



Article

Nondestructive Characterization of Dry Heat-Treated Fir (*Abies Alba* Mill.) Timber in View of Possible Structural Use

Aleš Straže * , Gorazd Fajdiga and Bojan Gospodarič

Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, 1000 Ljubljana, Slovenia; gorazd.fajdiga@bf.uni-lj.si (G.F.); bojan.gospodaric@bf.uni-lj.si (B.G.)

* Correspondence: ales.straze@bf.uni-lj.si; Tel.: +386-1-320-3635

Received: 14 November 2018; Accepted: 11 December 2018; Published: 15 December 2018



Abstract: The use of heat-treated timber for building with wood is of increasing interest. Heat treatment improves the durability and dimensional stability of wood; however, it needs to be optimized to keep wood's mechanical properties in view of the possible structural use of timber. Therefore, dry vacuum heat treatment varying the maximum temperature between 170 °C and 230 °C was used on fir (Abies alba Mill.) structural timber, visually top graded according to EN 338, to analyze its final weight loss, hygroscopicity, CIELAB color, and dynamic elastomechanical properties. It turned out that weight loss and total color difference of wood positively correlates with the increasing intensity of the heat treatment. The maximum 40% reduction of the hygroscopicity of wood was already reached at 210 °C treatment temperature. The moduli of elasticity in longitudinal and radial direction of wood, determined by ultrasound velocity, increased initially up to the treatment temperature of 210 °C, and decreased at higher treatment temperature. Equally, the Euler-Bernoulli modulus of elasticity from free-free flexural vibration of boards in all five vibration modes increased with the rising treatment temperature up to 190 °C, and decreased under more intensive treatment conditions. The Euler-Bernoulli model was found to be valid only in the 1st vibration mode of heat-treated structural timber due to the unsteady decrease in the evaluated moduli of elasticity related to the increasing mode number.

Keywords: heat treatment; wood; structural changes; nondestructive testing; ultrasound; Euler-Bernoulli; modulus of elasticity

1. Introduction

Thermal treatment at high temperature, i.e., between $160\,^{\circ}\text{C}$ to $260\,^{\circ}\text{C}$, is one of the eco-friendly methods for the enhancement of the biological durability of wood and lignocellulosic composites. Heat treatment processes vary in terms of furnace design, type and condition of heating medium, and treatment schedules, and mostly depend on final usage of heat-treated material. The common factor of these processes is a modification of the chemical structure of timber, which has consequences on the physical and mechanical properties of wood [1–7].

With the improved hygroscopicity and dimensional stability of heat-treated wood, there is a desire to use it for structural purposes, especially in more demanding climates. However, the important aspects in a case of thermally treated wood are strength reduction and stiffness alteration, which vary with the anatomical direction of wood, testing method, and wood species. Many studies have shown a reduction in the bending stiffness and strength of heat-treated wood, combined with the reduced wood density [8–14], since the latter is the main influencing factor in the mechanical properties of wood [15]. However, exceptions are found to be related to the significant decrease in modulus of elasticity only

when the weight loss of wood exceeds a particular value [16]. The latter is related significantly to the treatment conditions, since material cracking and degradation of the cell structure of heat-treated wood can be induced as well [12]. The important role of material changes during heat treatment mostly concerns the initial structure and density inhomogeneity, which is almost always present in real size solid wood. In the case of the use of such heat-treated solid wood for structural purposes, it is necessary to ensure reliable quality control based on non-invasive techniques [17], widely present in the management of wood quality in the whole forest-wood chain [18,19].

Therefore, the main goal of the study was to use non-destructive mechanical and physical testing methods to investigate possible internal structural changes of fir (*Abies alba* Mill.) real size quarter-sawn timber after vacuum heat treatment, having varying intensity. Additionally, the machine stress grading and dynamic mechanical response of structural timber before and after heat treatment was analyzed and compared with the weight loss of boards and their color changes.

2. Materials and Methods

2.1. Material

Forty-five radially-oriented fir wood boards (*Abies alba* Mill.) of 45 mm thickness (L_T), 120 mm wide (L_R) and 4 m long (L_L), Figure 1, were selected from the conditioned warehouse ($T = 20\,^{\circ}$ C; RH (Relative humidity) = 65%) of a local construction timber trade company. In the sample population, we included boards without present fissures, deformations, wane, rot, insect damages, or other abnormal defects. We only allowed the presence of single healthy knots up to a size of 15 mm, substantially below 1/5 of the cross-sectional area of the boards. This visual preselection and assessment of boards allowed us to grade the sample population into the S10 and S13 classes [20], and therefrom, to assign the C24 and C30 strength grading classes for the selected boards [21]. Most of the boards were initially visually graded into the top S13 class. However, some of the boards (n = 5; 11.1% of the samples), due to growth rings of widths greater than 6 mm, and therefore, lower wood density, were graded into the lower S10 grading class.

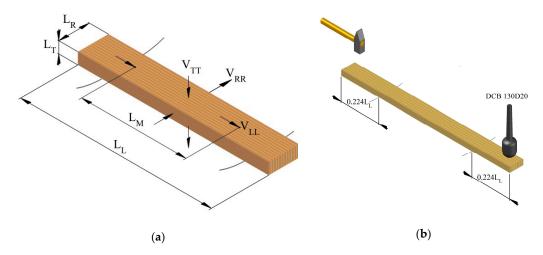


Figure 1. (a) The experimental setup for determination of velocity of ultrasound in longitudinal- (v_{LL}) , radial- (v_{RR}) and tangential (v_{TT}) wood direction; (b) principle of the analysis of flexural vibration response of structural timber specimens.

