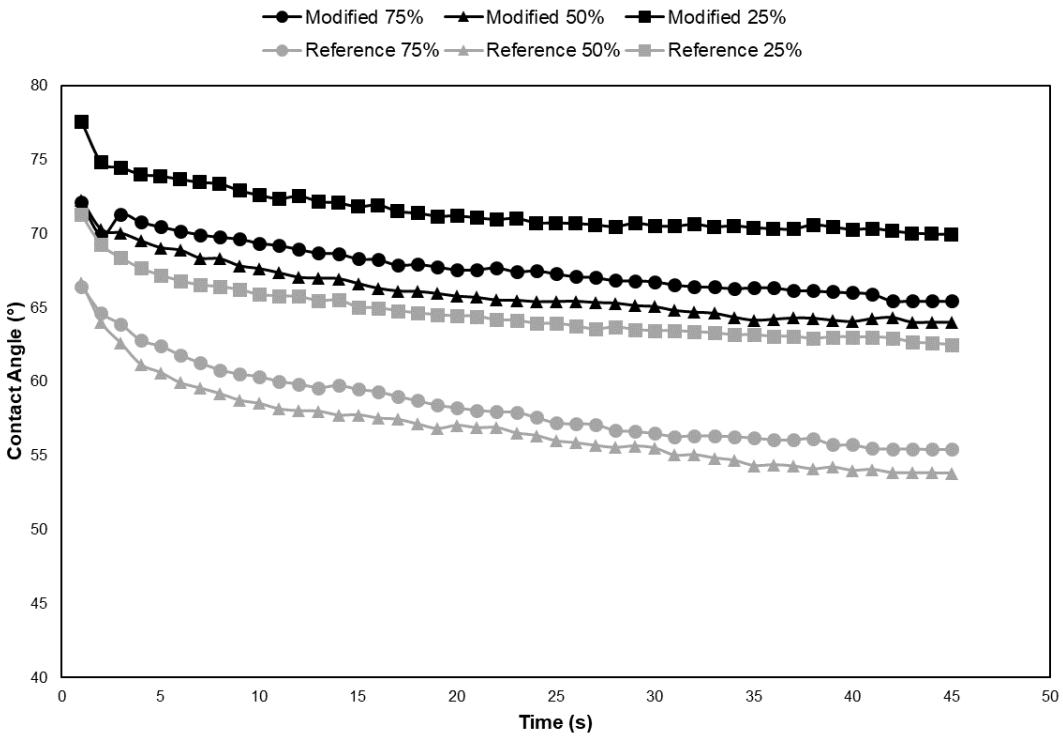

Fig. 3. Effect of the temperature on the contact angle during 45 seconds. Squares represent the 25% distance from pith, triangles the 50% distance from pith and circles the 75% distance. Grey represents wettability before modification, and black after modification.

Table 1. Properties of the Unmodified and Thermally Modified Samples

Modification Temperature	Distance from pith (%)	EMC (%)	Density (kg m^{-3})	R_a (µm)	R_z (µm)	Crystalline Ratio	Contact Angle (°)
Unmodified	**25**	10.241 ± 0.369 (a)	500 ± 12 (a)	3.309 ± 0.621 (a)	21.701 ± 3.309 (a)	0.480 ± 0.176 (a)	64.124 ± 1.978 (a)
	50	10.138 ± 0.310 (a)	528 ± 7 (a)	3.356 ± 0.503 (a)	22.472 ± 3.356 (a)	0.455 ± 0.172 (a)	57.063 ± 2.900 (b)
	75	10.209 ± 0.283 (a)	550 ± 10 (b)	3.358 ± 0.620 (a)	22.415 ± 3.358 (a)	0.511 ± 0.133 (a)	58.563 ± 2.730 (b)
190 °C	**25**	7.772 ± 0.311 (a)*	469 ± 11 (a)*	4.051 ± 0.749 (a)*	28.398 ± 4.051 (a)*	0.677 ± 0.193 (a)*	71.259 ± 1.789 (a)*
	50	7.635 ± 0.446 (a)*	505 ± 7 (a)	3.413 ± 0.684 (a)	23.539 ± 3.413 (a)	0.596 ± 0.194 (a)*	66.167 ± 2.041 (a)*
	75	7.656 ± 0.903 (a)*	509 ± 10 (b)*	4.736 ± 0.811 (b)*	32.479 ± 4.736 (b)*	0.700 ± 0.177 (a)*	69.590 ± 1.831 (a)*

