Chemical Structural Characteristics and Some Mechanical and Physical Properties of Thermally Modified *Nothofagus alpina* Thinning Wood from Three Different Silvicultural Conditions

Maximilian Wentzel,[a] Víctor Sepúlveda-Villarroel,[b] José Luis Barros,[c] Rubén A. Ananías,[b] and Aldo Rolleri [a,*]

Thermal modification processes are environmentally friendly methods used to improve certain properties of wood. Currently, wood from thinning of young plantations of *Nothofagus alpina* (raulí) in Chile is being evaluated to obtain value before the plantation has reached maturity. The objective of this paper was to assess selected properties of thermally modified wood of young (14- to 25-years-old) *N. alpina* wood that comes from thinning of two sites with intensive silviculture and one similar to a secondary growth forest. To achieve this, non-destructive tests were carried out to measure some chemical-crystalline characteristics, as well as physical and mechanical properties; the differences between the 25%, 50%, and 75% distance from pith to the bark in each site was studied. The modification temperatures used were 170, 190, and 210 °C. The results show that thinning wood from *N. alpina* can be thermally modified with favorable results, thus presenting an option to obtain value while the plantation reaches maturity, particularly the thinning wood from the intensive forestry regimes, which presented most homogeneous results, especially at the modification temperature of 190 °C.

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*Contact information: a: Universidad Austral de Chile, Facultad de Ciencias Forestales y Recursos Naturales, Instituto de Bosques y Sociedad, Valdivia, 5090000, Chile; b: Universidad del Bío-Bío, Facultad de Ingeniería, Departamento de Ingeniería en Maderas, Concepción, 4051381, Chile; c: Universidad Austral de Chile, Instituto de Acústica, Facultad de Ciencias de la Ingeniería, Campus Miraflores, Valdivia, 5090000, Chile; *Corresponding author: arolleri@uach.cl*

INTRODUCTION

Most of the solid wood used in Chile comes from plantations of introduced species (*Pinus radiata* and *Eucalyptus* spp.), while the native forest sawing industry consists mostly of old regrown forest and currently corresponds to only 2.2% of the total sawn wood in Chile (Instituto Forestal 2022). One of the most used species is *Nothofagus alpina*, which according to Donoso and Soto (2010) is characterized by having a greater productive potential than other *Nothofagus* species, and it has been used for experimental plantations with intensive forestry (felling, pruning, thinning, fertilization and weed control) (Reyes *et al*. 2007) to increase its commercial value. Wentzel *et al*. (2024) showed that the properties of wood obtained from thinning of plantations of *N. alpina* were comparable to other species used in Chile, such as *P. radiata*, and that the material could be used to obtain value

while the plantation reaches maturity. To further promote the use and management of this species, and potentially other native species, an early insertion of a sustainable technology would give alternatives to use the obtained material.

Thermal modification meets these characteristics, as it is a non-biocidal and environmentally friendly process, which allows the reuse of the material and facilitates recycling and easy disposal of it at the end of its useful life cycle. Fast-growing wood tends to contain higher proportion of juvenile wood, which has an effect on the wood quality, due to the growth rate, affecting properties such as density, dimensional stability and resistance to fungi and insects (Shmulsky and Jones 2019). Thermal modification can improve these properties (Esteves and Pereira 2009; Militz and Altgen 2014; Mai and Militz 2023). It has been used in plantation hardwood species, such as teakwood (*Tectona grandis*) (Lengowski *et al*. 2021; Brito *et al*. 2023), *Eucalyptus grandis* (Brito *et al*. 2023) *Eucalyptus nitens* (Wentzel *et al*. 2019a), among others.

These processes use treatment temperatures between 160 and 240 °C. The main differences of the thermal modification processes are the elements that limit the presence of oxygen during the modification, either with steam or nitrogen, and whether they are carried out at atmospheric pressure, under vacuum or at high pressure (Esteves and Pereira 2009; Militz and Altgen 2014). The mechanical properties of the material tend to decrease (Esteves and Pereira 2009; Militz and Altgen 2014; Mai and Militz 2023), but there are reports were the modulus of elasticity (MOE) presented higher values than the unmodified wood after the thermal modification process (Borrega and Kärenlampi 2008; Lekounougou *et al*. 2011). These changes are related to the chemical variations in the composition of cellulose, hemicelluloses, and lignin that occur during the thermal modification processes (Esteves and Pereira 2009; Hill *et al.* 2021; Mai and Militz 2023). These changes affect the crystallinity of the material, causing an apparent increase of it after the treatment (Wikberg and Maunu 2004; Boonstra and Tjeerdsma 2006). Crystalline cellulose, with its highly ordered and rigid structure, does not degrade as much in comparison to the amorphous cellulose during the thermal modification process. There is a slight increase of crystallinity at lower modification temperatures, then it falls, and tends to increase again as the modification temperature rises (Hill *et al*. 2021).