The initial weight and dimensions of the selected boards were determined afterwards for the ranging of timber into 9 density classes. We made nine density classes by ranking boards from the smallest to the highest density of wood. Five boards were placed successively in each density class. Small cut-off specimens (L = 25 mm; 300 mm from the board end) were made afterwards from each board to gravimetrically determine wood equilibrium moisture content.

2.2. Methods

2.2.1. Heat Treatment

Industrial dry vacuum heat treatment of wood was carried out by the Silvaprodukt company (Ljubljana, SI) according to patented SilvaproTM industrial vacuum procedure with a pre-drying phase (T = 105 °C; t = 24 h), stepwise heating phase ($\Delta T = +15$ °C/h), heating at maximum temperature for 3 hours, followed by cooling ($\Delta T = -15$ °C/h) and conditioning in normal climate (20 °C, RH = 65%). One board per wood density class was taken for this purpose of the control group and treated at 4 heat treatment intensities (9 boards per treatment), having the maximum temperature of 170 °C, 190 °C, 210 °C, and 230 °C. A one-month conditioning period (20 °C, 65%) was used prior to determining the final weight of the boards and their equilibrium moisture content (EMC) and wood density (ρ). The board weight loss (WT_{loss}) after heat treatment was calculated on the dry mass basis.

2.2.2. Determination of Wood Color

Standard color measurement (CIELAB) was performed on every board (3 measurements per sample) at the initial and heat treated state by X-Rite OptotronikTM SP62 (XRITE Inc., Rapids, MI, USA) spectrophotometer. The total color difference of wood before and after thermal modification was determined by the ΔE^* colorimetric parameter (Equation (1)).

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}},\tag{1}$$

where ΔL^* is a difference in color lightness, Δa^* is difference in green-red axis and Δb^* is difference in blue-yellow color axis.

2.2.3. Determination of Elastomechanical Properties of Structural Timber with Ultrasound

The velocity of ultrasound has been added to the measurement 3-times per board in the radial (v_{RR} , L_R = 120 mm), tangential (v_{TT} , L_T = 45 mm) and longitudinal (v_{LL} , L_M = 1500 mm) board direction by Proceq Pundit PL-200PE (Proceq Inc., Scharzenbach, Switzerland) pulse ultrasonic device, equipped with 54 kHz exponential transducers (Figure 1a). The velocity of ultrasound (v_{ii}) and wood density (ρ) were used to determine the moduli of elasticity (E_i) in longitudinal- (E_L), radial- (E_R) and tangential (E_T) direction of the boards (Equation (2)). Acoustic anisotropy was determined by ratios of ultrasound velocity in all three wood anatomical directions (v_{LL}/v_{RR} , v_{LL}/v_{TT} , v_{RT}/v_{TT} ; two-letter index: the first letter represents the direction of the ultrasonic wave, and the second represents its polarization).

$$E_{i} = \rho \cdot v_{ii}^{2}, \tag{2}$$

2.2.4. Analysis of Flexural Vibration of Structural Timber Boards and Strength Grading

For free-free flexural vibration, the test specimens were placed on soft thin rubber supports from their nodes of the 1st vibration mode (0.224 L) and excited using a steel hammer (mass 100 g) from a free end. The sound was recorded by unidirectional condenser microphone (PCB-130D20; PCB Piezotronics Inc, Depew, NY, USA) on the other free end of the board, and acquired by NI-9234 DAQ-module (National Instruments Inc, Austin, TX, USA) in 24-bit resolution with 51.2 kHz sampling frequency (Figure 1b). Euler-Bernoulli's moduli of elasticity (E_B) were determined based on each of the five initial modes ($1 \le n \le 5$) of flexural vibration (Equation (3)):

$$E_{B} = \frac{4 \cdot \pi^{2} \cdot L_{L}^{4} \cdot \rho \cdot f_{n}^{2} \cdot A}{I \cdot k_{n}^{4}},$$
(3)

where L_L is the length of a board, ρ is the mean density of a board, A is a board's cross section, I is the moment of inertia and k_n is a constant depending on vibration mode number n (k_n = ((2 n + 1)

Forests **2018**, 9, 776 4 of 12

 π)/2)). The analysis of the theoretical linear decreasing slope of the evaluated moduli of elasticity with increasing vibration mode number was accomplished by calculating the difference between sequential moduli ($\Delta E_{Bi} = \Delta E_{Bi} - \Delta E_{B\,(i-1)}$; $2 \le i \le 5$), and finally by calculating the coefficient of variation of the moduli difference between vibration modes (q) (Equations (4)–(6)):

$$\overline{\Delta E_B} = \frac{1}{n} \sum_{i=1}^{n} \Delta E_{Bi}, \tag{4}$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (\Delta E_{Bi} - \overline{\Delta E_{B}})^{2}}{n}},$$
 (5)

$$q = \frac{SD}{|\overline{\Delta E}_B|} \cdot 100\%, \tag{6}$$

where $\overline{\Delta E_B}$ is mean sequential moduli difference and SD is standard deviation of the sequential moduli difference.