Note: The average values followed by a different letter are statistically significant different from pith to bark at $p < 0.05$ utilizing an ANOVA test. The statistically significant differences between each position before and after being thermally modified are represented by (*). Data shown as average ± standard deviation. Equilibrium Moisture Content (EMC), density (kg m-3), arithmetic mean height (Ra), maximum height (Rz).

The decrease of the contact angle with the passage of time during the experiment is related to the liquid penetration and how it spreads on the wood surface, which is affected by the species, the location of the drop and if there was a treatment done to the surface (Shi and Gardner 2001). The contact angles in the modified wood were larger than the unmodified ones in all positions within the tree at all times of measurement. It also can be seen that in the unmodified samples, at 50 and 75% distance from the pith, the decrease of the contact angle continues until it reaches the end of the measurement, but at 25%, it looks similar to the modified samples.

As for the surface roughness, there was no significant difference between them before the modification, and there was a slight increase from pith to bark (Table 1). The modified samples show a difference between the 75% distance and the other positions, but no clear increase from pith to bark, with the sample at 50% presenting the lowest values, in both the arithmetic mean height (R_a) and maximum height (R_z), as shown in the averages presented in Table 1. The only position that did not show a significant difference before and after the modification process was at 50% from the pith. This could be explained by the change in density, as in that position it also was not statistically different before and after the modification process.

Table 2. Peak Heights of the Absorbance from Spectra Obtained from *N. alpina* that Showed Statistically Significant Differences from Pith to Bark and After the Thermal Modification Process

Modification Temperature	Distance from pith (%)	Band Wavelength (cm^{-1})				
		1742	1594	1375	1336	1040
Unmodified	25	1.039 ± 0.025 (a)	0.852 ± 0.024 (a)	0.189 ± 0.008 (a)	0.119 ± 0.010 (a)	0.043 ± 0.006 (a)
	50	1.037 ± 0.024 (a)	0.913 ± 0.026 (b)	0.198 ± 0.011 (a)	0.124 ± 0.009 (b)	0.057 ± 0.008 (b)
	75	1.048 ± 0.029 (a)	0.915 ± 0.283 (b)	0.209 ± 0.007 (a)	0.130 ± 0.008 (b)	0.055 ± 0.007 (b)
190 °C	25	0.946 ± 0.023 (a)*	0.828 ± 0.040 (a)*	0.182 ± 0.009 (a)*	0.115 ± 0.009 (a)	0.052 ± 0.009 (a)
	50	0.960 ± 0.023 (a)*	0.845 ± 0.037 (a)*	0.182 ± 0.010 (a)*	0.116 ± 0.007 (a)*	0.059 ± 0.005 (a)
	75	0.959 ± 0.032 (a)*	0.859 ± 0.030 (a)*	0.190 ± 0.007 (a)*	0.123 ± 0.008 (b)*	0.056 ± 0.008 (a)

Note: The average values followed by a different letter are statistically significant different from pith to bark at $p < 0.05$ utilizing an ANOVA test. The statistically significant differences between each position before and after being thermally modified are represented by (*). Data shown as average ± standard deviation. Band wavelength (cm^{-1}).