A quick non-destructive alternative method to measure the chemical and structural properties of the wood is Fourier transform infrared spectroscopy (FTIR). The absorption obtained by the FTIR spectra can be assigned to a combination of the functional groups (C, H, and O) that are present in celluloses, hemicelluloses, extractives, lignin and water that compose lignocellulosic materials (Evans 1991; Pandey 1999). Several studies have employed FTIR spectroscopy to evaluate changes in the chemical-crystalline structure of thermally modified wood (Wentzel *et al*. 2019b; Feng *et al*. 2022; Rolleri *et al*. 2024).

There are also non-destructive mechanical tests that have been used to measure the changes in those properties in thermally modified wood. The vibroacoustic test has been used to evaluate properties such as modulus of elasticity in modified wood in a wide range of temperatures (Pfriem 2015; Ahmed and Adamopoulos 2018; Rolleri *et al*. 2024). The advantages of non-destructive tests are that they can be done on the same samples before and after the modification processes, and that the same samples can be used for the chemical and physical tests.

This study is a continuation of the work done by Wentzel *et al*. (2024) in unmodified *N. alpina* wood that comes from the thinning process of three selected sites with different ages, silvicultural interventions, and positions within the tree. There has been no information on thermal modification of this species; therefore, the evaluation of the

properties could show the potential to use wood from *N. alpina* plantations, and particularly show alternative uses of wood from thinning, to give more options to incentive the plantation of this species and to generate additional value during the time the plantation reaches maturity, as the thermally modified wood could be used, as an example, for decking, flooring, doors or windows. Thus, the objective of this study was to evaluate the thermal modification of *N. alpina* wood from the thinning process, from two sites with intensive afforestation and one similar to a secondary growth forest, and three positions from pith to bark within the tree, through non-destructive measurements of the chemical structural characteristics, as well as the physical and mechanical properties.

EXPERIMENTAL

Nothofagus alpina Wood from Three Selected Sites

Nothofagus alpina wood that originated of the thinning process of three selected sites were used in this study, all located in the Los Ríos region in southern Chile. There were two sites with intense silviculture: Catanlí (39°38'S and 72°21'E), and Las Vertientes, (39°31' S and 72°44' W), aged 21 and 14 years respectively. The other site was similar to a secondary regrowth forest: Pelchuquín (39°36' S and 73°4' E), aged 25 years at the time of harvesting. Due to the limited availability of plantations of age that could be thinned and that coincided with the time frame of the study, the sites had to have different ages. The trees that were going to be thinned had to be at least 22 cm of breast height diameter, so that they could be sawn without issues with horizontal band saw to obtain boards of 320 cm.

Specimens for the characterization of the wood properties were taken from pith to bark and were proportionally separated in boards at three percentiles, 25%, 50% and 75% of the distance from pith to bark, to be able to compare within trees from the same sites. Overall, 72 samples per site, 216 in total, were obtained for their respective measurements and thermal modifications. A further explanation of the selection of the trees and sampling was presented in a previous study (Wentzel *et al*. 2024).

Thermal Modification Process

The thermal modification process was done in a prototype chamber (Model Lab3.5e, Neumann, Concepción, Chile) with a capacity of 3.5 m^3. The modification temperatures were 170, 190, and 210 °C. For each temperature, 72 specimens of *N. alpina* were selected per site, which were separated in 24 specimens per distance from the pith (25%, 50%, 75%). To fill the chamber, the specimens were stacked inside the middle of a pile of 50 mm wood pieces of other species, following the procedure presented by Herrera-Builes *et al*. (2021).

The prototype chamber operated under an atmosphere of steam, with a constant current flow without pressure. The thermal modification process was adapted from Herrera-Díaz *et al*. (2019), where the temperature increase rate was of 1 °C min^{-1} until it reached 100 °C. Afterwards, a temperature increase rate of 0.7 °C min^{-1} was applied to reach the modification temperatures. The treatment temperature was kept for approximately 3 h, followed by a cooling down and stabilizing process during 9 h inside the modification chamber.

Chemical Analysis

The same samples as those used by Wentzel *et al*. (2024) were used in this study for the measurement of the chemical structural characteristics of the modified samples. The data previously obtained from the unmodified samples were used in this study for comparison purposes.

A FTIR chemical imaging system (PerkinElmer, Waltham, MA, USA) consisting of a spectrophotometer Frontier that has two detectors, type DTGS NIR and MIR, both covering a range between (14700 cm^{-1} and 350 cm^{-1}) with a spectral resolution of 4 cm^{-1} was used. The imager Spotlight 400, with a detector type MCT MIR (7800 cm^{-1} to 720 cm^{-1}) that has a resolution > 2 cm^{-1}, was used. The system can generate chemical spectra directly on the surface of the wood through chemical images. For this study, diffuse reflectance mode was used to obtain the spectra with a resolution of 4 cm^{-1} and 16 scans, with a pixel resolution of 50 µm. The spectra were baseline corrected using an interactive baseline correction and then normalized considering maximum ordinate value in the spectrum.