We used the Euler-Bernoulli's modulus of elasticity in 1st vibration mode (E_{B1}) and wood density for the strength grading of boards according to standards EN 14081 [22] and EN 338 [23]. As a criterion for classification in a particular strength class, we took into account the achievement of the characteristic value of the wood density (ρ_c) and 95% of the average modulus of elasticity (E_m). The ANOVA (Analysis of variance) statistical tool and Duncan's multiple range test at the 95% level of significance were used for all the tested properties, to analyze the difference among group means in the sample of boards.

3. Results

3.1. Impact of Heat Treatment on Wood Density, Weight Loss, Hygroscopicity and Color of Fir Structural Timber

The rising of the heat treatment temperature induced a significant increase in the weight loss of fir wood (*Abies alba* Mill.; ANOVA, $p = 1.42 \times 10^{-12}$). This caused a drop in the mean density of wood after the heat treatment of 2.5% at a temperature of 170 °C ($\rho_{170} = 415 \text{ kg/m}^3$) and up to 10.3% at the heat treatment temperature of 230 °C ($\rho_{230} = 392 \text{ kg/m}^3$; ANOVA, p = 0.07). The hygroscopic nature of wood was significantly improved by the heat treatment (EMC; ANOVA, $p = 1.11 \times 10^{-16}$). Even after the lightest thermal modification (T = 170 °C), the equilibrium moisture content of the wood in the normal climate dropped to 8.0%. Only slightly lower values, i.e., between 6.9% and 7.6%, we recorded in stronger heat-treated wood (Table 1, Figure 2a).

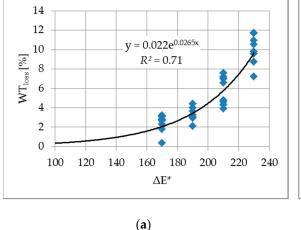
Table 1. Average wood density (ρ), weight loss (WT_{loss}), equilibrium moisture content (EMC) and color parameters (L*—lightness, a*, b*—chromaticity on green-red and blue-yellow axis; Δ E—total color difference) of wood after heat treatment (2nd row present Coef. of variation (%)).

Heat Treatment (°C)	ρ (kg/m ³)	WT _{loss} (%)	EMC (%)	L*	a*	b*	ΔΕ*
Control	425		12.4	74.9	6.1	25.1	
	(6.4)		(4.1)	(2.8)	(10.5)	(5.7)	
170	415	2.5	8.0	57.8	13.0	31.5	19.6
	(6.7)	(36.6)	(12.7)	(6.2)	(9.2)	(4.8)	(24.0)
190	415	3.1	7.5	47.6	11.7	24.8	28.0
	(7.3)	(26.8)	(11.9)	(7.1)	(6.5)	(10.9)	(13.9)
210	397	5.9	6.9	44.2	11.6	23.5	31.3
	(6.5)	(24.9)	(8.1)	(6.0)	(5.8)	(4.9)	(10.8)
230	392	10.3	7.6	37.6	10.3	18.8	38.2
	(6.7)	(15.9)	(13.9)	(4.4)	(8.5)	(9.9)	(8.6)

By increasing the intensity of the heat treatment, the color lightness of the wood was significantly reduced (ANOVA, $p = 1.1 \times 10^{-16}$). The mean color lightness was the highest in the control samples

Forests **2018**, 9, 776 5 of 12

(L* = 74.9), and the lowest in the samples after the heat treatment at 230 °C (L* = 37.6) (Table 1). Changes in the color parameters a* and b* were not as large, and were insignificant with respect to the intensity of the treatment (ANOVA, p = 0.13). Otherwise, the values of the two parameters under mild treatment conditions (\leq 190 °C) increased slightly, while for the more intensively heat-treated wood they dropped again. The total color difference in wood (Δ E*), compared to the color of the test specimens, was largely due to the change in color lightness. With the intensity of the heat treatment, the total color difference Δ E* was significantly increased (ANOVA, $p = 1.47 \times 10^{-9}$). It has also been shown that there is a positive correlation of Δ E* with the weight loss of test specimens (Table 1, Figure 2b).



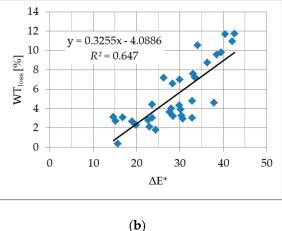


Figure 2. (a) The relationship between the individual weight loss (WT_{loss}) of wood and the intensity of the heat treatment; (b) the relationship between the individual weight loss (WT_{loss}) of wood and its total color difference (ΔE^*).

3.2. Elastomechanical Properties and Anisotropy of Heat-Treated Structural Timber

The ultrasound velocity was significantly improved in the longitudinal (v_{LL}) and radial direction (v_{RR}) of the heat-treated structural timber, up to a treatment temperature of 210 °C (ANOVA, p = 0.049). The velocity of ultrasound in these two anatomical directions was again slightly lower only in the most intense heat-treated structural timber (T = 230 °C). In the tangential anatomical wood direction (v_{TT}), the velocity of ultrasound didn't significantly change with the intensity of the heat treatment (Table 2; ANOVA, p = 0.82).

A somewhat smaller increase than in ultrasound velocity was recorded in the longitudinal- (E_L ; ANOVA, p = 0.014) and radial direction of wood (E_R ; ANOVA, p = 0.046) with the intensity of heat treatment of structural timber. This difference in trends in ultrasound velocity and stiffness of wood is attributed to the simultaneous decrease in the density of structural timber by increasing the intensity of the treatment. The latter also causes a reduction, however statistically insignificant (ANOVA, p = 0.15), in the modulus of elasticity in the tangential direction of the wood (E_T) by increasing the intensity of the thermal process (Table 2).