The peak intensities of FT-IR spectra of the structural elements that exhibited significant differences are shown in Table 2. The values from pith to bark, before modification, were: the 1594 cm^{-1} band, which represents the aromatic skeletal vibrations in lignin (Faix 1991; Casas *et al*. 2012), the 1336 cm^{-1} band, which represents the CH vibrations in cellulose (Colom and Carrillo 2005; Popescu *et al*. 2007), and the 1040 cm^{-1}

band, which represents the guaiacyl type lignin (Faix 1991; Lionetto *et al*. 2012). This was also shown in a previous report utilizing unmodified *N. alpina* wood from the same plantation (Wentzel *et al*. 2024a). This increase in lignin from pith to bark was also observed in plantation loblolly pine (Shupe *et al.* 1997), but there was also a decrease in other pine species (longleaf pine) (Via *et al.* 2007). Thus, the changes in lignin have to be considered in relation to the species used. These differences in the chemical composition from pith to bark could explain the decrease in the contact angle (increasing the wettability) from pith to bark in Table 1, as the less hydrophilic components of wood, such as lignin (Piao *et al*. 2010), can have an effect on the formation of water droplets (Young 1976). After the modification the only band showing significant differences from pith to bark was the 1336 cm^{-1} band, which confirms that after a thermal modification, there was an apparent homogenization of the chemical structure of the material, which was also shown in a previous report utilizing modified *N. alpina* wood (Wentzel *et al*. 2024b).

Table 2 shows the significant differences by ANOVA, before and after the modification at each position. The 1742 cm^{-1} band (Faix 1991; Kubovský *et al*. 2020), which represents the lignin, the polysaccharides, which are represented by the 1594 cm^{-1} band and cellulose bands at 1375 cm^{-1} (Schwanninger *et al*. 2004; Popescu *et al*. 2007) and at 1336 cm^{-1} (Colom and Carrillo 2005; Popescu *et al*. 2007), with exception of the closest to the pith (25%). This means that the chemical structure of the material was degraded after modification, particularly the structure of the lignin and hemicelluloses.

There was a hemicellulose band, 1158 cm^{-1} (Colom and Carrillo 2005), where the hemicelluloses showed values closer to zero after the modification, similar to what was previously shown in modified *N. alpina* (Wentzel *et al*. 2024b). This may mean that the changes in polysaccharides may have a stronger influence in surface wettability, as the disappearance of thus band can be probably related to the beginning of the degradation process of the cellulose (Kubovský *et al*. 2020).

The removals of hydroxyl groups present in the hemicelluloses, which are strongly related to the variations in wood wetting (Mitsui et al. 2008), shown in the changes of the polysaccharide band, is related to an increase in the contact angle, which was also shown in poplar wood by Chu *et al*. (2016). These changes are also related to the organic acid released by the degradation of the hemicellulose, reducing the hydroxyl groups (Kocaefe *et al*. 2010). This reduction of hydroxyl groups also changes the surface from hydrophilic to hydrophobic (Wang and Piao 2011).

The changes present in the lignin bands also affect the wettability, which was shown in the studies of Candan *et al*. (2012) and Bakar *et al*. (2013), where they infer that the plasticization of the lignin at higher temperatures causes changes in the surface of the material. The degradation of the cellulose, which was shown in the changes of the bands after modification, and possibly the migration of extractives to the surface of the material (Bakar *et al*. 2013). The relative crystalline ratio (crystallinity) showed no significant difference from pith to bark in either modified or unmodified samples (Table 1), but there was a statistically significant increase in the crystalline ratio after the modification process. This increase in crystallinity affects the surface roughness and wettability of the wood surface (Pétrissans *et al*. 2003). The increase of the crystalline cellulose, which is more hydrophobic than the amorphous cellulose, caused by the increase in cellulose crystallinity (Skaar 1988), in combination with the reduction of the hydroxyl groups, by the changes in hemicelluloses, lignin and cellulose, made the material that was relatively hydrophilic to a hydrophobic one.

A Pearson correlation analysis was conducted to explore the relationships between wettability (contact angle), surface roughness, and chemical composition (Table 3). Prior to thermal modification, the roughness parameter R_a exhibited a strong negative correlation with the contact angle at distances of 50% and 75% from the pith. After thermal modification, this negative correlation remained strong at 25% and 50% distances but shifted to a positive correlation at the 75% distance. These changes suggest that the effect of thermal modification altered the relationship between surface roughness and wettability, possibly due to the underlying chemical transformations.