The size of the specimens was 20 mm × 40 mm × 340 mm (radial × tangential × longitudinal). The pieces were conditioned at 20 ± 3 °C and 65 ± 5% relative humidity (RH) for a month prior to the FTIR analysis. The radial surface was chosen for each analysis. The obtained spectra were processed with an interactive baseline correction, normalization, and deconvolution. The chemical structural characteristics were interpreted based on the spectra. For evaluation of the relative crystallinity index, the ratio between spectra bands 1317 cm^{-1} and 1336 cm^{-1}, which represent the ratio between crystalline cellulose and amorphous cellulose (Colom and Carrillo 2002; Colom *et al*. 2003) was used. For each specimen, five repetitions were made.

Mechanical and Physical Properties

The modulus of elasticity (MOE) of the unmodified and thermally modified material was measured with a vibroacoustic method that utilizes a free-free beam measurement setup. A piezoelectric transducer Lightweight Accelerometer Type 4518-003 (Brüel & Kjaer, Nærum, Denmark) was placed to capture the vibrations at one end of the wood sample, which was then excited at the other end using an Impact Hammer Type 8206 (Bruel & Kjaer, Nærum, Denmark). The piezoelectric transducer used in this method is extra light (1.45 g) and has a wide frequency range (1 Hz to 20 kHz) so that it does not affect the response of the probe.

The wood sample was supported at the location of the vibration nodes of the first mode of flexural or bending vibration, located, in this case, at an approximate distance of 76 mm from each end of the specimen. The signal obtained by the piezoelectric transducer, connected to an Isotron signal conditioner model 4416B (Endevco, Depew, NY, United States), was captured by use of an analog-to-digital conversion interface USB Audio-Interface (Focusrite, High Wycombe, United Kingdom) to input it to a computer utilizing the software ARTA v 1.9.6, using a sampling rate of 16 kHz. The number of specimens used was 216, before and after the thermal modification, with five repetitions to record the impulse responses.

Using the Fourier transform of the measured impulse response, the frequency response function (FRF) was obtained, from which the frequency of the first mode was determined. Modulus of elasticity (MOE) in MPa, was calculated from the frequency of the first mode by Eq. 1,

$$MOE = \frac{{f_1}^2 l^4 \rho}{\left(\frac{9\pi}{8\sqrt{12}}h\right)^2} \quad (1)$$

where f_1 is the frequency of the first mode (Hz), l is the length of the beam (m), ρ is the density of the material (kg m^{-3}), and h is the thickness of the beam (m).

The density was measured by dividing the weight by the volume after conditioning at 20 ± 3 °C and 65 ± 5% RH, from each thermal modification temperature and each tree at their respective plantation site. The specimen size was 20 mm × 20 mm × 40 mm (radial × tangential × longitudinal). The same specimens were used to measure the equilibrium moisture content (EMC), where the weight was measured after conditioning at 20 ± 3 °C and 65% ± 5% RH and when oven-dry at 103 °C or until constant weight. The differences in weight divided by the oven-dry weight were used to calculate EMC.

Statistical Analysis

The statistical analysis consisted of a Shapiro-Wilks test to determine whether a data set is parametric or non-parametric, to either use a variance analysis (ANOVA), or a Kruskal-Wallis test to analyze possible differences of the measured wood properties within the trees of the same site. To compare the data sets before and after the thermal modification, a student's T test was used when the data were parametric, while a Mann-Whitney test was used when the data were non-parametric. The significance level was tested at p = 0.05. Pearson's correlation analysis was used to estimate the degree of linear correlation among density, and the chemical and mechanical properties.

RESULTS AND DISCUSSION

Physical and Mechanical Properties

The average values of the measured properties of each site from pith to bark are presented in Table 1. In all sites, the EMC and density decreased in comparison to the unmodified reference. As the modification temperature increased, both EMC and density also decreased in all sites. The MOE decreased at 170 °C and 210 °C in all positions, but at 190 °C, in all sites, it was increased at certain positions within the tree. In Las Vertientes, although it showed significant differences from pith to bark in the unmodified wood, there was not a significant difference of EMC from pith to bark in all the modification temperatures. Catanlí showed significant differences between the 25% and 50 to 75% distances from pith of the EMC in the unmodified wood samples, but that changed in all the thermal modifications, as they showed no significant differences from pith to bark. In Pelchuquín, the only property that showed significant differences was MOE at 210 °C.