The elastomechanical anisotropy of the structural timber changed slightly but insignificantly with the intensity of the thermal process (ANOVA, p = 0.21). The largest anisotropy was determined in the longitudinal-tangential plane (4.7 to 5.4) and somewhat smaller in the longitudinal-radial plane (3.5 to 3.9). As expected, elastomechanical anisotropy was the smallest in the radial-tangential plane (1.2 to 1.5) of structural timber (Table 2).

Forests **2018**, 9, 776 6 of 12

Table 2. Mean velocity of ultrasound in longitudinal- (v_{LL}), radial- (v_{RR}) and tangential wood direction (v_{TT}), elastomechanical anisotropy (v_{LL}/v_{RR} , v_{LL}/v_{TT} , v_{RR}/v_{TT}) and mean moduli of elasticity (E_L —longitudinal, E_R —radial, E_T —tangential) of heat-treated structural timber (2nd row present Coef. of variation (%)).

Heat Treatment (°C	v _{LL} C) (m/s)	v _{RR} (m/s)	v _{TT} (m/s)	v _{LL} /v _{RR}	v_{LL}/v_{TT}	v _{RR} /v _{TT}	E _L (GPa)	E _R (GPa)	E _T (GPa)
Control	4991	1399	1079	3.7	4.7	1.3	10.6	0.88	0.51
	(6.8)	(22.8)	(14.8)	(25.0)	(16.4)	(13.0)	(15.5)	(50.3)	(35.8)
170	5424	1610	1090	3.5	5.0	1.5	12.2	1.13	0.50
	(6.3)	(21.1)	(10.7)	(21.6)	(14.6)	(15.0)	(10.5)	(44.3)	(22.8)
190	5365	1473	1045	3.8	5.4	1.5	12.0	0.93	0.39
	(4.1)	(21.7)	(7.7)	(24.6)	(14.1)	(21.7)	(11.7)	(40.1)	(20.3)
210	5520	1587	1071	3.5	5.0	1.5	11.7	0.99	0.49
	(4.2)	(17.4)	(9.7)	(28.6)	(15.6)	(18.2)	(10.4)	(31.0)	(26.3)
230	5161	1225	1028	3.9	4.7	1.2	10.1	0.60	0.42
	(6.5)	(13.4)	(8.5)	(24.8)	(17.6)	(15.4)	(13.5)	(30.1)	(21.3)

3.3. Vibration Response of Heat-Treated Structural Timber

The modulus of elasticity in the test specimens increased initially with the intensity of heat treatment (\leq 190 °C); however, at higher temperatures, i.e., particularly at 230 °C, it was significantly reduced compared to control samples (ANOVA, p = 0.021). This trend was present at the modulus of the elasticity of the specimens in all five vibration modes (E_{B1} to E_{B5}) (Table 3).

Table 3. Mean moduli of elasticity of heat-treated structural timber determined by flexural vibration at individual vibration mode ($1 \le n \le 5$) and its mean bending strength according to EN 338 (2nd row present Coef. of variation (%)).

Heat Treatment (°C)	E _{B1} (GPa)	E _{B2} (GPa)	E _{B3} (GPa)	E _{B4} (GPa)	E _{B5} (GPa)	Bending Strength Grade (MPa)
Control	12.74	13.01	12.38	11.83	11.45	31.6
	(12.2)	(12.6)	(12.9)	(12.7)	(12.4)	(21.2)
170	13.58	13.48	12.96	12.47	12.06	34.1
	(9.6)	(11.1)	(10.7)	(10.2)	(10.3)	(17.6)
190	13.59	13.73	12.96	12.50	12.12	34.9
	(12.5)	(10.6)	(10.3)	(10.2)	(10.1)	(20.3)
210	12.94	12.81	12.12	11.71	11.40	29.4
	(14.5)	(10.8)	(11.7)	(11.8)	(11.4)	(20.9)
230	11.58	12.45	11.69	11.21	10.92	26.8
	(23.4)	(17.8)	(18.9)	(18.2)	(18.3)	(36.6)

The uniform, close to the linear decreasing slope of the flexural moduli of elasticity with increasing vibration mode number was confirmed only for the control structural timber (Table 3; Figure 3a). The sequential moduli difference between 1st and 2nd vibration modes was initially significantly changed for the structural timber already after the low intense heat treatment (\leq 190 °C). Major changes between the sequencing moduli with regard to vibration mode, especially for higher modal numbers, occurred at greater heat treatment temperatures (\geq 210 °C). The variation of the modulus of elasticity (q-coefficient) of heat-treated structural timber at 210 °C significantly increased (ANOVA, p = 0.045) compared to the rest of the tested population (Figure 3b).

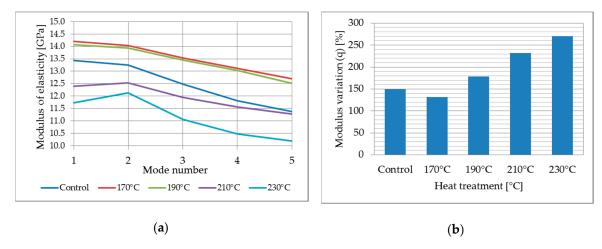


Figure 3. (a) Modal evaluated values of modulus of elasticity of heat-treated structural timber; (b) the coefficient of variation of the moduli difference in-between vibration modes (q-coefficient) of heat-treated wood.