Regarding the crystallinity index, it showed strong positive correlations with the contact angle at 50% and 75% distances from the pith. However, after thermal modification, it only maintained a strong positive correlation with the contact angle at 25% distance. This could mean that the chemical changes and roughness had a bigger influence on wettability than the changes of crystallinity. Nonetheless, the changes in crystallinity also have an effect on the surface roughness, thus is also an important influence on the changes after modification.

Table 3. Pearson Correlation Coefficients of the Relations between the Contact Angle and Maximum Height (R_z), Arithmetic Mean Height (R_a), Crystalline Ratio, and Cellulose/Lignin Ratio from Pith to bark at the 25%-50%-75% Distance Before and After the Thermal Modification

		Contact Angle		
	Distance from pith	**25%**	**50%**	**75%**
Before modification	**R_z**	-0.891	-0.740	-0.848
	R_a	-0.635	-0.968*	-0.910*
	Crystalline ratio	-0.614	0.926*	0.997*
After modification	**R_z**	-0.977*	-0.999*	0.987*
	R_a	-0.922*	-0.936*	0.989*
	Crystalline ratio	-0.962*	0.193	0.682

Note: *The values followed by (*) show a strong correlation between them and the contact angle.

An increase in surface roughness should reduce the contact angle, something that occurs before modification, but in the modified wood, the roughness increases and the contact angle also increased. It has to be taken into consideration that, although the same samples were measured for the chemical composition and roughness, there could be some discrepancies in the interpretation of the chemical composition of the surface and how it affects the roughness, as both are dependent on the way they were measured. However, the results presented similar tendencies of an increased roughness and contact angle shown by Budakçı *et al*. (2011), Candan *et al*. (2012), and Chu *et al*. (2016). On the other hand, other authors presented a decrease in surface roughness after modification (Korkut *et al*. 2012; Pinkowski *et al*. 2016; Shukla 2019). These differences could be related to the methodology of roughness measurement, the type of modification, and the species used. By having a strict control over the machining process, as implemented in this study, was essential for making accurate comparisons between pre- and post-modification conditions. This methodological consistency may also explain discrepancies in literature of the effects of roughness before and after the modification process.

The findings shown in this study suggest that the chemical-structural variation determines the behavior of the wettability from pith to bark, before and after the thermal modification process. From pith to bark, the increase of the relative crystallinity (related to a more brittle material) generates a greater roughness, which exposed the mostly

hydrophilic nature of wood (Piao *et al*. 2010). When the data before and after is compared, it indicates that the greater crystallinity of the modified wood (a material that tends to be more brittle), even while generating a greater surface roughness, they presented more degraded hydrophilic components and a structural order with a lower amorphous proportion of cellulose, thus a smaller contact angle (better wettability).

After the modification process, wettability from pith to bark tended to homogenize, thus it could be said that, in terms of surface quality, it would be possible to use wood from any position within the tree after modification, which could be advantageous for a better use of the material from thinned wood.

CONCLUSIONS

1. The chemical-structural variation was the mayor factor on the behavior of wettability before and after the modification process. The contact angle showed significant differences from pith to bark before the thermal modification, but they were all considered statistically similar after the process. After modification, although there were no significant differences from pith to bark, showing a homogenization of the wettability due to the thermal modification.
2. There were no significant differences from pith to bark in relative crystallinity before and after the modification process, but after modification, it increased. This can explain why the surface roughness showed only significant differences from pith to bark in one position (75% distance from pith) after the modification process, as it was the position with higher relative crystallinity, therefore, was more brittle than and had a lower amorphous proportion of cellulose than the other positions. Thus, a smaller contact angle was measured close to the bark.
3. The contact angle tended to be higher closer to the pith in the wood of thinning from young hardwood (*Nothofagus alpina*) plantations. This suggests that using wood from the outer regions of the tree may be more advantageous—both in its unmodified and thermally modified states—in applications that benefit from higher wettability by water.

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