In general, the samples at 75% distance from the pith modified at 190 °C showed better results in all studied sites, with higher densities and vibrational MOE, and lower EMC values. At 210 °C, though it presented the highest decrease in EMC, the MOE values were the lowest for all positions in all sites when compared to the unmodified reference. Thus, this modification temperature, with the technology that was utilized, may not be recommended for this species.

Due to a lack of research in modified *Nothofagus* species of younger ages, it was difficult to compare results with other modifications, but wood from fast-growing hardwood species plantations of similar ages could be used as a reference. Thermal modification at 160 °C of 15-to 18-year plantation teak showed a higher decrease in density

(19%) after the modification (Brito *et al*. 2023) than in the modification at 170 °C in all positions in Las Vertientes (4%, 7%, and 5% from pith to bark respectively), and Catanlí (3.5%, 3.9%, and 3.6% from pith to bark, respectively). Other plantation species, 17-year-old *Eucalyptus grandis* and *Eucalyptus regnans*, showed almost no difference in density after being modified at 180 °C and 200 °C (de Cademartori *et al*. 2015), which was in line with what *N. alpina* showed in this study.

Table 1. Average Equilibrium Moisture Content (EMC), Density and Vibrational Modulus of Elasticity (MOE) from Pith to Bark in Their Respective Site, Taken from the Same Samples Before and After Modification

Modification temperature	Distance from pith (%)	EMC (%)	Density (kg m^{-3})	Vibrational MOE (MPa)
Las Vertientes				
Unmodified	25	12.62 ± 0.12 (a)	550 ± 54 (a)	6655 ± 1249 (a)
	50	12.69 ± 0.11 (a)	576 ± 65 (a)	7973 ± 1712 (b)
	75	12.66 ± 0.23 (a)	587 ± 48 (a)	8920 ± 2002 (c)
170 °C	25	9.30 ± 1.54 (a)	526 ± 39 (a)	6130 ± 2025 (a)
	50	8.02 ± 1.04 (a)	535 ± 62 (a)	6971 ± 1766 (a)
	75	8.22 ± 1.02 (a)	555 ± 54 (a)	6973 ± 1785 (a)
190 °C	25	7.69 ± 0.27 (a)	524 ± 42 (a)	7875 ± 851 (a)
	50	7.59 ± 0.28 (a)	530 ± 45 (a)	7773 ± 1727 (a)
	75	7.50 ± 0.38 (a)	555 ± 54 (a)	10238 ± 1520 (b)
210 °C	25	7.24 ± 0.63 (a)	453 ± 35 (a)	3501 ± 158 (a)
	50	6.55 ± 1.88 (a)	506 ± 51 (a)	5698 ± 528 (b)
	75	6.93 ± 0.66 (a)	511 ± 45 (a)	6563 ± 160 (b)
Catanlí				
Unmodified	25	11.12 ± 0.40 (a)	508 ± 45 (a)	8456 ± 1167 (a)
	50	10.80 ± 0.14 (b)	515 ± 47 (a)	9923 ± 1705 (b)
	75	10.66 ± 0.12 (b)	524 ± 39 (a)	10751 ± 1113 (c)
170 °C	25	7.69 ± 0.79 (a)	490 ± 38 (a)	7619 ± 974 (a)
	50	7.98 ± 0.82 (a)	495 ± 47 (a)	8702 ± 1187 (a)
	75	7.87 ± 0.46 (a)	505 ± 42 (a)	9133 ± 1477 (a)
190 °C	25	7.67 ± 0.07 (a)	481 ± 38 (a)	8082 ± 932 (a)
	50	7.62 ± 0.19 (a)	495 ± 35 (a)	9961 ± 2406 (b)
	75	7.60 ± 0.35 (a)	502 ± 56 (a)	11123 ± 1469 (c)
210 °C	25	7.58 ± 0.41 (a)	461 ± 48 (a)	7309 ± 360 (a)
	50	7.67 ± 0.48 (a)	458 ± 43 (a)	7421 ± 453 (a)
	75	7.53 ± 0.22 (a)	445 ± 35 (a)	7783 ± 237 (a)