Strength Grading of Heat-Treated Structural Timber

The small reduction in wood density and significant increase in the modulus of elasticity in the moderate heat-treated construction wood (\leq 190 °C) cause improved classification, i.e., into the EN 338 strength classes. In the case of a moderate heat-treated structural timber (\leq 190 °C), the resulting mean bending strength was greater (Table 3, Figure 4a).

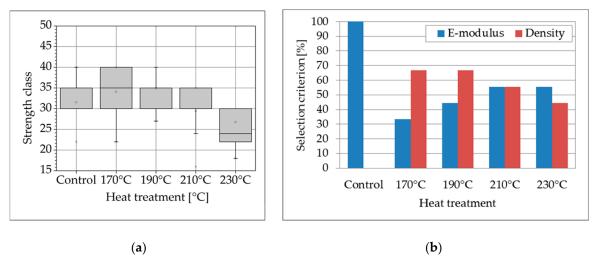


Figure 4. (a) Strength class distribution of heat-treated structural timber; (b) the decision making selection criteria for strength grading of heat-treated structural timber.

Classification into lower strength grades was required for heat-treated structural timber with a temperature of $210\,^{\circ}\text{C}$ or more. The estimated mean bending strength of the wood in this case is typically reduced below the values of the control specimens (Figure 4a), having also asymmetric distribution. In control specimens, the determining classification criterion was exclusively the individual modulus of elasticity. For heat-treated structural timber, the wood density was more often used for strength grading criteria (Figure 4b).

4. Discussion

The weight loss of various wood species and, consequently, the decrease in the wood density, was confirmed in both dry heat treatments, as well as in hydrothermal heat treatment processes [24–28].

Studies confirmed smaller degradation of heat-treated wood in a vacuum than under nitrogen or water vapor under the same conditions [26]. This is explained by the effect of vacuum allowing removal the of volatile degradation products limiting the acidic degradation of polysaccharides due to formation of acetic acid and the recondensation of volatile degradation products within the wood structure. Therefore, in the used dry vacuum heat treatment, the weight loss of wood is attributed mainly to the degradation of hemicelluloses, i.e., the most reactive wood components that hydrolyze into oligomeric and monomeric structures [29,30]. However, it is also suggested that other phenomena, such as structural modifications and chemical changes of lignin, also play an important part [31].

In comparable heat treatment in conifers, a similar increase in the weight loss of the wood was observed with increasing treatment temperature, and was dominant over the impact of the treatment time. As in previous studies, we also confirmed a rising decrease in mass correlated with EMC reduction [14,25,27,32]. This is explained by less moisture-accessible hydroxyl groups of the heat-treated specimens compared with untreated controls [33]. However, the EMC remained stable beyond the limit value of approximately 3% decrease in weight reached at 190 °C treatment temperature. This achieved limit value is lower compared to the data from related studies, ranging between 6% and 9%; however, it indicates the completion of decomposition of moisture-accessible hydroxyl groups by the heat treatment [25,32]. In these heat treatment processes, we achieved up to 40% reduction in EMC of wood, while research indicates that the EMC can be reduced in thermally-treated timber even up to 60% [28,34].

Color changes in wood during the heat treatment were found to be related to the process intensity. The excellent but non-linear negative relationship was observed between the lightness of wood (L*) and the used temperature of heat treatment, which was confirmed also in some previous studies [25,35–37]. Researchers even proposed more reliable means of measuring the intensity of a thermal modification process by combining parameter L*+b* and by milling of wood, to prevent scattering of color parameters on real wood surfaces [35]. Additionally, the relation between chemical composition and lightness decrease for heat-treated wood is reported [38]. However, the total color difference ΔE^* is most often used, and was found also in this study to have the same exponential relationship with the increase of the treatment temperature, determined even in a case of wood weight loss (Figure 2a,b).

The increase in the ultrasound velocity, significantly in the longitudinal and partially in the radial direction of fir wood, coincided with its weight loss and overall color difference ΔE^* , but just up to the treatment temperature of 210 °C. The effect of heat treatment on the longitudinal and radial sound velocity may vary, since it also increases greatly, i.e., up to 0.8% with a decrease of 1% of EMC, in the range of 5 to 30% equilibrium moisture content of wood [39,40]. Otherwise, the ultrasound velocity in the tangential direction of wood (v_{TT}) remained unchanged at these conditions, which induced the increase of elastomechanical anisotropy of heat-treated fir wood with respect to its tangential plane (v_{LL}/v_{TT} , v_{RR}/v_{TT}). In the heat treatment of wood up to approx. 200 °C, the increase in the ultrasound velocity, especially in the longitudinal direction of the wood, which is equivalent to a specific modulus of elasticity (E/ρ), is also indicated by other studies [41,42]. Elastomechanical anisotropy of heat-treated wood has not been widely studied so far. However, some researchers report the increase in the mechanical anisotropy of wood, but already in the area of plastic deformations, where they determined the increase in the ratio of compression strength of wood along- and transverse to the grain [43,44].

The positive correlation of the modulus of elasticity with the treatment temperature up to 190 $^{\circ}$ C, and then its decrease at higher treatment temperatures (\geq 210 $^{\circ}$ C), were equivalent regardless of the method used, i.e., at the ultrasound velocity and flexural vibration. A similar trend in heat-treated wood is reported by some related studies [45]. Otherwise, we measured on average a 14% lower modulus of elasticity in in the 1st flexural vibration mode compared to the ultrasound velocity measurements. Lower values of modulus of elasticity determined by ultrasound can be a consequence of a small distance between sensors ($L_{\rm M}$ = 1500 mm). The surface wave propagation may have affected

the compression wave passage lengthwise, and skewed the final passage time of the wave through material, as reported elsewhere [41].

The control specimens showed a steady and semi-uniform decrease in the evaluated moduli of elasticity from flexural vibration related to the increasing mode number, which suggests an approximation to properties of homogeneous axial isotropic (orthotropic) material [46,47]. After the heat treatment, this steady decrease line showed some breakages (Figure 3a), determined also by the increase of the q-coefficient, as the measure of modulus variation in-between vibration modes (Figure 3b). The latter finding indicates the possible presence and increase of structural inhomogeneity in the heat-treated wood, intensified also by increasing of the heat treatment temperature. The principle of slope breakage of modally evaluated moduli of elasticity was, in the past, already successfully used to recognize the severity of artificially made defects in wooden beams [48], or for the determination of density inhomogeneity along the boards of various wood species [49]. The same methodology has been proposed for detecting concentrated mass due to knottiness in solid wood [50], as well as at the determination of surface- and end-cracks in kiln dried wood [51]. This research suggests that the evaluation of moduli of elasticity from flexural vibration can be successfully used to determine inhomogeneous structural changes in full size heat-treated wood, which are likely present in material at increased treatment temperature. Depending on treatment parameters such as treatment temperature, the heating rate, the holding time at the maximum temperature, or the gas humidity, cracks can appear and the cell structure can be partially degraded as well [13,24,28,52].

The q-coefficient was found to be in a negative relationship, however, not significant, with the strength grading class of heat-treated wood after the treatment. It is important to note that the increase in q-coefficient by increasing the treatment temperature is also likely to be due to the change in the density of the heat-treated wood. Wood density, however, was a common decision criterion for strength grading of the heat-treated wood. The findings indicate the potential of both, i.e., density and q-coefficient, together with the modal evaluation of the modulus of elasticity, for use in strength grading of the heat-treated structural timber.

5. Conclusions

The weight loss and the total CIELAB color difference ΔE^* of structural fir timber positively correlate with the increase of the heat treatment temperature, in the range between 170 °C and 230 °C. The maximum 40% reduction of hygroscopicity of fir wood is already reached at 210 °C treatment temperature.

The ultrasound velocity, and consequently, modulus of elasticity, increases initially in the longitudinal and partially in the radial direction of fir structural timber, up to the treatment temperature of 210 $^{\circ}$ C, and decreases under more intensive heat treatment conditions. Due to the constant ultrasound velocity in the tangential direction (v_{TT}) of heat-treated wood, the increase of its elastomechanical anisotropy with respect to the tangential plane is confirmed.

As with the ultrasonic method, an initial positive correlation exists of the modulus of elasticity from the flexural vibration of boards in all vibration modes with heat treatment temperatures up to $^{\circ}$ C, which then decreases at higher treatment temperatures.

The Euler-Bernoulli model, used in free-free flexural vibration, was found to be valid only in the 1st vibration mode at structural timber. This discovery has potential for use in timber strength grading. The visually highly-graded preselected structural timber, having minimal structural anomalies, shows a steady decrease in the evaluated moduli of elasticity related to the increasing mode number. After the heat treatment, this steady decrease line has some breakages, with increased modulus variation between vibration modes.

Author Contributions: Conceptualization and experiments design, A.S., G.F. and B.G.; A.S. and B.G. performed the experiments; A.S. and B.G. analyzed the data; validation and formal analysis, G.F.; A.S., writing—original draft preparation; G.F. and B.G., writing—review and editing.

Funding: This work was supported by Ministry of Education, Science and Sport of the Republic of Slovenia within the framework of the Program P4-0015 and Program P2-0182.

Acknowledgments: Thanks are to the Breza Commerce d.o.o. Company (Todraž, Slovenia) for providing the timber for this study and to the Silvaprodukt d.o.o. Company (Ljubljana, Slovenia) for the heat treatment of wood.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