Pelchuquín				
Unmodified	25	12.41 ± 0.10 (a)	537 ± 41 (a)	10058 ± 2112 (a)
	50	12.30 ± 0.46 (a)	560 ± 21 (a)	10935 ± 1363 (a)
	75	12.03 ± 0.34 (a)	561 ± 33 (a)	11548 ± 2002 (a)
170 °C	25	8.02 ± 0.69 (a)	511 ± 51 (a)	9034 ± 2282 (a)
	50	8.07 ± 0.71 (a)	544 ± 47 (a)	9625 ± 1220 (a)
	75	7.71 ± 0.79 (a)	538 ± 42 (a)	9976 ± 1592 (a)
190 °C	25	7.58 ± 0.26 (a)	505 ± 44 (a)	9548 ± 2099 (a)
	50	7.58 ± 0.23 (a)	546 ± 28 (a)	11465 ± 1149 (a)
	75	7.52 ± 0.33 (a)	526 ± 52 (a)	11622 ± 1848 (a)
210 °C	25	7.43 ± 0.37 (a)	492 ± 35 (a)	7876 ± 103 (a)
	50	7.30 ± 0.39 (a)	487 ± 15 (a)	8186 ± 1036 (a)
	75	7.10 ± 0.72 (a)	497 ± 35 (a)	6408 ± 329 (b)

*The average values followed by a different letter are statistically significant different from pith to bark at $p < 0.05$ utilizing an ANOVA test. Data shown as average ± standard deviation.

The EMC increased less in younger teak (13%) (Brito *et al*. 2023) than in *N. alpina* from Las Vertientes and Catanlí (average 28% and 35% from pith to bark respectively). In 25-year-old plantation teak, the EMC decreased 42% at 160 °C (Lengowski *et al*. 2021), close to what Pelchuquín presented at 210 °C (loss of 40% EMC in all positions). The 17-year-old plantation eucalypts showed higher decrease in EMC, averaging 50% and 66% at 180 °C and 200 °C modification temperatures respectively (de Cademartori *et al*. 2015) for similarly aged *N. alpina* wood.

The increase of MOE in *N. alpina* wood at 190 °C was also seen in other species utilizing non-destructive measurements. European beech showed this increase in vibrational MOE at a modification temperature of 160 °C (Zauer *et al.* 2016), and in *Pinus radiata* it increased at 170 °C and tended to decrease at 220 °C (Rolleri *et al.* 2024). Other fast-growing hardwood species also showed the tendency to increase MOE in certain modification temperatures, although the MOE measurements were done with destructive tests. Wood from a 19-year-old *Eucalyptus nitens* plantation showed an increase in MOE at 160, 180, and 200 °C in an open system thermal modification (Wentzel *et al.* 2019a), teakwood from a 25-year-old plantation showed an increase at 160 °C (Lengowski *et al.* 2021) and wood from *E. saligna* showed this increase in modifications ranging from 180 °C to 240 °C (de Cademartori *et al.* 2015).

This increase in MOE in certain temperatures, following by a decrease at higher modification temperatures, could be explained by the increase in cellulose crystallinity and the reduction of the equilibrium moisture in the modified wood (Esteves and Pereira 2009). Another theory of this effect in MOE is the increase in cross-linking in the lignin network, as an increased cross-linking is expected to improve the rigid structure around the cellulose microfibrils (Lekounougou *et al.* 2011).

Chemical Structural Characteristics

Figure 1 shows an example of the intensities of FTIR spectra at 25% distance from the pith in Catanlí, to see the differences between the unmodified and modified spectra. However, for the purposes of this study, the data values obtained from them were used to compare within the sites and before and after the modification process.

The unmodified samples were studied in a previous report (Wentzel *et al*. 2024), with significant differences from pith to bark in the bands 1336 and 1158 cm^{-1}, which

represent the cellulose and hemicelluloses (Colom and Carrillo 2005; Pandey 1999) and the band 1040 cm^{-1}, which represents the guaiacyl type lignin (Faix 1991; Lionetto *et al.* 2012). Additionally, the band at 1635 cm^{-1}, representing the adsorbed water (Marchessault 1962), also showed significant differences.

At the modification temperature of 170 °C, all sites showed significant differences from pith to bark at the 2100 cm^{-1} band, which represents the vibrations from the scission and rocking of water (Olsson and Salmén 2004). Catanlí and Pelchuquín presented significant differences in the 1158 cm^{-1} band. Additionally, Catanlí also showed significant differences at the 1040 cm^{-1} band. At 190 °C, Las Vertientes only showed significant differences at the 2100 cm^{-1} band, while Catanlí and Pelchuquín also only had one band with significant differences from pith to bark, the 1040 cm^{-1} band.

At 210 °C, Catanlí Las Vertientes showed no significant differences from pith to bark in any band. Only Pelchuquín presented a significant difference, which was at the band at 1336 cm^{-1}, which represents the amorphous cellulose (Pandey 1999; Lionetto *et al.* 2012). Additionally, the band at 1158 cm^{-1}, completely disappeared at 190 °C and 210 °C modification temperature in all the sites.