- 1. Stamm, A.J. Themal degradation of wood and cellulose. Ind. Eng. Chem. 1956, 48, 413–417. [CrossRef]
- 2. Kollmann, F.; Schneider, A. Über das Sorptionsverhaltnis wärmebehandelter Hölzer. *Holz Roh- Werkst.* **1963**, 21, 77–85. (In German) [CrossRef]
- 3. Tjeerdsma, B.F.; Boonstra, M.; Pizzi, A.; Tekely, P.; Militz, H. Characterisation of thermally modified wood: Molecular reasons for wood performance improvement. *Holz Roh- Werkst.* **1998**, *56*, 149–153. [CrossRef]
- 4. Metsä-Kortelainen, S.; Antikainen, T.; Viitaniemi, P. The water absorption of sapwood and heartwood of Scots pine and Norway spruce heat-treated at 170 °C., 190 °C., 210 °C. and 230 °C. *Holz Roh- Werkst.* **2006**, 64, 192–197. [CrossRef]
- 5. Hakkou, M.; Pétrissans, M.; Zoulalian, A.; Gérardin, P. Investigation of wood wettability changes during heat treatment on the basis of chemical analysis. *Polym. Dégrad. Stab.* **2005**, *89*, 1–5. [CrossRef]
- 6. Burmeister, A. Einfluss einer Wärme-Druck-Behandlung halbtrockenen Holzes auf eine seine Formbeständigkeit. *Holz Roh- Werkst.* **1973**, *31*, 237–243. (In German) [CrossRef]
- 7. Cetera, P.; Negro, F.; Cremonini, C.; Todaro, L. Physico-Mechanical Properties of Thermally Treated Poplar OSB. *Forests* **2018**, *9*, 345. [CrossRef]
- 8. Santos, J.A. Mecanical behaviour of Eucalyptus wood modified by heat. *Wood Sci. Technol.* **2000**, *34*, 39–43. [CrossRef]
- 9. Shi, J.L.; Kocaefe, D.; Zhang, J. Mechanical behaviour of Quebec wood species heat-treated using ThermoWood process. *Holz Roh- Werkst.* **2007**, *65*, 255–259. [CrossRef]
- 10. Bengtsson, C.; Jermer, J.; Brem, F. Bending strength of heat-treated spruce and pine timber. In Proceedings of the IRG/WP 02-40242, Jackson Lake, WJ, USA, 20–24 May 2007.
- 11. Giebeler, E. Dimensionstabilisierung von Holz durch eine Feuchte/Wärme/Druck- Behandlung. *Holz Roh- Werkst.* **1983**, *41*, 87–94. (In German) [CrossRef]
- 12. Kubojima, Y.; Okano, T.; Ohta, M. Bending strength and toughness of heat-treated wood. *J. Wood Sci.* **2000**, 46, 8–15. [CrossRef]
- 13. Poncsak, S.; Kocaefe, D.; Bouazara, M.; Pichette, A. Effect of high temperature treatment on the mechanical properties of birch (*Betula papyrifera*). *Wood Sci. Technol.* **2006**, *40*, 647–663. [CrossRef]
- 14. Borůvka, V.; Zeidler, A.; Holeček, T.; Dudik, R. Elastic and Strength Properties of Heat-Treated Beech and Birch Wood. *Forests* **2018**, *9*, 197. [CrossRef]
- Zeidler, A.; Borůvka, V.; Schönfelder, O. Comparison of Wood Quality of Douglas Fir and Spruce from Afforested Agricultural Land and Permanent Forest Land in the Czech Republic. Forests 2017, 9, 13. [CrossRef]
- 16. Rusche, H. Festigkeitseigenschaften von trockenem Holz nach thermischer Behandlung. *Holz Roh- Werkst.* **1973**, *31*, 273–281. (In German) [CrossRef]
- 17. Widman, R.; Fernandez-Cabo, J.L.; Steiger, R. Mechanical properties of thermally modified beech timber for structural purposes. *Eur. J. Wood Wood Prod.* **2012**, *70*, *775*–784. [CrossRef]
- 18. Newton, P.F. Acoustic-Based Non-Destructive Estimation of Wood Quality Attributes within Standing Red Pine Trees. *Forests* **2017**, *8*, 380. [CrossRef]
- 19. Škorpik, P.; Konrad, H.; Geburek, T.; Schuh, M.; Vasold, D.; Eberhardt, M.; Schuler, S. Solid Wood Properties Assessed by Non-Destructive Measurements of Standing European Larch (*Larix decidua* Mill.): Environmental Effects on Variation within and among Trees and Forest Stands. *Forests* **2018**, *9*, 276. [CrossRef]
- 20. German Institute for Standardisation. *Strength Grading of Wood—Part 1: Coniferous Sawn Timber;* German Institute for Standardisation: Berlin, Germany, 2012; Volume DIN 4071-1, p. 8.

21. European Committee for Standardization. *Structural timber—Strength classes—Assignment of visual grades and species*; CEN: Brussels, Belgium, 2007; Volume EN 1912: 2004, p. 16.

- 22. European Committee for Standardization. *Timber Structures—Strangth Graded Structural Timber with Rectangular Cross Section—Part 1: General Requirements*; CEN: Brussels, Belgium, 2010; Volume EN 14081-1: 2005, p. 12.
- 23. European Committee for Standardization. *Structural Timber—Stress Classes*; CEN: Brussels, Belgium, 2009; Volume EN 338: 2009, p. 10.
- 24. Boonstra, M.; van Acker, J.; Tjeerdsma, B.F.; Kegel, E.V. Strength properties of thermally modified softwoods and its relation to polymeric structural wood constituents. *Ann. For. Sci.* **2007**, *64*, 679–690. [CrossRef]
- 25. Welzbacher, C.R.; Brischke, C.; Rapp, A.O. Influence of treatment temperature and duration on selected biological, mechanical, physical and optical properties of thermally modified timber. *Wood Mater. Sci. Eng.* **2007**, *2*, 66–76. [CrossRef]
- 26. Candelier, K.; Dumarcay, S.; Pétrassans, A.; Desharnais, L.; Gérardin, P. Comparison of chemical composition and decay durability of heat treated wood cured under different inert atmospheres: Nitrogen or vacuum. *Polym. Dégrad. Stab.* **2013**, *98*, 677–681. [CrossRef]
- 27. Alén, R.; Kotilainen, R.; Zaman, A. Thermochemical behaviour of Norway spruce (*Picea abies*) at 180 to 225 °C. *Wood Sci. Technol.* **2002**, *36*, 163–171. [CrossRef]
- 28. Esteves, B.M.; Pereira, H. Wood modification by heat treatment: A. review. BioResources 2009, 4, 370-404.
- 29. Bobleter, O.; Binder, H. Dynamischer hydrothermaler Abbau von Holz. *Holzforschung* **1980**, *34*, 48–51. [CrossRef]
- 30. Tjeerdsma, B.F.; Militz, H. Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood. *Holz Roh- Werkst.* **2005**, *63*, 102–111. [CrossRef]
- 31. Repellin, V.; Guyonnet, R. Evaluation of heat treated wood swelling by differential scanning calotrimetry in relation with chemical composition. *Holzforschung* **2005**, *59*, 28–34. [CrossRef]
- 32. Paul, W.; Ohlmeyer, M.; Leithoff, H.; Boonstra, M. Optimising the properties of OSB by one-step heat pre-treatment process. *Holz Roh- Werkst.* **2006**, *64*, 227–234. [CrossRef]
- 33. Boonstra, M.; Tjeerdsma, B.F. Chemical analysis of heat treated softwoods. *Holz Roh- Werkst.* **2006**, *64*, 204–211. (In German) [CrossRef]
- 34. Esteves, B.; Marques, A.V.; Domingos, I.; Pereira, H. Influence of steam heating on the properties of pine (*Pinus pinaster*) and eucalypt (*Eucalyptus globulus*) wood. *Wood Sci. Technol.* **2006**, 41, 193–207. [CrossRef]
- 35. Brischke, C.; Welzbacher, C.R.; Brandt, K.; Rapp, A.O. Quality control of thermally modified timber: Interrelationship between heat treatment intensities and CIEL*a*b* color data on homogenized wood samples. *Holzforschung* **2007**, *61*, 19–22. [CrossRef]
- 36. Bekhta, P.; Niemz, P. Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood. *Holzforschung* **2003**, *57*, *539–546*. [CrossRef]
- 37. Wei, Y.; Zhang, P.; Liu, Y.; Chen, Y.; Gao, J.; Fan, Y. Kinetic Analysis of the Color of Larch Sapwood and Heartwood during Heat Treatment. *Forests* **2018**, *9*, 289. [CrossRef]
- 38. Esteves, B.; Marques, A.V.; Domingos, I.; Pereira, H. Heat-induced colour changes of pine (*Pinus pinaster*) and eucalypt (*Eucalyptus globulus*) wood. *Wood Sci. Technol.* **2008**, 42, 369–384. [CrossRef]
- 39. Sandoz, J.L. Grading of construction timber by ultrasound. Wood Sci. Technol. 1989, 23, 95–108. [CrossRef]
- 40. Llana, D.F.; Iniguez-Gonzales, G.; Arriaga, F.; Niemz, P. Influence of Temperature and Moisture Content in Non-destructive values of Scots pine (*Pinus sylvestris* L.). In Proceedings of the 18th International Nondestructive Testing and Evaluation of Wood Symposium, Madison, WI, USA, 24–27 September 2013; pp. 451–458.
- 41. Holeček, T.; Gašparik, M.; Lagaňa, R.; Borůvka, V.; Oberhofnerová, E. Measuring the Modulus of Elasticity of Thermally Treated Spruce Wood using the Ultrasound and Resonance Methods. *BioResources* **2017**, *12*, 819–838. [CrossRef]
- 42. Del Menezzi, C.H.S.; Amorim, M.R.S.; Costa, M.A.; Garcez, L.R.O. Evaluation of Thermally Modified Wood by Means of Stress Wave and Ultrasound Nondestructive Methods. *Mater. Sci.* **2014**, *20*, 61–66. [CrossRef]
- 43. Heräjärvi, H. Effect of Drying Technology on Aspen Wood Properties. *Silva Fennica* **2009**, 43, 433–445. [CrossRef]
- 44. Straže, A.; Fajdiga, G.; Pervan, S.; Gorišek, Ž. Hygro-mechanical behaviour of thermally treated beech subjected to compression loads. *Constr. Build. Mater.* **2016**, *113*, 28–33. [CrossRef]

45. Kubojima, Y.; Okano, T.; Ohta, M. Vibrational properties of Sitka spruce heat-treated in nitrogen gas. *J. Wood Sci.* **1998**, *44*, 73–77. [CrossRef]

- 46. Bodig, J.; Jayne, B. *Mechanics of Wood and Wood Composites*; Krieger Publishing Co.: Malabar, India, 1993; p. 712.
- 47. Harris, C.M.; Paez, T.L. *Harris' Shock and Vibration Handbook*, 6th ed.; McGraw-Hill: New York, NY, USA, 2009; p. 1168.
- 48. Roohnia, M.; Tajdini, A. Identification of the Severity and Position of a Single Defect in a Wooden Beam. *BioResources* **2014**, *9*, 3428–3438. [CrossRef]
- 49. Kubojima, Y.; Tonosaki, M.; Yoshihara, H. Young's modulus obtained by flexural vibration test of a wooden beam with inhomogeneity of density. *J. Wood Sci.* **2006**, *52*, 20–24. [CrossRef]
- 50. Kubojima, Y.; Suzuki, S.; Tonosaki, M. Effect of Additional Mass on the Apparent Young's Modulus of a Wooden Bar by Longitudinal Vibration. *BioResources* **2014**, *9*, 5088–5098. [CrossRef]
- 51. Roohnia, M.; Yavari, A.; Tajdini, A. Elastic parameters of poplar wood with end-cracks. *Ann. For. Sci.* **2010**, 67, 409. [CrossRef]
- 52. Johansson, D. Influence of drying on internal checking of spruce (*Picea abies* L.) heat-treated at 212°C. *Holzforschung* **2006**, *60*, 558–560. [CrossRef]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).