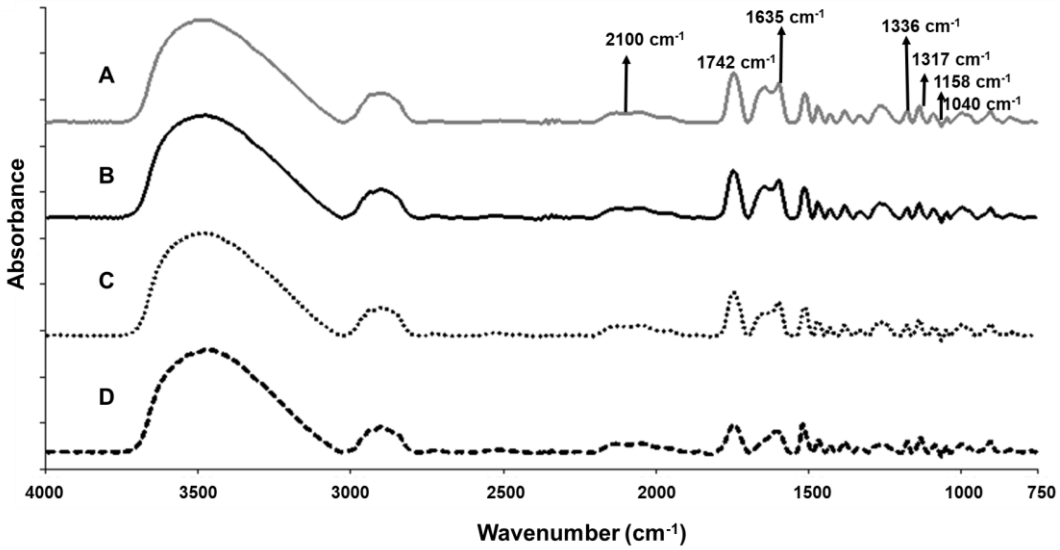

Fig. 1. Example of infrared FTIR spectra at 25% distance from the pith of *N. alpina* from Catanlí indicating selected bands that showed significant differences. Grey line represents the unmodified sample (A), black line represents the modification at 170 °C (B), black dotted line represents the modification at 190 °C (C) and the dashed black line represents the modification at 210 °C (D).

In all sites, there was a homogenizing effect of the chemical composition from pith to bark as the modification temperature increased, because of the decrease of significant differences between the bands compared to the unmodified wood samples.

When comparing the chemical composition before and after the thermal modification, there were significant differences in all temperatures with the lignin bands at 1040 cm^{-1} and 1742 cm^{-1}. The differences around the band 1742 cm^{-1} can be related to a cleavage of ether bonds and the production of C=O bonds (Esteves *et al.* 2013). These changes can be related to either lignin or hemicelluloses, as they represent the ketones and free aldehydes present in those structures (Michell and Higgins 2002). These bands also decreased in absorbance as the temperature increased in other hardwood species (Kubovský *et al.* 2020; Wentzel *et al.* 2019b).

The disappearance of the band at 1158 cm^{-1}, which represents the polysaccharides, was probably related to the beginning of the cellulose degradation process (Kubovský *et al.* 2020). This could be explained by the significant difference before and after the modification process of the bands at 1317 cm^{-1} and 1336 cm^{-1}, which represent the cellulose (Colom and Carrillo 2002; Colom *et al*. 2003). The bands related to water, vibrations from the scission and rocking of water (2100 cm^{-1}) and the adsorbed water (1635 cm^{-1}), also showed a significant difference before and after the modification.

The changes in hemicelluloses and lignin network modification (cross-linking) indirectly influence the EMC (Chaouch *et al.* 2013; Fu *et al.* 2019). The changes in EMC can also be correlated to the changes in oxygen/carbon ratio (O/H) (Chaouch *et al.* 2013; Hill *et al.* 2021), which can be seen in the differences in lignin, hemicelluloses, and cellulose after the thermal modification of *N. alpina*, and their decrease as the modification temperature increases, similar to what was shown in EMC for each site (Table 1).

The decrease in the bands that represent water, especially the 1635 cm^{-1} band of adsorbed water, can affect the EMC of the modified wood. A study indicated that a thermal modification affects the water adsorption of the wood (Fu *et al.* 2019), which is a property that directly affects the EMC of the material, thus relating the changes of this band with the decrease of EMC as the modification temperature increases.

The chemical composition changes are also related to the changes in MOE, as the degradation and depolymerization of the hemicelluloses and the cross-links caused by the changes in the composition of lignin influence this property (Boonstra *et al.* 2007; Kocaefe *et al.* 2008; Hill *et al.* 2021).

It is known that there is a relative increase of cellulose crystallinity when the wood is thermally modified, mostly due to the degradation of the amorphous part of the cellulose (Yildiz and Gümüşkaya 2007; Sikora *et al*. 2022). The average relative crystallinity before and after the modification process, utilizing the same samples before and after the modification thanks to the use of non-destructive methods, are shown in Table 2.

In all the sites, there was no significant difference from pith to bark in the relative crystalline ratio, for the unmodified and modified samples. In Las Vertientes at 170 °C, the crystallinity only increased at the 75% distance from the pith while at the 210 °C modification it only decreased at that distance from the pith, but the unmodified values at that position were high, thus the decrease in value could be related to chemical changes at that temperature. At 190 °C, there was an increase in the crystallinity in all positions. Catanlí showed an increase in crystallinity in all temperatures and positions. The crystallinity tended to increase from pith to bark; only the modification at 210 °C did not show this tendency. This could be explained due to the low crystalline ratio of the unmodified samples. Pelchuquín showed a decrease of crystallinity in all modifications and positions, with the only exception being the 75% distance from the pith at 190 °C. This was the only site that clearly decreased in crystallinity, meaning that the modified wood turned more amorphous as it was thermally modified.

The modified wood that came from plantation *N. alpina* wood showed similar tendencies to other modified hardwood species. Lopes *et al.* (2018), for thermally modified teak juvenile wood, presented an increase in relative cellulose crystallinity in heartwood and sapwood at modifications of 180 and 200 °C. Sikora *et al.* (2022), for isolated cellulose from thermally modified *Robinia pseudoacacia*, showed a relative increase of crystallinity from 160 to 210 °C. At higher temperatures (210 to 230 °C modified with nitrogen), Tuong and Li (2010) reported that the relative crystallinity index values of a thermally modified acacia hybrid slightly increased in all temperatures, with the highest crystallinity values

tending to be present at 215 °C, and not at the highest modification temperature. No other report presented similar tendencies to what was shown in Pelchuquín, the site closely similar to a regrowth forest. This could mean that there is an effect of the silvicultural management of the other sites on the properties, or it could be an effect of the age of Pelchuquín.

The changes shown in the chemical structure (represented by the relative crystalline ratio) in the modified wood of *N. alpina* can be related to the variations in the measured vibrational MOE, as previous reports (Kubojima *et al.* 1998; Rolleri *et al.* 2024) show that the variation of crystallinity was closely related to the changes that occur in MOE.

There was a tendency for an increase in crystallinity from 170 to 210 °C in all studied sites, with some cases of higher crystallinity at 190 °C at the 50% distance from pith to bark. There can be a light increase in crystallinity at lower modification temperatures, followed by a decrease of it as the temperature increases, and in some cases, it increases again as the temperature keeps rising (Hill *et al.* 2021).

Table 2. Average Relative Crystalline Ratio from Pith to Bark in Their Respective Site, Taken from the Same Samples Before and After Modification

Site	Distance from pith (25%)	Unmodified	170 °C	Unmodified	190 °C	Unmodified	210 °C
Las Vertientes	25	0.589 ± 0.334 (a)	0.564 ± 0.187 (a)	0.507 ± 0.341 (a)	0.664 ± 0.439 (a)	0.653± 0.497 (a)	0.701 ± 0.362 (a)
	50	0.737 ± 0.380 (a)	0.549 ± 0.242 (a)	0.601 ± 0.223 (a)	0.776 ± 0.293 (a)	0.606 ± 0.138 (a)	1.065 ± 0.701 (a)
	75	0.764 ± 0390 (a)	0.867 ± 0.560 (a)	0.811 ± 0.356 (a)	0.818 ± 0.316 (a)	0.839 ± 0.707 (a)	0.751 ± 0.395 (a)
Catanlí	25	0.449 ± 0.224 (a)	0.600 ± 0.325 (a)	0.434 ± 0.145 (a)	0.736 ± 0.303 (a)	0.522 ± 0.174 (a)	0.996 ± 0.410 (a)
	50	0.523 ± 0.179 (a)	0.726 ± 0.452 (a)	0.540 ± 0.307 (a)	0.808 ± 0.300 (a)	0.565 ± 0.216 (a)	0.753 ± 0.491 (a)
	75	0.571 ± 0.226 (a)	0.976 ± 0.771 (a)	0.505 ± 0.327 (a)	0.919 ± 0.464 (a)	0.741 ± 0.438 (a)	1.011 ± 0.552 (a)
Pelchuquín	25	0.601 ± 0.297 (a)	0.563 ± 0.278 (a)	1.011 ± 0.544 (a)	0.769 ± 0.513 (a)	0.837 ± 0.202 (a)	0.763 ± 0.300 (a)
	50	0.902 ± 0.319 (a)	0.604 ± 0.374 (a)	0.803 ± 0.172 (a)	0.801 ± 0.340 (a)	0.879 ± 0.383 (a)	0.813 ± 0.298 (a)
	75	0.731 ± 0.286 (a)	0.713 ± 0.329 (a)	0.750 ± 0.342 (a)	0.876 ± 0.407 (a)	0.833 ± 0.449 (a)	0.809 ± 0.228 (a)

*The average values followed by a different letter are statistically significant different from pith to bark at $p < 0.05$ utilizing an ANOVA test. Data shown as average ± standard deviation.

Table 3. Pearson Correlation Coefficients of the Relations Between Density and Crystallinity with Equilibrium Moisture Content (EMC) and Vibrational Modulus of Elasticity (MOE) from Pith to Bark in Their Respective Site at Each Thermal Modification Temperature

	Unmodified		**170 °C**		**190 °C**		**210 °C**	
Las Vertientes	Density	Crystallinity	Density	Crystallinity	Density	Crystallinity	Density	Crystallinity
EMC	0.742	0.387	-0.616	-0.333	-0.939*	-0.973*	-0.791	-0.943*
MOE	0.991*	0.954*	0.723	0.465	0.973*	0.685	0.980*	0.365
	Unmodified		**170 °C**		**190 °C**		**210 °C**	
Catanlí	Density	Crystallinity	Density	Crystallinity	Density	Crystallinity	Density	Crystallinity
EMC	-0.957*	-0.991*	0.48	0.453	-0.996*	-0.923*	-0.791	-0.943*
MOE	0.973*	0.997*	0.920*	0.908*	0.999*	0.967*	0.980*	0.365
	Unmodified		**170 °C**		**190 °C**		**210 °C**	
Pelchuquín	Density	Crystallinity	Density	Crystallinity	Density	Crystallinity	Density	Crystallinity
EMC	-0.748	-0.998*	-0.235	-0.923*	-0.021	-0.960*	-0.577	-0.769
MOE	0.927*	0.921*	0.86	0.920*	0.834	0.775	-0.934*	-0.284

*Significant correlations ($p < 0.05$) utilizing a Pearson's correlation analysis were marked with an asterisk (*).

As suggested by Esteves and Pereira (2009), this increase in crystallinity, in conjunction with a decrease of the EMC, could explain the increase of vibrational MOE at 190 °C. Additionally, in Las Vertientes, Catanlí and Pelchuquín, the band representing guaiacyl type lignin (1040 cm^{-1}) showed the highest values in peak intensity at the modification at 190 °C in comparison to the other modification temperatures. This is the same temperature where, in most positions from pith to bark, the vibrational MOE increased. This could be related to the possible increase of cross-linking that could increase the rigidity around the cellulose microfibrils (Lekounougou *et al.* 2011).

Statistical analysis of the variation within the trees

A Pearson correlation test was run to determine any relationship between density, EMC, vibrational MOE, and the relative crystalline ratio (Table 3) with data from the unmodified samples (taken from Wentzel *et al.* (2024)) and from each modification temperature for each site. It is important to mention that the vibrational MOE was partially calculated with the density of the specimen, so these properties will tend to have strong correlations.

Table 3 shows the Pearson correlation coefficients between the characteristics and properties of the wood for each site considered in this study. According to Wentzel *et al*. (2024), the Catanli produces the most homogeneous wood when considering the level of association between the studied properties. In the modified wood, the correlations tend to decline when the wood was subjected to thermal modifications of 170 and 210 °C, regardless of its origin. Nevertheless, the intermediate treatment (190 °C) modified the characteristics and properties of the wood to such a level that they were again significantly associated. It was notable that the wood from Catanli manages to maintain a similar level of association before and after thermal modification at 190 °C. The second site that generates the most homogeneous wood, considering the correlations, was Pelchuquin, a secondary regrowth forest, but it fails to recover the level given by growth when treated at 190 °C. Finally, the wood from Las Vertientes, which comes from a silvicultural condition similar to Catanli, improves its associations at 190 °C.

Due to the limited geography of the sites used in this study, it would be suggested to expand the locations of future studies, to cover more sites across southern Chile where *N. alpina* naturally grows, and focus in both plantations with intensive silviculture and young regrowth forests of this species.

CONCLUSIONS

1. The increase of vibrational modulus of elasticity (MOE) and decrease of equilibrium moisture content (EMC), density and relative crystalline ratio in the modification at 190 °C in most positions from pith to bark in all sites, in addition to the apparent homogenization of those properties and their chemical structure at that temperature, would suggest that this modification temperature may be the optimum for this species.
2. Among the studied sites, Catanlí, the 21-year-old plantation with intensive silviculture, presented the most homogeneous results, especially at the modification temperature of 190 °C, where the chemical wood structure and physical-mechanical properties were strongly associated. These results could be related to the longer influence of a silvicultural intervention in this site, thus suggesting a positive influence of this practice in young *N. alpina* wood.

3. The material from thinning of *N. alpina* plantation and regrowth sites can be used for thermal modification processes, thus giving alternatives of uses for this kind of wood. This further shows that this material could be used to generate additional value during the time the plantation reaches maturity.

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